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# Did ocean warming, acidification or saturation state control coccolithophorids production through time?

Alessandro Menini

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# **Did ocean warming, acidification or saturation state control coccolithophorids production through time ?**

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## **Le réchauffement, l'acidification ou l'état de saturation des océans ont-ils contrôlé la production de coccolithophores au fil du temps ?**

### RESUME

Les émissions de dioxyde de carbone devraient avoir un impact important sur la chimie des océans au cours des prochaines décennies. Les conséquences les plus importantes sont l'augmentation des températures des eaux de surface et l'acidification des océans, c'est-à-dire la diminution du  $pH$  de l'eau de mer, de la concentration en ions carbonate et de l'état de saturation du carbonate de calcium. En particulier, l'acidification des océans a un impact profond sur les organismes marins, notamment sur les organismes calcifiants (par exemple les coraux, les foraminifères et les coccolithophores) et est considérée comme une menace majeure pour la biominéralisation (Beaufort et al., 2011). Les espèces de coccolithophoridés (algues haptophytes) vivant dans les couches océaniques de surface sont particulièrement sensibles aux conditions chimiques et physiques des eaux peu profondes. Les coccolithophoridés sont les seuls organismes phytoplanctoniques à effectuer à la fois la photosynthèse et la biocalcification, participant aux pompes de carbone organique et inorganique (Rost et Riebesell, 2004). Des travaux récents montrent que la biocalcification pourrait être gravement affectée par l'acidification actuelle des océans, ce qui entraînerait à terme de profonds changements dans les écosystèmes marins (Fabry et al., 2008). Cependant, certaines études soulignent une résilience particulière des coccolithophores aux événements passés d'acidification des océans, et suggèrent que les températures pourraient être le principal facteur environnemental contrôlant la biocalcification (Gibbs, 2016).

Bien que la réponse des coccolithophores aux changements à court terme de température, de la  $pCO_2$  ou du  $pH$  est bien connue par le nombre croissant d'études sur des échantillons d'eau de culture ou de surface, la résilience au niveau spécifique à long terme face aux changements de ces paramètres environnementaux, ainsi que le potentiel séculaire de surmonter les conditions critiques, sont mal connus. La réponse à long terme des coccolithophores aux changements de température, de  $pCO_2$  ou de  $pH$  ne peut être abordée qu'en étudiant le record fossile. La principale question scientifique de mon doctorat concerne le rôle joué par les changements

sévères de  $p\text{CO}_2$  passés sur la calcification des coccolithophores. Mon hypothèse de travail est que ce paramètre n'a pas agi directement sur le potentiel de biocalcification mais indirectement, en augmentant la température et l'altération des continents qui, à leur tour, ont affecté l'alcalinité des océans. En fait, en période d'altération accrue, des flux accrus de  $\text{Ca}^{2+}$  et de  $\text{HCO}_3^-$  se sont produits dans les eaux de surface des océans. Nous avons sélectionné deux événements caractérisés par une perturbation du cycle du carbone probablement associé aux fluctuations du  $\text{CO}_2$ , notamment le Pliensbachien-Toarcien (~183 My ago ; PI-To event et T-OAE) et le Paléocène-Eocène (~55 My ; PETM). Ils sont également associés au réchauffement de l'océan et de l'atmosphère (hyperthermique), mais ils diffèrent car seulement le premier enregistre des dépôts de matière organique plus importants, appelés *black shales*.

Une première partie importante de mon doctorat a été de développer une biostratigraphie à haute résolution des nanofossiles calcaires pour les deux événements. Pour les deux cas d'études, j'ai représenté les événements à nanofossiles par rapport à la courbe des isotopes stables du carbone afin de corréliser des localités éloignées.

Afin d'évaluer l'impact des perturbations du carbone, de l'acidification des océans ou des variations de température sur les coccolithophores, et d'évaluer le retour éventuel aux conditions d'avant l'événement, j'ai analysé les changements dans la composition des assemblages de coccolithes fossiles, les abondances absolues (nanofossiles/gramme de roche) et les flux (ou NAR ; nanofossil accumulation rate ; nanofossiles/mètre carré/an) pour ces deux événements. Pour l'intervalle Pliensbachien-Toarcien, j'ai étudié trois sections d'Espagne (La Almunia), de France (Anse St. Nicolas) et du Royaume-Uni (Mochras). Pour le PETM, je me suis concentré sur l'étude des sites ODP de référence 1209 (Shatsky Rise), situés dans le Pacifique tropical et 1263, dans l'océan Atlantique (Walvis Ridge). De plus, je compare les enregistrements des sites océaniques du PETM à une section proximale en Tunisie (Kharouba) afin de comprendre la réponse des nanofossiles calcaires dans des environnements de dépôt similaires au cours des deux intervalles de temps. Pour les deux événements, je compare ces sections aux données de la littérature afin de fournir une perspective globale des changements paléocéanographiques qui ont affecté ces organismes planctoniques. Pour les deux événements, les assemblages de nanofossiles suggèrent que la stratification des océans induite par le réchauffement et la diminution de la disponibilité des nutriments sont les principaux facteurs déclenchant

la diminution de l'export de carbonate dans l'océan profond. En utilisant une méthodologie récemment développée au Laboratoire de Géologie de Lyon (Brazier et al., 2015), j'ai étudié les changements de la chimie des carbonates océaniques pour le PETM en utilisant la composition isotopique du calcium des coquilles d'une espèce de foraminifères planctoniques, qui s'est avérée suivre les changements de la saturation en carbonate et des concentrations en ions carbonate.

Nos résultats corroborent également les données empiriques et de modélisation suggérant que la stratification des océans induite par le réchauffement anthropique aura un impact important sur la productivité primaire, les bilans carbonés et les écosystèmes.

Mots-clés : PETM, T-OAE, Pliensbachien-Toarcien, nanofossiles calcaires, production de carbonate pélagique, cycle du carbone, cycle du calcium

Discipline: Sciences de la Terre, Biostratigraphie, Paleoceanographie

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## **Did ocean warming, acidification or saturation state control coccolithophorids production through time?**

### ABSTRACT

Ongoing carbon dioxide emissions are expected to severely impact ocean chemistry in the next few decades. The most important consequences are rising sea-surface temperatures and ocean acidification, i.e., decreases in sea-water  $pH$ , carbonate ion concentration and saturation state of calcium carbonate. In particular, ocean acidification deeply impacts marine organisms, especially calcifying biota (e.g. corals, foraminifera and coccolithophorids) and is considered as a major threat for biomineralization (Beaufort et al., 2011). Coccolithophorids (Haptophyte algae) species living in surface oceanic layers are particularly sensitive to chemical and physical conditions in shallow waters. Coccolithophorids are the only phytoplanktonic organisms to perform at the same time photosynthesis and biocalcification, participating to the carbon organic and inorganic pumps (Rost and Riebesell, 2004). Recent works show that biocalcification could be severely hampered under the current ocean acidification eventually leading to profound changes in marine ecosystems (Fabry et al., 2008). Some studies, however, point to a particular resilience of coccolithophorids to past ocean acidification events, and suggest that temperatures could be the main environmental factor controlling biocalcification (Gibbs, 2016).

Although the response of coccolithophorids to short term changes in temperature,  $pCO_2$  or  $pH$  is well constrained by the increasing number of studies on cultured or surface-water samples, the long term species-specific resilience to change in these environmental parameters, as well as the secular potential to overcome critical conditions, is poorly known. The long-term response of coccolithophorids to changes in temperature,  $pCO_2$  or  $pH$  can be only approached by studying the fossil record. The main scientific question of my PhD regards the role played by past severe  $pCO_2$  changes on coccolithophore calcification. Our working hypothesis is that this parameter did not act directly on biocalcification potential but indirectly, by enhancing temperature and continental weathering which in turn affected ocean alkalinity. In fact, in times of enhanced weathering, increased fluxes occurred of  $Ca^{2+}$  and  $HCO_3^-$  to ocean surface waters.

We selected two past global events characterized by perturbation of the carbon

cycle likely associated with fluctuations of CO<sub>2</sub>, namely the Pliensbachian-Toarcian (~183 My ago; PI-To event and T-OAE) and the Paleocene-Eocene (~55 My; PETM). They are also associated to warming (hyperthermal), but they differ because only the former records more widespread organic matter deposits, referred to as black shales. A first important part of my PhD was to develop a high-resolution calcareous nanofossils biostratigraphy for the two events, given that this is the basis for any paleoceanographic study. For both case studies, I plotted the nanofossil events against the  $\delta^{13}\text{C}$  stable isotopes curve in order to define the precise ranking of the bioevents and correlate remote localities.

In order to assess the impact of carbon perturbations, ocean acidification or temperature variations on coccolithophorids, and to appraise the eventual recovery to pre-event conditions, we analyzed changes in fossil coccoliths assemblage composition, absolute abundances (nanofossils/grams of rock) and fluxes (nanofossils/square meter/year) for these two events. For the Pliensbachian-Toarcian interval I studied three sections from Spain (La Almunia), France (Anse St. Nicolas) and United Kingdom (Mochras). For the PETM I focused on the study of the references ODP Sites 1209 (Shatsky Rise), located in the Tropical Pacific and 1263, in the Atlantic Ocean (Walvis Ridge). Also, I compare PETM deep-sea records to a proximal section in Tunisia (Kharouba) in order to compare the response of calcareous nanofossils in similar depositional environments across the two-time interval. For both events, I compare these sections to literature data in order to provide a global perspective of the paleoceanographic changes that affected these planktonic organisms. For both events, nanofossils assemblages suggest to warming-induced ocean stratification and lowered nutrient availability as main triggers for diminished calcium carbonate export into the ocean. Using a methodology recently developed in the host institute (Brazier et al., 2015), I investigated changes in ocean carbonate chemistry for the PETM through the use of the calcium isotope composition of the shells of one species of planktonic foraminifera, which has been shown to track changes in carbonate saturation and carbonate ions concentrations.

Our findings also corroborate empirical and modeling data suggesting that anthropogenic warming-induced ocean stratification will strongly impact primary productivity, carbon budgets and ecosystems.

Keywords : PETM, T-OAE, Pliensbachian-Toarcian, calcareous nannofossils, pelagic carbonate production, carbon cycle, calcium cycle

Discipline: Earth Sciences, Biostratigraphy, Paleoceanography



## Résumé étendu en français

Les émissions de dioxyde de carbone devraient avoir un impact important sur la chimie des océans au cours des prochaines décennies. Les conséquences les plus importantes sont l'augmentation des températures des eaux de surface et l'acidification des océans, c'est-à-dire la diminution du  $pH$  de l'eau de mer, de la concentration en ions carbonate et de l'état de saturation du carbonate de calcium. En particulier, l'acidification des océans a un impact profond sur les organismes marins, notamment sur les organismes calcifiants (par exemple les coraux, les foraminifères et les coccolithophores) et est considérée comme une menace majeure pour la biominéralisation (Beaufort et al., 2011). Les espèces de coccolithophoridés (algues haptophytes) vivant dans les couches océaniques de surface sont particulièrement sensibles aux conditions chimiques et physiques des eaux peu profondes. Les coccolithophoridés sont les seuls organismes phytoplanctoniques à effectuer à la fois la photosynthèse et la biocalcification, participant aux pompes de carbone organique et inorganique (Rost et Riebesell, 2004). Des travaux récents montrent que la biocalcification pourrait être gravement affectée par l'acidification actuelle des océans, ce qui entraînerait à terme de profonds changements dans les écosystèmes marins (Fabry et al., 2008). Cependant, certaines études soulignent une résilience particulière des coccolithophores aux événements passés d'acidification des océans, et suggèrent que les températures pourraient être le principal facteur environnemental contrôlant la biocalcification (Gibbs, 2016).

Bien que la réponse des coccolithophores aux changements à court terme de température, de la  $pCO_2$  ou du  $pH$  est bien connue par le nombre croissant d'études sur des échantillons d'eau de culture ou de surface, la résilience au niveau spécifique à long terme face aux changements de ces paramètres environnementaux, ainsi que le potentiel séculaire de surmonter les conditions critiques, sont mal connus. La réponse à long terme des coccolithophores aux changements de température, de  $pCO_2$  ou de  $pH$  ne peut être abordée qu'en étudiant le record fossile, étant donné que les coccolithophores possèdent un enregistrement fossile excellent depuis leur apparition au Trias supérieur. La principale question scientifique de mon doctorat concerne le rôle joué par les changements sévères de  $pCO_2$  passés sur la calcification des coccolithophores. Mon hypothèse de travail est que ce paramètre n'a pas agi

directement sur le potentiel de biocalcification mais indirectement, en augmentant la température et l'altération des continents qui, à leur tour, ont affecté l'alcalinité des océans. En fait, en période d'altération accrue, des flux accrus de  $\text{Ca}^{2+}$  et de  $\text{HCO}_3^-$  se sont produits dans les eaux de surface des océans.

J'ai sélectionné deux événements caractérisés par une perturbation du cycle du carbone probablement associé aux fluctuations du  $\text{CO}_2$ , notamment le Pliensbachien-Toarcien (~183 My ago ; PI-To event et T-OAE) et le Paléocène-Eocène (~55 My ; PETM). Ils sont également associés au réchauffement (hyperthermique), mais ils diffèrent car seulement le premier enregistre des dépôts de matière organique plus importants, appelés *black shales*. En utilisant une méthodologie récemment développée au Laboratoire de Géologie de Lyon (Brazier et al., 2015), j'ai étudié les changements de la chimie des carbonates océaniques pour le PETM en utilisant la composition isotopique du calcium des coquilles d'une espèce de foraminifères planctoniques, qui s'est avérée suivre les changements de la saturation en carbonate et des concentrations en ions carbonate.

Nos résultats corroborent également les données empiriques et de modélisation suggérant que la stratification des océans induite par le réchauffement anthropique aura un impact important sur la productivité primaire, les bilans carbonés et les écosystèmes.

Dans ce résumé étendu je synthétise les résultats principaux pour chaque chapitre de la thèse.

Une première partie importante de mon doctorat a été de développer une biostratigraphie à haute résolution des nanofossiles calcaires pour les deux événements, parce que les zonations standards ne fournissent pas une résolution suffisante pour étudier de courts événements (200-500 kyrs) comme le PETM ou le T-OAE. Pour les deux cas d'études, j'ai représenté les événements à nanofossiles par rapport à la courbe des isotopes stables du carbone afin de trouver les événements qui permettent de corréler des localités éloignées. Pour l'intervalle Pliensbachien-Toarcien, j'ai étudié une section d'Espagne (La Almunia) et de France (Anse St. Nicolas). Pour le PETM, je me suis concentré sur l'étude des sites ODP de référence 1209 (Shatsky Rise), situés dans le Pacifique tropical et 1263, dans l'océan Atlantique (Walvis Ridge).

**Biostratigraphie pour l'intervalle Pliensbachien-Toarcien :** Plusieurs études ont porté sur la réponse des nanofossiles calcaires à l'événement anoxique de Toarcien (T-OAE), l'un des événements les plus dramatiques des perturbations environnementales de l'ère mésozoïque. Néanmoins, l'impact des perturbations environnementales marquées sur le nannoplancton calcaire pendant la transition Pliensbachien/Toarcien (PI/To ; ~183 Ma), légèrement avant le T-OAE, reste comparativement moins bien documenté. Je présente une étude biostratigraphique et chimiostratigraphique à haute résolution de deux sections où la limite Pliensbachien/Toarcien est bien représenté. Une section est située dans le centre de l'Espagne (La Almunia) et la seconde dans le nord-ouest de la France (Anse St. Nicolas). Bien que les deux localités aient été paléographiquement proches l'une de l'autre au Jurassique Inferieur, les dissimilitudes dans les assemblages de nanofossiles suggèrent des conditions paléoenvironnementales différentes. Au-dessus de la limite PI/To, les abondances absolues (nanofossiles/gramme de roches) et les placolites ont augmenté de manière substantielle dans les deux sections. De même, les isotopes du carbone montrent une tendance à la hausse et une excursion négative à la limite. La comparaison de nos nouvelles données avec sept autres sections de la marge nord et sud de Téthys, montre que le PI/To correspondait à un événement majeur de diversification des coccolithes. La spéciation du PI/To a provoqué une réorganisation majeure des assemblages, notamment les murolithes dominant au Pliensbachien Supérieur alors que les placolithes deviennent le groupe dominant à partir du Toarcien Inferieur. Quelques différences sont observées d'une section à l'autre, mais plusieurs premières apparitions (FO) d'espèces sont biostratigraphiquement utiles pour la définition de la limite PI/To, comme la FO de *Biscutum intermedium*, *Zeughrabdothus erectus* et *Discorhabdus ignotus*. La perturbation du cycle du carbone à la limite PI/To s'est produite lors d'un épisode de transgression après un refroidissement prononcé et une baisse du niveau marin qui ont déclenché des hiatus dans de nombreuses localités. La spéciation des nanofossiles calcaires au PI/To est étroitement lié à tous ces phénomènes. Ainsi, cet événement doit être considéré comme le début de profondes perturbations paléoenvironnementales qui ont culminent avec le T-OAE.

**Biostratigraphie pour le PETM :** La limite Paléocène-Eocène est caractérisée par une excursion négative importante des isotopes du carbone qui correspond au

maximum thermique de l'éocène du paléocène (PETM). La forte excursion négative des isotopes stables du carbone a été retenue comme marqueur de la limite Paléocène-Éocène. Bien qu'elles aient été enregistrées dans plusieurs milieux océaniques et terrestres, les phases du PETM définies par Zachos et al., 2005 et Röhl et al., 2007 (*onset*, *core* de l'événement et *recovery*), ne sont pas correctement datées par les nanofossiles calcaires car les biozonations standard disponibles ne nous permettent pas d'obtenir une résolution suffisante. Je présente de nouvelles données biostratigraphiques à haute résolution provenant des sites 1209 (Shatsky Rise, océan Pacifique tropical) et 1263 (Walvis Ridge, océan Atlantique sud-est) afin de reconstruire précisément la succession des événements biostratigraphiques (première et dernière apparitions, changements dans la composition de l'assemblage), et de les ancrer à un proxy indépendant représenté par la courbe des isotopes stables du carbone. Grâce à une comparaison soignée de nos données avec des événements nanofossiles provenant de six sections situées à différentes (paléo)latitudes et dans différents contextes géologiques (de l'océan ouvert aux coupes néritiques) j'ai reconnu 26 événements sur un intervalle de 250 kyrs couvrant le PETM, et je présente une biozonation à haute résolution de cet intervalle. Les événements de nanofossiles calcaires représentés par rapport à la courbe de  $\delta^{13}\text{C}$  disponibles montrent un certain degré de diachronisme, même en tenant compte des marqueurs de zone précédemment établis. De plus, des discontinuités (*unconformities*) se produisent au début du PETM dans la plupart des sites océaniques, mais dans une moindre mesure dans les sections qui affleurent sur les continents. Je propose une nouvelle biozonation, basée sur des événements reproductibles dans différentes localités, afin d'obtenir une subdivision chronostratigraphique à haute résolution pour cet événement hyperthermique. Je définis ainsi quatre nouvelles zones couvrant le Paléocène supérieur et l'Éocène inférieur qui permettent de corréliser les localités proximales et distales, et deux sous-zones principalement utiles dans les environnements proximaux. Ces nouvelles zones sont corrélées aux principales tendances de la courbe des isotopes stables du carbone ( $\delta^{13}\text{C}$ ) et définissent l'intervalle de pré-excursion (PE-1), l'excursion négative du  $\delta^{13}\text{C}$  définissant la base de l'Eocène (PE0), le *core* de l'événement et la phase de récupération I (*recovery* I ; PE1) et les intervalles de la phase de récupération II (*recovery* II ; PE2)

Un deuxième aspect fondamental de mon travail de thèse a été l'étude de l'impact des perturbations du cycle du carbone, de l'acidification des océans ou des variations de température sur la biocalcification des coccolithophores au cours des temps géologiques, et d'évaluer le retour aux conditions précédentes à ces perturbations. Pour ce faire, j'ai analysé les changements dans la composition des assemblages de coccolithes fossiles, les abondances absolues (nanofossiles/gramme de roche) et les flux ou NAR (*nannofossil accumulation rate* ; nanofossiles/mètre carré/an) pour ces deux événements. Pour l'intervalle Pliensbachien-Toarcien, j'ai étudié trois sections d'Espagne (La Almunia), de France (Anse St. Nicolas) et du Royaume-Uni (Mochras). Pour le PETM, je me suis concentré sur l'étude des sites ODP de référence 1209 (Shatsky Rise), situés dans le Pacifique tropical et 1263, dans l'océan Atlantique (Walvis Ridge). De plus, je compare les enregistrements du PETM en eaux profondes à une section proximale en Tunisie (Kharouba) afin d'examiner la réponse des nanofossiles calcaires dans des environnements de dépôt similaires sur l'intervalle de deux temps. Pour les deux événements, je compare ces sections aux données de la littérature afin de fournir une perspective globale des changements paléocéanographiques qui ont affecté ces organismes planctoniques. Pour les deux événements, les assemblages de nanofossiles suggèrent que la stratification des océans induite par le réchauffement et la diminution de la disponibilité des nutriments sont les principaux facteurs déclenchant la diminution de l'export de carbonate dans l'océan profond.

**Assemblages et paleocénographie pour le Pliensbachien-Toarcien :** Le scénario classique d'interprétation de l'événement anoxique de Toarcien Inférieur (T-OAE ; ~183 Ma) et de l'excursion négative associée est généralement lié à la libération massive de carbone léger ( $^{12}\text{C}$ ) dans les réservoirs de surface, en raison de la mise en place des larges provinces magmatiques des Karoo-Ferrar, de la déstabilisation des hydrates de méthane des marges continentales, ou de la libération thermogénique de méthane due à la mise en place des filons-couches au Karoo-Ferrar. Quelle qu'en soit la cause, on pense que cette libération massive de carbone a favorisé les conditions d'effet de serre, l'amélioration du cycle hydrologique et l'altération des continents. Ces conditions ont finalement favorisé l'apport de nutriments aux bassins peu profonds, soutenant la productivité primaire et, en raison de la consommation

d'oxygène par la respiration de la matière organique, le développement de l'anoxie océanique.

Cependant, plusieurs travaux ont montré que les producteurs primaires, comme les nanofossiles calcaires et les dinoflagellés, ont connu une crise grave pendant le T-OAE, qui a culminé avec une panne de phytoplancton. Par ailleurs, les flux de matière organique ne semblent pas exceptionnels. L'analyse de la taille des nanofossiles dans le trou de forage de Mochras (foré par la BGS en Pays de Galle, Royaume Uni) peut nous aider à résoudre cette énigme. La récupération sédimentaire de la carotte est excellente, la section est continue et bien datée et a fait l'objet d'analyses à haute résolution, ce qui en fait un candidat idéal pour analyser l'évolution combinée de la production de carbonate et de la production primaire. Grâce à la combinaison de la biométrie et des abondances absolues (spécimens par g de roche), nous pouvons estimer les flux de carbonates et de matière organique d'origine nanofossile vers les sédiments. Nous pouvons comparer ces résultats au  $\delta^{13}\text{C}$ , qui reflète les perturbations du cycle du carbone au Toarcien inférieur. Cette étude devrait nous permettre de mieux évaluer les mécanismes d'exportation du carbone inorganique et organique des eaux océaniques de surface vers les sédiments lors des changements climatiques et environnementaux majeurs qui se sont produits au Toarcien.

**Assemblages et paléocéanographie pour le PETM :** Le réchauffement climatique et la perturbation du cycle du carbone autour de la limite Paléocène-Éocène (PETM, environ 56 Ma) ont été liés à une libération massive de carbone dans le système océan-atmosphère. Des études précédentes ont invoqué une augmentation de la productivité du phytoplancton pour provoquer une baisse de la  $p\text{CO}_2$ , un refroidissement et favoriser une récupération du système (*recovery*). Toutefois, les interprétations des données géochimiques et biotiques divergent quant au moment et au lieu où cette productivité accrue s'est produite. Je présente des données en haute résolution sur les assemblages de nanofossiles, y compris les abondances relatives et absolues (nanofossiles/gramme de roche) d'une section proximale située dans la Tethys (Kharouba) et de deux sites océaniques (sites ODP 1209 et 1263, situés respectivement dans les océans Pacifique et Atlantique) afin de suivre les tendances globales et locales des assemblages de nanofossiles. Ces données, combinées aux enregistrements biotiques publiés, indiquent une accentuation transitoire des gradients trophiques entre le *onset* et le *core* du PETM, avec une diminution de la

productivité dans les sites océaniques oligotrophes, parallèlement à une augmentation de la disponibilité des nutriments dans les zones proximales. Les niveaux de productivité se sont rétablis en domaine pélagique au cours du *recovery*, ce qui pourrait avoir joué un rôle important dans la séquestration du carbone et le retrait du CO<sub>2</sub> en association avec l'intensification de la météorisation continentale.

**Modulation du cycle du carbone par le phytoplancton pendant le PETM :** Le Maximum thermique à la limite Paléocène/Eocène du Paléocène (PETM, ~56 Ma), est considéré comme l'un des meilleurs analogues pour les émissions anthropiques de CO<sub>2</sub>. Pourtant, les principales rétroactions négatives qui ont éliminé l'excès de carbone lors de l'arrêt du PETM restent controversées. La saturation et l'enfouissement des CaCO<sub>3</sub>, dus à une altération accrue des silicates, sont communément acceptés comme les principaux processus moteurs. Par ailleurs, une baisse de la production nette de CaCO<sub>3</sub> des algues induites par le CO<sub>2</sub> pourrait avoir déclenché l'accumulation d'alcalinité et la sursaturation, mais ce mécanisme n'est toujours pas étayé par des preuves indirectes. Je présente une étude *multiproxy* des enregistrements des eaux profondes tropicales du Pacifique et de l'Atlantique qui démontre que l'enfouissement des carbonates s'est rétabli aux niveaux pré-PETM environ 30 000 ans plus tard que la saturation. Nous attribuons ce découplage à un effondrement spectaculaire (>60 %) et durable (>80 000 ans) de la production nette de CaCO<sub>3</sub> en raison de la stratification des océans induite par le réchauffement et de la diminution de la disponibilité des nutriments. Nos enregistrements montrent que l'excès d'alcalinité qui en résulte a été rapidement consommé lorsque la production et l'enfouissement du CaCO<sub>3</sub> ont finalement repris, déclenchant un retrait rapide et massif du carbone tant inorganique qu'organique. Nos conclusions en élucident certains des mécanismes biogéochimiques clés qui ont conduit à la récupération du PETM et soulignent l'importance négligée mais cruciale des seuils biologiques dans la régulation des événements passés et actuels du réchauffement de l'effet de serre.

**Conclusion et synthèse :** Le dernier chapitre de la thèse vise à comparer les deux intervalles de temps pour discuter des aspects similaires et des différences. Pour les deux événements les données biostratigraphiques ont été représentés par rapport à la courbe des isotopes stables du carbone ( $\delta^{13}\text{C}$ ). Pour le Pliensbachien-Toarcien, j'ai pu mettre en évidence qu'il y a un épisode majeur d'apparitions autour de la limite



Pliensbachien-Toarcien, contrairement au T-OAE. Ceci est en partie lié à l'augmentation des placolithes, qui domineront les assemblages pour le reste Mésozoïque et Cénozoïque et en partie liés à des condensations dans plusieurs bassins de la Tethys autour de la limite. Pour le PETM, j'ai pu mettre en évidence que le record sédimentaire a une influence majeure sur l'ordre des événements. Similairement au Pliensbachien-Toarcien, la présence de discontinuités à la limite explique certaines différences d'une localité à l'autre. Cependant, il existe un certain degré de diachronisme, affectant également les marques biostratigraphiques utilisées dans les zonations standards. La limite Paléocène-l'Éocène est caractérisée par plusieurs origines et extinctions, et aussi par des changements au sein des communautés de nanofossiles calcaires. Certains de ces événements, jamais pris en compte dans les biozonations antérieures, se sont avérés cohérents, avec un degré de diachronisme moindre que les marqueurs biostratigraphiques utilisés précédemment. Finalement j'obtiens un nouveau schéma de biozonation à haute résolution avec une résolution moyenne de 50-100 kyrs par zone. De plus, je corrèle les événements biostratigraphiques et les nouvelles zones aux différentes phases caractérisant l'excursion négative des isotopes du carbone définissant le Paléocène/Éocène.

En terme d'implications paleoceanographiques, malgré certaines différences, comme par exemple le fait que pour le Jurassique Inférieur nous ne disposons pas d'enregistrement d'océan ouvert, les changements des abondances absolues et des flux durant les deux événements, suggèrent une iperstratification et oligotrophie des eaux de surface. L'oligotrophie était plus marquée pendant le T-OAE, car même les zones plus proximales montrent une tendance à l'oligotrophie. Au PETM, l'oligotrophie était particulièrement accentuée dans les sites océaniques, loin des apports des rivières tandis que dans les coupes proximales on enregistre des conditions fluctuantes.

Un aspect fondamental de ce travail de thèse est l'étude *multiproxy* des enregistrements des eaux profondes tropicales du Pacifique et de l'Atlantique ; ces données démontrant que l'enfouissement des carbonates s'est rétabli à des niveaux pré-PETM environ 30 000 ans après la saturation. Ce découplage entre saturation et enfouissement des carbonates est expliqué par un effondrement spectaculaire (>60 %) et durable (>80 000 ans) de la production nette de  $\text{CaCO}_3$ , dû à la stratification des océans induite par le réchauffement et à la diminution de la disponibilité des nutriments. L'excès d'alcalinité qui en résulte a été rapidement consommé lorsque la



production et l'enfouissement du  $\text{CaCO}_3$  ont finalement repris, déclenchant un retrait rapide et massif du carbone tant inorganique qu'organique. Ces conclusions élucident certains des mécanismes biogéochimiques clés qui ont conduit à la récupération du PETM et soulignent l'importance négligée mais cruciale des seuils biologiques et donc de la biologie dans la régulation des événements passés et actuels du réchauffement de l'effet de serre.



# Chapitre 1. Introduction

## Introduction

### 1. Les perturbations présentes et futures du cycle inorganique du carbone.

Les émissions de dioxyde de carbone devraient avoir un impact important sur la chimie des océans au cours des prochaines décennies. Les conséquences les plus importantes sont l'augmentation des températures des eaux de surface et l'acidification des océans, c'est-à-dire la diminution du  $pH$  de l'eau de mer, de la concentration en ions carbonate et de l'état de saturation du carbonate de calcium. La valeur du  $CO_2$  atmosphérique aujourd'hui est supérieure de 100 ppmv à la valeur préindustrielle (280 ppmv), et le  $pH$  moyen de la surface de l'océan a baissé de 0,1 unité, ce qui représente une augmentation d'environ 30 % de  $[H^+]$ . Selon les prévisions du GIEC (Houghton et al., 2001), le  $pH$  moyen de l'océan de surface pourrait diminuer de 0.3-0.4 unité par rapport aux valeurs préindustrielles à la fin de ce siècle (Caldeira et Wickett, 2005).

En particulier, l'acidification des océans a un impact profond sur les organismes marins, notamment sur les organismes calcifiants (par exemple les coraux, les foraminifères et les coccolithophores) et est considérée comme une menace majeure pour la biominéralisation (Beaufort et al., 2011). Les espèces de coccolithophoridés (algues haptophytes) vivant dans les couches océaniques de surface sont particulièrement sensibles aux conditions chimiques et physiques des eaux peu profondes. Les coccolithophoridés sont les seuls organismes phytoplanctoniques à effectuer à la fois la photosynthèse et la biocalcification, participant aux pompes de carbone organique et inorganique (Rost et Riebesell, 2004). Des travaux récents montrent que la biocalcification pourrait être gravement affectée par l'acidification actuelle des océans, ce qui entraînerait à terme de profonds changements dans les écosystèmes marins (Fabry et al., 2008). Cependant, certaines études soulignent une résilience des coccolithophores aux événements passés d'acidification des océans (Iglésias-Rodríguez et al., 2008), et suggèrent que les températures pourraient être le principal facteur environnemental contrôlant la biocalcification (Gibbs, 2016).

Grace au nombre croissant d'études sur des échantillons d'eau de culture ou de surface, la réponse des coccolithophores aux changements à court terme de température, de la  $pCO_2$  ou du  $pH$  est bien connue mais la résilience au niveau

spécifique à long terme face aux changements de ces paramètres environnementaux, ainsi que le potentiel séculaire de surmonter les conditions critiques, sont difficiles à quantifier. La réponse à long terme des coccolithophores aux changements de température, de  $p\text{CO}_2$  ou de  $\text{pH}$  ne peut être abordée qu'en étudiant le record fossile.

## **2. Les coccolithophores dans les océans**

Les coccolithophores sont des algues unicellulaires de taille micrométrique du domaine Eukaryota, de l'embranchement Haptophyta et de la classe Prymniophyceae (Billard et Inouye, 2004). Ces algues photosynthétiques produisent à l'intérieur de leur cellule à l'aide de l'appareil de Golgi des plaques composées de carbonate de calcium ( $\text{CaCO}_3$ ) appelées coccolithes. Ces plaques sont ensuite transportées sur la bordure externe de la cellule pour former un teste appelé coccosphère. Les coccolithophores sont des organismes pélagiques exclusivement marins, très diversifiés en nombre d'espèces et extrêmement abondant dans les océans. A la base de la chaîne alimentaire dans les océans, ils participent à la fois par la photosynthèse et la biocalcification au cycle organique et inorganique du carbone. Malgré leur petite taille, leur contribution dans le cycle du carbone est extrêmement importante puisqu'ils produisent environ la moitié du carbonate pélagique total, notamment par le biais de *blooms*. Un *bloom* correspond à la multiplication massive d'une espèce pendant une courte période et lorsque les conditions environnementales sont favorables. Ces événements entraînent une production phénoménale de carbonate de calcium. Les coccolithophores ont une position clés dans les environnements marins actuels, de par leur base dans la chaîne alimentaire et leur rôle majeur dans le cycle du carbone.

## **3. Une longue histoire évolutive**

Les coccolithophores sont très souvent préservées sous forme de coccolithes isolées dans les sédiments et font partie des nanofossiles calcaires. Ce groupe inclut tous les restes minéralisés issus d'organismes pélagiques micrométriques à test calcaire, indifféremment de leur affinité taxinomique. Les plus anciens nanofossiles calcaires sont représentés par des calcisphères du Carnien (Trias supérieur, 228 Ma) ; les plus anciens coccolithes datent du Norien (Trias supérieur, 210 Ma) (Bown, 1987-1998), appartenant au groupe morphologique des murolithes. Les placolithes, la forme la plus répandue dans l'histoire de coccolithes, n'apparaissent qu'au début du Pliensbachien (Jurassique Inférieur, 190 Ma) et se diversifient très rapidement à la limite

Pleinsbachien-Toarcien (183 Ma). La longue histoire évolutive des nanofossiles calcaires a été affectée par de nombreux épisodes de crise drastique (e.g., la limite Crétacé/Paléocène ; la limite Paléocène/Eocène) et d'épisodes de diversification (e.g., la limite Pliensbachien/Toarcien, Jurassique moyen ; Suchéras-Marx et al., 2019) qui sont associés à des perturbations des principaux cycles biogéochimiques, tels que des changements de la  $p\text{CO}_2$ , de température ou du  $\text{pH}$ . Bien que la réponse des coccolithophores aux changements à court terme de température, de la  $p\text{CO}_2$  ou du  $\text{pH}$  est bien connue par le nombre croissant d'études sur les coccolithophores actuelles, la résilience au niveau spécifique à long terme face aux changements de ces paramètres environnementaux, ainsi que le potentiel séculaire de surmonter les conditions critiques, sont mal connus. La réponse à long terme des coccolithophores aux changements de température, de  $p\text{CO}_2$  ou de  $\text{pH}$  ne peut être abordée qu'en étudiant le record fossile. La principale question scientifique de mon doctorat concerne le rôle joué par les changements sévères de  $p\text{CO}_2$  passés sur la calcification des coccolithophores. Mon hypothèse de travail est que ce paramètre n'a pas agi directement sur le potentiel de biocalcification mais indirectement, en augmentant la température et l'altération des continents qui, à leur tour, ont affecté l'alcalinité des océans. En fait, en période d'altération accrue, des flux accrus de  $\text{Ca}^{2+}$  et de  $\text{HCO}_3^-$  se sont produits dans les eaux de surface des océans.

#### **4. Cas d'études : le PETM et le Pliensbachien/Toarcien**

Pour répondre à la question scientifique de ce projet de recherche, j'ai sélectionné deux cas d'études : le Maximum Thermique à la limite Paléocène-Eocène (PETM ; 56 Ma) et le Pliensbachien-Toarcien (limite Pliensbachien-Toarcien et l'événement anoxique océanique du Toarcien inférieur ou T-OAE; 183 Ma). Des études précédentes ont mis en évidence que les deux événements présentent de nombreuses caractéristiques communes (Cohen et al., 2007) :

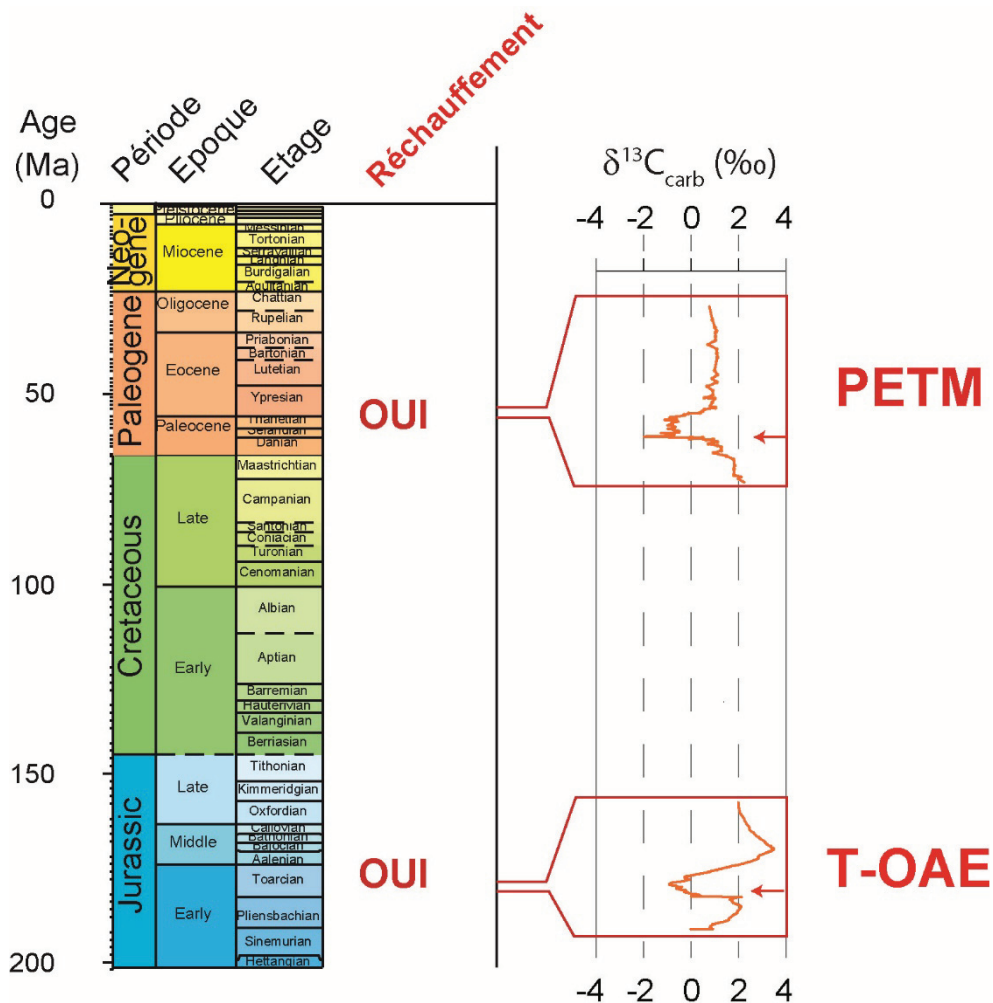


Fig. 1. Représentation des deux cas d'études par rapport à l'échelle des temps géologiques (Gradstein et al., 2012).

- Le grand nombre des enregistrements couvrant le PETM démontre que la perturbation du cycle du carbone a eu une portée mondiale (e.g., Kennet and Stott, 1991 ; Zachos et al., 2003 ; Zachos et al., 2005), et la reconnaissance de l'excursion négative des isotopes du carbone de Toarcien dans les sections de plateformes continentales appartenant à tous les océans, dans des sections épicontinentales et dans des échantillons de bois fossilisé indiquent très probablement un événement mondial (Jenkyns, 1985; Jenkyns et al. 2002).
- Le shift négative du  $\delta^{13}\text{C}$  qui définit les excursions négatives des isotopes du carbone au PETM et pendant le Toarcien était entre 2 ‰ et 7 ‰ et est observé dans les enregistrements de  $\delta^{13}\text{C}$  mesuré sur des carbonates  $\delta^{13}\text{C}_{\text{bulk carbonate}}$  (e.g., Hesselbo et al., 2007; Bains et al., 1999; Zachos et al., 2005) et sur la

matière organique totale  $\delta^{13}\text{C}_{\text{TOC}}$  qui couvrent les deux intervalles (Pagani et al., 2006; Sluijs et al., 2006; Xu et al., 2018)

- Les deux excursions négatives des isotopes du carbone ont été associées à des accumulations exceptionnellement élevées de carbone organique dans les plateformes continentales et dans les environnements marins épicontinentaux, le COT atteignant environ 15 % à environ 20 % dans certaines sections (Sluijs et al., 2006).
- Les deux excursions négatives des isotopes du carbone ont été associées à des extinctions d'espèces et phytoplancton dans les océans, avec des réorganisations majeures des espèces sur les continents, et avec la preuve d'une soudaine crise mondiale (Bown, 1987 ; Bralower et al., 2002 ; Gibbs et al., 2006b ; Mattioli et al., 2008).
- L'augmentation du lessivage continentale, comme l'indiquent des changements soudains dans la minéralogie des argiles et par une excursion des isotopes de l'osmium au PETM (Ravizza et al., 2001 ; Dickson et al., 2015), et par des excursions abruptes et importantes de isotopes du strontium, de l'osmium et du calcium (McArthur et al., 2000; Cohen et al., 2004 ; Brazier et al., 2015 ; Percival et al., 2016) pendant le T-OAE.

Bien que plusieurs études se sont focalisées sur la réponse du phytoplancton calcaire aux changements environnementaux durant le PETM et le Pliensbachien-Toarcien, la quantification de la productivité carbonatée versus productivité primaire en réponse aux perturbations du cycle du carbone, de température et de chimie des océans ainsi que l'étude approfondie du rôle du phytoplancton calcaire dans le mécanismes de récupération du système aux conditions précédentes n'a jamais été faite auparavant.

Une première partie importante de mon doctorat a été de développer une biostratigraphie à haute résolution des nanofossiles calcaires pour les deux événements, parce que les zonations standards ne fournissent pas une résolution suffisante pour étudier de courts événements tels que le PETM ou le T-OAE. Pour les deux cas d'études, j'ai représenté les événements à nanofossiles par rapport à la courbe des isotopes stables du carbone afin de trouver les événements qui permettent de corréler des localités éloignées. Pour l'intervalle Pliensbachien-Toarcien, j'ai étudié



une section d'Espagne (La Almunia) et de France (Anse St. Nicolas). Pour le PETM, je me suis concentré sur l'étude des sites océaniques ODP (Ocean Drilling Program) 1209 (Shatsky Rise), situés dans le Pacifique tropical et 1263, dans l'océan Atlantique (Walvis Ridge). Ces deux sites enregistrent très finement l'excursion négative des isotopes du carbone et en étant les sites océaniques les moins profonds de l'Atlantique et du Pacifique, sont véritablement les moins affectés par la dissolution généralisée des carbonates due à la remontée de la CCD pendant le PETM (Zachos et al., 2003 ; Zachos et al., 2005 ; Takeda et Kaiho, 2007 ; Bralower et al., 2014). En étant deux sections de référence pour cette intervalle de temps, de nombreuses études de littérature (e.g., géochimie, micropaléontologie, sédimentologie) existent déjà

Un deuxième aspect fondamental de mon travail de thèse était l'étude de l'impact des perturbations du cycle du carbone, de l'acidification des océans ou des variations de température sur les coccolithophores au cours des temps géologiques, et d'évaluer le retour aux conditions d'avant l'événement. Pour ce faire, j'ai analysé les changements dans la composition des assemblages de coccolithes fossiles, les abondances absolues (nanofossiles/gramme de roche) et les flux (ou NAR, nanofossil accumulation rates ; nanofossiles/mètre carré/an) pour ces deux événements. Pour l'intervalle Pliensbachien-Toarcien, j'ai étudié trois sections d'Espagne (La Almunia), de France (Anse St. Nicolas) et du Royaume-Uni (Mochras). Pour le PETM, je me suis concentré sur l'étude des sites ODP 1209 (Shatsky Rise), situés dans le Pacifique tropical et 1263, dans l'océan Atlantique (Walvis Ridge). De plus, je compare les enregistrements du PETM en eaux profondes à une section proximale en Tunisie (Kharouba) afin d'examiner la réponse des nanofossiles calcaires dans des environnements de dépôt similaires sur l'intervalle de deux temps. Pour les deux événements, je compare ces sections aux données de la littérature afin de fournir une perspective globale des changements paléocéanographiques qui ont affecté ces organismes planctoniques. Pour les deux événements, les assemblages de nanofossiles suggèrent que la stratification des océans induite par le réchauffement et la diminution de la disponibilité des nutriments sont les principaux facteurs déclenchant la diminution de l'export de carbonate dans l'océan profond.

## 5. Biostratigraphie pour l'intervalle Pliensbachien-Toarcien

Dans ce chapitre du manuscrit, je me suis intéressé à la construction d'une biostratigraphie à très haute résolution pour la limite Pliensbachien-Toarcien. Ce chapitre a fait l'objet d'une publication dans la revue internationale *Newsletters on Stratigraphy* en 2019. Plusieurs études ont porté sur la réponse des nanofossiles calcaires à l'événement anoxique de Toarcien (T-OAE), l'un des événements les plus dramatiques des perturbations environnementales de l'ère Mésozoïque. Néanmoins, l'impact des perturbations environnementales marquées sur les nanofossiles calcaires pendant la transition Pliensbachien/Toarcien (PI/To ; ~183 Ma), légèrement avant le T-OAE, reste comparativement moins bien documenté. Dans ce chapitre, je présente une étude biostratigraphique et chemostratigraphique à haute résolution de deux sections où le PI/To est bien représenté. Une section est située dans le centre de l'Espagne (La Almunia) et la seconde dans le nord-ouest de la France (Anse St. Nicolas). Bien que les deux localités aient été proches l'une de l'autre au Jurassique précoce, les dissimilitudes dans les assemblages de nanofossiles suggèrent des conditions paléoenvironnementales différentes. Après la limite PI/To, les abondances absolues (nanofossiles/gramme de roches) et les placolithes (un groupe de coccolithes à structure emboîté, Young et al., 1994) augmentent de manière substantielle dans les deux sections. De même, les isotopes du carbone montrent une tendance à la hausse et une excursion négative est constatée à la frontière. La comparaison de nos nouvelles données avec sept autres sections de la marge nord et sud de Téthys, montre que le PI/To correspondait à un événement majeur de diversification des coccolithes. La spéciation du PI/To a provoqué un passage prononcé des murolithes aux placolithes. Quelques différences sont observées d'une section à l'autre, mais plusieurs premières apparitions (FO) d'espèces et une réorganisation des assemblages sont documentées dans toutes les localités. Certaines de ces FO sont biostratigraphiquement utiles pour la définition de la limite PI/To, comme la FO de *Biscutum intermedium*, *Zeugrhabdothus erectus* et *Discorhabdus ignotus*. La perturbation du cycle du carbone à la limite PI/To s'est produite lors d'un épisode de transgression après un refroidissement prononcé et une baisse du niveau de la mer qui ont déclenché des hiatus dans de nombreuses localités. L'événement à l'origine des nanofossiles calcaires est étroitement lié à tous ces phénomènes. Ainsi, l'événement PI/To doit être considéré comme le début de profondes perturbations paléoenvironnementales qui ont culminé avec le T-OAE.

## 6. Biostratigraphie pour le PETM.

Dans ce chapitre du manuscrit, je me suis intéressé à la construction d'une biostratigraphie à très haute résolution pour la limite Paléocène-Eocène, similairement au chapitre précédent. Ce chapitre fait l'objet d'une publication qui est actuellement en cours de révision dans la revue internationale *Newsletters on Stratigraphy*. La limite Paléocène-Eocène est caractérisée par une excursion négative importante des isotopes du carbone qui correspond au maximum thermique de l'éocène du paléocène (PETM). La forte excursion négative des isotopes stables du carbone a été retenue comme marqueur de la limite Paléocène-Éocène. Bien qu'elles aient été enregistrées dans plusieurs milieux océaniques et terrestres, les phases du PETM, notamment le *onset*, le *core* de l'événement et la *recovery*, ne sont pas correctement datées par les nanofossiles calcaires car les biozonations standard disponibles ne nous permettent pas d'obtenir une résolution suffisante. Je présente de nouvelles données biostratigraphiques à haute résolution provenant des sites 1209 (Shatsky Rise, océan Pacifique tropical) et 1263 (Walvis Ridge, océan Atlantique sud-est) afin d'évaluer précisément la succession des événements biostratigraphiques (première et dernière apparitions, changements dans la composition de l'assemblage), et de les ancrer à un proxy indépendant représenté par la courbe des isotopes du carbone. Grâce à une comparaison soignée de nos données avec des événements nanofossiles provenant de six sections situées à différentes (paléo)latitudes et dans différents contextes géologiques (du large au plateau continental) j'ai reconnu 26 événements à nanofossiles calcaires sur un intervalle de 250 kyrs couvrant le PETM, et je présente une subdivision à haute résolution de cet intervalle. Les événements de nanofossiles calcaires tracés par rapport aux courbes de  $\delta^{13}\text{C}$  disponibles montrent un certain degré de diachronisme, même en tenant compte des marqueurs zonaux précédemment établis. De plus, des non-conformités se produisent au début du PETM dans la plupart des sites océaniques, mais dans une moindre mesure dans les sections qui affleurent sur les continents. Je propose une nouvelle biozonation, basée sur des événements reproductibles dans différentes localités, afin d'obtenir une subdivision chronostratigraphique à haute résolution pour cet événement hyperthermique. Je définis ainsi quatre nouvelles zones couvrant le Paléocène supérieur et l'Éocène inférieur qui permettent de corréler les localités proximales et distales, et deux sous-zones principalement utiles dans les environnements proximaux. Ces nouvelles zones

sont corrélées aux principales tendances de la courbe des isotopes stables du carbone ( $\delta^{13}\text{C}$ ) et définissent l'intervalle de pré-excursion (PE-1), l'excursion négative du  $\delta^{13}\text{C}$  définissant la base de l'Eocène (PE0), le *core* de l'événement et la phase de récupération I (*recovery* I ; PE1) et les intervalles de la phase de récupération II (*recovery* II ; PE2).

## 7. Assemblages et paléocéanographie pour le Pliensbachien-Toarcien

Une fois obtenue une biostratigraphie à une résolution suffisante, je me suis intéressé à la réponse des assemblages à nanofossiles calcaires aux perturbations environnementales durant l'évènement à la limite Pliensbachien-Toarcien et l'évènement océanique anoxique du Toarcien Inferieur (183 Ma). Ce chapitre fait l'objet d'un papier qui sera soumis en Octobre au volume spécial intitulé « Carbon Cycle and Ecosystem Response to the Jenkyns Event in the Early Toarcian (Jurassic) » qui sera publié dans le Journal of the Geological Society of London.

Le Jurassique Inferieur a été marqué par de multiples périodes de changements climatiques et paléocéanographiques, de changements d'assemblages au sein des écosystèmes benthiques et planctoniques et de perturbations des principaux cycles géochimiques, généralement liés au volcanisme des grandes provinces ignées. Des études antérieures portant sur les nanofossiles calcaires montrent que l'intervalle de temps couvrant le Pliensbachien inférieur et le Toarcien inférieur est caractérisé par une diversification majeure de ce groupe d'algues planctoniques. Au cours des dernières décennies, plusieurs études ont porté sur la réponse des nanofossiles calcaires aux perturbations environnementales du Pliensbachien Supérieur et du Toarcien Inferieur dans le sud de l'océan Téthys. Des études récentes se sont focalisées sur des localités éloignées de la Tethys, tels que le bassin de Néquen, le bassin andin et le Tibet.

Je présente de nouvelles données sur les nanofossiles calcaires provenant du forage Mochras, la section la plus épaisse du Jurassique Inferieur, afin de comprendre les changements de la production primaire et carbonatée en réponse aux changements paléoenvironnementaux dans le Pliensbachien Supérieur et le Toarcien Inferieur. Pour ce faire, j'ai calculé l'abondance absolue et les flux des nanofossiles et je les compare aux données géochimiques et sédimentologiques disponibles. Enfin, en comparant le forage de Mochras avec d'autres sections du même âge, je discute la relation entre les changements paléoenvironnementaux et la production primaire.

## 8. Assemblages et paléocéanographie pour le PETM

Le réchauffement climatique et la perturbation du cycle du carbone autour de la limite Paléocène-Éocène (PETM, environ 56 Ma) ont été liés à une libération massive de carbone dans le système océan-atmosphère. Des études précédentes ont invoqué une augmentation de la productivité du phytoplancton pour provoquer une baisse de la  $p\text{CO}_2$ , un refroidissement et une récupération environnementale. Toutefois, les interprétations des données géochimiques et biotiques divergent quant au moment et au lieu où cette productivité accrue s'est produite. Je présente des données en haute résolution sur les assemblages de nanofossiles, y compris les abondances relatives et absolues (nanofossiles/gramme de roche) d'une section proximale située dans la Tethys (Kharouba) et de deux sites océaniques (sites ODP 1209 et 1263), situés respectivement dans les océans Pacifique et Atlantique) afin de suivre les tendances globales et locales des assemblages de nanofossiles. Ces données, combinées aux enregistrements biotiques publiés, indiquent une accentuation transitoire des gradients trophiques entre le *onset* et le *core* du PETM, avec une diminution de la productivité dans les sites océaniques oligotrophes, parallèlement à une augmentation de la disponibilité des nutriments dans les zones proximales. Les niveaux de productivité se sont rétablis en domaine pélagique au cours du *recovery*, ce qui pourrait avoir joué un rôle important dans la séquestration du carbone et le retrait du  $\text{CO}_2$  en association avec l'intensification de la météorisation continentale.

## 9. Modulation du cycle du carbone par le phytoplancton pendant le PETM

Ce chapitre représente un travail fondamental de ce manuscrit, car il vise à clarifier le rôle de la productivité primaire sur le cycle du carbone. De par son interdisciplinarité, ce papier sera prochainement soumis à la revue *Nature* car ces résultats permettent d'expliquer la phase de récupération du PETM, qui reste jusqu'à maintenant objet de profonds débats au sein de la communauté scientifique.

Le Maximum thermique à la limite Paléocène/Eocène du Paléocène (PETM, ~56 Ma), est considéré comme l'un des meilleurs analogues pour les émissions anthropiques de  $\text{CO}_2$ . Pourtant, les principales rétroactions négatives qui ont éliminé l'excès de carbone lors de l'arrêt du PETM restent controversées. La saturation et l'enfouissement des  $\text{CaCO}_3$ , dus à une altération accrue des silicates, sont communément acceptés comme les principaux processus moteurs. Par ailleurs, une

baisse de la production nette de  $\text{CaCO}_3$  des algues induite par le  $\text{CO}_2$  pourrait avoir déclenché l'accumulation d'alcalinité et la sursaturation, mais ce mécanisme n'est toujours pas étayé par des preuves indirectes. Je présente une étude *multiproxy* des enregistrements des eaux profondes tropicales du Pacifique et de l'Atlantique qui démontre que l'enfouissement des carbonates s'est rétabli aux niveaux pré-PETM environ 30 000 ans plus tard que la saturation. Ce découplage est expliqué par un effondrement spectaculaire (>60 %) et durable (>80 000 ans) de la production nette de  $\text{CaCO}_3$  en raison de la stratification des océans induite par le réchauffement et de la diminution de la disponibilité des nutriments. Grâce à la mesure des isotopes du calcium ( $\delta^{44/40}\text{Ca}$ ) sur des coquilles de l'espèce de foraminifères planctoniques *Morozovella velascoensis*, et à la fragmentation des nannofossiles calcaires ainsi que des foraminifères planctoniques au Sites ODP 1209 (Pacifique tropical) et 1263 (Atlantique tropical), il est possible de tracer les changements d'alcalinité de l'océan pendant le PETM. Ces enregistrements montrent que l'excès d'alcalinité qui en résulte a été rapidement consommé lorsque la production et l'enfouissement du  $\text{CaCO}_3$  ont finalement repris, déclenchant un retrait rapide et massif du carbone tant inorganique qu'organique. Mes conclusions élucident certains des mécanismes biogéochimiques clés qui ont conduit à la récupération du PETM et soulignent l'importance négligée mais cruciale des seuils biologiques dans la régulation des événements passés et actuels du réchauffement climatique.

## 10. Conclusion et synthèse

Le dernier chapitre de la thèse vise à comparer les deux intervalles de temps pour discuter des aspects similaires et des différences. Pour les deux événements les données biostratigraphiques ont été représentés par rapport à la courbe des isotopes stables du carbone ( $\delta^{13}\text{C}$ ). Pour le Pliensbachien-Toarcien, j'ai pu mettre en évidence qu'il y a un épisode majeur d'apparitions autour de la limite Pliensbachien-Toarcien, contrairement au T-OAE. Ceci est en partie lié à l'augmentation des placolithes, qui domineront les assemblages pour le reste Mésozoïque et Cénozoïque et en partie liés à des condensations dans plusieurs bassins de la Tethys autour de la limite. Pour le PETM, j'ai pu mettre en évidence que le record sédimentaire a une influence majeure sur l'ordre des événements. Similairement au Pliensbachien-Toarcien, la présence de discontinuités à la limite explique certaines différences d'une localité à l'autre. Cependant, il existe un certain degré de diachronisme, affectant également les

marques biostratigraphiques utilisés dans les zonations standards. La limite Paléocène-l'Éocène est caractérisée par plusieurs origines et extinctions, et aussi par des changements au sein des communautés de nanofossiles calcaires. Certains de ces événements, jamais pris en compte dans les biozonations antérieures, se sont avérés cohérents, avec un degré de diachronisme moindre que les marqueurs biostratigraphiques utilisés précédemment. Finalement j'obtiens un nouveau schéma de biozonation à haute résolution avec une résolution moyenne de 50-100 kyrs par zone. De plus, je corrèle les événements biostratigraphiques et les nouvelles zones aux différentes phases caractérisant l'excursion négative des isotopes du carbone définissant le Paléocène/Éocène.

En terme de implications paleoceanographiques, malgré certaines différences, comme par exemple le fait que pour le Jurassique Inferieur nous ne disposons pas d'enregistrement d'océan ouvert, les changements des abondances absolues et des flux durant les deux évènements, suggèrent iperstratification et oligotrophie des eaux de surface. L'oligotrophie était plus marqué pendant le T-OAE, car même les zones plus proximales montrent une tendance à l'oligotrophie. Au PETM, l'oligotrophie était particulièrement accentuée dans les sites océaniques, loin des apports des rivières tandis que dans les coupes proximales on enregistre des conditions fluctuantes, notamment des phases de stratification alternées à des phases de brassage des eaux. Un aspect fondamental de ce travail de thèse est l'étude multiproxy des enregistrements des eaux profondes tropicales du Pacifique et de l'Atlantique ; ces données démontrant que l'enfouissement des carbonates s'est rétabli à des niveaux pré-PETM environ 30 000 ans après la saturation. Ce découplage entre saturation et enfouissement des carbonates est expliqué par un effondrement spectaculaire (>60 %) et durable (>80 000 ans) de la production nette de  $\text{CaCO}_3$ , dû à la stratification des océans induite par le réchauffement et à la diminution de la disponibilité des nutriments. L'excès d'alcalinité qui en résulte a été rapidement consommé lorsque la production et l'enfouissement du  $\text{CaCO}_3$  ont finalement repris, déclenchant un retrait rapide et massif du carbone tant inorganique qu'organique. Ces conclusions élucident certains des mécanismes biogéochimiques clés qui ont conduit à la récupération du PETM et soulignent l'importance de la biologie dans la régulation des événements passés et actuels du réchauffement climatique.





**Chapitre 2.1. New calcareous nannofossil and carbon isotope data for the Pliensbachian/Toarcian undary (Early Jurassic) in the western Tethys and theirpaleoenvironmental implications.**



# New calcareous nannofossil and carbon isotope data for the Pliensbachian/Toarcian boundary (Early Jurassic) in the western Tethys and their paleoenvironmental implications

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Bernard Pittet<sup>1</sup> and Guillaume Suan<sup>1</sup>

With 5 figures, 2 plates and 2 tables

**Abstract.** Several studies have focused on the response of calcareous nannofossils to the Toarcian anoxic event (T-OAE), one of the most dramatic events of environmental perturbations of the Mesozoic Era. Nevertheless, the impact of marked environmental perturbations on calcareous nannofossils during the Pliensbachian/Toarcian transition (PI/To; ~183 Ma), slightly before the T-OAE, remain comparatively less well documented. Here, we present a high-resolution biostratigraphical and chemostratigraphic study of two sections where the PI/To is well represented. One section is located in Central Spain (La Almunia) and the second one is in North-Western France (Anse St. Nicolas). Although the two localities were paleogeographically close to each other during the Early Jurassic, dissimilarities in the nannofossil assemblages suggest different paleoenvironmental conditions. Across the PI/To boundary, absolute abundances (nannofossils/gram of rock) and placolith-coccoliths increased substantially in both sections. Equally, carbon isotopes show a negative excursion at the boundary followed by a trend to more positive values. The comparison of our new data to seven sections located in both Northern and Southern Tethyan margins, shows that the PI/To corresponded to a major diversification event of coccoliths. The PI/To speciation caused a pronounced shift from muroliths to placoliths. Some differences are observed from one section to another, but several first occurrences (FO) of species and a reorganization of the nannofossil community are documented in all the localities. Some of these FOs are biostratigraphically useful for the definition of the PI/To boundary, like the FOs of *Biscutum intermedium*, *Zeugrhabdothus erectus* and *Discorhabdus ignotus*. The carbon cycle perturbation at the PI/To occurred during a transgressive event after a pronounced cooling event and a sea-level drop that triggered hiatuses in many localities. The origination event of calcareous nannofossils is closely linked to all these phenomena. Thus, the PI/To event has to be seen as the onset of profound paleoenvironmental perturbations that culminated with the T-OAE.

**Key words.** Pliensbachian, Toarcian, PI/To event, calcareous nannofossils, biostratigraphy, carbon and oxygen stable isotopes

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## 1. Introduction

In the last decade, numerous studies have focused on Lower Jurassic calcareous nannofossil assemblages and biostratigraphy (e. g., Mailliot et al. 2006, Mattioli et al. 2008, 2009, 2013, Reggiani et al. 2010, Fraguas et al. 2010, 2012, Casellato et al. 2015, Peti et al. 2017), with the large majority being dedicated to the Toarcian Anoxic Event (T-OAE; Jenkyns, 1988). Conversely, in spite of recent ratification of the Toarcian GSSP (Rocha et al. 2016), the palaeoenvironmental events occurring across the Pliensbachian/Toarcian boundary (PI/To) remain poorly investigated. The PI/To is a prominent event because it precedes the T-OAE by about 800–1000 kyrs (Suan et al. 2008a, Huang and Hesselbo 2014, Martinez et al. 2017) and coincides with a perturbation of the carbon cycle and marked changes in paleotemperature, as respectively reflected by prominent negative carbon isotope excursion (CIE) and a shift toward more negative oxygen isotope values in bulk rock carbonates and brachiopod shells (Hesselbo et al. 2007, Suan et al. 2008a, 2010, Bodin et al. 2010, 2016, Dera et al. 2011 a, Ferreira et al. 2015). Geochemical studies were also performed on belemnite rostra calcite (Gomez et al. 2008) but, for the PI/To, they did not deliver the same negative carbon excursion as brachiopods. Also, sea-level changes have been documented at the PI/To (Hesselbo 2008, Sabatino et al. 2009, Suan et al. 2010, Pittet et al. 2014), possibly linked to the growth and decay of polar ice caps (Morard et al. 2003, Suan et al. 2010, Korte and Hesselbo 2011). These sea-level changes drove in turn condensation or hiatuses in many epicontinental basins that make the definition of the PI/To boundary even more complicated (e. g., Blomeier and Reijmer 1999, Léonide et al. 2012, Sandoval et al. 2012, Pittet et al. 2014). Given the recent analysis of sections located outside the western Tethys, which has so far been the most extensively studied region, and due to the recent improvement of our knowledge of remote Toarcian settings, e. g. South America (Nequén Basin in Argentina, Al-Suwaidi et al. 2016, Andean Basin in Chile, Fantasia et al. 2018), North America (Martindale et al. 2017, Them II et al. 2017) and Tibet (Wignall et al. 2006, Fu et al. 2016), there is a growing need for improving the PI/To stratigraphy in order to perform supraregional correlations. In this study we present data from two successions where the PI/To boundary is well expressed, namely at Anse St. Nicolas, located in the western margin of France and at La Almunia, in central Spain in the region of Zaragoza. No apparent

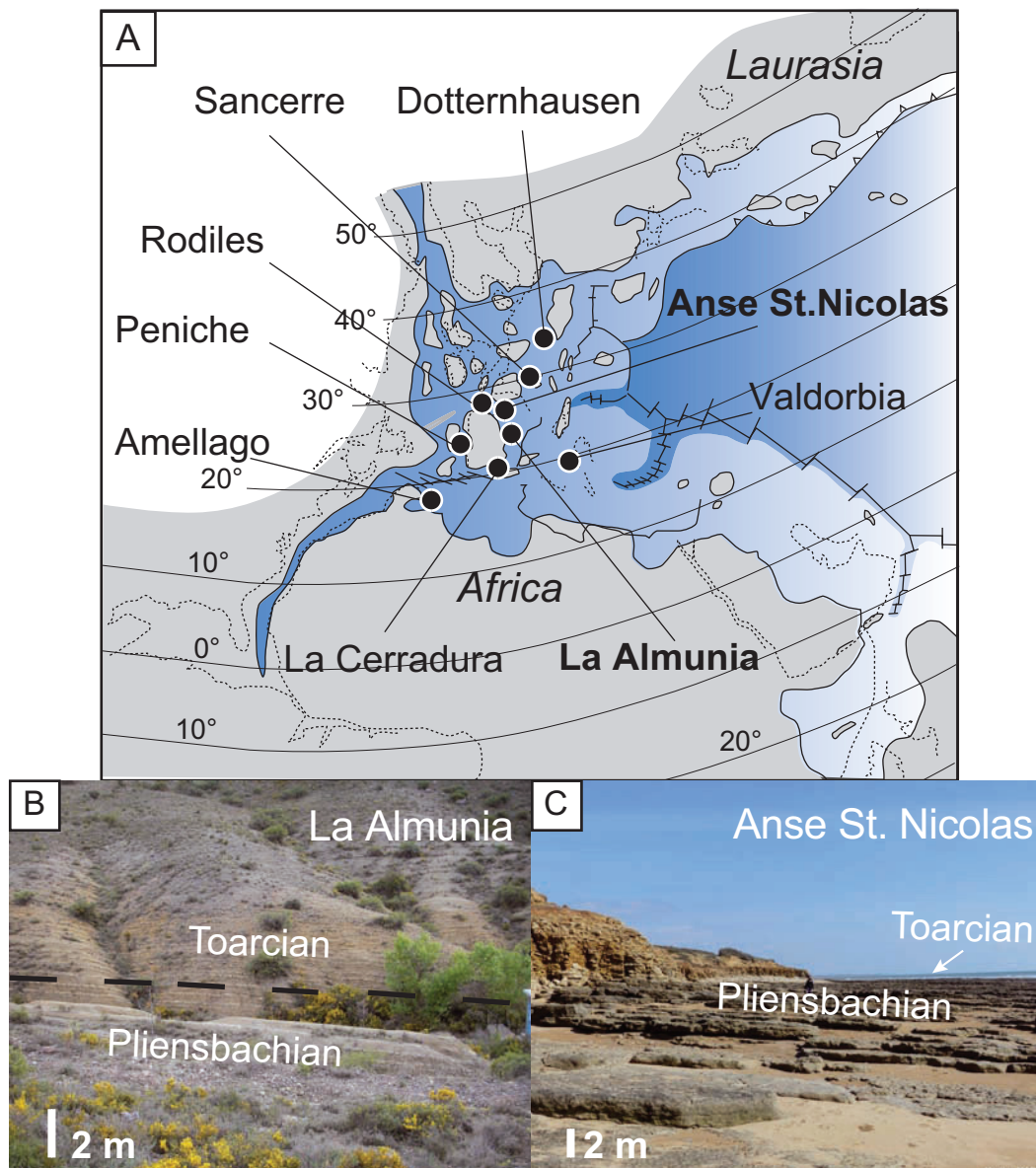
discontinuities occur in these two sections at the PI/To transition (Gabilly 1976, Elmi 2007, Gómez et al. 2008).

Besides their continuous PI/To record, these two sections were located in a key position in the western Tethys, at the crossway between the northern and the southern margins that bring significant differences in terms of floral and faunal assemblages and in terms of environmental conditions (van de Schootbrugge et al. 2005, Mattioli et al. 2008). We present a precise comparison between the new calcareous nannofossil events, assemblages and C isotope data from these two areas. We then compare our data with ones from other sections from both northern and southern Tethyan domains where ammonite, carbon isotopes and nannofossil data are available (including the recently ratified GSSP at Peniche in Portugal) to provide a comprehensive stratigraphic framework for the Pliensbachian/Toarcian boundary.

## 2. Geological setting

During the Early Jurassic, the western Tethys consisted of shallow epicontinental seas extending between the Laurasian and the African landmasses (Fig. 1A). Several lines of evidence indicate significant paleoclimatic and paleoceanographic differences between the northern subtropical margin (~27–35 °N) and the southern tropical margin (~17–23 °N). Water masses with different properties have been interpreted for the two domains to explain the different ammonite faunas (Cecca and Macchioni 2004 and references herein) and substantial differences in calcareous nannofossil assemblages (Bown 1987, Mattioli et al. 2008). Belemnite oxygen isotope composition, clay mineral and fossil wood assemblages indicate more humid climate conditions in the northern margin, opposed to a more arid climate for the southern part (van de Schootbrugge et al. 2005, Rosales et al. 2006, Dera et al. 2009, Philippe et al. 2017). Consequently, the northern Tethyan margin is characterized by siliciclastic deposits, while the southern margin is dominated by carbonates, likely indicating more arid conditions. Paleogeographic reconstructions show that the southern Tethyan margin featured relatively shallow basins separated by large carbonate platforms (Bassoulet et al. 1993, Thierry and Barrier 2000).

The two sections studied here were located in a key area at the transition between the northern and the southern margins of the Tethys in the Early Jurassic. La

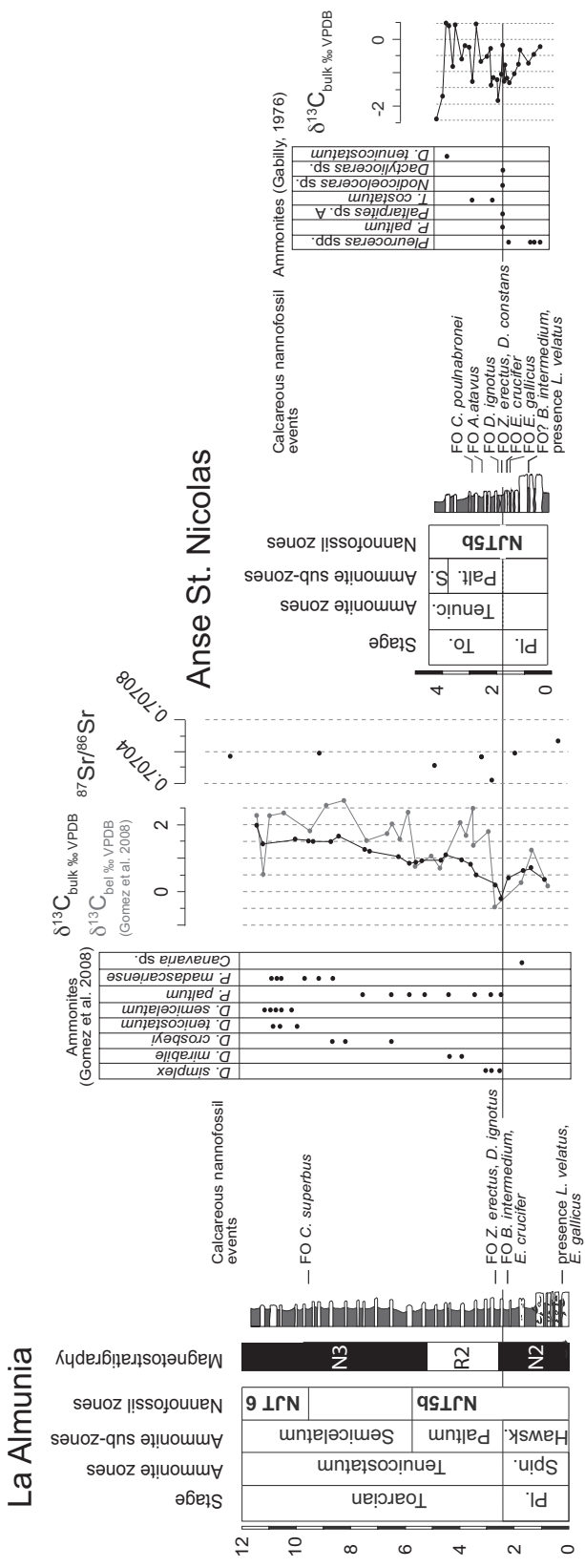


**Fig. 1.** A: Paleogeographic reconstruction of western Tethys at about 183 Ma (after Bassoullet et al. 1993) showing location of the sections studied or used for comparison in this study. La Almunia, La Cerradura, Valdorbria, and Amellago are located in the Southern Tethyan margin. Anse St. Nicolas, Rodiles, Sancerre, and Dotternhausen are located in the Northern Tethyan margin. Peniche was located in the Lusitanian Basin, a N-S elongated corridor in connexion with both Tethyan and NW European regions. B: Field view of La Almunia section, located in central Spain in the region of Zaragoza. The lithology is constituted of marl/limestone alternations. Dashed line represents the Pliensbachian/Toarcian boundary. Scale bar is 2 meter. C: Field view of Anse St. Nicolas section, located in North-West France in the department Vendée. The lithology is constituted of marl/limestone alternations. Pliensbachian beds are well exposed, while Toarcian strata are only accessible during low tides. Scale bar is 2 meters.

Almunia (Fig. 1B) was located in the Iberian Range (Central Spain), while Anse St. Nicolas (Fig. 1B) was located along the north-western epicontinental margin (NW France). Both sections present ammonite assemblages of the Northwestern European Province,

although in the La Almunia section taxa both from the NW European and the Mediterranean provinces are recorded (Comas-Rengifo et al. 2010).

La Almunia section is located in central-eastern Spain, at 267.5 km of the National II road Madrid to



Barcelona, along the “Camino de Las Conchas”. Paleogeographically, the section was located to the East of the Iberian Massif. The succession (Fig. 2) consists of marl-limestone alternations and the thickness of the studied interval is 12 m. It records the Hawskerense (upper Pliensbachian), Paltum and Semicelatum (lower Toarcian) sub-zones (Gautier and Mouterde 1964, Goy and Martinez 1990). Ostracod (Arias 1991, 1995) and foraminifer (Herrero 1992) assemblages have also been studied. The ammonite assemblages and stable oxygen and carbon isotope composition of belemnite rostra from this succession have been reported by Gómez et al. (2008).

The Anse St. Nicolas section is located in the western Atlantic margin (NW France), close to Jard in Vendée. Paleogeographically, this area represented the southern, distal margin of the Armorican Massif. In this region, different sections record a relatively complete Pliensbachian/Toarcian transition (Gabilly 1964, 1976, Bécaud 2002, 2005, 2006) based on their ammonite and brachiopod contents. Anse St. Nicolas represents the most complete and expanded section in western France (Gabilly 1976). In particular, this section records a relatively expanded (~10 m) lower Toarcian interval (Gabilly 1976) compared to the nearby historical Toarcian stratotype at Thouars, where the same interval is represented by 0.50 m of sediments

**Fig. 2.** Geochemical and biostratigraphic data for La Almunia and Anse St. Nicolas sections. Ammonite zones and sub-zones in the two sections are after Elmi et al. (1997). The Pliensbachian/Toarcian boundary corresponds to the passage between Spinatum and Tenuicostatum ammonite zones. Calcareous nanofossil zones are after Mattioli and Erba (1999). The zone NJT5 b is recorded in both sections based on the record of *Lotharingius sigillatus* which is present from the lowest studied samples. Only at La Almunia is recognized the zone NJT6, given the first occurrence of *Carinolithus superbus*. Many first occurrences of calcareous nanofossils are reported. In particular, the first occurrences of *Ethmorhabus crucifer*, *Zeugrhabdotus erectus* and *Discorhabus ignotus* well approximate the Pliensbachian/Toarcian boundary (PI/To). Carbon isotopes on bulk rock samples are expressed relative to the international standard VPDB. A negative excursion characterizes the PI/To boundary, followed by a positive recovery phase. Magnetostratigraphy and strontium isotopes of La Almunia are after Comas-Rengifo et al. (2010). The PI/To boundary lies just below the passage from N2 to R2 magnetozone. Strontium isotope ratios display lower values in correspondence of the PI/To.



(Courtinat et al. 2007). The succession is represented by marl-limestone alternations characteristic of outer carbonate platform environments (Fig. 2). For the lowermost Toarcian, the ammonite biostratigraphy permits the recognition of the two subzones Paltum and Semicelatum, belonging to the Tenuicostatum zone. At Anse St. Nicolas, the Spinatum zone (uppermost Pliensbachian) is not recognized. The upper Pliensbachian is characterized by the occurrence of ammonites of the *Pleuroceras* genus. These disappear at the Pl/To boundary, when the mass occurrence of *Dactyloceras* is observed (Gabilly 1976). Such an assemblage change attests for the completeness of the boundary, although condensation is not excluded (Rocha et al. 2016). Gabilly (1976) inferred that no discontinuities occur between the last Pliensbachian bed and the first Toarcian level, making the section very suitable for a detailed study of the Pliensbachian/Toarcian event. Such a completeness made of Anse St. Nicolas one of the discussed possible candidates as the stratotype for the Toarcian (Gabilly 1973, 1976, Rocha et al. 2016).

Additional Pliensbachian-Toarcian sections are considered here for comparison of their nannofossil assemblages, namely Dotternhausen (SW Germany), Sancerre (N France), Rodiles (N Spain), the GSSP of the Toarcian at Peniche (Portugal), La Cerradura (S Spain), Valdorbja (Central Italy), and Amellago (Morocco). All these sites benefit from high-resolution carbon isotope data and good nannofossil and ammonite biostratigraphic control (e. g., Mattioli et al. 2008, 2013, Bodin et al. 2010, Fraguas et al. 2012, Reolid et al. 2014, Clemence et al. 2015) and are remarkable for their continuity at the Pl/To boundary. However, in the Sancerre core a discontinuity (D1) was noticed by Pittet et al. (2014; figure 10), and a hiatus was inferred in correspondence of the Pl/To boundary. La Cerradura, Valdorbja and Amellago belong to the southern margin of the Tethys and display ammonites from the Mediterranean Province; Peniche and La Almunia show a mixing of Mediterranean and NW Europe ammonite fauna; Anse St. Nicolas and Dotternhausen belong to the northern margin of Tethys and yield ammonites of the NW Europe Province (see for a synthesis Rocha et al. 2016); the Rodiles section shows a high proportion of common taxa with the UK sections (Gomez et al. 2008).

### 3. Materials and methods

The calcareous nannofossils and bulk rock carbon and oxygen isotopes were analysed for thirty-two samples for the section Anse St. Nicolas, and for twenty-five samples for the section La Almunia, covering the upper Pliensbachian-lower Toarcian transition. Samples were collected every 10 cm for the section Anse St. Nicolas and every 30 cm for the section La Almunia, with a higher sampling density near the boundary (every 5 cm at Anse St. Nicolas; every 10 cm at La Almunia).

#### 3.1. Stable isotope analyses

Stable carbon and oxygen isotopes on bulk rock carbonates were analysed at the Institute of Earth Surface Dynamics of the University of Lausanne, Switzerland. Stable carbon ratios ( $\delta^{13}\text{C}_{\text{carb}}$  values) were measured in whole rock samples containing >10 wt.%  $\text{CaCO}_3$  following the procedure of Spangenberg and Herlec (2006). Samples with clear evidence of diagenetically neoformed or recrystallized carbonates (calcite or dolomite) were not analysed. The analyses were performed in aliquots of powdered whole rock samples (variable weight depending on the  $\text{CaCO}_3$  content). Sample powders were analysed using a Thermo Fisher Scientific Gas Bench II (Bremen, Germany) carbonate preparation device connected to a Delta Plus XL isotope ratio mass spectrometer that was operated in the continuous helium flow mode (Révész and Landwehr 2002). The  $\text{CO}_2$  extraction was done by reaction with anhydrous phosphoric acid at 70 °C. Stable carbon isotope ratios are reported in the delta ( $\delta$ ) notation as the per mil (‰) deviation relative to the Vienna Pee Dee belemnite standard (VPDB). The normalization of the measured isotope ratios to the VPDB scale was performed by replicate analyses of an in-house working standard Carrara marble (UNIL-CM,  $\delta^{13}\text{C} = 2.05\text{‰}$ ) and international reference materials (RMs) in each run. The  $\delta^{13}\text{C}$  values of the reference gas and the UNIL-CM were normalized with the RMs NBS-19 limestone with  $\delta^{13}\text{C} = 1.95\text{‰}$ , NBS-18 carbonatite with  $\delta^{13}\text{C} = -5.04\text{‰}$ , and LSVEC lithium carbonate with  $\delta^{13}\text{C} = -46.65\text{‰}$  (Brand et al. 2014). The repeatability and intermediate precision of the analyses ( $2\sigma$ ), monitored by replicate analyses of the laboratory standard UNIL-CM and the RMs was better than  $\pm 0.05\text{‰}$ . The accuracy of the analyses was checked periodically through the analyses of the RMs.

### 3.2. Calcareous nannofossils

Samples for calcareous nannofossils were prepared following the technique described by Beaufort et al. (2014), slightly modified here. A cover slide was weighed before and after a homogeneous suspension of dried rock-powder and water (supersaturated with respect to  $\text{CaCO}_3$  and with a basic pH) was let to settle on the cover slide for 2 hours in a Petri-dish. After settling of the powder, water was carefully aspirated with a water pump related to a micro-pipette, avoiding any turbulence in the Petri-dish. The residual water on the cover slide was dried, the cover slide was recovered and attached on a microscope slide using Rhodopass resine. This technique allowed the quantification of absolute abundances of nannofossils per gram of rock using the following formula:

$$x = \frac{n * (l * h)}{m * A}$$

where  $x$  is the absolute abundance value,  $n$  is the number of counted specimens in a slide,  $l$  is the length of the cover slide,  $h$  is the height of the cover slide,  $m$  is the mass of the weighted sample and  $A$  is the studied surface of the sample.

For each sample, 300 specimens of calcareous nannofossils have been counted using a Leica DM750P microscope with a 1000 X magnification. In samples where the richness was extremely low, ~100 nannofossils have been counted. Counting 300 specimens per sample provides us with a limited probability (less than 5%) not to recover a rare species having a relative abundance of 1% in the total assemblage (Hay 1972). Each slide was further scanned over two transverses of the slide in order to detect the presence of rare but biostratigraphically significant specimens. For the poorest samples, a threshold of 100 specimens per sample has proven to be significant due to the limited number of species (~50) recorded in the studied interval. Counts of 100 specimens have a satisfactory statistical reliability according to Fatela and Taborda (2002). Also, rarefaction graphs have been constructed in our paper based on the method described by Krebs (1998) and Hammer et al. (2001). These graphs allow the evaluation of theoretical diversity of samples with respect to a reference sample where species richness is higher. It is thus possible to estimate when the sampling size is significant. This is namely when the confidence interval of the tested samples is superimposed to the confidence interval of the reference sample.

The relative abundances of species expressed as percentages were calculated for *Schizosphaerella*, an *incertae sedis* probably corresponding to a dinoflagellate cyst (Bown 1987), with respect to the total nannofossil counts (i. e., coccoliths plus *Schizosphaerella*), while the percentage of coccoliths is calculated with respect to the total coccoliths. Fatela and Taborda (2002) have calculated the confidence interval for species with a proportion of 0.1 (i. e., 1%) when counting 100 individuals. The confidence interval extends from 0.041 to 0.159 around the value of 1%. This is the reason why in the rest of the manuscript we only discuss taxa representing more than 5% in the assemblage.

Nannofossil preservation was evaluated for each sample based on the degree of etching and overgrowth following the classification of Roth et al. (1984). Three classes have been recognized: poor nannofossil assemblages when strong etching is observed along with overgrowth or fragmentation; moderate and good when *Schizosphaerella* fragmentation appears to be limited and delicate coccoliths still present intact structures.

We also calculated the Shannon Index (H), a mathematical expression of species diversity in a community (Shannon and Weaver 1949). It is calculated as follows:

$$H = - \sum_{i=1}^s P_i * (\ln(P_i))$$

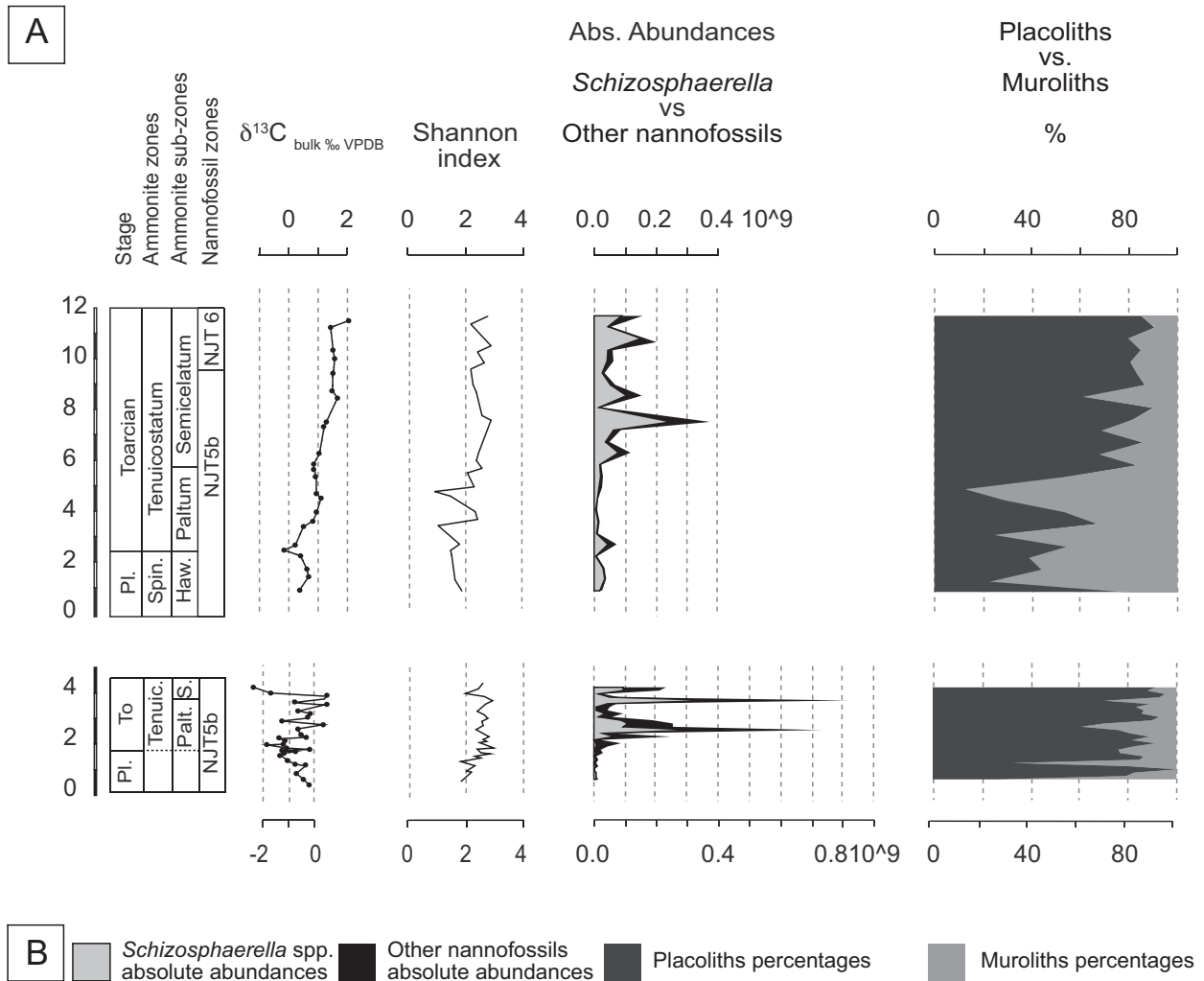
where  $i$  is a species,  $s$  is the number of species in the interval (i. e., species richness),  $P_i$  is the relative abundance of each species.

The nannofossil biostratigraphic record has been compared to the standard ammonite zones taking into account for the two studied sections.

## 4. Results

### 4.1. Stable carbon isotope results

Stable carbon isotopes values range from  $-0.5$  to  $2.0$  ‰ VPDB at La Almunia and from  $-2.0$  to  $0.5$  ‰ VPDB at Anse St. Nicolas (Fig. 2 and supplementary data). The two sections show the same trend, namely a general  $1.5$ ‰ increase of the  $\delta^{13}\text{C}_{\text{carb}}$  values from the Pliensbachian to the Toarcian, interrupted by a  $0.5$  to  $1$ ‰ negative excursion at the Pl/To boundary (PT-CIE). The bulk carbonate carbon isotope profile at Almunia shows a very similar trend with that of belemnites from



**Fig. 3.** A: La Almunia section. From the Pliensbachian to the Toarcian, an increase in Shannon Index is documented as well as an increase in absolute abundances (nannofossil/gram of rock). Placolith-coccoliths increase in percentage relatively to muroliths and the result is a turnover from murolith- to placolith-dominated assemblages. B: The same trend is observed at Anse St. Nicolas. Two peaks in absolute abundances are seen and these are interpreted as an evidence of sedimentary starvation and nannofossil increased accumulation.

the same section (Gómez et al. 2008). Carbon isotope values show a larger variability at Anse St. Nicolas than at La Almunia (Fig. 2), probably reflecting a lithological control on the signal, with marls displaying lower  $\delta^{13}C_{\text{carb}}$  than argillaceous limestones. At Anse St. Nicolas the carbon isotope values show a 3‰ negative shift in topmost samples (Fig. 2).

Even though the general trend is very similar in both sections, the  $\delta^{13}C_{\text{carb}}$  values are overall lower at Anse St. Nicolas compared to La Almunia. This is probably due to the higher organic matter content at Anse St. Nicolas, as organic debris (both wood fragments and algal remains) are commonly observed in nannofossil

slides. Given the light isotopic composition of organic matter, a contribution of inorganic carbon produced by oxidative degradation of organic compounds may explain the lower  $\delta^{13}C_{\text{carb}}$  values as well as the highly fluctuating  $\delta^{13}C_{\text{carb}}$  trend in Anse St. Nicolas.

#### 4.2. Calcareous nannofossils

In both sections, nannofossil preservation is generally moderate to good (see also Plates 1 and 2). In spite of the overall satisfactory preservation of nannofossils, four samples at the base of Anse St. Nicolas (SN 0.05, 0.13, 0.20, 1.12) are barren of nannofossils (see



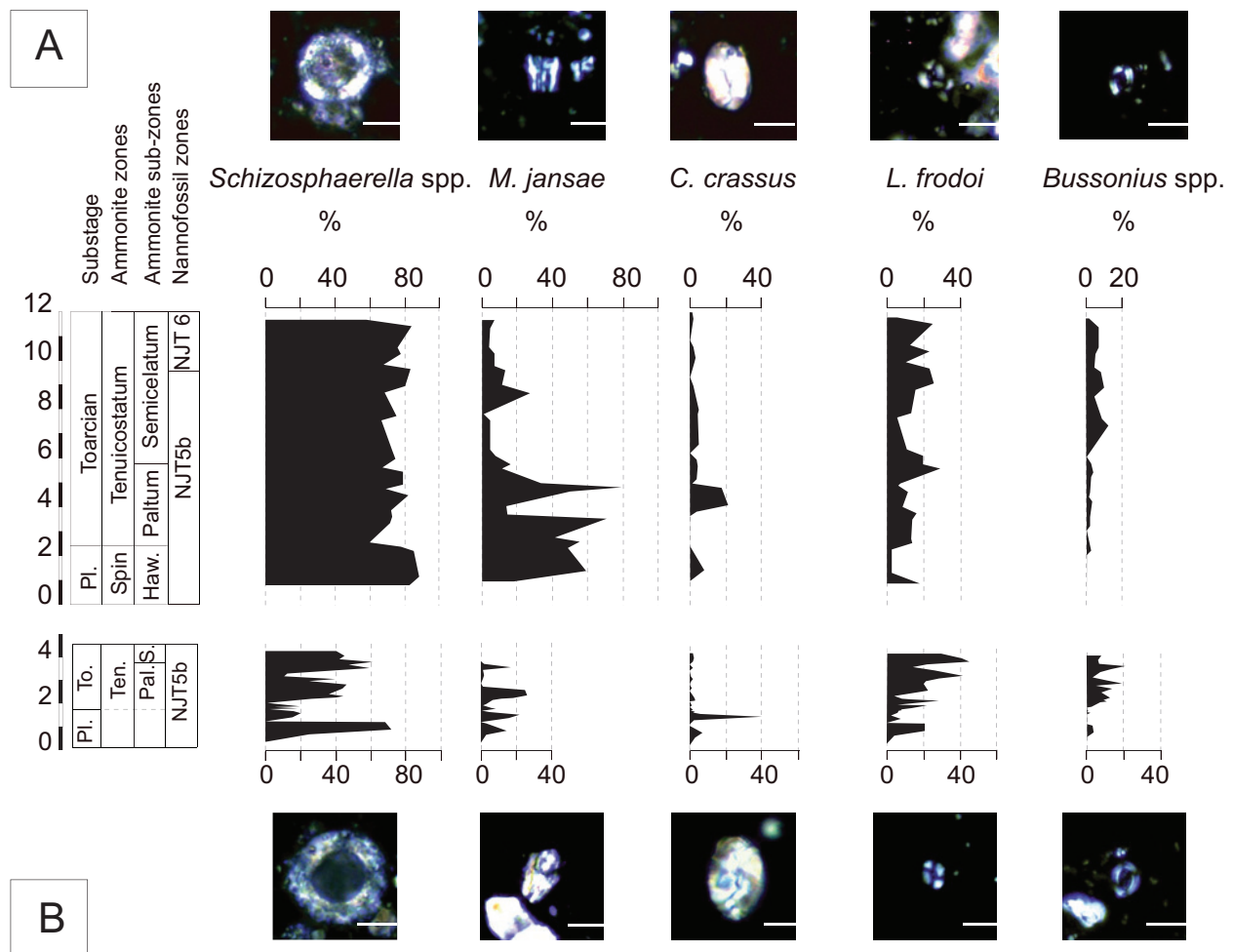
supplementary data). The Shannon index shows similar values and evolution in the two sections, and the most interesting feature is an increase from values around 2 in the Pliensbachian to values around 3 in the Toarcian (Fig. 3).

The two sections yielded a quite rich and diversified nannofossil assemblage, and even very rare species are sporadically present (e. g., *Diductius constans*). Total relative and absolute abundances are comparable for the two sections with a few differences. A remarkable point is the different contribution of *Schizosphaerella* spp. and coccoliths (Figs. 3 and 4). Indeed, at La Almunia *Schizosphaerella* spp. is the most abundant taxon and constitute between 60 and 90 % of the entire assemblage, with up to  $200 \times 10^6$  specimens per gram of rock (Figs. 3 and 4). Conversely, at Anse St. Nicolas *Schizosphaerella* spp. is abundant before and after the PI/To, reaching relative abundances up to 60 % and absolute abundances up to  $800 \times 10^6$ , but its abundance does not exceed 20 % (absolute abundances  $50 \times 10^6$ ) in several samples and this taxon is even totally absent in some upper Pliensbachian samples. Other quantitatively significant taxa recorded in both sections are *Lotharingius* spp., *Mitrolithus jansae*, *Crepidolithus crassus*, *Similiscutum cruciulus* group, *Similiscutum finchii*, *Biscutum intermedium*, *Biscutum grande*, *Bussonius prinsii*, *Bussonius leufuensis*, *Tubirhabdus patulus*, *Parhabdolithus liasicus* (Tables 1 and 2).

The PI/To boundary records a major turnover in the calcareous nannofossil assemblages. The upper Pliensbachian samples are dominated by muroliths (such as *M. jansae*, *C. crassus*, *T. patulus*, *P. liasicus*), while lower Toarcian samples record an increase in abundance of the placolith-coccoliths. Muroliths are characterised by a simple structure with calcite elements of the distal shield extending vertically, and represent the earliest coccoliths to have appeared in the Late Triassic (Bown 1987, Gardin et al. 2012). The placolith structure is defined by two shields which lie on top of one another, and are connected by a central tube; the two shields show radial calcite elements (Bown 1987). Taxa such as *Lotharingius* spp., *Similiscutum* spp., *Biscutum* spp. or *Bussonius* spp. became more abundant in the Toarcian. However, this increase of placoliths does not correspond to an effective decrease of muroliths, although their relative abundance decreased. This decrease is a closed-sum effect as muroliths absolute abundances remain more or less constant through the studied interval, while placoliths rapidly increased (Fig. 4).

*Lotharingius* spp. are the most common coccoliths, as recorded in many other lower Jurassic sections. The different species of *Lotharingius* spp. (*L. hauffii*, *L. frodoii*, *L. sigillatus*, *L. crucicentralis*, *L. barozii*, *L. velatus*) account between 30 and 50 % of the assemblage in both sections. *Mitrolithus jansae* is very abundant at La Almunia, where it reaches between 60 and 70 % of total coccoliths, while at Anse St. Nicolas it is present but never exceeds 20 % of coccoliths. *Biscutum* spp. and *Similiscutum* spp., are more abundant at Anse St. Nicolas than at La Almunia: these two genera never exceed 10 %, with the exception of the species *S. finchii*, that reaches peaks of 20 % in both sections. *Bussonius* spp. are more abundant at Anse St. Nicolas; they account for 10–15 % of the assemblage, though at La Almunia they never exceed 10 %. Other taxa are rare and their percentage ranges from 1 % to 5 %.

In both sections, many first occurrences (FO) are recorded around the PI/To (Fig. 2). *Lotharingius velatus*, which is documented to occur in the uppermost part of the Pliensbachian (Mattioli et al. 2013), is present in the lowermost samples studied both at Anse St. Nicolas and at La Almunia; therefore the FO of this taxon certainly occurs below these samples and cannot be recognized in the studied material. At Anse St. Nicolas, *B. intermedium* is found in the upper Pliensbachian just above the basal barren samples, at the base of the PT-CIE; this horizon may correspond to the FO of the species. At La Almunia, the FO of *B. intermedium* is recorded just below the PI/To boundary, at the base of the PI/To negative CIE. The FO of *Ethmorhabdus gallicus* at Anse St. Nicolas is found just below the PI/To, concomitant with the negative CIE, whereas at La Almunia this species is present from the lowermost sample studied. The FO of *Ethmorhabdus crucifer* is recorded in both sections just below the PI/To, concomitant with the negative CIE. Two FOs are well documented in both sections at the very base of the Toarcian, Tenuicostatum ammonite Zone (Paltum subzone), namely the FOs of *Zeughrabdothus erectus* and *Discorhabdus ignotus* (Fig. 2). In the Early Toarcian, the FOs of *Axopodorhabdus atavus*, *Diductius constans* and *Carinolithus poulabronei* are only recorded at Anse St. Nicolas (Paltum subzone). An important event in the early Toarcian is the FO of *Carinolithus superbus*. This event was not found at Anse St. Nicolas, while at La Almunia it is located in the upper part of the section (Semicelatum subzone).



**Fig. 4.** Relative abundances (%) of the most abundant species in the two sections. A: La Almunia section. B: Anse St. Nicolas. *Schizosphaerella* spp. (a probable calcareous dinoflagellate cyst) dominates the assemblages, even if at Anse St. Nicolas it is overall less abundant. The main feature passing from the Pliensbachian to the Toarcian is a general increase in percentage of placoliths, such as *Lotharingius frodoi* or *Bussonius* spp., and a decrease in muroliths, such as *Mitrolithus jansae* or *Crepidolithus crassus*. Scale bar is 5 microns.

## 5. Discussion

### 5.1. Calcareous nannofossil bioevents

Early Jurassic nannofossil biostratigraphy is based on two schemes that are, nowadays, accepted as standard; for the NW European sections the adopted scheme is the one by Bown (1987) modified by Bown and Cooper (1998), and for the south Tethyan settings the reference is Mattioli and Erba (1999). The sections studied here are at the transition between the southern and northern Tethys and, as far as ammonites are concerned, La Almunia displays a mixing of Mediterranean and NW Europe faunas, while Anse St.

Nicolas is part of the NW European Province. However, given the nannofossil assemblages and the constant presence or dominance of taxa which are typical of the S-Tethyan margin (i. e., *Schizosphaerella* and *M. jansae*; Bown 1987, Mattioli et al. 2008), the scheme that better applies to our dataset is that of Mattioli and Erba (1999). Based on this work, the base of the Anse St. Nicolas section is dated to the subzone NJT5 b, given the presence of *Lotharingius sigillatus* in the lowermost studied sample and the absence of *C. superbus*. La Almunia encompasses equally the subzone NJT5 b but the upper two meters of the section are attributed to NJT6 zone, given the FO of *C. superbus* in sample LAL 21.

The PI/To has been considered as a period of elevated evolutionary rates in nannofossils (Bown 1987, Bown and Cooper 1998, Bown et al. 2005) and numerous first occurrences are recorded across the boundary (Bown and Cooper 1998, Mattioli and Erba 1999, Mattioli et al. 2013). Across the PI/To are successively recorded the FOs of *L. velatus*, *A. atavus*, *B. intermedium*, *Z. erectus*, *D. ignotus*, *E. gallicus*, *E. crucifer* and *D. constans*. Most of these coccoliths are placoliths and only two are muroliths, namely *Z. erectus* and *D. constans*. This succession of events is very similar to the record of the Toarcian GSSP of Peniche (Mattioli et al. 2013, Rocha et al. 2016). *Lotharingius velatus* is present from the basal samples in both sections, while the FO of *A. atavus* is only recorded at Anse St. Nicolas. At La Almunia, *E. gallicus* is recorded from the basal sample but at Anse St. Nicolas the first occurrence is in the sample SN1.45, in the upper Pliensbachian. This species was originally described in the Oxfordian (Noël 1965) and subsequent studies extended the range of this species from Bathonian to Kimmeridgian (e.g., Medd 1982). According to Bown (1987), this species first occurred in the Toarcian. Our data show that its range can extend down to the uppermost Pliensbachian.

The FO of *E. crucifer* is recorded at Anse St. Nicolas and La Almunia in the uppermost Pliensbachian, just below the PI/To boundary. The holotype of this species was defined by Noël (1972) who noticed this species in lower Toarcian sediments. Other authors documented the total range of this species in the lower Toarcian (Bown 1987, Bown and Cooper 1998), and our data precise its FO just below the PI/To. A very good biohorizon in both sections, as well as in the GSSP section (Mattioli et al. 2013), is the FO of *Z. erectus*. This species first occurs slightly earlier than (Anse St. Nicolas) or in the same sample as (La Almunia) *D. ignotus* in the basal Toarcian, approximating very closely the PI/To boundary. Bown (1987) already reported a possible FO of *Z. erectus* in the Pliensbachian. Mattioli et al. (2013) show that, in the GSSP section of Peniche, this last taxon first occurred in the basal Toarcian (basal Polymorphum zone) while in previous works it was noticed in the upper part of Lower Toarcian (Bown 1987, Mattioli and Erba 1999, Mattioli et al. 2004b, 2008). The FO of *D. ignotus* is recorded in the Lower Toarcian in both the studied sections. In the lower Toarcian of the sections studied here, *D. ignotus* is very rare and discontinuous following its FO. Our results are consistent with the data of Mattioli et al. (2013). *Discorhabdus ignotus* behaved as

a Lazarus species, being absent from the sediments corresponding to the T-OAE in Peniche and other sections (Mattioli et al. 2013). The consistent occurrence of *D. ignotus* is then recorded by the end of the T-OAE (Mattioli et al. 2013).

Finally, the FO of *C. superbus* is recorded in the La Almunia section in the Semicelatum subzone. This event is consistently recorded below the negative CIE characterizing the T-OAE in southern Tethyan sections (Mattioli et al. 2013), but it is documented to occur after the T-OAE negative CIE in England (Bown 1987, Bucefalo Palliani et al. 2002, Boomer et al. 2009).

## 5.2. Calcareous nannofossil diversity and absolute abundance

The PI/To represents a significant acceleration of evolutionary rates in the history of calcareous nannofossils (Bown et al. 2004). The species richness increased at that time (Bown et al. 2004) but also the Shannon diversity attained significantly higher values in the Lower Toarcian (Fig. 2). The Shannon values recorded at the PI/To in the two sections studied here are comparable with literature data (Mattioli et al. 2008, Fraguas et al. 2012). Most of the new entries are represented by placolith-coccoliths that also show a remarkable increase in absolute abundances, whilst murolith-coccoliths originations were less numerous and absolute abundances stayed quite steady. Thus, taxa like *Biscutum/Similiscutum* and *Lotharingius* became dominant assemblage components.

Absolute abundances are twice higher passing from the Pliensbachian to the Toarcian in both studied sections (Fig. 3). A similar increase of absolute abundances in the basal Toarcian has already been reported in other sections (Mattioli et al. 2004, 2008), and likely corresponded to a rise in primary productivity (Mattioli et al. 2008). However, at La Almunia the absolute abundance increase is quite steady, while at Anse St. Nicolas two significant peaks are observed (from  $200 \times 10^6$  to  $700\text{--}800 \times 10^6$ ; Fig. 3). These two peaks of absolute abundances observed at Anse St. Nicolas are recorded in the same stratigraphic interval as the D1 and D3 discontinuities of Pittet et al. (2014), which have been interpreted as rapid marine transgressions. These two peaks may thus be attributed to condensation intervals due to these rapid transgressive events, as low sedimentary rates may result in a reduced dilution of nannofossils by other sedimentary components, hence causing peaks in abundance (Mattioli and Pittet 2002).

### 5.3. Comparisons of nannofossil bioevents between Tethyan sections across the PI/To CIE

Anse St. Nicolas and La Almunia sections are here compared to various sections where the PI/To is recorded continuously, ammonite and calcareous nannofossil biostratigraphy are well established and whole-rock stable carbon isotope are available (Fig. 5). The upper Pliensbachian and the lowest portion of lower Toarcian of all the considered sections can be assigned to the nannofossil zone NJT5 b because of the presence of *L. sigillatus* and the absence of *C. superbus*. We find the FO of *C. superbus* in all the sections but at Anse St. Nicolas because the interval studied is limited to the lowermost Toarcian. This event is recorded in all the sections in the lower Toarcian, during the positive excursion of C isotopes just before the onset of the T-OAE negative CIE as documented in the literature (Mattioli et al. 2013). However, at Rodiles and at Sancerre this event is found at the base of the CIE that characterizes the T-OAE (Fraguas et al. 2012, Clémence et al. 2015). It is possible that this is due to scarcity of *C. superbus* after its first occurrence.

Some other relevant events in the considered sections are the FO of *L. velatus*, *B. intermedium*, *D. ignotus*, *Z. erectus*, *E. gallicus* and *E. crucifer*. The FO of *L. velatus*, which is recorded in the uppermost Pliensbachian at Peniche, Valdorbja and Cerradura, is not detected in the two sections studied here, since *L. velatus* is found in the lowest nannofossil-bearing samples. The FO of *B. intermedium* is found in the uppermost Pliensbachian at La Almunia and potentially at Anse St. Nicolas as well as at Rodiles, Peniche, Valdorbja, Cerradura and Amellago. Both the FO of *L. velatus* and *B. intermedium* are recorded before the PI/To CIE. The FOs of *D. ignotus* and *Z. erectus* approximate very well the PI/To boundary as defined by ammonites, and they occur in concomitance of the negative CIE (Fig. 5). At Sancerre only the FO of *Z. erectus* is recorded in a lower interval compared to other sections. At Amellago and Dotternhausen the FO of *Z. erectus* was not found. At Rodiles neither *D. ignotus* nor *Z. erectus* are reported. Recently, Fantasia et al. (2018) studied a section from the Andean Basin which belonged to the Panthalassa Ocean domain. The comparison between ammonite zonation, carbon isotope curve and calcareous nannofossil events shows a succession of bio-horizons, which is very similar to the one we recorded in western Tethys,

unless the FO of *C. superbus* that was not found there (Fig. 5). Such a good correlation attests for the valuable potential of nannofossil biostratigraphy for supra-regional correlations in the Lower Jurassic.

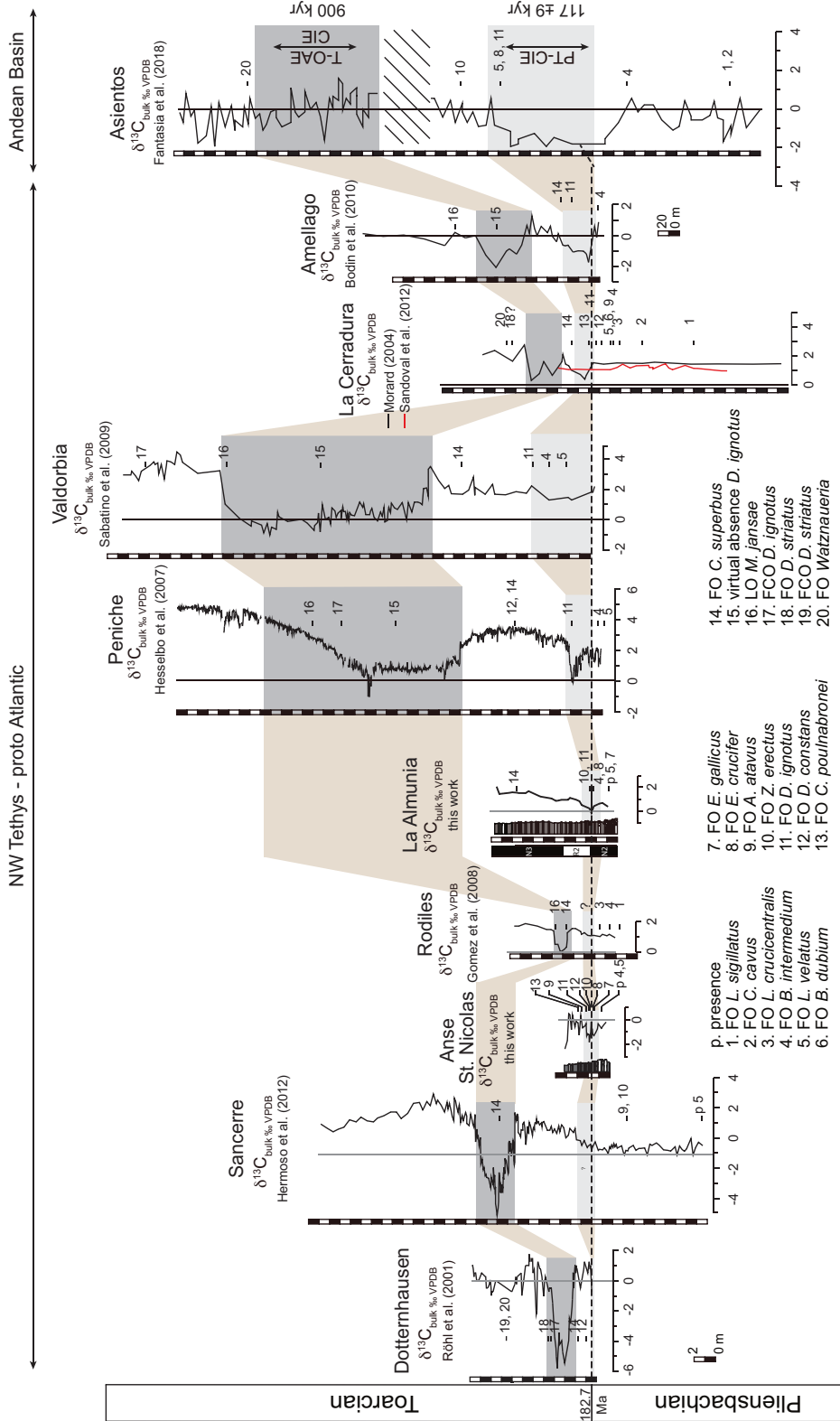
After its first record in bulk carbonate and fossil wood at the GSSP of Peniche (Hesselbo et al. 2007), the PI/To CIE was documented in other Tethyan sections, (e. g., Suan et al. 2008, Littler et al. 2010, Bodin et al. 2016). However, the PI/To CIE was not recorded in all the localities considered in this paper (e. g., Rodiles and Sancerre; Fig. 5). More puzzlingly, Bodin et al. (2016) have shown that the PI/To negative CIE recorded by the bulk carbonate fraction in three different successions from the High-Atlas in Morocco is not recorded by organic material from the same samples. They concluded that the PI/To negative CIE has a strong lithological control, and suggested that the negative CIE might reflect local changes in carbonate-producing sources rather than global carbon cycle perturbations. The negative CIE in the fossil wood profile recorded at the PI/To in the GSSP at Peniche (Hesselbo et al. 2007) suggests, on the contrary, that the perturbation affected terrestrial environments. It thus remains to be seen whether the PI/To negative CIE reflects global or local changes in carbon cycling.

The upper Pliensbachian has been interpreted as a cooling period (Morard et al. 2003, Suan et al. 2008, Korte et al. 2011, Gómez et al. 2016), and sea-level experienced a prominent fall followed by a rapid transgression in the earliest Toarcian (e. g., Pittet et al. 2014). The regression-transgression couplet gave rise in turn to hiatuses or condensations in many Tethyan localities and, especially, in those sections which were located in the most proximal settings (Pittet et al. 2014). The occurrence of hiatuses or condensation at the Pliensbachian/Toarcian transition may also account for the differences in terms of ranking of bioevents or of presence/absence of some species in the different sections considered here. Ultimately, the two sections studied here appear amongst the most complete for the PI/To (e. g., Comas Rengifo et al. 1999, Elmi 2007, Gabilly 1976).

### 5.4. Comparisons with independent proxies

To better constrain the PI/To nannofossil events recorded in the studied sections, we compared biostratigraphic and carbon isotope data with other additional stratigraphic techniques, namely strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and magnetostratigraphy. We take into





**Fig. 5.** Comparison between La Almunia, Anse St. Nicolas and other Northern and Southern Tethyan sections and proto-Atlantic (Peniche). The recently studied section of Asientos (Fantasia et al. 2018), located in the Andean Basin, is also considered here. Both calcareous nannofossil data and bulk carbonate carbon isotopes are presented. All sections are precisely dated by ammonite biostratigraphy. Nannofossil biostratigraphic data come from the following papers: Mattioli et al. 2008 (Dotternhäusen); Clémence et al. 2015 (Sancerre); Fraguas et al. 2012 (Rodiles); Mattioli et al. 2013 (Peniche and Valdorbja); Reolid et al. 2014 (La Cerradura); Bodin et al. 2010 (Amellago). On the right of the figure is reported the duration of the P/To CIE (after Martínez et al. 2017). Also the duration of the T-OAE CIE is shown (after Suan et al. 2008). Some of these section are more expanded (e. g., the Peniche GSSP or Amellago in Morocco) while some others are more condensed (e. g. Dotternhäusen); this can also be seen in the succession of first occurrence events, which can be either more spaced or more concentrated. Shaded area corresponds to the P/To event and the T-OAE no first occurrences are documented. Note that the Pliensbachian/Toarcian diversification event of nannofossils takes place across the P/To, while during the T-OAE no first occurrences are documented. The vertical scale is the same for all the sections but Amellago, which is the most expanded section.

account data from Comas Rengifo et al. (2010), who studied the Almunacid de la Cuba section, which is located at ca. 60 km to the SE of la Almunia (35 km South of Zaragoza). Both sections are precisely correlated each-other as well as with the GSSP at Peniche (see Rocha et al. 2016).  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope values of Almunacid de la Cuba section match with previously published data for England (McArthur et al. 2000) and Portugal (Hesselbo et al. 2007), showing a decrease during the Hawskerense ammonite subzone (latest Pliensbachian), reaching a minimum value at around the Pliensbachian/Toarcian boundary and a recovery in the lower Toarcian (Fig. 2).  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio shows distinctive changes across the PI/To, namely a negative trend that matches with the numerous calcareous nannofossil events recorded across the PI/To boundary. These combined bio- and chemostratigraphic events may be used as a reliable proxy to perform global correlations.

From the magnetostratigraphic record available at Almunacid de la Cuba, the PI/To is very close to the inversion in magnetozones N2/R2 of Comas-Rengifo et al. (2010). This interval also corresponds to minimum values of strontium isotopes and the peak in calcareous nannofossil originations. This magnetic record permits indirect correlation with the Karoo-Ferrar Traps reversed/normal polarity succession, and hence the possible projection of Karoo ages onto the PI/To. The PI/To might be correlated to the Karoo basalts from South Africa dated to  $182.7 \pm 0.8$  Ma  $^{40}\text{Ar}/^{38}\text{Ar}$  (Duncan et al. 1997). This is within the error interval but slightly younger than the age measured by Pálffy and Smith (2000), namely  $183 \pm 1.7$ – $1$ – $1$  Ma, or the  $182 \pm 1.5$  Ma estimated by Ogg (2004).

The PI/To was a biological key period not only for calcareous nannofossils, but also for many other fossils groups, such as marine invertebrates that experienced stepwise extinction and turnovers (e. g., Little et al. 1995, Morard et al. 2003, Cecca and Macchioni 2004). Nevertheless, for calcareous nannofossils and especially coccolithophorids the PI/To represents mostly an origination period (high number of FO) and, finally, the key point from which primitive coccolithophorid assemblages (dominated by muroliths) were replaced by the evolutionary successful placolith group still dominating in today oceans. The emergence of the placolith-coccoliths was important because it produced a locked coccosphere, meanwhile the murolith-coccoliths were presumably contiguous, not interlocking at the surface of the cell (Wiggan et al. 2018). Recently, astrochronology has been applied in order to

calculate the duration of ammonite and nannofossil zones in expanded sections of Morocco (Martinez et al. 2017). This study has revealed that the interval comprised between the PI/To and the FO of *C. superbus* lasts between  $433 \pm 25$  and  $505 \pm 44$  kyrs. Such an approach may be applied in the future to our high-resolution dataset in order to better constrain the time lag between single nannofossil events and, finally, calculate real diversification rates.

## 6. Summary and conclusions

The two sections studied here for calcareous nannofossil biostratigraphy and chemostratigraphy at Anse St. Nicolas in W France and La Almunia in central Spain offer the opportunity to perform a high-resolution study across the PI/To interval. The sections are well dated with ammonites and represent amongst the most continuous records for this time interval, given that often hiatuses and condensations occur in many Tethyan locations. The analysis of carbon stable isotopes reveal a negative excursion that corresponds to the PI/To event, as already documented in literature for other areas. Although the general trend in diversity and absolute abundance of calcareous nannofossils is very similar in the two section studied here, some differences are observed in assemblage composition (e. g., higher proportions of *Schizosphaerella* in La Almunia), but also in the morphology of the observed species. The two sections being located in different sedimentary basins but not very remote the one with respect to the other, the observed differences may indicate a certain extent of geographical segregation within western Tethys basins.

Calcareous nannofossils experienced at the PI/To a dramatic origination event. This is accompanied by an increase in species diversity and absolute abundances, and also corresponds to a change in the assemblage composition from murolith- to placolith-dominated coccoliths. All these observations are consistent with data coming from other Tethyan settings although some local differences are observed.

The PI/To represents a major turnover for several invertebrate groups, somehow more noteworthy than the T-OAE crisis, meaning that this event affected all marine biota and environments. Thus, the PI/To corresponded to a key evolutionary period, occurring concomitantly with major geochemical perturbations, a prominent sea-level fall, likely glacio-eustatic in origin, followed by a rise. The upper Pliensbachian–lo-

wermost Toarcian successions are characterized by numerous depositional hiatuses and condensed intervals (e. g., Wignall 1991, Morard et al. 2003, Röhl and Schmid-Röhl 2005, Léonide et al. 2012, Pittet et al. 2014, Rocha et al. 2016). Because of the incomplete nature of the boundary strata in many Tethyan areas, it is still unclear if such a high origination rate is uniquely linked to the evolutionary history of marine invertebrates, or if there is a superimposed effect of hiatuses or condensations. If this is the case, it is not excluded that the Pl/To origination event was partly amplified in the sedimentary record. However, the glacio-eustatic sea-level fall in the uppermost Pliensbachian could also have been at the origin of an allopatric speciation, because geographical barriers likely appeared between Western Tethyan basins. Astrochronological studies should be applied in the future to such a high-resolution dataset in order to constrain diversification and turnover rates of calcareous nannofossils.

## Species list

List of the species identified in the present work, mentioned both in the text and in the plates. Taxonomy follows Bown (1987) for muraliths, Mattioli (1996) for *Lotharingius*, and Mattioli et al. (2004 b) for *Similiscutum/Biscutum*. Some remarks about taxonomic concepts have been added when needed.

*Axopodorhabdus atavus* (Grün et al., 1974) Bown, 1987

*Axopodorhabdus cylindratus* (Noël, 1965) Wind and Wise in Wise and Wind, 1977

*Biscutum dubium* (Noël, 1965) Grün in Grün et al., 1974

*Biscutum grande* Bown, 1987

*Biscutum intermedium* Bown, 1987

*Bussonius leufuensis* Bown and Kielbowicz, 1987 in Bown, 1987

Remarks: *Bussonius* is included in the Watznaueriaceae family, the same as for *Lotharingius*. However, the two genera are different because the two cycles composing the distal shield are equally bright in *Lotharingius* appearing white in color, whilst for *Bussonius* the inner cycle is slightly brighter than the outer, which is slightly grey. Also, the cross structure in the central area of *B. leufuensis* is thicker than the cross in *L. barozii* or in *L. crucicentralis*. The arms of the cross in *Bussonius* are offset, thus the cross appears asymmetrical.

*Bussonius prinsii* (Noël, 1973) Goy, 1979

Remarks: *B. prinsii* differs from *B. leufuensis* for its more elliptical shape and narrower central area.

*Calyculus* spp. Noël, 1973

Remarks: thin and narrowly elliptical specimens are recorded, as well as thicker and broadly elliptical forms. These last likely represent transitional forms between *Calyculus* and *Carinolithus*.

*Carinolithus poul nabroni* Mattioli, 1996

Remarks: these are forms with an extended tube between proximal and distal shields. In side view, the central opening has an elongated V-shape.

*Carinolithus superbus* (Deflandre in Deflandre and Fert, 1954) Prins in Grün et al., 1974

Remarks: the central opening is very reduced and, in side view, the coccolith has a general T-shape.

*Crepidolithus cavus* Prins ex Rood et al., 1973

Remarks: in Plate 1 we show a *C. cavus/imponatus*. In fact, the difference between the two species is quite tenuous, and the bridge which characterizes *C. imponatus* is sometimes not preserved, although its insertions on the coccolith are visible.

*Crepidolithus crassus* (Deflandre in Deflandre and Fert, 1954) Noël, 1965

*Crepidolithus crucifer* Prins 1969

*Crepidolithus granulatus* Bown, 1987

Remarks: the specimens shown in Plate 1 is very thick, but we also have found forms with a much thinner wall.

*Diductius constans* Goy in Goy et al., 1979

*Crucirhabdus primulus* Prins, 1969 ex Rood et al., 1973 emend.

*Crucirhabdus minutus* Jafar, 1983

*Discorhabdus ignotus* (Górka, 1957) Perch-Nielsen, 1968

*Ethmorhabdus crucifer* Noël, 1965

*Ethmorhabdus gallicus* Noël, 1965

*Lotharingius barozii* Noël, 1973

Remarks: *L. barozii* is distinguished from all other *Lotharingius* because of its thin rim and very wide central area. The outer and inner cycles of distal shield are of equal thickness. The cross spanning the central area is very rarely preserved.

*Lotharingius crucicentralis* (Medd, 1971) Grün and Zweili, 1980

Remarks: this is differentiated from *L. barozii* because of its more reduced central area, which is sub-rectangular or oval in shape. Central area is spanned by a cross which is often not preserved. When the cross is absent, the four insertions on the coccolith are still observed. *L. crucicentralis* displays small dimensions in upper Pliensbachian and lower Toarcian material,

but its size increased from the lower/middle Toarcian transition (Ferreira et al. 2016).

*Lotharingius frodoi* Mattioli, 1996

Remarks: small coccolith, broadly elliptical-to-elliptical in shape, and presenting a very reduced central area filled with two buttresses mimicking a small bridge. If this central area structure is lacking, the insertions of the buttresses on both sides of the coccolith are still visible. It is differentiated from *L. barozii* and *L. crucicentralis* because of its reduced central area size.

*Lotharingius hauffii* Grün and Zweili in Grün et al., 1974

Remarks: small coccolith, elliptical-to-subcircular in shape, and presenting a reduced central area with a small button. It is differentiated from *L. barozii* and *L. crucicentralis* because of its reduced central area and more circular shape, and from *L. frodoi* because of less elliptical shape and central area structures.

*Lotharingius sigillatus* (Stradner, 1961) Prins in Grün et al., 1974

Remarks: elliptical coccolith, presenting a narrow and elongated central area, with a longitudinal buttress bulging in its middle part. It is differentiated from *L. barozii* and *L. crucicentralis* because of its narrower central area, from *L. frodoi* and *L. hauffii* because of slightly larger dimensions of the coccolith and more elongated central area. In a way similar to *L. crucicentralis*, *L. sigillatus* dimension is small in upper Pliensbachian and lower Toarcian material, but its size increased from the lower/middle Toarcian transition (Ferreira et al. 2016).

*Lotharingius umbriensis* Mattioli, 1996

Remarks: this is a quite rare but easy to recognize coccolith. It possesses a subcircular shape, a reduced central area spanned by a little cross. The optical discontinuity between the inner and outer cycle of distal shield is well-marked.

*Lotharingius velatus* Bown and Cooper, 1989

Remarks: this is the largest *Lotharingius* species. The general shape of coccolith and central area are oval. The wide central area is spanned by granulations that sometimes are not preserved. Sometimes, specimens with the diagnostic characters, but with a thin rim are observed (*L. aff. velatus* of Plate 2). As for the other *Lotharingius* species, its size is smaller in lower Toarcian material and increased from the lower/middle Toarcian transition (Ferreira et al. 2016).

*Mazaganella protensa* Bown, 1987

*Mitrolithus elegans* Deflandre in Deflandre and Fert, 1954

*Mitrolithus lenticularis* Bown, 1987

*Mitrolithus jansae* (Wiegand, 1984) Bown and Young in Young et al., 1986

*Orthogonoides hamiltoniae* Wiegand, 1984

*Parhabdololithus liasicus* Deflandre in Grassé, 1952

*Parhabdololithus liasicus* subsp. *distinctus* Bown, 1987

*Parhabdololithus liasicus* subsp. *liasicus* Deflandre in Grassé, 1952

*Schizosphaerella* Deflandre & Dangeard, 1938

*Similiscutum cruciulus* subsp. *avitum* Mattioli et al., 2004b

*Similiscutum cruciulus* subsp. *cruciulus* Mattioli et al., 2004b

*Similiscutum finchii* (Crux, 1984 emend. Bown, 1987) de Kænel and Bergren, 1993

Remarks: elliptical *Similiscutum* with light grey, striped birefringence colors. The central area is rectangular and elongated. It is differentiated from *S. cruciulus* group because of lighter grey colors, more elliptical shape and wider central area.

*Similiscutum novum* (Goy, 1979) Mattioli et al., 2004

Remarks: sub-circular *Similiscutum* with light grey, striped birefringence colors. The central area is sub-squared. It is differentiated from *S. finchii* because of smaller size, less elliptical shape and more reduced central area size, and from *S. cruciulus* group because of lighter grey colors.

*Similiscutum precarium* de Kænel and Bergen, 1993

*Sollasites* sp. Black, 1967

*Sollasites arctus* (Noël, 1973) Bown, 1987

*Stradnerlithus* Black, 1971

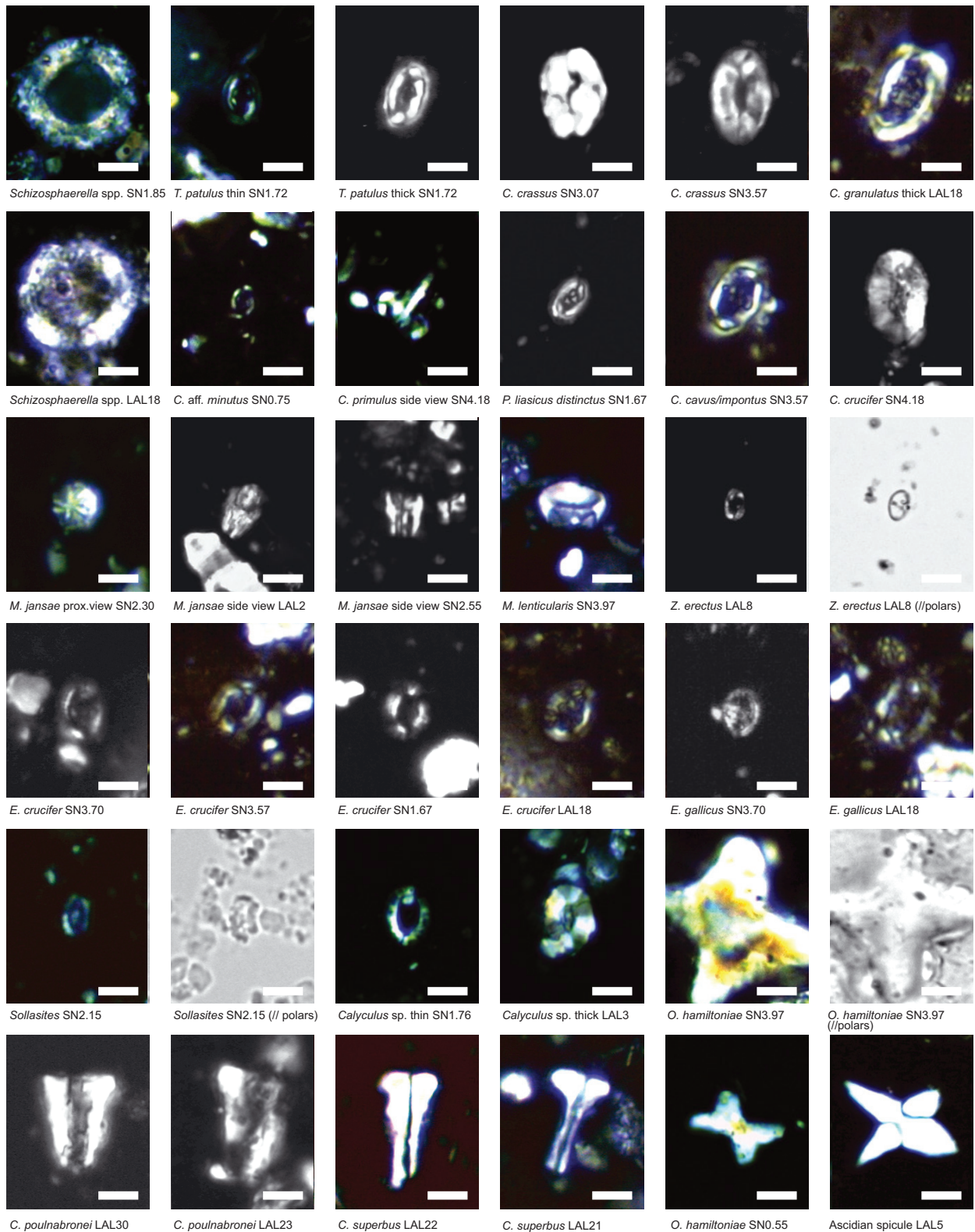
*Tubirhabdus patulus* Prins ex Rood et al., 1973

Remarks: specimens very thin occur along with thicker forms.

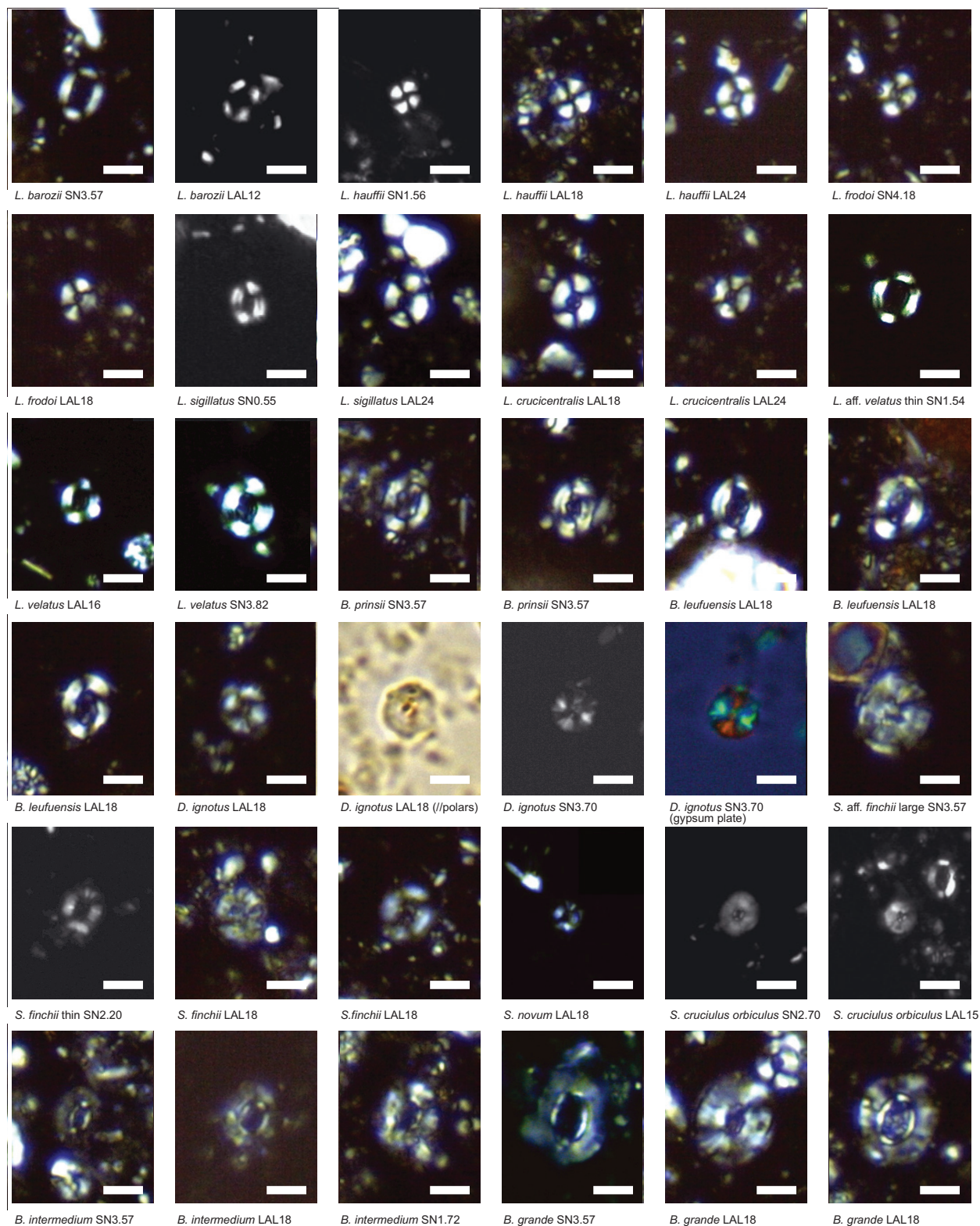
*Zeugrhabdotus erectus* (Deflandre in Deflandre and Fert, 1954) Reinhardt, 1965

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**Plate 1.** Microphotographs of common nannofossil taxa recored at La Almunia (LAL) and at Anse St. Nicolas (SN). Slight morphological differences may occur between nannofossils in the two regions. Scale bar is 5 microns.



**Plate 2.** Microphotographs of common nannofossil taxa recored at La Almunia (LAL) and at Anse St. Nicolas (SN). Slight morphological differences may occur between nannofossils in the two regions. Scale bar is 5 microns.

Table 1. Stratigraphic distribution of calcareous nannofossils recorded at La Almunia section. Large-sized square symbol is used for abundant species (>10% of the assemblage), intermediate-sized square is used for common species (1–10%) and small-sized square represents frequent species (0–1%). Species abundance concept is after Bown (1998).

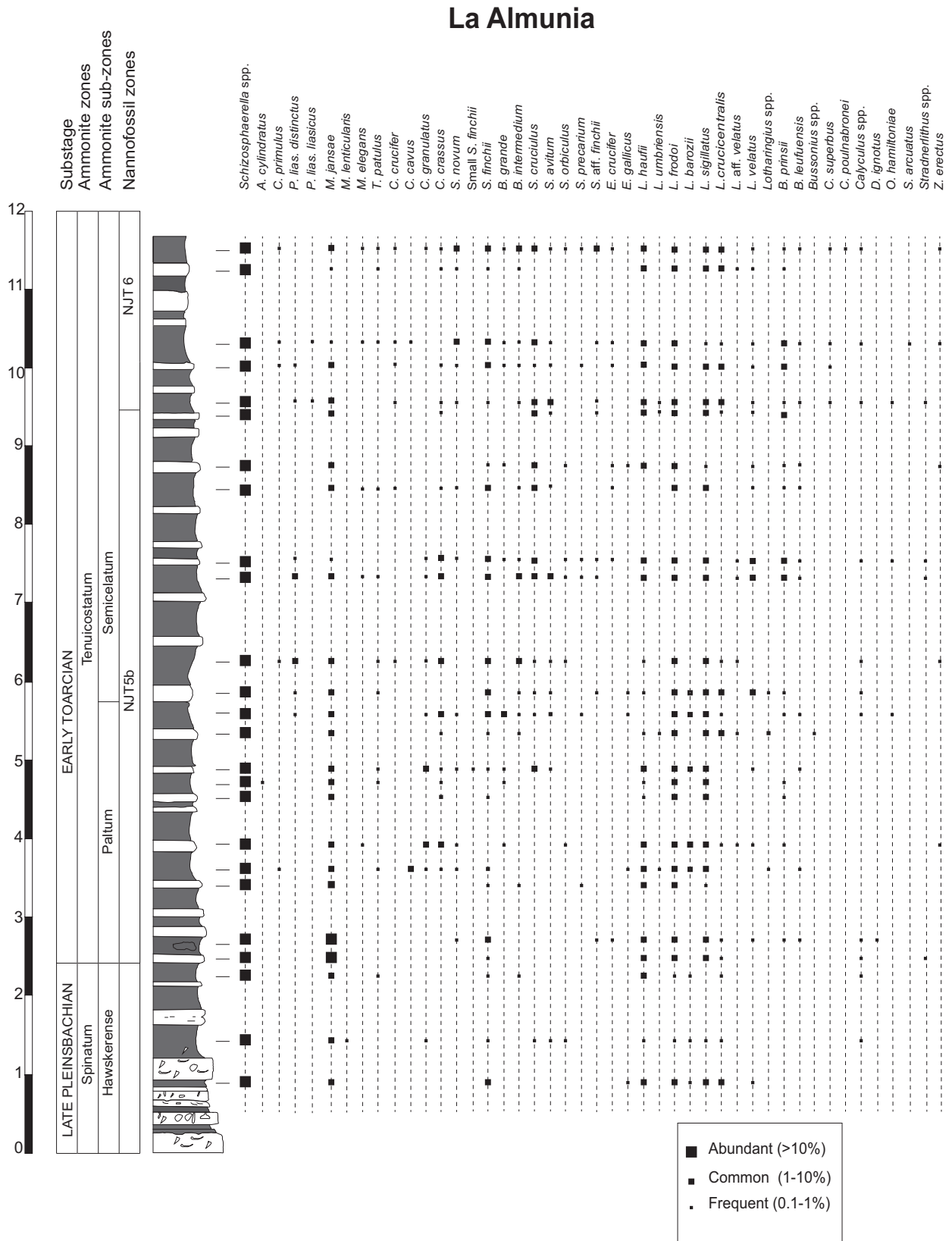
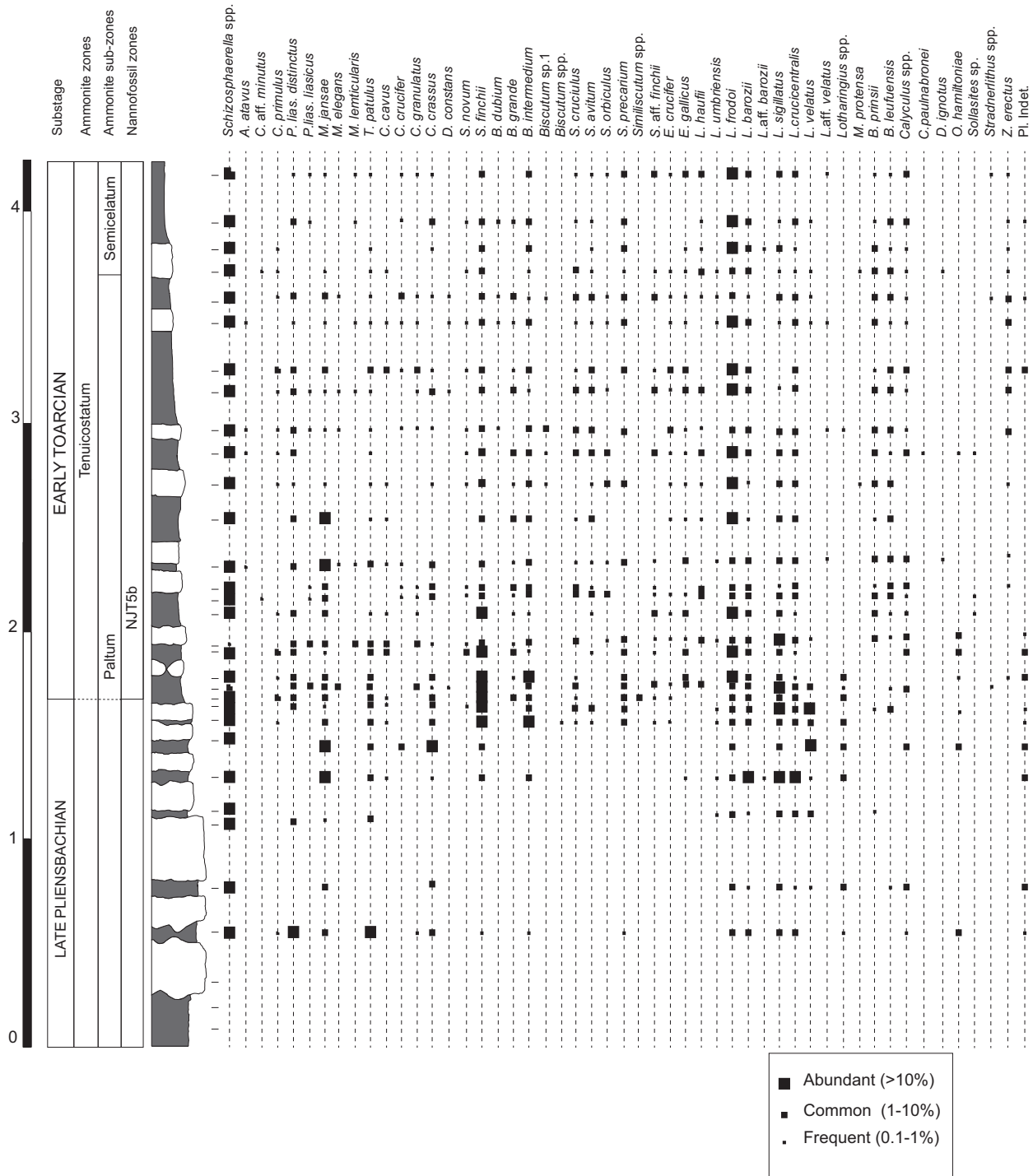




Table 2. Stratigraphic distribution of calcareous nannofossils recorded at Anse St. Nicolas section. Large-sized square symbol is used for abundant species (>10% of the assemblage), intermediate-sized square is used for common species (1–10%) and small-sized square represents frequent species (0–1%). Species abundance concept is after Bown (1998).

### Anse St. Nicolas



## References

- Al-Suwaidi, A. H., Hesselbo, S. P., Damborenea, S. E., Manceño, M. O., Jenkyns, H. C., Riccardi, A. C., Angelozzi, G. N., Baudin, F., 2016. The Toarcian Oceanic Anoxic Event (Early Jurassic) in the Neuquén Basin, Argentina: A Reassessment of Age and Carbon Isotope Stratigraphy. *The Journal of Geology*, doi: 10.1086/684831.
- Arias, C. F., 1991. Las asociaciones de ostrácodos del Domeriense superior y Toarciense inferior de la Cordillera Ibérica. *Coloquios de Paleontología* 43, 79–99.
- Arias, C. F., 1995. Los ostrácodos del Toarciense inferior en la Cordillera Ibérica. PhD Thesis, Fac. C. Geológicas. Univ. Complutense Madrid, Spain.
- Bassoullet, J. P., Elmi, S., Poisson, A., Cecca, F., Bellion, Y., Guiraud, R., Baudin, F., 1993. Mid Toarcian. In: Dercourt, J., Ricou, L. E., Vrielynck, B. (Eds.), *Atlas Tethys Palaeoenvironmental Maps*. BEICIPFRANLAB, Rueil-Malmaison.
- Beaufort, L., Barbarin, N., Gally, Y., 2014. Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature Protocols* 9, 633–642.
- Bécaud, M., 2002. Le Toarcien de la bordure sud et sud-est du Massif armoricain (Deux-Sèvres et Vendée). *Le naturaliste vendéen* 2, 3–33.
- Bécaud, M., 2005. Ammonites peu connues du Toarcien inférieur du sud-ouest de la Vendée. *Le naturaliste vendéen* 5, 45–48.
- Bécaud, M., 2006. Les Hildoceratidae (Ammonitina) du Toarcien de la bordure sud et sud est du Massif armoricain (France). *Docum. Lab. Géologie Lyon* 162, 1–148.
- Blomeier, D. P. G., Reijmer, J. J. G., 1999. Drowning of a lower Jurassic carbonate platform: Jbel Bou Dahar, High Atlas, Morocco. *Facies* 41, 81–110.
- Bodin, S., Krencker, F. N., Kothe, T., Hoffmann, R., Mattioli, E., Heimhofer, U., Kabiri, L., 2016. Perturbation of the carbon cycle during the late Pliensbachian – early Toarcian: New insight from high-resolution carbon isotope records in Morocco. *Journal of African Earth Sciences* 116, 89–104, <https://doi.org/10.1016/j.jafrearsci.2015.12.018>.
- Bodin, S., Mattioli, E., Fröhlich, S., Marshall, J. D., Boutib, L., Lahsini, S., Redfern, J., 2010. Documentation of Early Toarcian (Jurassic) carbon isotope negative shifts and nutrient changes along the Northern Gondwana margin (High Atlas, Morocco): palaeoenvironmental implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* 297, 377–390.
- Boomer, I., Lord, A. R., Page, K. N., Bown, P. R., Lowry, F. M. D., Riding, J. B., 2009. The biostratigraphy of the Upper Pliensbachian–Toarcian (Lower Jurassic) sequence at Ilminster, Somerset. *Journal of Micropalaeontology* 28, 67–85.
- Bown, P. R., 1987. Taxonomy, evolution and biostratigraphy of Late Triassic-early Jurassic calcareous nannofossils. *Special Papers in Paleontology* 38, 1–118.
- Bown, P. R., Cooper, M. K. E., 1998. Jurassic. In: Bown, P. R. (Ed.), *Calcareous Nannofossil Biostratigraphy*, British Micropalaeontological Society Series. Chapman and Hall/Kluwer Academic Publishers, London, 86–131.
- Brand, W. A., Coplen, T. B., Vogl, J., Rosner, M., Prohaska, T., 2014. Assessment of international reference materials for isotope-ratio analysis. *Pure and Applied Chemistry* 86, 425–467.
- Casellato, C. E., Erba, E., 2015. Calcareous nannofossil biostratigraphy and paleoceanography of the toarcian oceanic anoxic event at colle di sogno (Southern Alps, Northern Italy). *Rivista Italiana di Paleontologia e Stratigrafia* 121, 297–327.
- Cecca, F., Macchioni, F., 2004. The two Early Toarcian (Early Jurassic) extinction events in ammonoids. *Lethaia* 3, 35–56, <https://doi.org/10.1080/00241160310008257>.
- Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Herrero, C., Osete, M. L., Palencia, A., 2010. A complementary section for the proposed Toarcian (Lower Jurassic) global stratotype: the Almonacid de la Cuba sections (Spain). *Stratigraphy and Geological Correlation* 18, 133–152.
- Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Herrero, C., Perilli, N., Rodrigo, A., 1999. El Jurásico Inferior en la sección de Almonacid de la Cuba (Sector central de la Cordillera Ibérica), Zaragoza, España. *Cuad. Geol. Ibér.* 25, 27–57.
- Courtinat, B., Pittet, B., Mattioli, E., Rio, M., 2007. Marine microplankton and calcareous nannofossil palaeoecology of the Toarcian stratotype. *Geobios* 40, 785–800.
- Dera, G., Neige, P., Dommergues, J.-L., Brayard, A., 2011. Ammonite paleobiogeography during the Pliensbachian–Toarcian crisis (Early Jurassic) reflecting paleoclimate, eustasy, and extinctions. *Global and Planetary Change* 78, 92–105.
- Dera, G., Pellenard, P., Neige, P., Deconinck, J.-F., Pucéat, E., Dommergues, J.-L., 2009. Distribution of clay minerals in Early Jurassic Peritethyan seas: Palaeoclimatic significance inferred from multiproxy comparisons. *Palaeogeography, Palaeoclimatology, Palaeoecology* 271, 39–51.
- Duncan, R. A., Hooper, P. R., Rehacek, J., Marsh, J. S., Ducan, A. R., 1997. The timing and duration of the Karoo igneous event, southern Gondwana. *Journal of Geophysical Research* 102, 127–138.
- Elmi, S., 2007. Pliensbachian/Toarcian boundary: the proposed GSSP of Peniche (Portugal). *Ciências da Terra (UNL)* 16, 7–16.
- Elmi, S., Rulleau, L., Gabilly, J., Mouterde, R., 1997. Ammonites: Toarcien. In: Cariou, E., Hantzpergue, P. (Eds.), *Biostratigraphie du Jurassique ouest-européen et méditerranéen: Zonations parallèles et distribution des invertébrés et microfossiles*. Groupe Français d'Etude du Jurassique. *Bulletin du Centre de Recherches, Elf Exploration Production* 17, 25–36 + 120–125.
- Fantasia, A., Föllmi, K. B., Adatte, T., Bernárdez, E., Spangenberg, J. E., Mattioli, E., 2018. The Toarcian Oceanic Anoxic Event in southwestern Gondwana: An example from the Andean Basin, northern Chile. *Journal of the*

- Geological Society, doi: <https://doi.org/10.1144/jgs2018-008>.
- Fatela, F., Taborda, R., 2002. Confidence limits of species proportions in microfossil assemblages. *Marine Micropaleontology* 45, 169–174, [10.1016/S0377-8398\(02\)00021-X](https://doi.org/10.1016/S0377-8398(02)00021-X).
- Ferreira, J., Mattioli, E., Pittet, B., Cachão, Spangenberg, J.E., 2015. Palaeoecological insights on Toarcian and lower Aalenian calcareous nannofossils from the Lusitanian Basin (Portugal). *Paleogeography, Paleoclimatology, Paleocology* 436, 245–262.
- Ferreira, J., Mattioli, E., van de Schootbrugge, B., 2016. Palaeoenvironmental vs. evolutionary control on size variation of coccoliths across the Lower-Middle Jurassic. *Paleogeography, Paleoclimatology, Paleocology*, [http://dx.doi.org/10.1016/j.palaeo.2016.10.029](https://doi.org/10.1016/j.palaeo.2016.10.029).
- Fraguas, Á., Erba, E., 2010. Biometric analyses as a tool for the differentiation of two coccolith species of the genus *Crepidolithus* (Pliensbachian, Lower Jurassic) in the Basque-Cantabrian Basin (Northern Spain). *Marine Micropaleontology* 77, 125–136.
- Fraguas, Á., Comas-Rengifo, M. J., Gómez, J. J., Goy, A., 2012. The calcareous nannofossil crisis in Northern Spain (Asturias province) linked to the Early Toarcian warming-driven mass extinction. *Marine Micropaleontology* 94–95, 58–71.
- Fu, X., Wang, J., Feng, X., Wang, D., Chen, W., Song, C., Zeng, S., 2016. Early Jurassic carbon-isotope excursion in the Qiangtang Basin (Tibet), the eastern Tethys: Implications for the Toarcian Oceanic anoxic event. *Chemical Geology* 442, 62–72.
- Gabilly, J., 1964. Stratigraphie et limite de l'étage Toarcien Thouars et dans les régions voisines. *Coll. Jurassique, Luxembourg (1962)*. C.R. Mém. Inst. Grand Duc., Sect. Sci. Nat. Phys. Math., 193–201.
- Gabilly, J., 1973. Le Toarcien du Poitou. *Biostratigraphie de la région du stratotype. Évolution des Hildocerataceae (Ammonitina)*. Doctoral dissertation, Poitiers, 546 p.
- Gabilly, J., 1976. Le Toarcien à Thouars et dans le Centre-Ouest de la France. *Biostratigraphie. Évolution de la faune (Harpoceratinae – Hildoceratinae)*; collection: Comité français de Stratigraphie. Les stratotypes français vol. 3. CNRS, Paris, 217 p.
- Gautier, F., Mouterde, R., 1964. Stratigraphie – lacunes et irrégularités des dépôts à la limite du Jurassique inférieur et du jurassique moyen de la bordure nord des chaînes ibériques (Espagne). *Comptes rendus hebdomadaires des séances de l'académie des sciences* 258, 3064.
- Gómez, J. J., Comas-Rengifo, M. J., Goy, A., 2016. Palaeoclimatic oscillations in the Pliensbachian (Early Jurassic) of the Asturian Basin (Northern Spain). *Climate of the Past* 12, 1199–1214, doi: [10.5194/cp-12-1199-2016](https://doi.org/10.5194/cp-12-1199-2016).
- Gómez, J. J., Goy, A., Canales, M. L., 2008. Seawater temperature and carbon isotope variations in belemnites linked to mass extinction during the Toarcian (Early Jurassic) in Central and Northern Spain. Comparison with other European sections. *Paleogeography, Palaeoclimatology, Palaeoecology* 258, 28–58.
- Goy, A., Martínez, G., 1990. Biozonación del Toarciense en el área de La Almunia de Doña Godina-Ricla (Sector Central de la Cordillera Ibérica). *Cuadernos Geología Ibérica* 14, 9–44.
- Hammer, Ø., Harper, D. A. T., Ryan, P. D., 2001. Past: Paleontological Statistics Software Package for education and data analysis. *Palaeontologia Electronica* 4 (1), 9, [http://palaeo-electronica.org/2001\\_1/past/issue1\\_01.htm](http://palaeo-electronica.org/2001_1/past/issue1_01.htm).
- Hay, W. W., 1972. Probabilistic stratigraphy. *Eclogae Geologicae Helveticae* 65, 255–266.
- Hermoso, M., Minoletti, F., Rickaby, R. E. M., Hesselbo, S. P., Baudin, F., Jenkyns, H. C., 2012. Dynamics of a stepped carbon-isotope excursion: Ultra high-resolution study of Early Toarcian environmental change. *Earth and Planetary Science Letters* 319–320, 45–54.
- Herrero, C., 1992. Los foraminíferos del Toarciense inferior de la Cordillera Ibérica. Tesis Doctoral. Facultad de Ciencias Geológicas, Universidad Complutense de Madrid, 523 pp.
- Hesselbo, S. P., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. *Proceedings of the Geologists' Association* 119, 19–34.
- Hesselbo, S. P., Jenkyns, H. C., Duarte, L. V., Oliveira, L. C. V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth Planet. Sci. Lett.* 253, 455–470.
- Huang, C., Hesselbo, S. P., 2014. Pacing of the Toarcian Oceanic Anoxic Event (Early Jurassic) from astronomical correlation of marine sections. *Gondwana Research* 25, 1348–1356.
- Jenkyns, H. C., 1988. The Early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. *Am. J. Sci.* 288, 101–151.
- Korte, C., Hesselbo, S., 2011. Shallow marine carbon and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic. *Paleoceanography* 26, 1–18, PA4219, doi: [10.1029/2011PA002160](https://doi.org/10.1029/2011PA002160).
- Krebs, C. J., 1998. *Ecological methodology* (2nd edition). Addison Wesley Longman (Eds., Pearson Education), 620 pp.
- Léonide, P., Floquet, M., Durlet, C., Baudin, F., Pittet, B., Lécuyer, C., 2012. Drowning of a carbonate platform as a precursor stage of the Early Toarcian global anoxic event (Southern Provence sub-Basin, South-east France). *Sedimentology* 59, 156–184.
- Little, C. T. S., Benton, M. J., 1995. Early Jurassic mass extinction: a global long term event. *Geology* 23, 495–498.
- Littler, K., Hesselbo, S. P., Jenkyns, H. C., 2010. A carbon-isotope perturbation at the Pliensbachian–Toarcian boundary: evidence from the Lias Group, NE England. *Geological Magazine* 147 (2), 181–192.
- Mailliot, S., Mattioli, E., Guex, J., Pittet, B., 2006. The Early Toarcian anoxia, a synchronous event in the Western Tethys? An approach by quantitative biochronology (Unitary Associations), applied on calcareous nannofos-

- sils. *Palaeogeography, Palaeoclimatology, Palaeoecology* 240 (3–4), 562–586, <https://doi.org/10.1016/j.palaeo.2006.02.016>.
- Martindale, R. C., Aberhan, M., 2017. Response of macrobenthic communities to the Toarcian Oceanic Anoxic Event in northeastern Panthalassa (Ya Ha Tinda, Alberta, Canada). *Palaeogeography, Palaeoclimatology, Palaeoecology* 478, 103–120, <https://doi.org/10.1016/j.palaeo.2017.01.009>.
- Martinez, M., Krencker, F.-N., Mattioli, E., Bodin, S., 2017. Orbital chronology of the Pliensbachian – Toarcian transition from the Central High Atlas Basin (Morocco). *Newsletters on Stratigraphy* 50 (1), 47–69, <https://doi.org/10.1127/nos/2016/0311>.
- Mattioli, E., Erba, E., 1999. Synthesis of calcareous nannofossil events in tethyan lower and middle Jurassic successions. *Rivista Italiana di Paleontologia e Stratigrafia* 105, 343–376.
- Mattioli, E., Pittet, B., Palliani, R., Rohl, H.-J., Schmid-Rohl, A., Morettini, E., 2004a. Phytoplankton evidence for the timing and correlation of palaeoceanographical changes during the early Toarcian oceanic anoxic event (Early Jurassic). *Journal of the Geological Society* 161 (4), 685–693, <https://doi.org/10.1144/0016-764903-074>.
- Mattioli, E., Pittet, B., Petitpierre, L., Mailliot, S., 2009. Dramatic decrease of pelagic carbonate production by nannoplankton across the Early Toarcian anoxic event (T-OAE). *Global and Planetary Change* 65 (3–4), 134–145, <https://doi.org/10.1016/j.gloplacha.2008.10.018>.
- Mattioli, E., Pittet, B., Suan, G., Mailliot, S., 2008. Calcareous nannoplankton changes across the early Toarcian oceanic anoxic event in the western Tethys. *Paleoceanography* 23 (3), 1–17, <https://doi.org/10.1029/2007PA001435>.
- Mattioli, E., Pittet, B., Young, J. R., Bown, P. R., 2004b. Biometric analysis of Pliensbachian-Toarcian (Lower Jurassic) coccoliths of the family Biscutaceae: intra- and interspecific variability versus palaeoenvironmental influence. *Marine Micropalaeontology* 52, 5–27.
- Mattioli, E., Plancq, J., Boussaha, M., Duarte, L. V., Pittet, B., 2013. Calcareous nannofossil biostratigraphy: new data from the Lower Jurassic of the Lusitanian Basin. *Comunicacoes Geologicas T. 100, 100 (Especial I)*, 69–76.
- McArthur, J. M., Donovan, D. T., Thirwall, M. F., Fouke, B. W., Matthey, D., 2000. Strontium isotope profile of early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belmnite palaeotemperature. *Earth Planet. Sci. Lett.* 179, 269–285.
- Medd, A. W., 1982. Nannofossil zonation of the English Middle and Upper Jurassic. *Marine Micropalaeontology* 7, 73–95.
- Mensik, H., 1965. Stratigraphie und Paläogeographie des marinen Jura in den nord-westlichen Iberischen Ketten (Spanien). *Beih. Geol. Jb.*, 55–102.
- Morard, A., Guex, J., Bartolini, A., Morettini, E., De Wever, P., 2003. A new scenario for the Domerian – Toarcian transition. *Bull. Soc. géol. Fr.* 4, 351–356.
- Noël, D., 1965. Sur les Coccolithes du Jurassique Européen et d'Afrique du Nord. Éditions du Centre National de la Recherche Scientifique, Paris, 110–111.
- Noël, D., 1972. Nannofossiles calcaires de sediments jurassiques finement laminés. *Bull. Mus. Hist. Natur.* 3 e sér. 75, 95–116.
- Pálffy, J., Smith, P. L., 2000. Synchrony between Early Jurassic extinction, oceanic anoxic event, and the Karoo-Ferrar flood basalt volcanism. *Geology* 28, 747–750.
- Peti, L., Thibault, N., Clémence, M.-E., Korte, C., Dommergues, J.-L., Bougeault, C., Pellenard, P., Jelby, M. E., Ullmann, C. V., 2017. Sinemurian–Pliensbachian calcareous nannofossil biostratigraphy and organic carbon isotope stratigraphy in the Paris Basin: Calibration to the ammonite biozonation of NW Europe. *Palaeogeography, Palaeoclimatology, Palaeoecology* 468, 142–161.
- Philippe, M., Pujjalón, S., Suan, G., Mousset, S., Thévenard, F., Mattioli, E., 2017. The palaeolatitudinal distribution of fossil wood genera as a proxy for European Jurassic terrestrial climate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 466, 373–381.
- Pittet, B., Suan, G., Lenoir, F., Vitor, L., Mattioli, E., 2014. Carbon isotope evidence for sedimentary discontinuities in the lower Toarcian of the Lusitanian Basin (Portugal): Sea level change at the onset of the Oceanic Anoxic Event. *Sedimentary Geology* 303, 1–14, <https://doi.org/10.1016/j.sedgeo.2014.01.001>.
- Reggiani, L., Mattioli, E., Pittet, B., Duarte, L. V., Veiga de Oliveira, L. C., Comas-Rengifo, M. J., 2010. Pliensbachian (Early Jurassic) calcareous nannofossils from the Peniche section (Lusitanian Basin, Portugal): A clue for palaeoenvironmental reconstructions. *Marine Micropalaeontology* 75 (1–4), 1–16, <https://doi.org/10.1016/j.mar-micro.2010.02.002>.
- Reolid, M., Emanuela, M., Nieto, L. M., Rodriguez-Tovar, F. J., 2014. The Early Toarcian Oceanic Anoxic Event in the External Subbetic (Southiberian Palaeomargin, Westernmost Tethys): Geochemistry, nannofossils and ichnology. *Palaeogeography, Palaeoclimatology, Palaeoecology* 411, 79–94, <https://doi.org/10.1016/j.palaeo.2014.06.023>.
- Révész, K., Landwehr, J. M., 2002.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic composition of  $\text{CaCO}_3$  measured by continuous flow isotope ratio mass spectrometry: statistical evaluation and verification by application to Devils Hole core DH-11 calcite. *Rapid Communications in Mass Spectrometry* 16, 2102–2114.
- Rocha, R., Mattioli, E., Duarte, L. V., Pittet, B., Elmi, S., Mouterde, R., Cabral, M. C., Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Hesselbo, S. P., Jenkyns, H. C., Littler, K., Mailliot, S., Veiga, Oliveira, L. C., Osete, M. L., Perilli, N., Pinto, S., Ruget, C., Suan, G., 2016. Base of the Toarcian Stage of the Lower Jurassic defined by the Global Boundary Stratotype Section and Point (GSSP) at the Peniche section (Portugal). *Episodes* 39, 460–481.
- Röhl, H. J., Schmid-Röhl, A., Wolfgang, O., Frimmel, A., Lorenz, S., 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: An oxygen-depleted ecosystem con-



- trolled by sea level and palaeoclimate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 165, 27–52, doi: 10.1016/S0031-0182(00)00152-8.
- Rosales, I., Quesada, S., Robles, S., 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque – Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 203, 253–275.
- Roth, P.H., 1984. Preservation of calcareous nannofossils and fine-grained carbonate particles in mid-Cretaceous sediments from the southern Angola Basin. In: Hay, W.W. (Ed.), *Initial Reports of Deep Sea Drilling Project 75*. U.S. Government Printing Office, Washington, 651–655.
- Sabatino, N., Neri, R., Bellanca, A., Jenkyns, H., Baudin, F., Parisi, G., Masetti, D., 2009. Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria–Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. *Sedimentology* 56, 1307–1328.
- Sandoval, J., Bill, M., Aguado, R., O’Doherty, L., Doherty, L., Rivas, P., Morard, A., Guex, J., 2012. The Toarcian in the Subbetic basin (southern Spain): Bioevents (ammonite and calcareous nannofossils) and carbon-isotope stratigraphy. *Palaeogeography, Palaeoclimatology, Palaeoecology* 342–343, 40–63, <https://doi.org/10.1016/j.palaeo.2012.04.028>.
- Shannon, C.E., Weaver, W., 1949. *The Mathematical Theory of Communication*. Univ. of Ill. Press, Urbana, Ill.
- Spangenberg, J.E., Herlec, U., 2006. Hydrocarbon biomarkers in the Topla-Mežica zinc-lead deposits, northern Karavanke/Drau Range, Slovenia: Paleoenvironment at the site of ore formation. *Economic Geology* 101 (5), 997–1021.
- Suan, G., Mattioli, E., Pittet, B., Lécuyer, C., Suchéras-Marx, B., Duarte, L.V., Martineau, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* 290 (3–4), 448–458, <https://doi.org/10.1016/j.epsl.2009.12.047>.
- Suan, G., Mattioli, E., Pittet, B., Mailliot, S., Lécuyer, C., 2008a. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal. *Paleoceanography*, 23, PA1202, doi: 10.1029/2007PA001459.
- Them, T.R., Gill, B.C., Caruthers, A.H., Gröcke, D.R., Tulsy, E.T., Martindale, R.C., ... Smith, P.L., 2017. High-resolution carbon isotope records of the Toarcian Oceanic Anoxic Event (Early Jurassic) from North America and implications for the global drivers of the Toarcian carbon cycle. *Earth and Planetary Science Letters* 459, 118–126, <https://doi.org/10.1016/j.epsl.2016.11.021>.
- Thierry, J., Barrier, E., 2000. Middle Toarcian. In: Dercourt, J., Gaetani, M.E.A. (Eds.), *Atlas Peri-Tethys*. Palaeogeographical Maps CCGM/CGMW, Paris.
- van de Schootbrugge, B., McArthur, J.M., Bailey, J.M., Rosenthal, Y., Wright, J.M., Miller, K.G., 2005. Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records. *Paleoceanography* 20, PA3008, doi: 10.1029/2004PA001102.
- Wiggin, N.J., Riding, J.B., Fensome, R.A., Mattioli, E., 2018. The Bajocian (Middle Jurassic): A key interval in the early Mesozoic phytoplankton radiation. *Earth-Science Reviews* 180, 126–146.
- Wignall, P.B., Hallam, A., Newton, R.J., Sha, J.G., Reeves, E., Mattioli, E., Crowley, S., 2006. An eastern Tethyan (Tibetan) record of the Early Jurassic (Toarcian) mass extinction event. *Geobiology* 4, 179–190.

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**Table of contents – Electronic Supplementary Material (ESM)**

Calcareous nannofossils relative and absolute abundances as well as  $\delta^{13}\text{C}$  bulk rock data are available as supplementary material. The file can be requested to the corresponding author.



**Chapitre 2.2. Calcareous nannofossil  
biostratigraphy across the Paleocene-Eocene  
Thermal Maximum**

1 **Calcareous nannofossil biostratigraphy across the Paleocene-Eocene**

2 **Thermal Maximum**

3

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17

18 **Abstract**

19

20 The Paleocene-Eocene transition is characterized by a prominent negative carbon isotope  
21 excursion that corresponds to the Paleocene Eocene Thermal Maximum (PETM). The sharp  
22 negative shift of stable carbon isotopes has been retained as marker for the Paleocene/Eocene  
23 boundary. Although recorded in several oceanic and onland settings, the PETM phases namely  
24 the onset, the core of the event and the recovery, are not adequately dated by calcareous  
25 nannofossils because available standard biozonations do not provide us with a high-resolution

26 across the event. Here, we present new high-resolution biostratigraphic data from Sites 1209  
27 (Shatsky Rise, Tropical Pacific Ocean) and 1263 (Walvis Ridge, South Eastern Atlantic Ocean)  
28 in order to precisely assess the succession of biostratigraphic events (first and last occurrences,  
29 changes in the assemblage composition), and to anchor them to the independent proxy  
30 represented by the  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve. A tidy comparison of our data with nannofossil events  
31 from six sections located at different (paleo)latitudes and in different geological settings (open  
32 ocean-to-shelf) revealed 26 calcareous nannofossil events across a 250 kyrs long-lasting  
33 interval spanning the PETM, and allowed a high-resolution biozonal subdivision of this  
34 interval. Calcareous nannofossil events plotted against available  $\delta^{13}\text{C}_{\text{bulk carb}}$  curves show a  
35 certain degree of diachronism, even when considering previously established zonal markers.  
36 Also, unconformities occur at the onset of PETM in most oceanic sites, but to a lesser extent in  
37 onland sections. We propose here a new biozonation, based on reproducible events at different  
38 localities, to obtain a chronostratigraphic subdivision with a high-resolution for this short-  
39 lasting hyperthermal event. We define thus four new zones spanning the latest Paleocene and  
40 the earliest Eocene that allow correlation of shelf and open-ocean localities, and two subzones  
41 mainly useful in shelf environments. These new zones correlate to the main trends of the  
42  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve and define the pre-excursion interval (PE-1), the negative  $\delta^{13}\text{C}_{\text{bulk carb}}$  shift  
43 defining the base of the Eocene (PE0), the core of the event, the recovery phase I (PE1) and  
44 the recovery phase II intervals (PE2).

45

46 **Keywords;** calcareous nannofossils, biostratigraphy, PETM, biozonation, shelf, open ocean

47

## 48 **1. Introduction**

49 The Paleocene-Eocene transition (56 Ma) is characterized by a brief but intense carbon isotope  
50 negative excursion (CIE) associated with a global warming of 5-7°C (Kennet and Stott 1991,

51 Zachos et al. 2001). This transition is known as the Paleocene Eocene Thermal Maximum  
52 (PETM). Recent models estimated that this event lasted approximately 200 kyrs (Röhl et al.  
53 2000, Röhl et al. 2007). The input of isotopically light carbon either from methane release or  
54 volcanism (Dickens et al. 1995, 1997) led to enhanced  $p\text{CO}_2$  in the oceans, finally triggering  
55 acidification and shoaling of the carbonate compensation depth CCD (Zachos et al. 2004,  
56 Penman et al. 2014, Babila et al. 2018). Recent studies suggest that these changes happened  
57 during a 405 kyrs eccentricity maximum (Zeebe and Lourens 2019). Benthic communities  
58 suffered a dramatic extinction (Tjalsma and Lohmann 1983, Thomas and Shackleton 1996) and  
59 planktonic biota underwent a profound re-organisation (e.g., Bralower et al. 1995, Kelly et al.  
60 1996, Bralower et al. 2002, Gibbs et al. 2006, Raffi et al. 2009).

61 The number of continuous late Paleocene-early Eocene successions is still relatively limited;  
62 consequently, only partial information exists about the biostratigraphic ranges of marker  
63 species. Because the PETM is characterized by intense carbonate dissolution, preservation  
64 problems have compromised a precise biostratigraphic information in several ODP/IODP  
65 settings and land sections (e.g., Wei and Zhong 1996, Kroon et al. 1998, Aubry et al. 2000).

66 Thus, although the sequence of calcareous nannofossil bioevents (either the first or the last  
67 occurrence of taxa in a given stratigraphic section) is well-known across the PETM (Martini  
68 1971, Bukry 1973, Perch-Nielsen 1985), the precise range and the reliability of the  
69 biostratigraphic markers are inadequately known. Up-to-date, important differences have been  
70 reported in the range of the species between various settings (e.g., Aubry et al. 2000, Bralower  
71 et al. 2002, Raffi et al. 2005, Agnini et al. 2007, Gibbs et al. 2006, Self-Trail et al. 2012).

72 Furthermore, the repeated occurrence of condensation or hiatuses in both oceanic and onland  
73 settings makes the correlations difficult.

74 At ODP legs 198 (Site 1209, Shatsky Rise, Tropical Pacific Ocean) and 208 (Site 1263, Walvis  
75 Ridge, Southern-East Atlantic Ocean) intact composite sequences of the PETM from a wide

76 range of depths were recovered, providing very good material to establish a solid  
77 biostratigraphy. Site 1209 and 1263 are the shallowest sites in both Pacific and Atlantic Oceans  
78 and they are the best candidates for such a task. The close temporal succession of paleo-  
79 oceanographic and paleo-climatic events across the PETM (i.e., warming, C-isotope negative  
80 excursion, core of the event and recovery) call for a higher biostratigraphic resolution to be  
81 achieved, enabling us to more precisely date and more effectively correlate sections in various  
82 oceanic and onland areas.

83 Here, Sites 1209 and 1263 are compared to already published nannofossil data that we  
84 compiled, namely from the Sites 1260 (equatorial Atlantic; Mutterlose et al. 2007), 690 (South  
85 Atlantic; Bralower et al. 2002), South Dover Borehole (NW Atlantic; Self-Trail et al. 2012,  
86 Alamedilla (southern Spain; Monechi et al. 2000), and Cicogna (NE Italy; Agnini et al. 2016),  
87 TDP14 (Tanzania; Bown and Pearson 2009). All these sections and cores have been studied for  
88 calcareous nannofossil content and carbon isotope geochemistry and provide us with a supra-  
89 regional bio- and chemo-stratigraphic tool to precisely date the PETM in disparate localities.

90

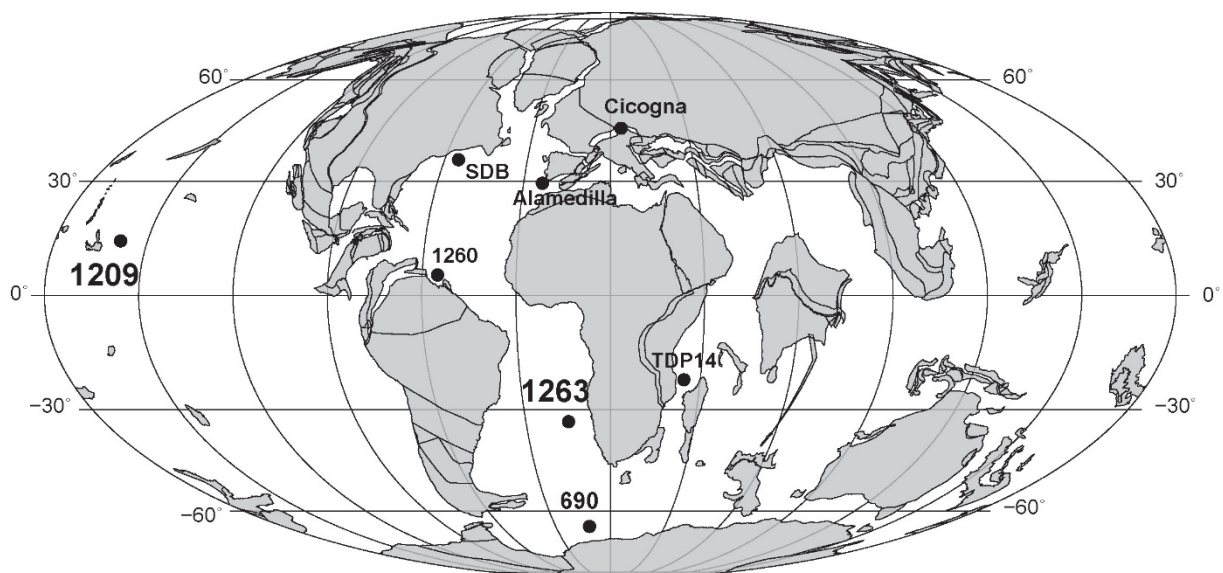


Figure 1

91

92

93 **2. Materials and methods**

94

95 **2.1. Calcareous nannofossils**

96 At Site 1209 (Fig. 1; 32°39.1'N, 158°30.4'E; 2387 water depth; 1900 paleodepth; Takeda and  
97 Kaiho 2007), we studied 20 samples over a 0.55 m interval spanning the PETM. The event lies  
98 in a ~25-cm-thick layer of clayey nannofossil ooze, with a sharp basal contact and a gradational  
99 contact with underlying and overlying chalk, respectively (Fig. 2). Samples were collected  
100 every 1-3 cm, with higher sampling rate across the PETM (1 cm). Core photos and carbonate  
101 concentration (Bralower et al., 2002; Farley, pers. comm.) are shown (Fig. 2).

102 At Site 1263 (Fig. 1, 28°32'S; 02°47'E; 2717 m water depth; 1500 m paleodepth; Zachos et al.  
103 2004), we studied 30 samples over a ~2 m section spanning the PETM. The position of the site  
104 relative to the Paleocene-Eocene paleogeography is shown in Zachos et al. (2004). The PETM  
105 onset is marked by a sharp contact between grayish brown, ash-bearing clay overlying light  
106 gray nannofossil ooze. Samples were collected every 5-10 cm, with higher sampling rate across  
107 the PETM (5 cm). Given higher sedimentation rate at Site 1263 relative to Site 1209, sampling  
108 resolution between both sites is comparable. Core photos and carbonate concentration (Zachos  
109 et al. 2005) are shown (Fig. 2). Because of paucity of material in the PETM onset (~10 cm),  
110 this interval is undersampled. We analyzed the Hole 1263C between 333.61 and 335.20 rmd,  
111 and Hole 1263D between 335.32 and 335.72 rmd.

112 Calcareous nannofossil slides were prepared following the Random Settling method (Beaufort  
113 et al. 2014), slightly modified here. A cover slide was weighted before and after the settling (4  
114 hours in a Petri-dish) of a homogeneous suspension of dry bulk sediment and water  
115 supersaturated with respect to CaCO<sub>3</sub>. Water was carefully aspirated with a water-pump  
116 connected to a micro-pipette to avoid any turbulence. After residual water drying, the cover  
117 slide was fixed on a microscope slide using Rhodopass B resin (Polyvinyl acetate). At least 500



118 nannofossils were counted in a total of 30 Fields of View (FOV) for each sample with a Leica  
119 DM750P microscope at 1000X magnification. Given the diameter of a single FOV (200 µm),  
120 the total studied area is 0.00942 cm<sup>2</sup>.

121 Each slide was further scanned over 10 transects in order to detect the presence of rare but  
122 biostratigraphically significant species. 10 transects correspond to ~1600 FOV as we used  
123 3.2x2.4 cm microscope slides. Each nannofossil slide was analysed twice over a year in order  
124 to check the consistency of the results.

125 To compare our data with previous studies, we generated relative abundance (%) data for all  
126 samples across the PETM using the formula:

$$127 \quad y = \frac{n}{N} * 100 \quad (1)$$

128 where  $y$  is the relative abundance value;  $n$  in the number of counted specimens of a species in  
129 a slide and  $N$  is the total number of nannofossils counted in a slide.

130 On the basis of relative abundances of the species and genera, distribution charts for Site 1209  
131 and 1263 were generated (Table 1, Table 2). Nannofossil abundances are expressed using the  
132 following notation: abundant (A, >10 %), common (C, 1-10 %), frequent (F, 1-0.1 %) and rare  
133 (R, <0.1 %).

134 The preservation of the studied nannofossil assemblages across the PETM at Sites 1209 and at  
135 1263 was further investigated using a Phenom SEM G2PRO microscope. 20 samples were  
136 studied at Site 1209, and 7 at Site 1263 all across the PETM. Powdered dry bulk sediment was  
137 gently placed on a stub. The powder was then coated with gold by using a Leica EM ACE200  
138 system.

139 Following Gradstein et al. (2012), the abbreviation FO (First Occurrence) is herein used for the  
140 first or stratigraphically lowest occurrence of a species in a section (or Base); LO (Last  
141 Occurrence) for the last or stratigraphically highest occurrence of a species in a section (or  
142 Top); FCO (First Consistent Occurrence) when a species previously discontinuous is recorded

143 in consecutive samples; LCO (Last Consistent Occurrence) when a species is no longer  
144 observed in consecutive samples; RI (Rapid Increase) for the stratigraphic horizon where a  
145 given taxon yields for the first time a relative abundance higher than 5% and maintains it  
146 throughout the subsequent samples; and RD (Rapid Decrease) when a quite common species  
147 decreases in relative abundance below the threshold of 5% (see also Ferreira et al., 2019).

148

## 149 **2.2. Carbon stable isotope measurements**

150 Stable isotope ratios of bulk-rock samples ( $\delta^{13}\text{C}_{\text{bulk carb}}$ ) analyzed for their nannofossil content  
151 in the archive half of 1209B-22H-1 were determined using an autosampler MultiPrep™ system  
152 coupled to a dual-inlet GV IsoPrime™ isotope ratio mass spectrometer (IRMS) at the  
153 Laboratoire de Géologie de Lyon (Université Lyon 1). For each sample, an aliquot of about  
154 100–500  $\mu\text{g}$  (depending on the  $\text{CaCO}_3$  content) of bulk-rock samples was reacted with  
155 anhydrous oversaturated phosphoric acid at 90°C for 20 min. Carbon isotope compositions are  
156 quoted in the  $\delta$  notation in per mil (‰) relative to Vienna Pee Dee Belemnite standard (V-PDB).  
157 All samples were measured in duplicate and normalized to the VPDB scales with an in-house  
158 working standard Carrara Marble (CAM,  $\delta^{13}\text{C}_{\text{V-PDB}} = 2.025$ ) and international reference  
159 standards analyzed during the same session. The CAM was normalized with the international  
160 references NIST NBS19 limestone ( $\delta^{13}\text{C}_{\text{V-PDB}} = +1.95\text{‰}$ ) and NBS18 carbonatite ( $\delta^{13}\text{C}_{\text{V-PDB}} =$   
161  $-5.01\text{‰}$ ). External reproducibility is better than  $\pm 0.05\text{‰}$  for  $\delta^{13}\text{C}$  values ( $2\sigma$ ).

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Site	Hole	Core	Section Interval	Depth relatively to LC		$\delta^{13}\text{C}_{\text{bulk rock}}$	$\delta^{13}\text{C}_{\text{bulk rock}}$ SD	<i>Bomolothus aquilius</i>	<i>Bomolothus megastypus</i>	<i>Bomolothus supremus</i>	<i>Braarudosphaera</i> spp.	<i>Campylospira dela</i>	<i>Campylospira eodela</i>	<i>Coccolithus bowinii</i>	<i>Coccolithus</i> spp.	<i>Cruci.</i> + <i>Chiasmolithus</i> spp.	<i>Discoaster araneus</i>	<i>Discoaster multiradiatus</i>	<i>Discoaster salisburgensis</i>	<i>Discoaster</i> spp.
				cm	m															
1209 B	22H	1A	90-91	0.42	1.94	0.04	R					F	F	F	A	F	F	C	F	C
1209 B	22H	1A	95-96	0.37	1.90	0.00		F				F	F	F	A	F	F	C		C
1209 B	22H	1A	100-101	0.32	1.81	0.02						F	F	F	A	F	F	C		C
1209 B	22H	1A	105-106	0.27	1.63	0.03	R	F				F	F	F	A	F	F	C		C
1209 B	22H	1A	110-111	0.22	1.47	0.05	R			C	C	F	C	A	F	C	C	C		C
1209 B	22H	1A	115-116	0.17	1.09	0.02		F		C		F		C		F	F	C	F	C
1209 B	22H	1A	120-121	0.12	1.00	0.02		F				F	F	C	A	C	F	C	F	C
1209 B	22H	1A	125-126	0.07	0.39	0.03						F	F	C	A	C	C	C	F	C
1209 B	22H	1A	129-130	0.03	0.28	0.00		F	R			F		C	A	C	C	C		F
1209 B	22H	1A	130-131	0.02	0.47	0.00		F	F			F	F	C	A	C	C	C		C
1209 B	22H	1A	131-132	0.01	1.02	0.03		F				F	F	C	A	C	C	C		C
1209 B	22H	1A	132-133	0	2.36	0.04			F			F			A	C	F	C		C
1209 B	22H	1A	133-134	-0.01	2.34	0.03		F				C	F	C	A	F	C	C		C
1209 B	22H	1A	134-135	-0.02	2.72	0.06						F	F	C	A	F	F	C		C
1209 B	22H	1A	135-136	-0.03	2.62	0.01		F				F		F	A	C	C	C		C
1209 B	22H	1A	136-137	-0.04	2.41	0.03		F				F	F	F	A	C		C		C
1209 B	22H	1A	137-138	-0.05	2.65	0.07						C	F		A	F		C		C
1209 B	22H	1A	140-141	-0.08	2.81	0.02		F				F	F		A	C		C		C
1209 B	22H	1A	142-143	-0.1	2.82	0.02		F				F	F		A	F		C		C
1209 B	22H	1A	145-146	-0.13	2.82	0.02		F	R			F	F		A	F		C		C
Site	Hole	Core	Section Interval																	
cm																				
				<i>Ericsonia</i> spp. <i>Fasciculithus</i> spp. <i>Fasciculithus clinatus</i> <i>Fasciculithus involutus</i> <i>Fasciculithus richardii</i> group <i>Fasciculithus thomasi</i> <i>Fasciculithus tympaniformis</i> <i>Rhombosphaera calcitrapa</i> group <i>Rhombosphaera</i> spp. <i>Sphenolithus</i> spp. <i>Toweius</i> + <i>Prinsius</i> spp. <i>Tribracliatius bramlettei</i> <i>Thoracosphaera</i> spp. <i>Z. bijugatus</i> Other nannofossils Reworking Cretaceous																
1209 B	22H	1A	90-91	A	C	F	F		F	F	R	F	C	A	F	F	C	C		
1209 B	22H	1A	95-96	A	C		F		F			F	C	A	F	F	C	C		
1209 B	22H	1A	100-101	A	C	F	C		C			F	C	C	F	C	C	C		
1209 B	22H	1A	105-106	C	C	F	F		F	R		F	C	C		F	A	C		
1209 B	22H	1A	110-111	A	C	F	C		F	C		F	A	C		F	A	C		
1209 B	22H	1A	115-116	A	C	F	F	F	F			F	C	A	F	C	A	C		
1209 B	22H	1A	120-121	A	C	F	C	F	C	R		F	C	C		C	A	C		
1209 B	22H	1A	125-126	C	C		F	C	F	F			C	C	F	C	C	C		
1209 B	22H	1A	129-130	C	C	F	C	C	C			F	C	C		C	F	A		
1209 B	22H	1A	130-131	C	C	F	C	C	C	R		F	C	C	F	C	F	C	C	
1209 B	22H	1A	131-132	C	C	F	C	C	F	C			A	C		C	C	C	C	
1209 B	22H	1A	132-133	A	C	C	C	C	F	C			C	C		F	F	C	F	
1209 B	22H	1A	133-134	A	C	F	C	C	F	C		F	C	C		F	C	C	F	
1209 B	22H	1A	134-135	A	C	F	C	C	C	C			C	C		F	C	F		
1209 B	22H	1A	135-136	A	C	F	C	C	C			F	C	C		F	F	C		
1209 B	22H	1A	136-137	A	C	F	C	C	F	C			C	C		F	F	C	F	
1209 B	22H	1A	137-138	A	C	F	C	C	F	C			C	C		F	F	C		
1209 B	22H	1A	140-141	A	C	F	C	C	F	C			C	C		F	F	C		
1209 B	22H	1A	142-143	A	C	F	C	C	F	C			C	C		F	F	C		
1209 B	22H	1A	145-146	A	C	F	C	C	C				C	C		F	C	C		

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Site	Hole	Core	Section	Interval	Rcmd		Depth to LC	<i>Bomolihus megastypus</i>	<i>Bomolihus supremus</i>	<i>Calcosolenia aperta</i>	<i>Campylosphaera dela</i>	<i>Campylosphaera eodela</i>	<i>Cruci. + Chiasmolithus</i> spp.	<i>Coccolithus bownii</i>	<i>Coccolithus</i> spp.	<i>Discoaster araneus</i>	<i>Discoaster multiradiatus</i>	<i>Discoaster</i> spp.	<i>Fasciculithus involutus</i>	<i>Fasciculithus richardii</i> group	<i>Fasciculithus tympaniformis</i>	<i>Rhombaster calceitrapa</i> gr.	<i>Rhombaster cuspis</i>	<i>Sphenolithus</i> spp.	<i>Towleus</i> + <i>Prinsius</i> spp.	<i>Tribrachiatulus bramletti</i>	<i>Zygnabolithus</i> spp.	Other nanofossils																		
					m	cm																																								
1263	C	14H	1A	129-130	333.61	1.66	R				C	F	C		A		C	C	C	C	C			F	A	A	C	C																		
1263	C	14H	1A	139-140	333.71	1.56					C	F	C		A		C	C	C	C	C	R		F	A	A	A	C	C																	
1263	C	14H	1A	149-150	333.81	1.46	R				C	F	C	F	A		C	C	C	A	C			F	A	A	A	A	C	C																
1263	C	14H	2A	09-10	333.90	1.37	R				C	F	C	F	A		C	C	C	A	C			F	A	A	A	A	A	C	C															
1263	C	14H	2A	19-20	334.00	1.27				F	F		F	C	A		C	C	C	C	C			F	A	A	A	A	A	A	C	C														
1263	C	14H	2A	29-30	334.10	1.17	R			F	F		F	C	A		C	C	C	C	C			F	A	A	A	A	A	A	A	C	C													
1263	C	14H	2A	39-40	334.20	1.07	R				C	F	C	F	A		C	C	C	C	C	R		C	A	A	A	A	A	A	A	A	C	C												
1263	C	14H	2A	49-50	334.30	0.97					C	F	C	F	A		C	C	C	C	C			C	A	A	A	A	A	A	A	A	A	C	C											
1263	C	14H	2A	59-60	334.40	0.87	R			F	F		F	C	A		C	C	C	C	C	R		F	A	A	A	A	A	A	A	A	A	A	C	C										
1263	C	14H	2A	69-70	334.50	0.77	R			F	F		F	C	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	C	C									
1263	C	14H	2A	79-80	334.60	0.67	R			F	F		F	C	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	C	C								
1263	C	14H	2A	89-90	334.70	0.57					F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C							
1263	C	14H	2A	99-100	334.80	0.47	R				F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C						
1263	C	14H	2A	104-105	334.85	0.42	R				C		C	F	A		C	C	C	C	C	R		F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C					
1263	C	14H	2A	109-110	334.90	0.37					C		F	C	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C					
1263	C	14H	2A	114-115	334.95	0.32	R				F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C				
1263	C	14H	2A	119-120	335.00	0.27	R				F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C				
1263	C	14H	2A	124-125	335.05	0.22	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C				
1263	C	14H	2A	129-130	335.10	0.17					F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C			
1263	C	14H	2A	134-135	335.15	0.12	R				F	F	F	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C			
1263	C	14H	2A	139-140	335.20	0.07	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C			
1263	D	4H	1A	72-73	335.32	-0.05					C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C			
1263	D	4H	1A	77-78	335.37	-0.10	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C		
1263	D	4H	1A	82-83	335.42	-0.15	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C	
1263	D	4H	1A	87-88	335.47	-0.20					C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C	
1263	D	4H	1A	92-93	335.52	-0.25	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C	
1263	D	4H	1A	97-98	335.57	-0.30					C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C	
1263	D	4H	2A	02-03	335.62	-0.35	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C	
1263	D	4H	2A	07-08	335.67	-0.40	R				C		C	F	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C
1263	D	4H	2A	12-13	335.72	-0.45	R				F		C	C	A		C	C	C	C	C			F	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C	C

Table 2

172 **3. Results**

173

174 **3.1. Preservation and assemblages at Site 1209 and Site 1263**

175 At Site 1209, optical (OM) and Scanning Electron Microscope (SEM) pictures (Plates 1 to 3)  
176 reveal an overall good preservation, with the contemporaneous presence of limited etching  
177 (mainly on coccoliths) and overgrowth effects (mainly on fasciculiths and discoasters). A slight  
178 deterioration in nannofossil preservation occurs between 1 cm below and above the Lithological  
179 Contact (LC), as previously suggested by Bralower et al. (2014). In those samples, etching  
180 prevails consistently with the concomitant maximum in nannofossil fragmentation. At Site  
181 1263, nannofossil preservation is moderate to good, but in a 6-cm thick interval from 0 to 6 cm  
182 above the LC, dissolution occurred as previously observed (Raffi et al. 2009). Although most  
183 of the coccoliths and nannoliths we observed in OM as well in SEM are moderately- to well-  
184 preserved, strongly etched specimens may coexist with fairly well preserved specimens in the  
185 same sample.

186 Calcareous nannofossil assemblages at both localities are similar in terms of percentage of  
187 different genera, although little disparities. Assemblages across the PETM at Site 1209 are rich  
188 except from the interval 1 cm below and 1 cm above the PETM. Assemblages are dominated  
189 by *Coccolithus* (abundant; Table 1) and *Ericsonia* (abundant) accompanied by *Toweius*  
190 (common to abundant). *Ericsonia* rapidly decreased from abundant to common at the onset of  
191 PETM. The rest of the assemblage is dominated by *Fasciculithus* (common to frequent),  
192 *Discoaster* (common) and *Sphenolithus* (common). *Zygrhablithus* rapidly increases from  
193 frequent to common 7 cm above the onset of PETM. Concomitantly, *Fasciculithus* decreases  
194 from common to frequent, as previously observed (Gibbs et al. 2006). These changes are not  
195 related with dissolution, as other robust taxa (e.g., *Discoaster* and *Sphenolithus*) do not increase  
196 in abundance.

197 At Site 1263, *Coccolithus* dominate the placolith-coccoliths (abundant; Table 2) as well as  
 198 *Toweius* (abundant). Small *Ericsonia* referred to as *E. orbis* (Bown et al. 2016) are present but  
 199 never reach abundance as high as at Site 1209. The rest of the assemblage is dominated by  
 200 *Fasciculithus* (abundant to common), *Discoaster* (common) and *Sphenolithus* (common)..  
 201 *Zygrhablithus* rapidly increases from common to abundant 0.87 cm above the onset of PETM,  
 202 alongside a *Fasciculithus* decrease from abundant to common as previously reported (Raffi and  
 203 De Bernardi 2008). These changes are not attributed to dissolution, as other robust taxa (e.g.,  
 204 *Discoaster* and *Sphenolithus*) do not increase in abundance.

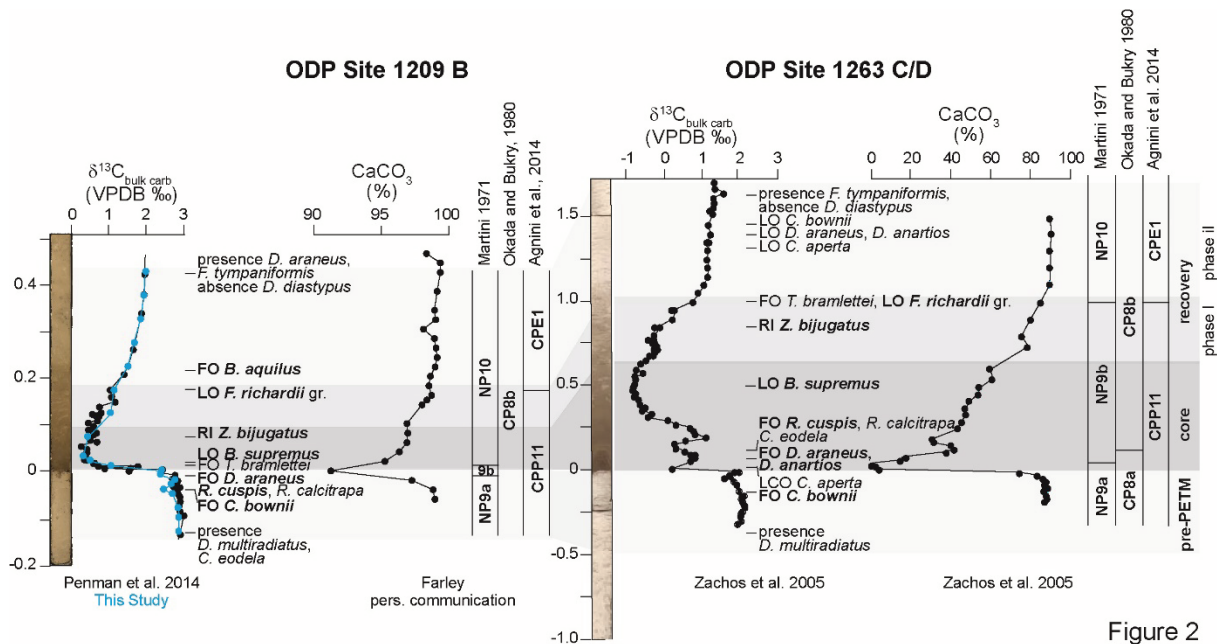


Figure 2

205  
 206 **3.2. Biostratigraphy**

207 Calcareous nannofossils biostratigraphy of late Paleocene and early Eocene is mostly based on  
 208 standard zonations of Martini (1971) and Okada and Bukry (1980). Recent studies propose to  
 209 subdivide the NP9 and NP10 of Martini (1971) in several subzones (Aubry et al. 1996, 1999)  
 210 in order to improve the biostratigraphic resolution around the Paleocene/Eocene. Agnini et al.  
 211 (2014) published a new biozonation frame for the Paleogene for low and middle latitudes. In  
 212 order to effectively compare the results from the two sites, we express our data in function of



213 the depth below the LC, which marks the onset of the PETM. The biozonation of the two  
214 sections is established following the different reference biozonations cited above.

215

### 216 3.2.1. ODP Site 1209

217 Several events were recorded spanning the Paleocene-Eocene transition (Fig. 2). *Discoaster*  
218 *multiradiatus* and *Campylosphaera eodela* are present in the assemblage from the lowermost  
219 sample. *Coccolithus bownii* first occurs at -0.04 m, just below the negative carbon excursion  
220 marking the onset of the PETM. The very onset of the PETM is characterized by the FO of  
221 *Discoaster araneus* in the same sample as *Rhomboaster cuspis* and *Rhomboaster calcitraba* (-  
222 0.03 m), shortly followed by the FO of *Tribrachiatus bramlettei* (0.02 m). The LO of  
223 *Bomolithus supremus* is at 0.03 m. The RI of *Zygrhablithus bijugatus* (>5%) is observed at 0.07  
224 m. The LO of *Fasciculithus richardii* group (see Appendix 1) at 0.17 m marks the inflexion of  
225  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve between the end of the PETM negative excursion and the return to steady  
226 values. The uppermost part of the studied interval is characterized by the presence of *D. araneus*  
227 and *Fasciculithus tympaniformis*, but the absence of *Discoaster diastypus* (Fig. 2).

228 The lower part of the section (-0.13 m to 0.01 m) is dated NP9 (Martini 1971) because of the  
229 presence of *D. multiradiatus* from the lowermost sample and the absence of *T. bramlettei*.

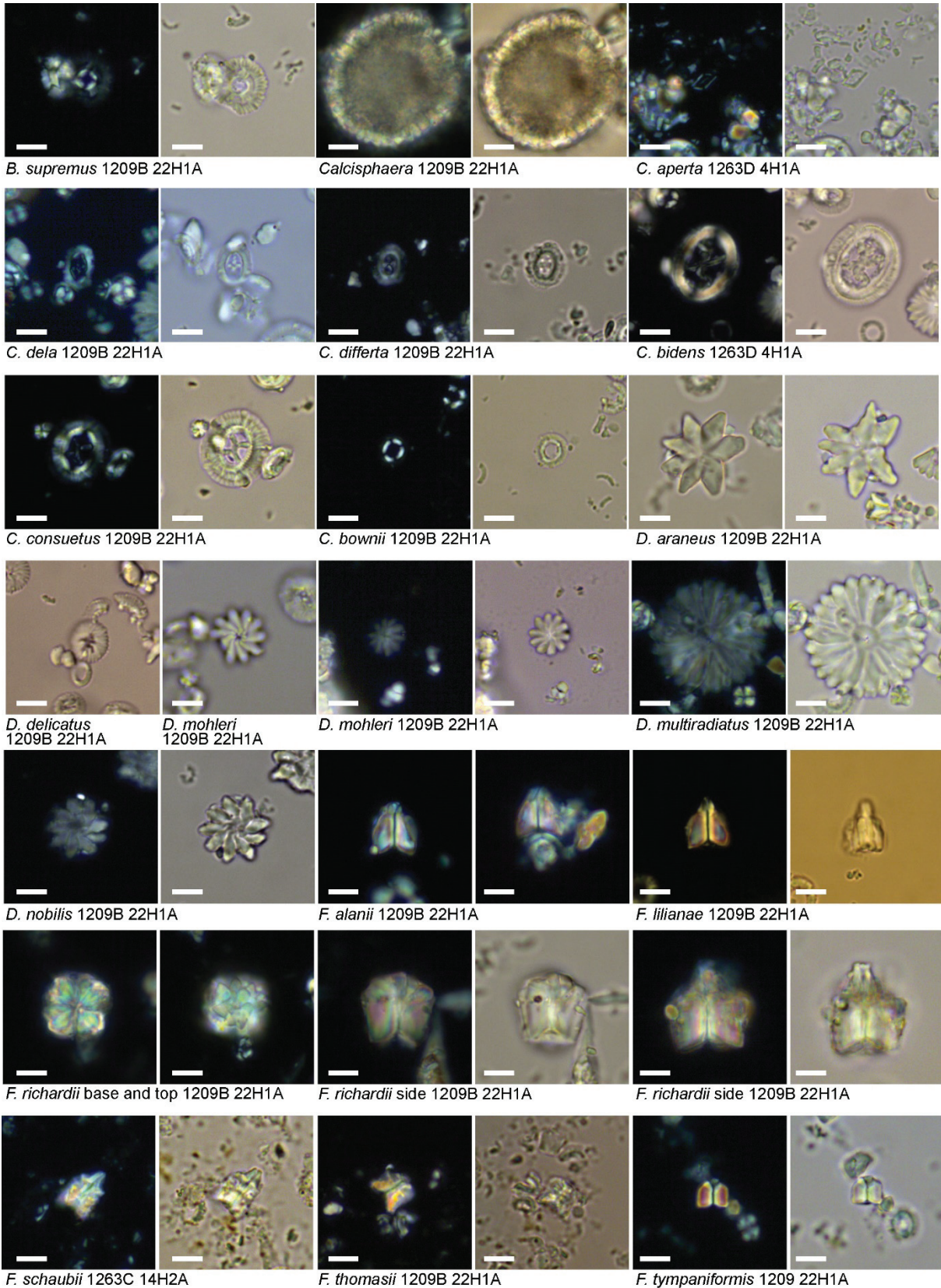
230 Based on Aubry et al. (1999), who subdivided the NP9 of Martini (1971) into two subzones,  
231 we attribute the lowest part of the section (-0.13 to -0.02 m) to the NP9a because of the presence

232 of *D. multiradiatus* and the FOs of *R. calcitraba*, *D. araneus* and *D. anartios* at -0.03 m. From  
233 -0.03 to 0.01 m, the section is dated NP9b (Aubry et al. 1996). According to Agnini et al. (2014),

234 the lower part of the section (-0.13 m to 0.17 m) is dated CNP11 because of the presence of *D.*  
235 *multiradiatus* from the lowermost sample and the LO of *F. richardii* group in sample 1209B-

236 22H-1-115-116 (0.17 m).







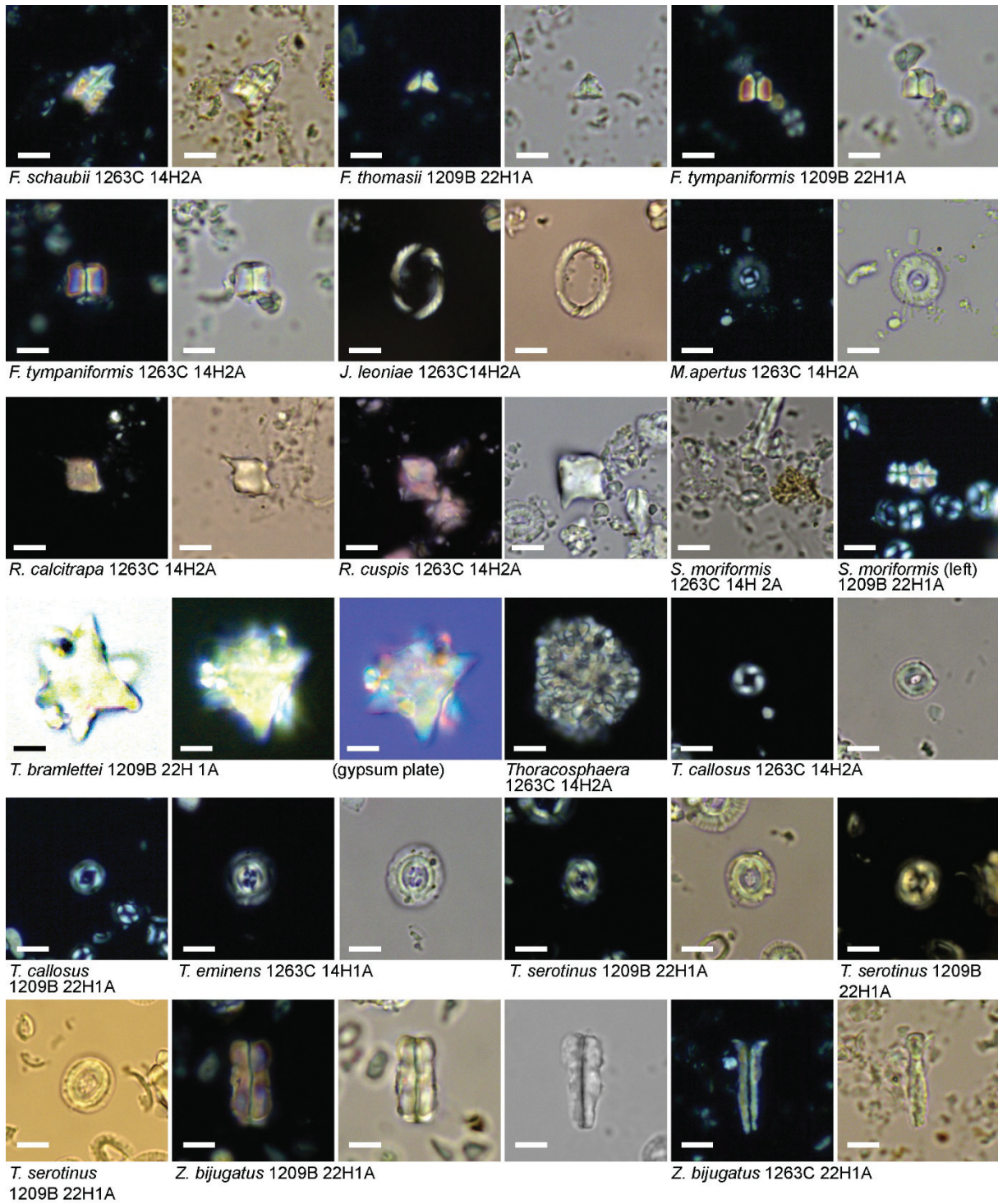


Plate 2

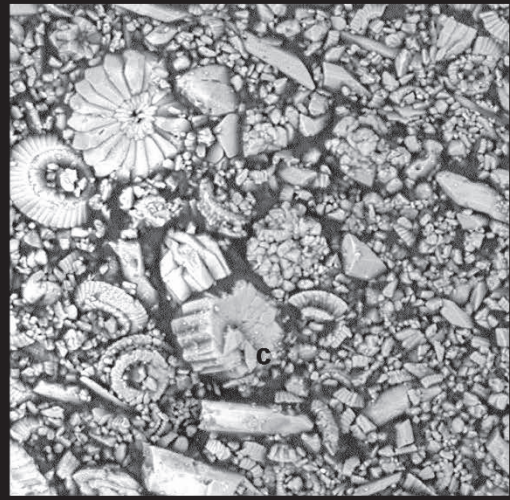
238

239

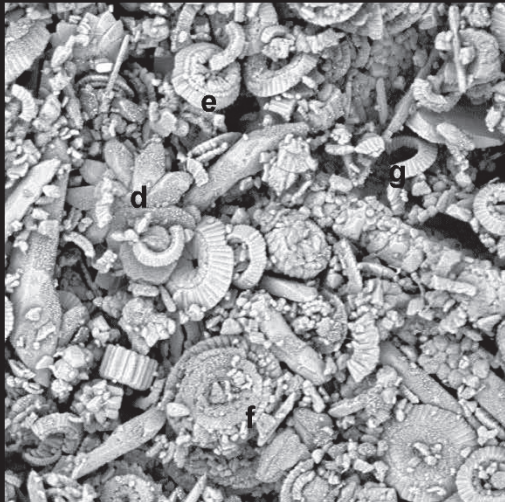




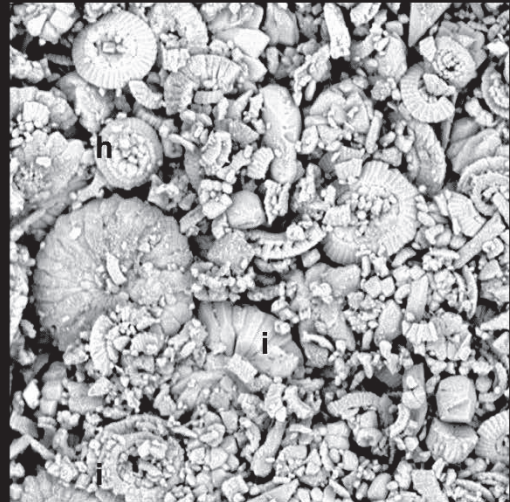
10 μm 6000x 1209 22H1



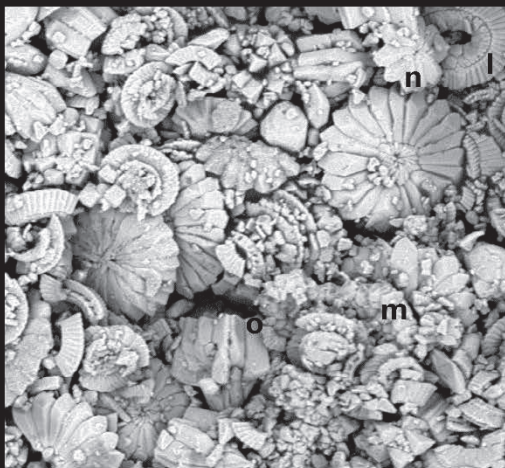
10 μm 6000x 1209 22H1



10 μm 6000x 1209 22H1



10 μm 6000x 1209 22H1



10 μm 6000x 1209 22H1



10 μm 6000x 1209 22H1

Plate 3

240

241

242 The interval comprised between 0.02 to 0.42 m is dated NP10 because of the FO of *T. bramlettei*  
243 in sample 1209B-22H-1-130-131 and the absence of *Tribrachiatus contortus* in the uppermost  
244 studied sample, whose FO marks the base of NP11. According to Aubry et al. (1996), this  
245 interval corresponds to NP10a because of the absence of *Tribrachiatus digitalis*, whose FO  
246 marks the base of NP10b. The upper part of the section (1.07-0.42 m) is dated CNE1 because  
247 of the LO of *F. richardii* group (0.97 m) and the presence of *F. tympaniformis* in the uppermost  
248 studied sample. According to Okada and Bukry (1980), the whole studied section is dated to  
249 CP8b because of the presence of *D. multiradiatus*, *C. eodela* from the lowermost sample and  
250 the absence of *D. diastypus* in the upper part of the studied section.

251

### 252 3.2.2. ODP Site 1263

253 Similar to Site 1209, *D. multiradiatus* is present from the base of the studied interval at Site  
254 1263 (Fig. 2). The FO of *C. bownii* at -0.20 m also lies just below the negative carbon excursion  
255 marking the onset of the PETM. The FOs of *D. araneus* and *D. anartios* are recorded at 0.07  
256 m, at the onset of the PETM. Conversely, *C. eodela* is not present from the base of the studied  
257 interval, but first occurs in the same sample as *R. cuspis*, at 0.12 m. The LO of *B. supremus* is  
258 at 0.27 m. The RI of *Z. bijugatus* (>5%) is observed at 0.87 m, above the core of the PETM, in  
259 an interval comparable to Site 1209. Also, similar to Site 1209, the LO of *F. richardii* group  
260 (0.97 m) occurs in the interval where the inflexion of the  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve occurs, between the  
261 end of the PETM negative excursion and the return to steady values. The FO of *T. bramlettei*  
262 (0.97 m) is conversely very different from the Site 1209. In the upper part of the studied interval,  
263 the successive LOs of *Calcisolenia aperta* (1.27 m) and of *D. araneus* and *D. anartios* (1.37  
264 m) are recorded.

265 The NP9 zone (-0.45 to 0.87 m) is recognized because of the presence of *D. multiradiatus* from  
266 the lowermost sample until the FO of *T. bramlettei* (0.97 m). Based on the subdivision of this



267 zone by Aubry et al. (1999), the NP9a subzone is recognized until the FOs of *D. araneus* and  
268 *D. anartios* (-0.45 to -0.05 m). From 0.07 to 0.87 m the section is dated NP9b (Aubry et al.  
269 1996) until the FO of *T. bramlettei* (0.97 m). According to the zonation of Okada and Bukry  
270 (1980), the interval from -0.45 m to 0.07 m is dated CP8a because of the presence of *D.*  
271 *multiradiatus* from the lowermost sample until the FO of *C. eodela* (0.12 m). According to  
272 Agnini et al. (2014), the interval from -0.45 to 0.97 m is dated CNP11 because of the LO of *F.*  
273 *richardii* group in sample 1263C-14-2A-49-50 (0.97 m). The upper part of the section (0.97 to  
274 1.66 m) is dated NP10 because of the FO of *T. bramlettei* in sample 1263C-14-2A-49-50 and  
275 the absence of *T. contortus* and of *T. digitalis*. The interval from 0.12 to 1.66 m is dated CP8b  
276 (Okada and Bukry 1980) because of the FO of *C. eodela* in sample 1263C-14-2A-134-135 (0.12  
277 m) and the absence of *D. diastypus* in the upper part of the studied section. The upper part of  
278 the section (1.07 to 1.66 m) is dated CNE1 (Agnini et al. 2014) because of the absence of *F.*  
279 *richardii* group and the presence of *F. tympaniformis*.

280

### 281 3.3. Carbon isotopes at Sites 1209

282 We have measured the  $\delta^{13}\text{C}_{\text{bulk carb}}$  on the samples analysed for their calcareous nannofossil  
283 content from the archive half of core 22H of Site 1209B to anchor them stratigraphically to  
284 already published  $\delta^{13}\text{C}_{\text{bulk carb}}$  measurements (See Table 1). These measurements indicate that  
285 the working half has been offset downward by 25 mm relative to the archive half, consistently  
286 with the downward offset of 25 mm relative to the archive half during sampling mentioned in  
287 Colosimo et al. (2006). The depths of the samples investigated in this study have therefore been  
288 shifted downward by a constant offset of 25 mm to facilitate comparisons with previously  
289 published data.

290 In agreement with previously published  $\delta^{13}\text{C}_{\text{bulk carb}}$  data (Colosimo et al. 2006, Penman et al.  
291 2014), values are stable between -0.2 and 0 m with respect to the LC and range from 2.82 to

292 2.34 ‰. From 0 to 0.3 m, values drastically decrease to 0.28 ‰, with a 2 ‰ negative excursion.  
293 Values stay low still up 0.10 m then recover from 0.10 to 0.40 m.  
294 The  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve of Paleocene-Eocene interval has been published by Zachos et al. (2005).  
295 The  $\delta^{13}\text{C}_{\text{bulk carb}}$  trend is the same as Site 1263, but the values record a general offset of  $\sim 0.8\%$   
296 with respect to Site 1209.

297

#### 298 **4. Discussion**

299

300 In order to check the reproducibility of nannofossil events and biostratigraphy from Sites 1209  
301 and 1263, we compiled a synthesis of eight already published sections located in different  
302 paleoceanographic settings and from several basins around the world, from low to high latitudes  
303 across the PETM (Fig. 1). All the sections dispose of  $\delta^{13}\text{C}$  isotopes measured on bulk-rock  
304 samples ( $\delta^{13}\text{C}_{\text{bulk carb}}$ ), besides detailed biostratigraphic data. The data used for comparison  
305 come from Sites 690 (Southern Atlantic Ocean; Bralower 2002), 1260 (Equatorial Atlantic  
306 Ocean; Mutterlose et al. 2007), that yield a reliable picture of open ocean records of the PETM.  
307 The sections providing a PETM record in shelf areas are: South Dover Bridge (SDB; New  
308 Jersey Coastal Plain; Self-Trail et al. 2012), Alamedilla (South-Spain; Monechi et al. 2000) and  
309 Cicogna (North-Italy; Agnini et al. 2016), all of them being located in the Tethys Ocean, and  
310 the Tanzania Drilling Project core 14 (TDP14; Bown and Pearson 2009). For TDP14 Site we  
311 integrate  $\delta^{13}\text{C}$  isotopes measured on *n*-alkanes because the CIE is not well expressed on bulk  
312 rock (Handley et al. 2008, Aze et al. 2014).  
313 Magnetostratigraphy is available for all the studied sections and shows that PETM encompasses  
314 magnetochron C24r of Cande and Kent (1995) (see also Ali et al. 2000, Aubry et al. 2000,  
315 Erbacher et al. 2004, Westerhold et al. 2007, Dallanave et al. 2009).

316 Differences and similarities between these sections provide us with a synthetic bio-  
317 chemostratigraphic framework across the event (Fig. 3). A new biostratigraphic subdivision is  
318 proposed here based on calcareous nannofossil FO and LO horizons, and on changes in  
319 assemblage composition. These include RI and RD of taxa. Also, FCO and LCO and switchover  
320 effects between taxa are taken into account.

321

#### 322 **4.1. Age model**

323 Carbon isotope stratigraphy is extensively used to correlate upper Paleocene-lower Eocene  
324 stratigraphic sections. Many records of magnetochron C24r have been "tuned" using the C-  
325 isotope excursions (assumed to represent the CIE) but purposely avoiding biostratigraphic  
326 datums because they are assumed to be somehow diachronous in nature (e.g., Pak and Miller  
327 1992, Zachos et al. 1993, Thomas and Shackleton. 1996, Pak et al. 1997). However, a  
328 comprehensive synthesis of nannofossil events and the carbon isotope curves in order to obtain  
329 a precise overview and explain the supposed diachronism has never been attempted. Here, we  
330 present the stratigraphic position of each event plotted against the  $\delta^{13}\text{C}_{\text{bulk carb}}$  profiles of  
331 different sites. Despite the broad similarities, the studied sites reveal marked differences in the  
332 overall shape of their  $\delta^{13}\text{C}$  profiles (Fig. 3). The most striking difference relates to the shape  
333 and amplitude of the negative  $\delta^{13}\text{C}_{\text{bulk carb}}$  excursion spanning the core of the PETM. This  
334 excursion is indeed almost symmetrical at Alamedilla and Cicogna sections, but appears highly  
335 asymmetrical at the other sites considered, where the negative  $\delta^{13}\text{C}_{\text{bulk carb}}$  excursion is very  
336 sharp. Assuming a comparable  $\delta^{13}\text{C}_{\text{bulk carb}}$  variation in oceanic waters in times of global  
337 perturbations, although local paleoceanography may produce isotopic offsets, the  $\delta^{13}\text{C}_{\text{bulk carb}}$   
338 values of the considered sites were compared to that of Alamedilla and Cicogna where the CIE  
339 onset is more gradual (Fig. 3). This comparison clearly shows a very good consistency of  
340  $\delta^{13}\text{C}_{\text{bulk carb}}$  values between the sites if considering the existence of unconformities. In particular,



341 the sharp negative shift toward negative  $\delta^{13}\text{C}_{\text{bulk carb}}$  values in all the sites but Alamedilla and  
342 Cicogna, most likely indicate very reduced sedimentation rates related to dissolution intervals  
343 (i.e., Aubry et al. 2000, McCarren et al. 2008, Storme et al. 2012). Also, a major unconformity  
344 is recorded in the recovery interval at South Dover and TDP14. Although the PETM has already  
345 been reported as a period when sedimentary discontinuities did occur (e.g., Aubry et al. 2000)  
346 the impact of such unconformities on biostratigraphic record has never been explored in detail  
347 before.

348 The age model of Röhl et al. (2007) was applied. The authors proposed a state-of-the-art age  
349 model for the PETM derived from a orbital chronology developed with cycle stratigraphic  
350 records from sites drilled during ODP Leg 208 (Walvis Ridge, South-eastern Atlantic)  
351 integrated with already published records from Site 690 (Weddell Sea, Southern Ocean, ODP  
352 Leg 113). Bains et al. (1999) defined some carbon isotope tie points (from -B to H) from the  
353 isotopic record at Site 690 and this nomenclature was adopted for tuning Site 1263 (Röhl et al.  
354 2007). Here we integrate in Figure 3 the tie points defined by Röhl et al. (2007) for Site 690.  
355 Ages are defined relatively to the PETM onset, fixed at 0 kyrs. On the basis of the previous  
356 assumptions, we define four time intervals in agreement to Röhl et al. (2007) (Fig. 3): 1) the  
357 pre-PETM prior to 0 kyrs; 2) the core of the PETM; 3) the recovery phase I; and 4) recovery  
358 phase II. These intervals are tightly linked to the  $\delta^{13}\text{C}_{\text{bulk carb}}$  profile across the event, as defined  
359 by Zachos et al. (2005).

360 No detailed astrochronology exists for the PETM interval recovered during Leg 198 at Shatsky  
361 Rise, as obliquity and precession-related cycles are not obvious due to low sedimentation rate  
362 and bioturbational smoothing (Westerhold et al. 2008, Westerhold et al. 2018). Previous PETM  
363 age models for ODP Site 1209 were therefore established using stable isotope correlations with  
364 Atlantic Ocean and Southern Ocean sites (ODP Sites 1263 and 690).

365

#### 366 **4.2. Calcareous nannofossil bioevents across the PETM at Sites 1209 and 1263**

367 Both Sites 1209 and 1263 represent a very good biostratigraphic record of the PETM interval.

368 Although the accumulation rate is almost twice at Site 1263 with respect to 1209, a very similar

369 succession of biostratigraphic events is observed in both sites. These events (in bold; Fig. 2)

370 seem therefore to be very reproducible because they occur in comparable intervals from remote

371 sites, both in the Atlantic and Pacific oceans. Namely, the FO of *C. bownii* in the pre-PETM

372 interval is closely followed by the FO of *D. araneus* and *D. anartios* very close to the onset of

373 the core of the PETM. *R. cuspis* is recorded in the same sample as these malformed discoasters

374 at Site 1209, very likely due to sedimentary condensation, but 5 cm higher at Site 1263. The

375 LO of *B. supremus* is also recorded within the core of the event in both sites. The RI of *Z.*

376 *bijugatus* is in the uppermost part of the PETM core at Site 1209, but in the recovery interval

377 at Site 1263. The LO of *F. richardii* group is recorded in the upper part of the recovery interval

378 in both 1209 and 1263 sites.

379 Conversely, other events appear to be slightly diachronous and, unfortunately, such events are

380 the ones used in standard biozonations. Thus, the FO of *T. bramlettei* occurring close to the

381 PETM onset at Site 1209, but at the end of the recovery phase I interval at Site 1263 makes

382 diachronous the base of the NP10 zone of Martini (1971). Also, the presence of *C. eodela* from

383 the lowermost studied sample at site 1209, while this species is first recorded at the PETM onset

384 at Site 1263 makes diachronous the base of CP8b Zone of Okada and Bukry (1980). Conversely,

385 the CPP11/CPE1 boundary, based on the LO of *F. richardii* group, is consistently synchronous

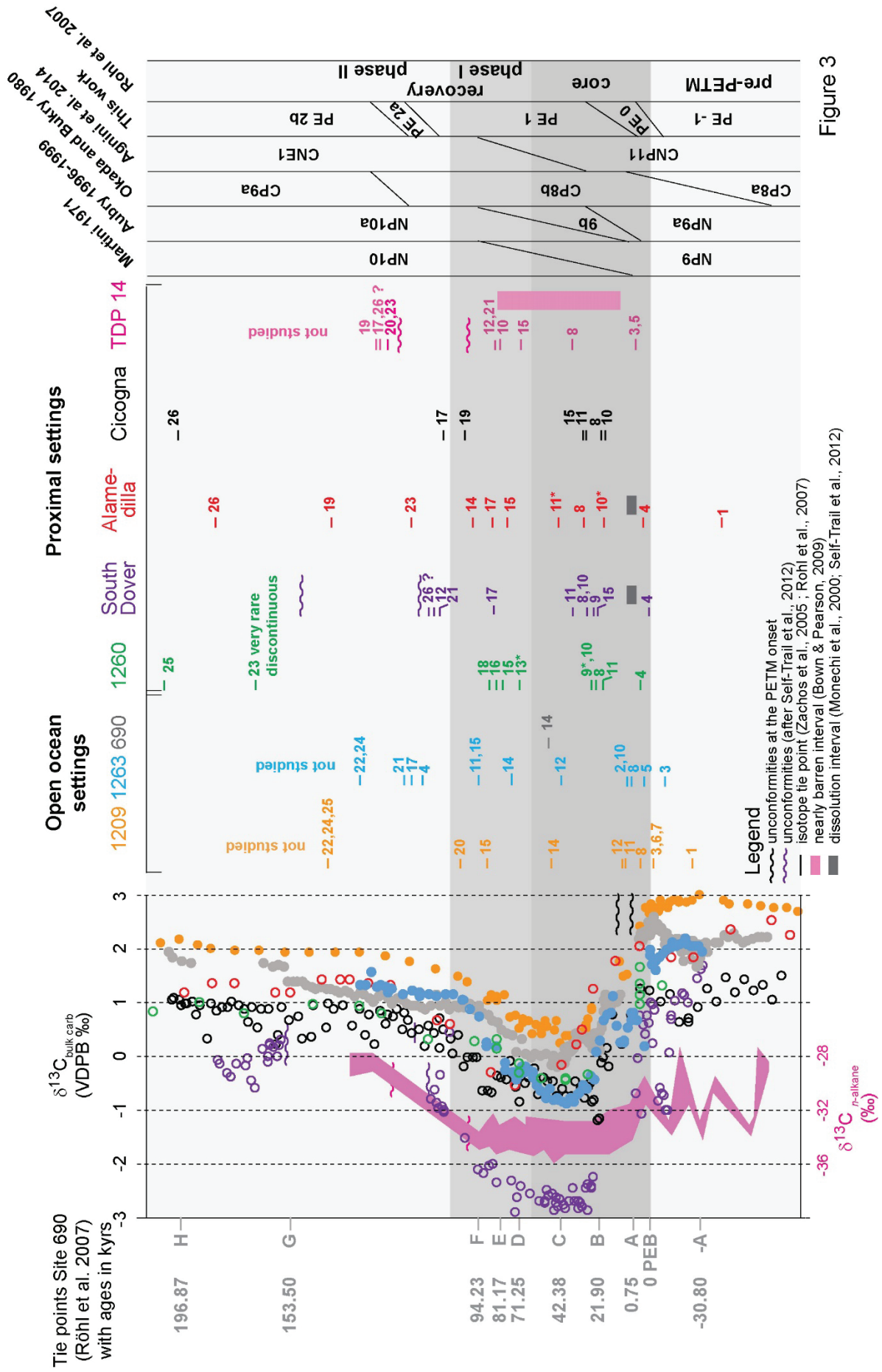
386 in both section occurring at the transition between the recovery phase I and the recovery phase

387 II intervals.

388

389

390



### 392 4.3. Comparison of Sites 1209 and 1263 with literature

393 A synthesis of all biostratigraphic events reported across the Paleocene-Eocene is plotted  
394 against  $\delta^{13}\text{C}_{\text{bulk carb}}$  records for various localities considered here (Fig. 3). The age model used  
395 is based on detailed foraminifer and calcareous nannofossil biostratigraphies available for each  
396 site (Monechi et al. 2000, Bralower 2002, Mutterlose et al. 2007, Bown and Pearson 2009, Self  
397 Trail et al. 2012, Agnini et al. 2016). The shape of isotopic curves allowed precise placement  
398 of the different phases, namely pre-event, core of the PETM, recovery phase I and recovery  
399 phase II. For all of the considered papers, we took into consideration the bioevents (namely,  
400 FO, LO) reported in synthetic figures by the authors. However, in order to better integrate all  
401 biostratigraphic information, we also carefully checked the distribution charts for single  
402 species. We could therefore detect more biostratigraphic events than the ones indicated in  
403 synthetic figures by the authors.

404 The synthesis we made is based upon a careful revision of taxonomic concepts used in various  
405 papers, in order to ensure taxonomic stability. Thus, *T. bramlettei*, whose FO is used as zonal  
406 marker by Martini (1971), was subdivided into various morphotypes by Monechi et al. (2000),  
407 namely with short- and long-arms and variety T, which have successive FOs across the PETM.  
408 A careful analysis of published images (plate 1, micrograph 20, p. 484) was thus necessary for  
409 assessing that only *T. bramlettei* variety T of Monechi et al. (2000) corresponds to the forms  
410 reported as *T. bramlettei* by other authors. Also, the specimens of *T. bramlettei* long-arms  
411 figured by Monechi et al. (2000) (plate 1, micrographs 17 and 19, p. 484) very much resembles  
412 to *R. calcitraba*, and some of the specimens of *T. bramlettei* short arms (plate 1, micrographs 6  
413 and 11, p. 484) might be attributed to *R. cuspis*. The FO or LO of these species is shown with  
414 an asterisk in Figure 3 to mark the taxonomic choice we made. However, some papers show  
415 the distribution of *Rhombaster* instead of that of the different species of the genus (e.g., Bown  
416 and Pearson 2009, Self-Trail et al. 2012). This is the reason why we also used *Rhombaster* in

417 the synthesis of Figure 3. Also, according to Bown (2005a) we adopted the new combination  
418 of *Scapholithus apertus* into *Calcisolenia aperta*, whose LO is considered in Monechi et al.  
419 (2000). Also, *Scapholithus rhombiformis* reported in Mutterlose et al. (2007) is a synonym of  
420 *C. aperta* (cf. Bown 2005a).

421 From comparison of biostratigraphic events in various localities, it results that two events,  
422 namely the FO of *C. bownii* and the LCO or LO of *C. aperta* are recorded in almost all the sites  
423 at the transition between the pre-PETM and the core of the PETM. This is a very new datum,  
424 because *C. bownii* has been introduced only recently (Jiang and Wise 2007), therefore it was  
425 not taken into account by Monechi et al. (2000), Bralower et al. (2002), or Mutterlose et al.  
426 (2007), although this latter figured specimens of *C. subpertusus* (figure 5, micrograph 7, p. 19)  
427 that can be ascribed to *C. bownii*. Mutterlose et al. (2007) consider these forms as typical of the  
428 PETM negative CIE, thus we were able to tentatively place the RI and RD of *C. bownii* at Site  
429 1260 (with an asterisk; Fig. 3), which likely stratigraphically corresponds to its FO and LO as  
430 reported in various papers.

431 Contrarily to previous studies stating that *C. aperta* is absent in oceanic settings (Bown and  
432 Pearson 2009), this species is recorded in almost all the onland sections and oceanic sites  
433 considered here, unless Cicogna (Northern Italy; Agnini et al. 2016) and Site 1209 (central  
434 Pacific; this study). *C. aperta* is also present in Equatorial Pacific Ocean, as confirmed by  
435 preliminary observations of PETM sediments at Site 865 (Allyson Guyot, Alessandro Menini  
436 unpublished). At 1260, South Dover and Alamedilla the LO of *C. aperta* is recorded below the  
437 PETM onset. However, at Site 1263 and at TDP14 this species ranges up above the PETM,  
438 despite discontinuously. The LO of *C. aperta* occurred in the recovery phase II interval at Site  
439 1263. We postulate that the LO of *C. aperta* before the onset of the PETM in some sections is  
440 very likely synchronous with the LCO in Tanzania and at ODP Site 1263, given that in both

441 these exceptionally preserved sections this species is still present during the recovery phase II  
442 of the event.

443 *C. bownii* has a short range, restricted to the PETM interval. In fact, in most of oceanic sites  
444 considered here and at South Dover, it disappears at the base of the recovery phase II interval,  
445 whilst at the TDP14 its LO is earlier, in the latest part of the recovery phase I interval.  
446 Interestingly, the RD of *C. pertusus* (~ *C. bownii*) occurs at the base of the recovery phase I  
447 interval at Site 1260 (Mutterlose et al. 2007). Previous studies also suggested that *C. bownii* is  
448 typical of the carbon negative excursion characterizing the PETM (Jiang and Wise 2007).

449 *D. araneus* and *D. anartios* are considered as malformed discoasters, probably corresponding  
450 to adaptation to variable environmental conditions (Bralower et al. 2016), as they are recorded  
451 with a different palaeogeographic distribution (Aubry 2001, Kahn and Aubry 2004, Self-Trail  
452 et al. 2012). These malformed discoasters first occurred within the PETM core interval in all  
453 the considered sections. They have a short range within the CIE, disappearing at the base of the  
454 recovery phase II interval. These specimens are thus very useful for supraregional correlations.  
455 The malformed discoaster often co-occur along with species of *Rhomboaster* (e.g., *R.*  
456 *calcitrapa*, *R. cuspis*, *R. spineus*). These latter first occur close to the base of the PETM core,  
457 unless at TDP 14 core, where they are restricted to a short interval between the upper part of  
458 the recovery phase I and the base of the recovery phase II (Fig. 3). The *Rhomboaster-Discoaster*  
459 (RD) assemblage is well-known to be characteristic of the PETM interval (Kahn and Aubry  
460 2004). Both these forms can be sporadically present well after the PETM.

461 The FO of *T. bramlettei*, which is a marker used in the Martini (1971), seems to be consistently  
462 present in all the considered areas, but it is slightly diachronous within the interval  
463 corresponding to the PETM core, which lasts ~50 kyrs. The LO of *F. richardii* group *sensu*  
464 Agnini et al. (2014) (namely, *F. clinatus*, *F. aubertae*, *F. thomasii*, *F. involutus* and *F.*  
465 *tympaniformis*), approximates the transition between the recovery phase I and the recovery



466 phase II (~100 kyrs after the PETM onset ) in oceanic sites, whilst it occurs earlier within the  
467 recovery phase I interval (at ~70 kyrs after the PETM onset) at Alamedilla and TDP14, and  
468 even earlier in the Cicogna section (at the top of the core interval). The switchover between  
469 fasciculiths and zygrhabliths is a well-known pattern occurring in the PETM interval (Bralower  
470 2002, Tremolada and Bralower 2004, Gibbs et al. 2006, Agnini et al. 2007 2014), and it  
471 corresponds to the LO of *F. richardii* group and the RI of *Z. bijugatus*. This last event is reported  
472 at the boundary between the top of the PETM core and the base of the recovery phase I interval  
473 in oceanic sites, whilst in the Alamedilla it occurs later, nearly at the end of the recovery phase  
474 I interval. However, when considering the RI of *Z. bijugatus*, it might be somehow difficult to  
475 precisely place this event without knowing which is the threshold percentage values for  
476 different authors.

477 Other events having a supraregional significance are: the FO of *D. diastypus* in the middle part  
478 of the recovery phase II interval (Alamedilla, TDP14, Site 1260); the LO of *F. tympaniformis*,  
479 which seems to occur consistently at the top of the recovery phase II interval in proximal  
480 settings, while this taxon is still present in the considered interval of oceanic settings.

481 The FO of *D. diastypus* is synchronous at TDP14 and Site 1260 while it is slightly offset at  
482 Alamedilla (Fig. 3). However, the specimen figured by Monechi et al. (2000) and referred as to  
483 *D. diastypus* (plate 2, micrograph 1, p. 486) is more likely *D. salisburgensis* given that it has  
484 18 rays, whilst *D. diastypus* is reported to have maximum 16 rays (see Appendix 1). The  
485 specimen illustrated by Monechi et al. (2000) has been found at 13.7 m while in their chart the  
486 FO of both *D. salisburgensis* and *D. diastypus* occurs at 16.4 m. Given the poor preservation of  
487 nannofossils at Alamedilla (Aubry et al. 2000) it could be difficult to systematically distinguish  
488 between these two species. Some diachronism (~50 kyrs) between Alamedilla, TDP14 and Site  
489 1260 cannot be completely ruled out but, given the concomitant FO of well-preserved *D.*  
490 *diastypus* in disparate settings, this apparent diachronism might be explained by different



491 taxonomic concepts between authors. In any case, at Alamedilla, TDP14 and Site 1260 the FO  
492 of *D. diastypus* is reported in the recovery phase II interval and this record does not prevent its  
493 use in biostratigraphy.

494 Two other events are worth noticing, namely the LO of *Bomolithus supremus* and the FO of  
495 *Bomolithus aquilus*. These two species have been introduced, respectively, by Bown and  
496 Dunkley-Jones (2006) and by Bown (2010). Although these are not taken into account by older  
497 papers, the LO of *B. supremus* is recorded in both Sites 1209, 1263 and TDP 14 within the  
498 PETM negative CIE, while the FO of *B. aquilus* marks the base of recovery phase II interval in  
499 both Sites 1209 and TDP 14. These represent therefore promising events to be further confirmed  
500 in other localities.

501

#### 502 **4.4. Possible biases of preparation and counting methods**

503 Before discussing the possible causes, e.g. paleoenvironmental factors or sedimentary features,  
504 of the observed similarities and differences amongst the studied localities, this section considers  
505 a basic issue concerning calcareous nannofossil studies, namely the preparation and counting  
506 methods used in different works.

507 As discussed above, our samples are prepared using the settling boxes method (Beaufort et al.  
508 2014). Mutterlose et al. (2007) prepared the slides for ODP Site 1260 with a comparable settling  
509 method (Geisen et al. 1999). Settling provides slides with a very homogenous concentration of  
510 powder in each field of view (FOV) that is ideal for counting. Other datasets used here for  
511 comparison were acquired by studying standard smear-slides (Monechi et al. 2000, Bralower  
512 2002, Bown and Pearson 2009, Self-Trail et al. 2012, Agnini et al. 2016).

513 Despite smear-slides remain the quickest sample preparation method, they do not consistently  
514 deliver a homogeneous preparation that should provide us with a rather constant number of  
515 nannofossils per FOV. This is quite possible when the sediment powder is let settle on the cover

516 slip resulting in a quasi-homogenous slide, whereas smear slides often provide alternating very  
517 concentrated and poor FOVs.

518 In case of very poor FOV, it is certainly possible to recover all the species in a given assemblage  
519 but this can be time-consuming. In very rich FOV, some species can be missed especially the  
520 small-sized ones, which can be hidden by larger specimens.

521 Most papers dealing with nannofossil biostratigraphy count up to 300 or 500 specimens per  
522 sample, independently on the number of analyzed FOV. However, this counting can be  
523 problematic for biostratigraphic purposes, since 500 specimens can be easily achieved in very  
524 few fields of view and the presence of rare but biostratigraphically important species can be  
525 missed. Fatela and Taborde (2002) calculate that counting at least 300 specimens is statistically  
526 robust to record all the species making up  $>1.7\%$  of the total assemblage with a confidence  
527 level of 99.5%. Because biostratigraphic markers are often rare and scattered after their first  
528 occurrence, as well as close to their last occurrence, these precise horizons can be missed when  
529 counting 300 or 500 specimens. This is particularly true for the time interval studied here, where  
530 species such as *Coccolithus*, *Toweius* and *Fasciculithus* dominate the assemblages. We  
531 performed empirical tests showing that the quantitative method we applied, which consists of  
532 counting nannofossil specimens in 30 FOV plus 10 further transects scanned (~1600 FOV) is  
533 far more accurate for recovering rare species. For example, the presence of *C. aperta* in open  
534 ocean sections has been rarely reported. At Site 1263, previous studies did not report it (Raffi  
535 and De Bernardi 2008, Raffi et al. 2009) while we could recover various specimens per sample  
536 by scanning the slides over 10 transects.

537

#### 538 **4.5. Paleoceanographic biases**

539 Previous studies showed that the distinctive association of *Rhomboaster* spp., *D. araneus* and  
540 *D. anartios* (deformed *Discoaster*) has a marked provincialism, restricted to the Atlantic Ocean

541 and partially extending to the Tethys seaway and westernmost Indian Ocean (Kahn and Aubry  
542 2004). Raffi (2005) found that the association *Rhomboaster* spp. and *D. araneus* also occurred  
543 in the paleo-equatorial Pacific Ocean. At Site 1209, we document that the *Rhomboaster* spp.  
544 and deformed *Discoaster* association also occurred in tropical Pacific. Thus these species  
545 colonized the world ocean across the PETM and were not restricted to the Tethys, Atlantic and  
546 Indian Oceans. Conversely, as shown by Bralower et al. (2016), *D. araneus* and *D. anartios*  
547 can be considered as morphotypes of the same biological species adapted to different  
548 oceanographic settings, thus occurring in different localities.

549 The LO of *F. richardii* group is recorded consistently earlier in proximal localities compared  
550 to open-ocean sites, probably reflecting environmental parameters. The genus *Fasciculithus* has  
551 been previously interpreted as a species adapted to warm and oligotrophic surface waters  
552 (Aubry 1998, Bralower 2002, Tremolada and Bralower 2004). Enhanced continental runoff  
553 during the PETM has been previously inferred (Ravizza et al. 2001, Kelly et al. 2005) likely  
554 triggering eutrophication of shelf areas. The demise of *F. richardii* group in oceanic settings  
555 corresponds to the beginning of the PETM recovery, where temperatures decreased to pre-event  
556 values. The absence of the group at high-latitudes might suggest that it was better adapted to  
557 warm waters (Bralower 2002, Tremolada and Bralower 2004), then became disadvantaged in  
558 times of decreased temperatures during the recovery phase (Raffi et al. 2005, 2009).  
559 Alternatively, the increase in abundance of *Zygrhablithus* concomitant with the extinction of *F.*  
560 *richardii* group could be linked to a decreased competition for the same ecological niche  
561 (Monechi et al. 2000), and environmental conditions in the early Eocene were probably more  
562 favorable to *Zygrhablithus*.

563 In some regions, a relevant increase in percentage of *Z. bijugatus* is observed concomitant with  
564 a drastic decline of fasciculiths (Bralower 2002, Tremolada and Bralower 2004, Gibbs et al.  
565 2006, Agnini et al. 2007, 2014). The RI of *Z. bijugatus* is not recorded at Site 1260 but this is

566 coherent with other data from equatorial Atlantic (Raffi et al. 2005). In shelf sections, this event  
567 is well documented at Cicogna (Agnini et al. 2016) and Alamedilla (Monechi et al. 2000), but  
568 neither at TDP14 (Bown and Pearson 2009) nor at South Dover (Self-Trail et al. 2012) and  
569 hence it cannot be used for supraregional correlations. *Z. bijugatus* is interpreted as a species  
570 that thrived in oligotrophic conditions (Aubry 1998, Bralower 2002, Tremolada and Bralower  
571 2004, Gibbs et al. 2006, Self-Trail et al. 2012). Meso-eutrophic conditions occurring in the  
572 aftermath of the PETM were likely unfavourable to the development of this species (Self-Trail  
573 et al. 2012), explaining its rarity in proximal sections. Whatever the environmental trigger, the  
574 shift from *F. richardii* group ending with its LO and the RI of *Z. bijugatus* represents a reliable  
575 event approximating the transition from the core of the event and the recovery interval in several  
576 localities.

577 Contrarily to previous studies who stated that *C. aperta* is not present in oceanic localities  
578 (Bown and Pearson 2009), this characteristic species has been recorded in oceanic sediments  
579 from Site 1263 and Site 1260, as well as at Site 865 (Equatorial Pacific, Allyson Guyot,  
580 Alessandro Menini, unpublished). The LO of *C. aperta* is approximatively 150 ky after the  
581 PETM onset at Site 1263. This is coherent with the range presented by Bown and Pearson  
582 (2009) at TDP14, where *C. aperta* is recorded within the PETM interval. This species is  
583 however very tiny and rare (~1 specimen every 2 transects), thus it is not easily recovered. The  
584 new record here should enable us to consider a paleogeographic distribution of *C. aperta* wider  
585 than previously considered.

586 Previous studies pointed out that condensations or hiatuses frequently affected shelf PETM  
587 settings, a sedimentary feature possibly introducing artifacts in the biostratigraphic record.  
588 Short hiatuses have been reported at Alamedilla (Aubry et al. 2000), at South Dover (Aubry et  
589 al. 2000, Self-Trail et al. 2012), and in TDP 14 (Bown and Pearson 2009, Aze et al. 2014) across  
590 the PETM (Fig. 3), that could explain some of the apparent diachroneous events between shelf

591 and open-ocean sites. Unconformities are integral components of the PETM stratigraphic  
592 record, both in shelves and deep-sea basins (Aubry et al. 2000). The contemporaneous  
593 occurrence of *T. bramlettei*, the malformed *Discoaster* and *Rhomboaster* at Site 1260  
594 (Mutterlose et al. 2007) is almost certainly due to the presence of an unconformity. Also, the  
595 earlier LO of *C. bownii* at TDP14, within the core of the PETM, is possibly related to a  
596 prolonged interval where samples are nearly barren. In any case, in both shelf and open-ocean  
597 sections, this event is recorded in the core of the CIE. Other unconformities might be present,  
598 although not detected on the basis of sedimentary features, that might affect the slightly  
599 diachronous records of species. However, the method used in this paper, based on a precise  
600 intercalibration of isotopic curves from various localities, should enable us to minimize the  
601 effect of unconformities on the timing of the events.

602

#### 603 **4.6. Towards a new biozonation scheme for the PETM interval**

604 The comparison of nannofossil bioevents at Sites 1209 and 1263 with six other sections from  
605 both open-ocean and shelves allows testing the reliability and the resolution power of the  
606 existing standard zonations (i.e., Martini 1971, Okada and Bukry 1980, Agnini et al. 2014)  
607 when applied to the very short time interval (<250 kyrs) represented by the PETM.

608 Some of the taxa used in standard zonations proved to be largely diachronous (Fig. 3). As an  
609 example, the FO of *T. bramlettei* marking the NP9/NP10 boundary (Martini 1971), spans an  
610 interval as long as the entire PETM negative CIE. Aubry et al. (1999) proposes a subdivision  
611 of the Martini's zones into NP9a and NP9b subzones, based on the FO of malformed *Discoaster*  
612 and of *Rhomboaster*. The boundary between these two subzones is also diachronous, but limited  
613 to the core of the PETM. Such a diachronism might be only apparent to some extent, resulting  
614 from the presence of unconformities, dissolution effects or barren intervals within the core of  
615 the event. The FO of *D. diastypus*, marker of the CP8/CP9 boundary (Okada and Bukry 1980),

616 seems to be also largely diachronous. This event is recorded in some sites (e.g., 1209, 1263,  
617 Cicogna) very high stratigraphically, above the interval considered here, making the boundary  
618 diachronous across the recovery phase II interval. *C. eodela*, whose FO marks the base of CP8b  
619 (Okada and Bukry 1980), is not considered by some authors (e.g., Mutterlose et al. 2007, Bown  
620 and Pearson 2009, Self-Trail et al. 2012, Agnini et al. 2016), or when taken into account it has  
621 a very wide range, either first appearing before the pre-PETM interval (Site 1209; Alamedilla  
622 section) or in the core of the PETM (Site 1263). *C. eodela* resembles to *C. dela* but with a  
623 narrow central area largely filled by the axial cross. Its range matches with the lower part of the  
624 range of *C. dela* (e.g., Shamrock and Watkins 2012). Future biometry studies should test the  
625 robustness of differences between them in order to investigate their biostratigraphic value as  
626 markers. Agnini et al. (2014) considered open-ocean settings located at low-to-middle latitudes.  
627 The LO of *F. richardii* group used by Agnini et al. (2014) for the base CNE1 zone is also partly  
628 diachronous in various localities spanning all the recovery interval. Standard biohorizons  
629 appear therefore inaccurate to precisely dating and correlating the different phases of the PETM,  
630 as defined by  $\delta^{13}\text{C}_{\text{bulk carb}}$  curve.

631 Most primary markers for GSSPs are biostratigraphic events, but some have utilized other  
632 global stratigraphic episodes (e.g., the CIE onset for the base-Eocene). Given that the  $\delta^{13}\text{C}_{\text{bulk}}$   
633  $\text{carb}$  curve is an independent stratigraphic proxy, we subdivided the time interval spanning the  
634 PETM and anchored the zones we established to the different phases recognized in the  $\delta^{13}\text{C}_{\text{bulk}}$   
635  $\text{carb}$  trends, namely the pre-event, core of the PETM, recovery phase I and recovery phase II.  
636 Criteria for the biozone definitions follow Agnini et al. (2014). We propose four new zones and  
637 two subzones for the Paleocene-Eocene transition that are defined as follows:

638

639 **PE-1**

640 Name: *Calcisolenia aperta* zone

641 Definition: Interval from FO of *D. multiradiatus* to FO of *C. bownii*  
642 Reference section: Site 1209 (Shatsky Rise, Tropical Pacific; 32°39.1'N, 158°30.4'E).  
643 Remarks: The FO of *C. bownii* is a very good marker approximating the top of the NP9 and the  
644 transition between the pre-excursion and the PETM onset in both shelves and oceanic sections.  
645 The sections we considered are stratigraphically above the extinction of *Ericsonia robusta*  
646 (morph. B, *sensu* Garzarella and Raffi 2018) in the lowermost CNP11 (Agnini et al. 2014),  
647 which shortly follows the base of magnetochron C24r (Garzarella and Raffi 2018). In this zone,  
648 it is also recorded the LCO or LO of *C. aperta*. This event is almost contemporaneous to the  
649 FO of *C. bownii* and can be used as auxiliary event.  
650 This zone encompasses the upper part of NP9 of Martini (1971) and CP8a of Okada and Bukry  
651 (1980) and corresponds to an interval of background conditions according to the  $\delta^{13}\text{C}_{\text{bulk carb}}$   
652 curve, before the PETM onset. Assemblages are dominated by placoliths *Coccolithus* and  
653 *Toweius* as well as *Chiasmolithus*, *Campylosphaera* and *Cruciplacolithus*. In some sections,  
654 small *Ericsonia* are abundant (*E. orbis*, *E. aliquanta*). *Fasciculithus* are the most abundant  
655 nannoliths. Sphenoliths are represented by *S. moriformis* group (*sensu* Agnini et al. 2014) and  
656 *S. anarrhopus*. Several species of the genus *Discoaster* are present, such as *D. nobilis*, *D.*  
657 *falcatus*, *D. mohleri*, *D. lenticularis*, *D. delicatus*. and *D. multiradiatus*, whose FO is the  
658 standard marker for NP9 base (Martini 1971).

659

## 660 **PE0**

661 Name: *Discoaster araneus* zone

662 Definition: Interval from FO of *C. bownii* to FO of *D. araneus* or FO of malformed discoasters  
663 or FO of *Rhomboaster* spp..

664 Reference section: Site 1209 (Shatsky Rise, Tropical Pacific; 32°39.1'N, 158°30.4'E).



665 Remarks: This subzone approximates the uppermost part of NP9 and the PETM onset in both  
666 shelves and open-ocean.  $\delta^{13}\text{C}_{\text{bulk carb}}$  shows a drastic  $\sim -3$  ‰ negative excursion in all the  
667 considered sections. Because of the definition of the Paleocene/Eocene, this zone also allows a  
668 precise placement of the boundary. The only site where *D. araneus* first occurs later in the  
669 PETM core is TDP14. However, most of the samples corresponding to the core of the event are  
670 barren there and the biohorizons recorded are poorly reliable. Assemblages are similar to what  
671 reported for the zone PE-1.

672 The sharp decrease of  $\delta^{13}\text{C}_{\text{bulk carb}}$  values at the Paleocene/Eocene boundary very likely  
673 corresponds to an unconformity (Fig. 3), future studies should thus consider to use the base of  
674 PE0 as the marker for the Paleocene/Eocene.

675

#### 676 **PE1**

677 Name: *Fasciculithus richardii* group zone

678 Definition: Interval from FO of *D. araneus* to the LO of *C. bownii* but also characterized by the  
679 LO of *F. richardii* group

680 Reference section: Site 1263 (Walvis Ridge, Southern-East Atlantic; 28°32'S; 02°47'E).

681 Remarks:

682 The PE1 spans most of the PETM core and recovery interval phase I. The disappearance of the  
683 *F. richardii* group represents an easily observable evolutionary change among the nannofossil  
684 assemblages, where different species (*F. alanii*, *F. hayii*, *F. liliana*, *F. mitreus*, *F. richardii*,  
685 *F. schaubii* and *F. tonii*) concomitantly disappear. Agnini et al. (2014) used this event to define  
686 the top of CNP11. The disappearance of the last species of the plexus is, however, slightly  
687 diachronous within the recovery interval. This is the reason why we use the LO of *C. bownii*,  
688 which shows a lower degree of diachronism between proximal and oceanic sites. The base of  
689 PE1 is also characterized by the LO of *B. aquilus*, reported in a limited number of sites.

690 The fasciculiths group underwent an abrupt extinction across the PETM in Atlantic, Pacific and  
691 Tethyan area (Monechi et al. 2000, Zachos et al. 2005, Raffi et al. 2005, Agnini et al. 2006,  
692 2007). Despite their scarcity in shelf sections, both these taxa clearly last occurred during the  
693 core of the PETM, as also observed at South Dover.

694 In some regions, *Z. bijugatus* occurred concomitant with the abundance decline of fasciculiths  
695 (Bralower 2002, Tremolada and Bralower 2004, Gibbs et al. 2006, Agnini et al. 2007, 2014).  
696 *Z. bijugatus* can attain 40% of total assemblage. This event can be useful for correlating high-  
697 and low-latitude sections (e.g., Site 690) where the LO of *F. richardii* group is not well defined  
698 due to its rarity.

699

## 700 **PE2**

701 Name: *Zygrhablithus bijugatus* zone

702 Definition: Interval from LO of *C. bownii* to LO of *F. tympaniformis*

703 Reference section: Site TDP 14 (Tanzania; 14 (9°16'59.89"S, 39°30'45.04"E)

704 Remarks: this zone is subdivided into two subzones described below.

## 705 **PE2a**

706 Name: *Coccolithus bownii* subzone

707 Definition: Interval from LO of *C. bownii* to FO of *D. diastypus*

708 Reference section: Site TDP 14 (Tanzania, 9°16'59.89"S, 39°30'45.04"E)

709 Remarks: This subzone represents the recovery phase II interval only in shelf sections.

710 The FO of *D. diastypus* also marks the base of CNP9a (Okada and Bukry 1980). It is sporadic  
711 at the beginning of its range and its position relative to the  $\delta^{13}\text{C}$  is somehow variable. This taxon  
712 was not recorded neither at Sites 1263 or 1209. However, at Site 1209 Gibbs et al. (2006)  
713 recorded its FO approximately 1.5 m above the LC, and this is far above the interval we  
714 studied here. Because the first occurrence of this species is recorded in the recovery phase II

715 interval only in proximal settings (Site 1260, Alamedilla, TDP 14), this zone has somehow a  
716 limited value and can be applied only locally.

## 717 **PE2b**

718 Name: *Fasciculithus tympaniformis* subzone

719 Definition: Interval from FO of *D. diastypus* to LO of *F. tympaniformis*

720 Reference section: Site TDP 14 (Tanzania; 14 (9°16'59.89"S, 39°30'45.04"E))

721 Remarks: This subzone represents the recovery phase II interval in both shelf sections and open-  
722 ocean localities. At Site 1260 and at TDP 14, the FO of *D. diastypus* is synchronous while at  
723 Alamedilla it occurs ~50 kyrs earlier. Different taxonomic concepts might explain this apparent  
724 diachronism. Thus, the base of PE2b is probably not diachronous upon a uniform taxonomic  
725 definition of *D. diastypus*. The LO of *F. tympaniformis* can be a slightly diachronous event,  
726 which due to the limited interval considered in this paper, has not been recorded at Sites 1209  
727 and 1263.

728

## 729 **5. Conclusions**

730 Newly acquired biostratigraphic data from the Paleocene-Eocene Thermal Maximum (PETM)  
731 of ODP Sites 1209 (Tropical Pacific Ocean) and 1263 (South East Atlantic Ocean) were  
732 compared to available high-resolution records from various ODP cores and onland marine  
733 sections from Atlantic, Pacific, Southern oceans and Tethys region. All the considered records  
734 dispose of  $\delta^{13}\text{C}_{\text{bulk carb}}$  geochemistry, which biostratigraphic data were plotted to. Such a tidy  
735 comparison revealed two main issues, namely: i) unconformities are present in all the  
736 considered sites but two onland localities (Alamedilla, Cicogna) at the onset of the PETM C-  
737 isotope negative excursion; ii) most of the considered bioevents, including the ones used in  
738 standard biozonations, are diachronous to some extent. These discoveries have profound  
739 implications, first because the C-isotope negative excursion is used to define the

740 Paleocene/Eocene boundary. Also, it appears that standard calcareous nannofossil biozonations  
741 fail to bracket the PETM at an adequate resolution, because the zone duration averages 1-2  
742 Myrs whilst the PETM is a short hyperthermal lasting some 250 kyrs. Because of the combined  
743 effect of relatively low-resolution and diachronous nature of the events, standard calcareous  
744 nannofossil biozonations may provide us with an apparent contradictory correlation of the  
745 PETM in various sites. The inconsistency and partly diachronous nature of standard  
746 biostratigraphic markers are either due to primary environmental factors or to preservation  
747 biases. In fact, dissolution intervals are also well-known during the PETM.

748 The late Paleocene and early Eocene are characterized by several originations and extinctions,  
749 and also by dominance shifts within the calcareous nannofossil communities. Some of these  
750 events, never considered in earlier biozonations, proved to be consistent, with a lesser degree  
751 of diachronism than the previously-used biostratigraphic markers. By reviewing the original  
752 datasets available for each section, we end up with a new high-resolution biozonation scheme  
753 with an average resolution of 50-100 kyrs per zone. More importantly, we anchor the  
754 biostratigraphic events and new zones to the different phases characterizing the CIE defining  
755 the Paleocene/Eocene. Thus, the pre-excursion interval is comprised in the PE-1 new  
756 nannofossil zone. The onset of the CIE is bracketed by the PE0, which might be considered in  
757 future works as the main marker for the Paleocene/Eocene boundary. The PE1 corresponds to  
758 the core of the event and to the recovery interval phase I. The recovery interval phase II is  
759 characterized by the PE2 zone, which can be subdivided into two subzones at least valuable in  
760 epicontinental areas.

761 For dating and correlating paleoceanographic events occurring on short-term geological time  
762 scales (< 1 Myrs), an enhanced biostratigraphy is crucial. Because of diachronism of the events,  
763 some studies on the PETM have avoided the use of calcareous nannofossil biostratigraphy in  
764 order to recognize the PETM. However, precise biostratigraphy cannot be neglected and

765 remains fundament for modern research in paleoclimatology/paleoceanography studies aiming  
766 at a better understanding of extreme events such as the PETM.

767

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774 de Géologie de l'Université de Lyon (FSL number 717458).

775

## 776 **Appendix 1**

### 777 **Species list and taxonomic-stratigraphic remarks**

778 This list includes all the taxa cited in the paper. The taxonomy and bibliographical references  
779 follow Perch-Nielsen (1985) and Bown (2005a). Potential biases when dealing with PETM  
780 biostratigraphy may derive from the inconsistency between authors in the taxonomic concepts  
781 adopted. We thus clarify the taxonomic concepts adopted here, which are consistently based on  
782 the holotype of the species and its original description.

783

784 *Bomolithus* Roth 1973

785 *Bomolithus aquilus* Bown 2010

786 *Bomolithus megastypus* (Bramlette and Sullivan 1961) Bown 2010

787 *Bomolithus supremus* Bown and Dunkley Jones 2006

788 *Braarudosphaera* Deflandre 1957

789 *Calciosolenia aperta* (Hay and Mohler 1967) Bown 2005a

790 For synonymies prior to 2005, we refer to Bown 2005a  
791 2007 *Scapolithus apertus* Mutterlose et al. 2007  
792 We follow the taxonomic concept of Bown (2005a), who combined *S. apertus* and *S.*  
793 *rhombiformis* into *C. aperta*. The genus *Scapholithus* is a junior synonym of the extant genus  
794 *Calciosolenia* (see discussion by Bown in Kennedy et al. 2000; Young et al. 2003). This species  
795 of *Calciosolenia* has a central solid rod extending almost to the ends of the scapolith. This  
796 structure is very fragile and can be easily lost. However, this species cannot be confused with  
797 others of the same genus, because it is the only present in the late Paleocene. *C. aperta* can be  
798 easily recognized by using the gypsum plate: the four sides of the scapolith show an alternating  
799 extinction pattern every 90°. Namely, when the long sides of the lozenge show yellow  
800 birefringence colors, the short sides show blue-yellow colors and *vice-versa*.  
801 Just below the onset of the CIE, several authors reported the last occurrence of *C. aperta* in  
802 shelf settings, but its presence in oceanic settings was never discussed so far. For the first time,  
803 we document the presence of *C. aperta* from the core of the PETM interval at Site 1263,  
804 following its LCO. Mutterlose et al. (2007) also observed this species in an Atlantic setting  
805 (ODP 1260). Thanks to its widespread distribution in Europe (Alamedilla), North America  
806 (South Dover) and Tanzania sections this event can be used in supraregional correlations. The  
807 last occurrence of *C. aperta* can be used to approximate the end of the NP9 of Martini (1971)  
808 and the NP9b of Aubry et al. (1999).  
809 *Campylosphaera* Kamptner 1963  
810 *Campylosphaera dela* (Bramlette and Sullivan 1961) Hay and Mohler 1967  
811 *Campylosphaera differta* Bown 2010  
812 *Campylosphaera eodela* Bukry 1971  
813 *Chiasmolithus* Hay et al. 1966  
814 *Chiasmolithus bidens* (Bramlette and Sullivan 1961) Hay and Mohler 1967



815 *Chiasmolithus consuetus* (Bramlette and Sullivan 1961) Hay and Mohler 1967  
816 *Coccolithus* Schwarz 1894  
817 *Coccolithus pelagicus* Schiller 1930  
818 *Coccolithus bownii* Jiang and Wise 2007  
819 2007 *Coccolithus subpertusus* Mutterlose et al. 2007 micrograph 7, figure 5.  
820 Among the “excursion-taxa”, Jiang and Wise (2007) described *C. bownii*. It is a broadly  
821 elliptical to subcircular *Coccolithus* with a large central opening, that occupies 40-50% of the  
822 coccolith diameter along the minor axis. In SEM, it possesses a very thin shield compared to  
823 *C. pelagicus*. This species possibly corresponds to the thin morphotypes of *C. pelagicus*  
824 observed at Bass River borehole (New Jersey) during the CIE (O’Dea et al. 2014).  
825 Based on observation of the light microscope pictures of Mutterlose et al. (2007) (micrograph  
826 7, figure 5), the specimens reported by the authors as *C. subpertusus* (= *Ericsonia subpertusa*)  
827 belong to *C. bownii*. *E. subertusa* has a narrow-to-closed central area, while the specimen  
828 figured by Mutterlose et al. (2007) has a clearly open central area that occupies at least 50% of  
829 the coccolith surface. If so, the range of *C. bownii* at Site 1260 is perfectly consistent with the  
830 record of Sites 1209, 1263, South Dover and TDP14.  
831 *Cruciplacolithus* Hay and Mohler 1967  
832 *Discoaster* Tan 1927  
833 *Discoaster anartios* Bybell and Self-Trail 1995  
834 *Discoaster araneus* Bukry 1971  
835 Despite the recent taxonomic revision of PETM malformed discoasters by Bralower and Self-  
836 Trail (2016), here we refer to the original species concepts of *D. araneus* and *D. anartios* since  
837 in our sections we only found specimens that fit these two end-members. Given that *D. araneus*  
838 is more consistently recorded across our studied sections, we chose to adopt it as a zonal marker.  
839 *D. araneus* is a large Discoaster (12-25  $\mu\text{m}$ ), with 7 to 9 tapering rays

840 that have a variable free length from 1/3 to 2/3 of the total ray length. The length of the  
841 individual rays, even on the same specimen, is not uniform and the angle between rays is  
842 likewise variable. The distinct taper of the rays, which terminate in points, and the large central  
843 knob are consistent characters in this morphologically plastic species. In overgrown specimens,  
844 the central knob is not easily recognizable, as overgrowth happens primarily in and around the  
845 central area of *Discoaster* (Adelsek et al. 1973). However, the tapering rays and the irregular  
846 angle between rays are still recognizable features. This taxon is typical in Pacific sediments and  
847 it corresponds to the specimens attributed to *Discoaster* cf. *araneus* by Bown (2005b) at Shatsky  
848 Rise. At Site 865 (Allyson Guyot), *D.* cf. *araneus* (*sensu* Bown 2005b) has been also found  
849 (Alessandro Menini preliminary observations), which we consider as *D. araneus*. This record  
850 indicates that this species was widespread in the Pacific Ocean. The specimens reported as *D.*  
851 cf. *araneus* (Bown 2005b) have exactly the same stratigraphic range as *D. araneus* in the  
852 sections studied here.

853 As already stated by Bukry (1971), *D. araneus* is easily distinguished from other Lower Tertiary  
854 species, such as *D. multiradiatus* or *D. nobilis* which show consistently regular ray  
855 arrangements, because of long tapering rays and large central knob, and the variability of the  
856 general proportions of the rays in a single specimen.

857 Previous studies stated that the distinctive *Rhomboaster* spp. - *D. araneus* association  
858 is considered to have a marked provincialism, restricted to the Atlantic Ocean and partially  
859 extending into the Tethys seaway and westernmost Indian Ocean (Kahn and Aubry 2004). Raffi  
860 (2005) reported that the distinct *Rhomboaster* spp. - *D. araneus* association also occurs in the  
861 paleo-equatorial Pacific Ocean. Thanks to our record from Site 1209, located in the Tropical  
862 Pacific Ocean, we can attest that the *Rhomboaster* spp. - *D. araneus* association also occurs in  
863 tropical Pacific settings. Thus possibly these organisms colonized the world ocean across the  
864 PETM and were not restricted to the Tethys, Atlantic and Indian Oceans.

- 865 *Discoaster delicatus* Bramlette and Sullivan 1961
- 866 *Discoaster diastypus* Bramlette and Sullivan 1961
- 867 *non* 2000 *Discoaster diastypus* Monechi et al. 2000 plate 2, micrograph 1, p. 486
- 868 *D. diastypus* is a large to very large species (11 to 20  $\mu\text{m}$  in diameter) of rosette-shaped
- 869 discoaster with 9 to 16 pointed rays. The rays are joined through most of their length (1/2 to
- 870 2/3) and typically they are curving. This species has two central knob, thus side views are
- 871 diagnostic and very peculiar. *D. diastypus* is distinguished from *D. salisburgensis* (Stradner
- 872 1961) by an overall higher number of rays in the latter (12 to 24) and presence of prominent
- 873 knob of one side only.
- 874 *Discoaster lenticularis* Bramlette and Sullivan 1961
- 875 *Discoaster multiradiatus* Bramlette and Riedel 1954
- 876 *Discoaster mohleri* Bukry and Percival 1971
- 877 *Discoaster nobilis* Martini 1961
- 878 *Discoaster salisburgensis* Stradner 1961
- 879 *Ericsonia* Black 1964
- 880 *Ericsonia aliquanta* Bown 2016
- 881 *Ericsonia orbis* Bown 2016
- 882 *Ericsonia robusta* (Bramlette and Sullivan 1961) Edwards and Perch-Nielsen 1975
- 883 *Ericsonia subpertusa* Hay and Mohler 1967
- 884 *Fasciculithus* Bramlette and Sullivan 1961
- 885 *Fasciculithus alanii* Perch-Nielsen 1971
- 886 *Fasciculithus hayi* Haq 1971
- 887 *Fasciculithus involutus* Bramlette and Sullivan 1961
- 888 *Fasciculithus mitreus* Gartner 1971
- 889 *Fasciculithus richardii* Perch-Nielsen 1971

890 *Fasciculithus schaubii* Hay and Mohler 1967

891 *Fasciculithus thomasi* Perch-Nielsen 1971

892 *Fasciculithus tonii* Perch-Nielsen 1971

893 *Fasciculithus tympaniformis* Hay and Mohler 1967

894 *Fasciculithus richardii* group *sensu* Agnini et al. 2014

895 Close to the top of the CIE, the Paleocene genus *Fasciculithus* drastically decreased in  
896 abundance. Such a decrease is driven by the successive extinctions of *F. richardii*, *F. hayi*, *F.*  
897 *liliana*, *F. schaubii*, *F. mitreus*, *F. tonii* (Romein 1979, Perch-Nielsen 1985, Agnini et al. 2007,  
898 Agnini et al. 2014). These species constitute the third and last major radiation event among the  
899 fasciculiths in the upper Thanetian. These taxa are here all included in the single *F. richardii*  
900 group, according to Agnini et al. (2014) given their similar conical shape and their very similar  
901 stratigraphic range. Some species have fenestrae (i.e., *F. schaubii*, *F. richardii*) and other do  
902 not (i.e., *F. alanii*, *F. liliana*) but the lack/presence of fenestrae is not of stratigraphic value  
903 (Romein 1979, Perch-Nielsen et al. 1985, Raffi et al. 2005, Agnini et al. 2014). Previous studies  
904 found that all these species have a similar stratigraphic range, with a common first appearance  
905 close to Chron C25n/C24r boundary and a last occurrence in correspondence with the onset of  
906 the PETM and hence the Paleocene-Eocene boundary (Raffi et al. 2005, Agnini et al. 2007,  
907 2014). In both ODP Sites 1209 and 1263 studied here, and in marine onland sections, the last  
908 occurrence of the different species of the genus *Fasciculithus* occurs in the core of the event  
909 (between 50-100 ky after the PETM).

910 *Fasciculithus tympaniformis* Hay and Mohler *in* Hay et al. 1967

911 It possesses a peculiar morphology consisting of a small-to-medium sized (5-7  $\mu\text{m}$  in length),  
912 squat cylindrical fasciculith, almost square in side-view, with gently convex upper surface. *F.*  
913 *tympaniformis* is distinguished from *F. involutus* because it is lacking of fenestrae. Wise and  
914 Wind (1977) showed that the *F. tympaniformis* morphotype could be produced through

915 overgrowth of *F. involutus* and considered the two forms as conspecific. Following this  
916 interpretation, they considered *F. tympaniformis* to be a junior synonym of *F. involutus*.  
917 However, most authors keep separated the two forms, and arguably the forms with fenestrae  
918 only occur in the upper part of the range of the group.

919 *Jakubowskia leoniae* Varol 1989

920 *Markalius apertus* Perch Nielsen 1979

921 *Rhomboaster* (Bramlette and Sullivan 1961) and *Tibrachiatus bramlettei* (Bronnimann and  
922 Stradner 1960) Proto-Decima et al. 1975

923 The taxonomy of most PETM taxa is generally well established, except for the much-debated  
924 genera *Rhomboaster* and *Tibrachiatus* (Perch-Nielsen 1985, Bybell and Self-Trail 1997,  
925 Aubry et al. 2000, Wei and Zhong 1996, von Salis et al. 2000, Raffi et al. 2005). Within the  
926 CIE, the genus *Rhomboaster* evolved with several species, finally giving rise to *Tibrachiatus*  
927 *bramlettei*. Although some investigators have gathered the two taxa under the genus  
928 *Rhomboaster* and recombined all the species within *Tibrachiatus* into *Rhomboaster*, we prefer  
929 to distinguish both genera, only recognizing the following *Rhomboaster* taxa: *R.cuspis* (with  
930 short rays) and *R. calcitraba* group, which includes the species *R. calcitraba*, *R. intermedia*, *R.*  
931 *bitrifida* and *R. spineus* (all possessing long rays). In literature *Rhomboaster* spp. are either  
932 distinguished at a specific level or lumped together. Despite the ray length could be partially  
933 due to a diagenetic artefact (Bybell and Self-Trail 1995, Wei and Zhong 1996), we prefer to  
934 distinguish morphotypes with short arms from long arms as previously proposed (Aubry et al.  
935 2000), and hence *R. cuspis* from *R. calcitraba* in order to avoid misrepresentation of the original  
936 data.

937 Despite the considerable debate on morphologic and evolutionary relationships between  
938 *Rhomboaster* and *Tibrachiatus* (e.g., Perch-Nielsen 1985, Bybell and Self-Trail 1995, 1997,  
939 Aubry 1995, Aubry et al. 1996, 2000; Angori and Monechi 1995, Wei and Zhong 1996, von

940 Salis et al. 2000), biostratigraphic studies have improved our understanding of known ranges  
941 of the different species (e.g., Bralower and Mutterlose 1995, Bybell and Self-Trail 1997,  
942 Monechi et al. 2000). By combining SEM and optical microscope study of type material where  
943 the holotypes of several *Rhomboaster* and *Tribrachiatus* species were described, Wei and  
944 Zhong (1996) showed that the transition from *Rhomboaster* to *Tribrachiatus* is expressed by a  
945 general flattening of the nannolith. The distinction between *Rhomboaster* and *Tribrachiatus* is  
946 justified by the existence of shape gradation between the two genera and the morphologic  
947 difference is very important in most cases (for example *T. orthostylus* from *R. cuspis*). Besides,  
948 different stratigraphic ranges exist between *Rhomboaster* and *Tribrachiatus*: while  
949 *Rhomboaster* are restricted to the PETM interval, *Tribrachiatus* evolve in the lower Eocene (*T.*  
950 *contortus*, *T. digitalis*, *T. orthostylus*, *T. absidatus*, *T. lunatus*) and, given that the nomenclature  
951 stability is still strongly encouraged by the IBCN, we keep separated the two genera.

952 *Rhomboaster cuspis* (Bramlette and Sullivan 1961)

953 2000 *Rhomboaster bramlettei* var. short arms Monechi et al. 2000 plate 3, micrograph 4, p. 488  
954 *R. cuspis* (Bramlette and Sullivan 1961) is a rhombic-shaped nannolith with little or no  
955 extension from the points of the rhomb. Faces are depressed and strongly concave. Polarized  
956 light shows that it is composed of a unique mass of calcite.

957 *Rhomboaster calcitraba* group *sensu* Raffi et al. 2005

958 2000 *Rhomboaster bramlettei* var. long arms Monechi et al. 2000 plate 1, micrograph 17-19, p.  
959 484

960 *R. calcitraba*, *R. intermedia*, *R. bitrifida* and *R. spineus* are all rhombic-shaped nannolith with  
961 long extensions from the points of the rhomb. *Rhomboaster bitrifida*, *R. intermedia* and *R.*  
962 *spineus* are rarely reported in the literature (Bybell and Self-Trail 1995, Wei and Zhong 1996)  
963 justifying our choice to lump these species into the *R. calcitraba* group.

964 *Sphenolithus* Deflandre in Grassé, 1952



- 965 *Sphenolithus anarrhopus* Bukry and Bramlette 1969
- 966 *Sphenolithus moriformis* group *sensu* Agnini et al. 2014
- 967 *Prinsius* Hay and Mohler 1967
- 968 *Thoracosphaera* Kamptner 1927
- 969 *Toweius* Hay and Mohler 1967
- 970 *Toweius callosus* Perch-Nielsen 1971
- 971 *Toweius eminens* (Bramlette and Sullivan, 1961) Perch-Nielsen, 1971
- 972 *Toweius serotinus* Bybell and Self Trail 1995
- 973 *Tibrachiatus* Shamrai 1963
- 974 *Tibrachiatus bramlettei* (Bronnimann and Stradner 1960) Proto-Decima et al. 1975
- 975 2000 *Rhomboaster bramlettei* var. T Monechi et al. 2000 plate 3, micrograph 1-2-3, p. 488.
- 976 *T. bramlettei* is a nannolith with two symmetrically offset and superimposed tri-radiate cycles.
- 977 These are very easy to observe by focusing under microscope in plane-polarized light or in XPL
- 978 light. In side view, it is flatter than species of *Rhomboaster* genus (Romein 1979, Wei and
- 979 Zhong 1996). The first occurrence of *T. bramlettei* defines the Subzone NP10a (=base NP10)
- 980 of Aubry et al. (1999).
- 981 *Zygrhablithus* Deflandre 1959
- 982 *Zygrhablithus bijugatus* Deflandre 1959

983

984 **References**

- 985 • Adelseck, C.G., Geehan, G.W., Roth, P.H., 1973. Experimental evidence for the selective
- 986 dissolution and overgrowth of calcareous nannofossils during diagenesis. Geological Society
- 987 of America Bulletin 84, 2755–2762.

- 988 • Agnini, C., Muttoni, G., Kent, D. V., Rio, D., 2006. Eocene biostratigraphy and magnetic  
989 stratigraphy from Possagno, Italy: The calcareous nannofossil response to climate  
990 variability. *Earth and Planetary Science Letters* 241, 815–830.
- 991 • Agnini, C., Fornaciari, E., Rio, D., Tateo, F., Backman, J., Giusberti, L., 2007. Responses of  
992 calcareous nannofossil assemblages, mineralogy and geochemistry to the environmental  
993 perturbations across the Paleocene/Eocene boundary in the Venetian Pre-Alps. *Marine*  
994 *Micropaleontology* 63, 19–38.
- 995 • Agnini, C., Fornaciari, E., Raffi, I., Catanzariti, R., Pälike, H., Backman, J., Rio, D., 2014.  
996 Biozonation and biochronology of Paleogene calcareous nannofossils from low and middle  
997 latitudes. *Newsletters on Stratigraphy* 47, 131–181
- 998 • Agnini, C., Spofforth, D.J.A., Dickens, G.R., Rio, D., Pälike, H., Backman, J., Muttoni, G.,  
999 Dallanave, E., 2016. Stable isotope and calcareous nannofossil assemblage record of the late  
1000 Paleocene and early Eocene (Cicogna section). *Climate of the Past* 12, 883–909.
- 1001 • Ali, J. R., Kent, D. V., Hailwood, E. A., 2000. Magnetostratigraphic reinvestigation of the  
1002 Palaeocene/Eocene boundary interval in Hole 690B, Maud Rise, Antarctica. *Geophysical*  
1003 *Journal International* 141(3), 639–646.
- 1004 • Angori, E., Monechi, S., 1995. High-resolution calcareous nannofossils biostratigraphy  
1005 across the Paleocene/Eocene boundary at Caravaca (southern Spain). *Israel Journal of Earth*  
1006 *Sciences* 44, 197– 206.
- 1007 • Aubry, M.-P., 1995. Towards an upper Paleocene–lower Eocene high resolution stratigraphy  
1008 based on calcareous nannofossils stratigraphy. *Israel Journal of Earth Sciences* 44, 239– 253.
- 1009 • Aubry, M.-P., 1998. Early Paleogene calcareous nannoplankton evolution: a tale of climatic  
1010 amelioration. In: Aubry, M.-P., Lucas, S., Berggren, W.A. (Eds.), *Late Paleocene and Early*  
1011 *Eocene Climatic and Biotic Evolution*. Columbia University Press, New York, 158–203.

- 1012 • Aubry, M.-P., 1999. Late Paleocene–early Eocene sedimentary history in western Cuba:  
1013 implications for the LPTM and for regional tectonic history. *Micropaleontology* 45, 5–18.
- 1014 • Aubry, M.-P., 2001. Provincialism in the photic zone during the LPTM. In: Ash, A., Wing,  
1015 S. (Eds.), *Climate and Biota of the Early Paleogene*. International Meeting, Powell,  
1016 Abstract Volume, Powell, p. 6.
- 1017 • Aubry, M.P., Cramer, B.S., Miller, K.G., Wright, J.D., Kent, D. V., Olsson, R.K., 2000. Late  
1018 Paleocene event chronology: Unconformities, not diachrony. *Bulletin de la Societ *  
1019 *Geologique de France* 171 (3), 367–378
- 1020 • Aze, T., Pearson, P.N., Dickson, A.J., Badger, M.P.S.S., Bown, P.R., Pancost, R.D., Gibbs,  
1021 S.J., Huber, B.T., Leng, M.J., Coe, A.L., Cohen, A.S., Foster, G.L., 2014. Extreme warming  
1022 of tropical waters during the Paleocene-Eocene thermal maximum. *Geology* 42 (9),739–742
- 1023 • Babila, T.L., Penman, D.E., H nisch, B., Kelly, D.C., Bralower, T.J., Rosenthal, Y., Zachos,  
1024 J.C., 2018. Capturing the global signature of surface ocean acidification during the  
1025 Palaeocene–Eocene Thermal Maximum. *Philosophical Transactions A* 376.
- 1026 • Bains, S., R. Corfield, M., Norris, R. D., 1999. Mechanisms of climate warming at the end  
1027 of the Paleocene, *Science* 285, 724–727.
- 1028 • Beaufort, L., Barbarin, N., Gally, Y., 2014. Optical measurements to determine the thickness  
1029 of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature*  
1030 *Protocols* 9 (3), 633–642
- 1031 • Blair, S., Watkins, D. K., 2009. High-resolution calcareous nannofossil biostratigraphy for  
1032 the Coniacian/Santonian Stage boundary, Western Interior Basin. *Cretaceous Research* 30,  
1033 367–384.
- 1034 • Bown, P. R., 2005a. Palaeogene calcareous nannofossils from the Kilwa and Lindi areas of  
1035 coastal Tanzania (Tanzania Drilling Project 2003-4). *J. Nannoplankton Res.* 27 (1), 2005,  
1036 21–95.

- 1037 • Bown, P.R., 2005b. Cenozoic calcareous nannofossils biostratigraphy, ODP Leg 198 Site  
1038 1208 (Shatsky Rise, northwest Pacific Ocean). In Bralower, T.J., Premoli Silva, I., and  
1039 Malone, M.J. Proceedings of the Ocean Drilling Program. Scientific Results 198, 1– 44.
- 1040 • Bown, P. R., 2010. Calcareous nannofossils from the Paleocene/Eocene Thermal Maximum  
1041 interval of southern Tanzania (TDP Site 14). *Journal of Nannoplankton Research*. 31(1), 11–  
1042 38.
- 1043 • Bown, P.R., 2016. Paleocene calcareous nannofossils from Tanzania (TDP sites 19, 27 and  
1044 38). *J. Nannoplankton Res*, The calcareous nannofossil genus *Ericsonia* in the upper  
1045 Paleocene 149 36 (1), 1–32.
- 1046 • Bown, P. R., Dunkley Jones, T., 2006. New Paleogene calcareous nannofossil taxa from  
1047 coastal Tanzania: Tanzania Drilling Project Sites 11 to 14. *Journal of Nannoplankton*  
1048 *Research* 28 (1), 17–34.
- 1049 • Bown, P., Pearson, P., 2009. Calcareous plankton evolution and the Paleocene/Eocene  
1050 thermal maximum event: New evidence from Tanzania. *Marine Micropaleontology* 71, 60–  
1051 70.
- 1052 • Bralower, T.J., 2002. Evidence of surface water oligotrophy during the Paleocene–Eocene  
1053 Thermal Maximum: nannofossil assemblage data from Ocean Drilling Program Site 690  
1054 Maud Rise, Weddell Sea. *Paleoceanography* 17, 1–13.
- 1055 • Bralower, T.J., Mutterlose, J., 1995. Calcareous nannofossil biostratigraphy of ODP Site  
1056 865, Allison Guyot, Central Pacific Ocean: a tropical Paleogene reference section. In:  
1057 Winterer, E.L., Sager, W.W., Firth, J.V. (Eds.), Proceedings of the Ocean Drilling Program.  
1058 Scientific Results 143, 31– 72.
- 1059 • Bralower, T.J., Self-Trail, J.M., 2016. Nannoplankton malformation during the Paleocene-  
1060 Eocene Thermal Maximum and its paleoecological and paleoceanographic significance.  
1061 *Paleoceanography* 31, 1423–1439.

- 1062 • Bralower, T.J., Kelly, D.C., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L., Smith, G.J.,  
1063 2014. Impact of dissolution on the sedimentary record of the Paleocene-Eocene thermal  
1064 maximum. *Earth and Planetary Science Letters* 401, 60–72
- 1065 • Bramlette, M. N., Sullivan, F. R., 1961. Coccolithophorids and related nannoplankton of the  
1066 early Tertiary in California. *Micropaleontology*, 129-188.
- 1067 • Bukry, D., 1973. Low-latitude coccolith biostratigraphic zonation. In: Edgar, N.T.,  
1068 Saunders, J.B., et al. *Initial Reports of the Deep Sea Drilling Project 15*. U.S. Government  
1069 Printing Office, Washington, 685–703.
- 1070 • Bukry, D., 1975. Coccolith and silicoflagellate stratigraphy, northwestern Pacific Ocean,  
1071 Deep Sea Drilling Project Leg 32. In: Larson, R.L., Moberly, R., et al. *Initial Reports of the*  
1072 *Deep Sea Drilling Project 32*. U.S. Government Printing Office, Washington, 677– 701.
- 1073 • Bybell, L.M., Self-Trail, J.M., 1995. Evolutionary, biostratigraphic, and taxonomic study of  
1074 calcareous nannofossils from a continuous Paleocene-Eocene boundary section in New  
1075 Jersey. *US Geological Survey Professional Paper* 1554.
- 1076 • Bybell, L.M., Self-Trail, J.M., 1997. Late Paleocene and early Eocene calcareous  
1077 nannofossils from three boreholes in an onshore-offshore transect from New Jersey to the  
1078 Atlantic Continental Rise. *Proceedings of the Ocean Drilling Program. Scientific results* 150,  
1079 91–110.
- 1080 • Cande, S.C., Kent, D.V., 1995. Revised calibration of the geomagnetic polarity timescale  
1081 for the Late Cretaceous and Cenozoic. *Journal of Geophysical Research* 100, 6093– 6095.
- 1082 • Colosimo, A.B., Bralower, T.J., Zachos, J.C., 2006. Evidence for lysocline shoaling at the  
1083 Paleocene/Eocene thermal maximum on Shatsky rise, northwest Pacific. *Proceeding of the*  
1084 *Ocean Drilling Program. Scientific Results* 198, 1–36.

- 1085 • Dallanave, E., Agnini, C., Muttoni, G., Rio, D., 2009. Magneto-biostratigraphy of the  
1086 Cicogna section (Italy): Implications for the late Paleocene-early Eocene time scale. *Earth  
1087 and Planetary Science Letters* 285, 39–51.
- 1088 • Dickens, G.R., O'Neil, J.R., Rea, D.K., Owen, R.M., 1995. Dissociation of oceanic methane  
1089 hydrate as a cause of the carbon isotope excursion at the end of the Paleocene.  
1090 *Paleoceanography* 10, 965–971
- 1091 • Dickens, G.R., Castillo, M.M., Walker, J.G.C., 1997. A blast of gas in the latest Paleocene:  
1092 Simulating first-order effects of massive dissociation of oceanic methane hydrate, *Geology*  
1093 25, 259–262.
- 1094 • Dickson, A.J., Cohen, A.S., Coe, A.L., Davies, M., Shcherbinina, E.A., Gavrillov, Y.O.,  
1095 2015. Evidence for weathering and volcanism during the PETM from Arctic Ocean and Peri-  
1096 Tethys osmium isotope records. *Palaeogeography, Palaeoclimatology, Palaeoecology* 438,  
1097 300–307.
- 1098 • Erbacher, J., Mosher, D.C., Malone, Berti, D., Bice, K. L., Bostock, H., Jürgen Brumsack,  
1099 H., Danelian, T., Glatz, C., Heidersdorf, F., Henderiks, J., Janecek, T., Junium, C., Le  
1100 Callonec, L., MacLeod, K., Meyers, P. A., Mutterlose, J., Nishi, H., Norris, R., Ogg, J. G.,  
1101 O'Regan, M., Rea, B., Sexton, P., Sturt, H., Suganuma, Y., Thurow, J.W., Wilson, P. A.,  
1102 Wise, S. W., 2004. Demerara rise: equatorial cretaceous and Paleogene paleoceanographic  
1103 transect, Western Atlantic (Leg 207, Sites 1257–1261). *Proceedings of the Ocean Drilling  
1104 Program* 207, 1–89.
- 1105 • Fatela, F., Taborda, R., 2002. Confidence limits of species proportions in microfossil  
1106 assemblages. *Marine Micropaleontology* 45, 169–174.
- 1107 • Ferreira, J., Mattioli, E., Suchéras-Marx, B., Giraud, F., Duart, L., V., Pitter, B., Hassler, A.,  
1108 Spangenberg, J., 2019. Western Tethys Early and Middle Jurassic calcareous nannofossils  
1109 biostratigraphy. *Earth-Science Reviews* 197, 1–19.



- 1110 • Garzarella, A., Raffi, I., 2018. Taxonomy and evolutionary relationships within the  
1111 calcareous nannofossil genus *Ericsonia* in the upper Paleocene. *Rivista Italiana di*  
1112 *Paleontologia e Stratigrafia* 124 (1), 129–150.
- 1113 • Geisen, M., Bollmann, J., Herrle, J.O., Mutterlose, J., Young, J.R., 1999. Calibration of the  
1114 random settling technique for calculation of absolute abundances of calcareous  
1115 nannoplankton. *Micropaleontology* 45, 437–442.
- 1116 • Gibbs, S.J., Bralower, T.J., Bown, P.R., Zachos, J.C., Bybell, L.M., 2006. Shelf and open-  
1117 ocean calcareous phytoplankton assemblages across the Paleocene–Eocene thermal  
1118 maximum: implication for global productivity gradients. *Geology* 34 (4), 233–236.
- 1119 • Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M., 2012. The geologic time scale, The  
1120 *Geologic Time Scale 2012*.
- 1121 • Handley, L., Pearson, P., McMillan, I.K., Pancost, R.D., 2008. Large terrestrial and marine  
1122 carbon and hydrogen isotope excursions in a new Paleocene/Eocene boundary section from  
1123 Tanzania. *Earth and Planetary Science Letters* 275, 17–25.
- 1124 • Jiang, S., Wise, S.W., 2006. Surface-water chemistry and fertility variations in the tropical  
1125 Atlantic across the Paleocene/Eocene Thermal Maximum as evidenced by calcareous  
1126 nannoplankton from ODP Leg 207, Hole 1259B. *Revue de Micropaléontologie* 49, 227–244.
- 1127 • Kahn, A., Aubry, M.P., 2004. Provincialism associated with the Paleocene/Eocene thermal  
1128 maximum: Temporal constraint. *Marine Micropaleontology* 52, 117–131.
- 1129 • Kelly, D.C., Bralower, T.J., Zachos, J.C., Premoli Silva, I., Thomas, E., 1996. Rapid  
1130 diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the  
1131 late Paleocene thermal maximum. *Geology* 24, 423–426.
- 1132 • Kelly, D.C., Zachos, J.C., Bralower, T.J., Schellenberg, S.A., 2005. Enhanced terrestrial  
1133 weathering/runoff and surface ocean carbonate production during the recovery stages of the  
1134 Paleocene-Eocene thermal maximum. *Paleoceanography* 20, 1–11.

- 1135 • Kennedy, J., Gale, A.S., Bown, P.R., Caron, M., Davey, R., Gröcke, D., Wray, D.S. 2000.  
1136 Integrated stratigraphy of the Aptian-Albian boundary interval in the Marnes Bleues, at the  
1137 Col de Pré-Guittard, Arnyon (Drôme), and at Tartonne (Alpes-de-Haute-Provence), France,  
1138 a candidate Global Boundary Stratotype Section and Boundary Point for the base of the  
1139 Albian stage. *Cretaceous Research* 21, 591–720.
- 1140 • Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and  
1141 benthic extinctions at the end of the Palaeocene. *Nature* 353, 225–229.
- 1142 • Kroon, D., Norris, R.D., Klaus, A., 1998. Proceeding of the Ocean Drilling Program. Initial  
1143 Reports 171B.
- 1144 • Lu G., Keller, G., Adatte T., Ortiz, N., Molina, E., 1996. Long-term ( $10^5$ ) or short-term  
1145 ( $10^3$ )  $\delta^{13}\text{C}$  excursion near the Palaeocene-Eocene transition: evidence from the Tethys. *Terra*  
1146 *Nova* 8, 347-355.
- 1147 • Martini, E., 1971. Standard Tertiary and Quaternary calcareous nannoplankton zonation. In:  
1148 Farinacci, A., Proceedings of the 2<sup>nd</sup> International Conference on Planktonic Microfossils 2,  
1149 739– 785
- 1150 • McCarren, H., Thomas, E., Hasegawa, T., Röhl, U., Zachos, J.C., 2008. Depth dependency  
1151 of the Paleocene-Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker  
1152 records (Ocean Drilling Program Leg 208, Walvis Ridge). *Geochemistry, Geophysics,*  
1153 *Geosystems* 9, 1–10.
- 1154 • Monechi, S., Angori, E., von Salis, K., 2000. Calcareous nannofossil turnover around the  
1155 Paleocene/Eocene transition at Alamedilla (southern Spain). *Bulletin de la Société*  
1156 *Géologique de France* 171 (4), 477–489.
- 1157 • Mutterlose, J., Linnert, C., Norris, R., 2007. Calcareous nannofossils from the Paleocene-  
1158 Eocene Thermal Maximum of the equatorial Atlantic (ODP Site 1260B): Evidence for  
1159 tropical warming. *Marine Micropaleontology* 65, 13–31.

- 1160 • O’Dea, S.A., Gibbs, S.J., Bown, P.R., Young, J.R., Poulton, A.J., Newsam, C., Wilson, P.A.,  
1161 2014. Coccolithophore calcification response to past ocean acidification and climate change.  
1162 Nature Communications 5 (5363).
- 1163 • Okada, H., Bukry, K., 1980. Supplementary modification and introduction of code numbers  
1164 to the low-latitude coccolith biostratigraphic zonation. *Marine Micropaleontology* 5, 321–  
1165 325.
- 1166 • Pak, D. K., Miller, K. G., 1992. Paleocene to Eocene benthic foraminiferal isotopes and  
1167 assemblages: Implications for deep water circulation, *Paleoceanography* 7, 405– 422.
- 1168 • Pak, D., Miller, K., Browning, J., 1997. Global significance of an isotopic record from the  
1169 New Jersey coastal plain: linkage between the shelf and deep sea in the late Paleocene to  
1170 early Eocene. In *Proceedings of the Ocean Drilling Program. Scientific results 156*, 305–  
1171 315.
- 1172 • Penman, D.E., Hönisch, B., Zeebe, R.E., Thomas, E., Zachos, J.C., 2014. Rapid and  
1173 sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum.  
1174 *Paleoceanography* 29, 357–369.
- 1175 • Penman, D.E., Turner, S.K., Sexton, P.F., Norris, R.D., Dickson, A.J., Boulila, S., Ridgwell,  
1176 A., Zeebe, R.E., Zachos, J.C., Cameron, A., Westerhold, T., Röhl, U., 2016. An abyssal  
1177 carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene Thermal  
1178 Maximum. *Nature Geoscience* 9, 575–580.
- 1179 • Perch-Nielsen, K., 1985. Cenozoic calcareous nannofossils. In: Bolli, H.M., Saunders, J.B.,  
1180 Perch-Nielsen, K. *Plankton Stratigraphy*. Cambridge University Press, Cambridge, 427–554.
- 1181 • Raffi, I., De Bernardi, B., 2008. Response of calcareous nannofossils to the Paleocene–  
1182 Eocene thermal maximum: observations on composition, preservation and calcification in  
1183 sediments from ODP Site 1263 (Walvis Ridge -SW Atlantic). *Marine Micropaleontology*  
1184 69, 119–138.

- 1185 • Raffi, I., Backman, J., Pälike, H., 2005. Changes in calcareous nannofossil assemblages  
1186 across the Paleocene/Eocene transition from the paleo-equatorial Pacific Ocean.  
1187 *Palaeogeography, Palaeoclimatology, Palaeoecology* 226, 93–126.
- 1188 • Raffi, I., Backman, J., Zachos, J.C., Sluijs, A., 2009. The response of calcareous nannofossil  
1189 assemblages to the Paleocene Eocene Thermal Maximum at the Walvis Ridge in the South  
1190 Atlantic. *Marine Micropaleontology* 70, 201–212.
- 1191 • Ravizza, G., Norris, R.N., Blusztajn, J., Aubry, M.P., 2001. An osmium isotope excursion  
1192 associated with the late Paleocene thermal maximum: Evidence of intensified chemical  
1193 weathering. *Paleoceanography* 16 (2), 155–163
- 1194 • Röhl, U., L. J. Abrams, 2000, High-resolution, downhole and non-destructive core  
1195 measurements from Sites 999 and 1001 in the Caribbean Sea: Application to the late  
1196 Paleocene thermal maximum, *Proceedings of the Ocean Drilling Program Sci. Results* 165,  
1197 191–203.
- 1198 • Röhl, U., Westerhold, T., Bralower, T.J., Zachos, J.C., 2007. On the duration of the  
1199 Paleocene–Eocene thermal maximum (PETM). *Geochemistry, Geophysics, Geosystems* 8,
- 1200 • Romein, A.J.T., 1979. Lineages in early Paleogene calcareous nannoplankton (Doctoral  
1201 dissertation, Utrecht University), 76–78.
- 1202 • Self-Trail, J. M., Powars, D. S., Watkins, D. K., Wandless, G., 2012. Calcareous nannofossil  
1203 assemblage changes across the Paleocene-Eocene thermal maximum: Evidence from a shelf  
1204 setting, *Marine Micropaleontology* 92–93, 61–80,
- 1205 • Shamrock, J. L., Watkins, D. K., 2012. Eocene calcareous nannofossil biostratigraphy and  
1206 community structure from Exmouth Plateau, Eastern Indian Ocean (ODP Site 762).  
1207 *Stratigraphy* 9 (1), 1–11.

- 1208 • Stradner, H., Papp, A., 1961. Tertiäre Discoasteriden aus Österreich und deren  
1209 stratigraphische Bedeutung mit Hinweisen auf Mexico, Rumanien und Italien. Jahrbuch der  
1210 Geologischen Bundesanstalt (Wien) 7, 1–159.
- 1211 • Storme, J.Y., Devleeschouwer, X., Schnyder, J., Cambier, G., Baceta, J.I., Pujalte, V., Di  
1212 Matteo, A., Iacumin, P., Yans, J., 2012. The Palaeocene/Eocene boundary section at Zumaia  
1213 (Basque-Cantabric Basin) revisited: New insights from high-resolution magnetic  
1214 susceptibility and carbon isotope chemostratigraphy on organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ). *Terra Nova*  
1215 24, 310–317.
- 1216 • Takeda, K., Kaiho, K., 2007. Faunal turnovers in central Pacific benthic foraminifera during  
1217 the Paleocene-Eocene thermal maximum. *Palaeogeography, Palaeoclimatology,*  
1218 *Palaeoecology* 251, 175–197.
- 1219 • Thomas, E., Shackleton, N.J., 1996. The latest Paleocene benthic foraminiferal extinction  
1220 and stable isotope anomalies. In: Knox, R.O., Corfield, R.M., Dunay, R.E. *Correlation of*  
1221 *the Early Paleogene in Northwest Europe. Geological Society of London Special Publication*  
1222 101, 40–441.
- 1223 • Tjalsma, R. C., Lohmann, G. P., 1983. Paleocene-Eocene bathyal and abyssal benthic  
1224 foraminifera from the Atlantic Ocean. *Micropaleontology Special Publication* 4, 1–90.
- 1225 • Tremolada, F., Bralower, T.J., 2004. Nannofossil assemblage fluctuations during the  
1226 Paleocene-Eocene Thermal Maximum at Sites 213 (Indian Ocean) and 401 (North Atlantic  
1227 Ocean): Palaeoceanographic implications. *Marine Micropaleontology* 52, 107–116.
- 1228 • von Salis, K., Monechi, S., Bybell, L.M., Young, J., 2000. Remarks on the calcareous  
1229 nannofossil markers *Rhomboaster* and *Tribrachiatus* around the Paleocene/Eocene  
1230 boundary. *Journal of the Geological Society of Sweden* 122, 138–140.
- 1231 • Wei, W., Zhong, S., 1996. Taxonomy and magnetobiochronology of *Tribrachiatus* and  
1232 *Rhomboaster*, two genera of calcareous nannofossils. *Journal of Paleontology* 70, 7– 22.

- 1233 • Westerhold, T., Röhl, U., Donner, B., Zachos, J.C., 2018. Global Extent of Early Eocene  
1234 Hyperthermal Events: A New Pacific Benthic Foraminiferal Isotope Record From Shatsky  
1235 Rise (ODP Site 1209). *Paleoceanography and Paleoclimatology* 33, 626–642.
- 1236 • Westerhold, T., Röhl, U., Laskar, J., Raffi, I., Bowles, J., Lourens, L.J., Zachos, J.C., 2007.  
1237 On the duration of magnetochrons C24r and C25n and the timing of early Eocene global  
1238 warming events: Implications from the Ocean Drilling Program Leg 208 Walvis Ridge depth  
1239 transect. *Paleoceanography* 22, 1–19.
- 1240 • Westerhold, T., Röhl, U., Raffi, I., Fornaciari, E., Monechi, S., Reale, V., Bowles, J., Evans,  
1241 H.F., 2008. Astronomical calibration of the Paleocene time. *Palaeogeography,*  
1242 *Palaeoclimatology, Palaeoecology* 257, 377–403.
- 1243 • Wise, S.W., Wind, F.H., 1977. Mesozoic and Cenozoic calcareous nannofossils recovered  
1244 by DSDP Leg 36 drilling on the Falkland Plateau, south-west Atlantic sector of the Southern  
1245 Ocean. *Initial Reports of the Deep Sea Drilling Project* 36, 269–491.
- 1246 • Zachos, J.C., Lohmann, K.C., Walker, J.C.G., Wise, S.W. Jr., 1993. Abrupt climate change  
1247 and transient climates during the Paleogene: A marine perspective, *J. Geol.* 101, 191 – 213.
- 1248 • Zachos, J.C., Kroon, D., Blum, P., Bowles, J., Gaillot, P., Hasegawa, T., Hathorne, E.C.,  
1249 Hodell, D. A., Kelly, D. C., Jung, J. H., Keller, S. M., Lee, Y. S., Leuschner, D. C., Lohmann,  
1250 K. C., Lourens, L., Monechi, S., Nicolo, M., Raffi, I., Riesselman, C., Röhl, U., Schellenber,  
1251 S. A., Schmidt, D., Slujis A., Thomas, D., Thomas, E., Vallius, H. , 2004. Early Cenozoic  
1252 extreme climates: the Walvis Ridge transect. *Proceedings of the Ocean Drilling Program.*  
1253 *Initial Reports* 208.
- 1254 • Zachos, J.C., Pagani, M., Sloan, L.C., Billups, K., Thomas, E., 2001. Trends, rhythms, and  
1255 aberrations in global climate 65 Ma to present. *Science* 292, 686–693.



- 1256 • Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas,  
1257 E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H., Kroon, D., 2005. Rapid acidification  
1258 of the ocean during the Paleocene–Eocene thermal maximum. *Science* 308, 1611–1615.
- 1259 • Zeebe, R.E., Lourens, L.J., 2019. Solar System chaos and the Paleocene–Eocene boundary  
1260 age constrained by geology and astronomy. *Science* 365, 926–929.

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1262

### 1263 **Figure captions**

1264

1265 Fig. 1. Location of the two studied sections on a paleogeographic map at 56 Ma  
1266 (<http://www.odsn.de/odsn/services/paleomap/paleomap.html>): Site 1209 (Shatsky Rise,  
1267 Tropical Pacific), and Site 1263 (Walvis Ridge, South Eastern Atlantic). Location of the sites  
1268 used for comparison is also shown: Site 690 (Southern Ocean) Site 1260 (Equatorial Atlantic),  
1269 SDB (New Jersey), TDP 14 (Tanzania), Cicogna (North Italy), Alamedilla (Spain).

1270

1271 Fig. 2. Core photo,  $\delta^{13}\text{C}_{\text{bulk carb}}$ ,  $\text{CaCO}_3$  (%) and calcareous nannofossil bioevents for Sites 1209  
1272 (left side) and 1263 (right side) in function of depth. Depth is expressed as relative to the  
1273 lithological contact (LC: from white nannofossils ooze to brown clayey nannofossil ooze).  
1274 Calcareous nannofossil biozonations are after Martini (1971), Okada and Bukry (1980) and  
1275 Agnini et al. (2014). The subdivision of NP9 (Martini 1971) in NP9a and NP9b is after Aubry  
1276 et al. 1999. Shaded area are used to subdivide the PETM interval in pre-PETM, core of the  
1277 PETM and recovery phase I and II according to Röhl et al. (2007).

1278

1279 Fig. 3. Compilation of biostratigraphic events in all the studied sections relative to the  $\delta^{13}\text{C}_{\text{bulk}}$   
1280 <sub>carb</sub> record (Alamedilla (red) Lu al. 1996, ODP 690 (grey) Bains et al. 1999 , ODP 1209 (orange)

1281 Penman et al. 2014, ODP 1263 (light blue) Zachos et al. 2005, ODP 1260 (green) Mutterlose  
1282 et al. 2007, South Dover (violet) Self Trail et al. 2012, Cicogna (black) Agnini et al. 2016). For  
1283 TDP 14 (pink) we used  $\delta^{13}C_{n\text{-alkane}}$  record (isotopes of C-25, C-27, C-29 and C-31 alkanes),  
1284 since  $\delta^{13}C_{\text{bulk carb}}$  did not provide satisfying results (Bown and Pearson 2009, Aze et al. 2014).  
1285 Tie-points of the  $\delta^{13}C_{\text{bulk carb}}$  at Site 690 as defined by Zachos et al. (2005) and Röhl et al. (2007)  
1286 from –A to H are shown. These authors reviewed the original definition of the  $\delta^{13}C_{\text{bulk carb}}$   
1287 inflection points of Site 690 by Bains et al. (1999). Ages of tie-points ages are after Röhl et al.  
1288 (2007). Biostratigraphic events from 1 to 26 are expressed as first or last occurrence (FO, LO),  
1289 LCO (last consistent occurrence), RI, RD (rapid increase, rapid decrease) according to  
1290 Gradstein et al. (2012). These events are from the earliest to the latest: 1. Presence of *C. eodela*;  
1291 2. FO *C. eodela*; 3. FO *C. bownii*; 4. LO *C. aperta*; 5. LCO *C. aperta*; 6. FO *R. cuspis*; 7. FO  
1292 *R. calcitrata*; 8. FO malformed *Discoaster* (*D. araneus*, *D. anartios*); 9. RI *C. bownii*; 10. FO  
1293 *Romboaster* spp.; 11. FO *T. bramlettei*; 12. LO *B. supremus*; 13. RD *C. bownii*; 14. RI *Z.*  
1294 *bijugatus*; 15. LO *F. richardii*; 16. LCO malformed *Discoaster*; 17. LO malformed *Discoaster*;  
1295 18. LCO *Rhomboaster* spp.; 19. LO *Rhomboaster* spp.; 20. FO *B. aquilus*; 21. LO *C. bownii*;  
1296 22. Absence of *D. diastypus*; 23. FO *D. diastypus*; 24. Presence of *D. araneus*; 25. Presence of  
1297 *F. tympaniformis*; 26. LO *F. tympaniformis*. The presence of uncorformities is also represented  
1298 based on literature data. On the left side we show the biostratigraphic synthesis across the  
1299 PETM after Martini (1971), Aubry et al. (1999), Okada and Bukry (1980), Agnini et al. (2014)  
1300 and the new PETM zones and sub-zones (PE)

1301  
1302 Plate. 1. Micrographs under optical microscope, crossed polars, at 1000X magnification of  
1303 selected specimens in alphabetic order. Scale bar is 5  $\mu\text{m}$   
1304

1305 Plate. 2. Micrographs under optical microscope, crossed and parallel polars, at 1000X  
1306 magnification of selected specimens in alphabetic order. Scale bar is 5  $\mu\text{m}$

1307

1308 Plate. 3. SEM pictures from selected samples from Site 1209B-22H-1A. Photos were acquired  
1309 with Phenom SEM G2 PRO microscope at 6000X magnification. Overgrown is clearly visible  
1310 on *Discoaster* specimens. Early overgrowth occurs in and around the central area of the  
1311 discoasters then it proceeds outwards along the rays, until the entire ray becomes overgrown  
1312 (Adelsek et al. 1973). a. Calcite blade; b. Overgrown *Fasciculithus*; c. *F. tympaniformis*; d.  
1313 Overgrown *D. nobilis*; e. *T. pertusus*; f. Overgrown placolith; g. Nannofossil fragment; h.  
1314 Overgrown *Toweius*; i., Overgrown *D. multiradiatus*; l. *C. pelagicus*; m. Broken *Calcisphaera*;  
1315 n. Overgrown *D. mohleri*; o. Overgrown *Fasciculithus*; p. Overgrown placolith

1316

### 1317 **Table captions**

1318

1319 Table. 1. Distribution of the counted calcareous nannofossils at Site 1209 B. Nannofossil  
1320 abundances are expressed as follows: abundant (A, >10 %), common (C, 1-10 %), frequent (F;  
1321 1-0.1 %) and rare (R; <0.1 %). Stable isotope ratios of bulk-rock samples ( $\delta^{13}\text{C}_{\text{bulk carb}}$ ) measured  
1322 on the archive-half of core 22H-1 (see text for details).

1323

1324 Table. 2. Distribution of the counted calcareous nannofossils at Site 1263 C/D. Nannofossil  
1325 abundances are expressed as follows: abundant (A, >10 %), common (C, 1-10 %), frequent  
1326 (F; 1-0.1 %) and rare (R; <0.1 %).



# **Chapitre 3. 1. Primary and carbonate productivity changes across the Pliensbachian-Toarcian interval in Mochras Borehole**

1 Primary and carbonate productivity changes across the Pliensbachian-  
2 Toarcian interval in Mochras Borehole

3

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11

12 1. Abstract

13

14 **The classical scenario for interpreting the lower Toarcian anoxic event (T-OAE;**  
15 **~183 Ma) and the associated negative carbon isotope event is commonly related**  
16 **to the massive release of <sup>12</sup>C to the surface reservoirs, because of the**  
17 **emplacement of Karoo-Ferrar LIP, the destabilization of methane hydrates from**  
18 **continental margins, or the thermogenic methane release due to sill**  
19 **emplacement in Karoo-Ferrar. Whatever the cause, this massive carbon release**  
20 **is thought to have favored greenhouse conditions, enhanced hydrological cycle**  
21 **and continental weathering. These conditions finally promoted the delivery of**  
22 **nutrients to shallow basins, supporting the primary productivity and, because**  
23 **of O<sub>2</sub> consumption by organic matter respiration, the development of oceanic**  
24 **anoxia.**

25 **However, several works showed that primary producers, like calcareous**  
26 **nannoplankton and dinoflagellates, experienced a severe crisis during the T-**  
27 **OAE, culminating with a phytoplankton blackout. Also, organic matter fluxes**  
28 **seem to be not exceptional. The analysis of nannofossil size in the Mochras**  
29 **borehole (drilled by the BGS) can help us to solve this conundrum. The**  
30 **sedimentary recovery of the core is excellent, the section is continuous and well-**  
31 **dated and has been the object of high-resolution analyses, that makes it an ideal**  
32 **spot where to analyze the combined evolution of carbonate and primary**  
33 **production. Through combination of biometry and absolute abundances**



34 **(specimens per g of rock) we can estimate the fluxes of nannofossil-derived**  
35 **carbonates and organic matter to the sediments. We can compare these results**  
36 **to the total organic content of sediments and to the  $\delta^{13}\text{C}$ , which reflects the**  
37 **perturbations of the carbon cycle occurred in the lower Toarcian. This study**  
38 **should enable us to better assess the mechanisms of mineral and organic**  
39 **carbon export from the upper ocean to the sediments during the major climate**  
40 **and environmental changes that occurred in the Toarcian.**

41

## 42 2. Introduction

43 The Early Jurassic was a time of extreme environmental changes: there are well-  
44 documented examples of rapid transitions from cold climates to greenhouse events  
45 (Price, 1999; Dera et al., 2009; Suan et al., 2010; Korte and Hesselbo, 2011), such as  
46 the early Toarcian oceanic event (T-OAE) (~183 Ma ago). The T-OAE (Jenkyns, 1988)  
47 is one of the most intense and geographically extensive events of oceanic redox  
48 change and organic-carbon burial in the Mesozoic era. A perturbation of the carbon  
49 cycle is evidenced by carbon isotopes excursions as recorded in marine carbonate,  
50 organic matter, biomarker and fossil wood (e.g., Jenkyns and Clayton, 1997; Hesselbo  
51 et al., 2007; Xu et al., 2017-2018, Storm et al., 2020). Organic rich deposits are found  
52 across the T-OAE especially in the northern Tethys and these may have resulted from  
53 enhanced primary productivity, either from intensified upwelling (Jenkyns, 1988) or  
54 from increased continental weathering and runoff (Cohen et al., 2004; Brazier et al.,  
55 2015). The alternation between icehouse and greenhouse events caused global sea-  
56 level changes (Hesselbo et al., 2000; Hesselbo, 2008; Suan et al., 2010; Pittet et al.,  
57 2014) and major biological changes in marine ecosystems (Little and Benton, 1995;  
58 Menini et al., 2019). Then, sea-level changes led to condensations and or hiatus in  
59 many localities (Pittet et al., 2014; Menini et al., 2019). However, there are evidences  
60 that paleoenvironmental perturbations started before the T-OAE, namely at the  
61 Pliensbachian-Toarcian boundary (PI-To) (Bodin et al., 2016; Martinez et al., 2017;  
62 Menini et al., 2019). There are several proofs that the paleoenvironmental changes  
63 occurring at the time were driven by increased volcanism, linked to the emplacement  
64 of large igneous provinces in the Karoo-Ferrar region (Duncan et al., 1997; Hesselbo  
65 et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Svensen et al., 2007; Percival  
66 et al., 2015). Besides volcanism, other mechanisms might explain the excess of light

67 carbon inferred by  $\delta^{13}\text{C}$  records across the T-OAE. Namely, this might be due to  
68 thermogenic methane ( $\text{CH}_4$ ) from sill intrusion into Gondwanan coal and organic-rich  
69 shale, and/or biogenic methane from dissociation of sub-seafloor methane clathrates.  
70 The early Toarcian CIE is supposed to have induced a wetter climate in mid latitudes:  
71 this drove to an accelerated hydrological cycle that caused an increase in silicate  
72 weathering on the continents, and consequent increased fluvial supply of nutrients to  
73 the oceans and large inland lakes (Jenkyns et al., 2002; Cohen et al., 2004; Jenkyns,  
74 2010; Dera et al., 2011  
75 ; Kemp et al., 2011; Brazier et al., 2015; Xu et al., 2017; Izumi et al., 2018). Enhanced  
76 nutrient fluxes caused an increase in primary productivity in the oceans and large lakes  
77 as well as enhanced burial of organic matter in these reservoirs, facilitated by local  
78 water-column stratification. Organic-carbon burial, coupled to an increase in silicate  
79 weathering, eventually drew down the excess of  $\text{CO}_2$ , conducting to an inverse  
80 greenhouse effect and global cooling (Schouten et al., 2000; Cohen et al., 2004). There  
81 are evidences, especially in northern Europe, of widespread development of anoxic–  
82 euxinic (sulphide-rich) bottom waters in restricted basins which intensely affected  
83 marine ecosystems (Jenkyns, 2003, 2010; Caswell and Coe, 2013; Hermoso et al.,  
84 2013; Ullmann et al., 2014; Danise et al., 2015). Also, globally significant burial of  
85 photosynthetically derived ( $^{12}\text{C}$ -rich) organic matter took place, and this gave rise to  
86 a positive (higher  $\delta^{13}\text{C}$ ) carbon-isotope excursion (CIE) of  $\sim 3\text{‰}$  in marine carbonate  
87 and  $\sim 4\text{‰}$  in bulk sedimentary organic matter (Jenkyns et al., 2002; Gradstein et al.,  
88 2012; Hermoso et al., 2013). This observed early Toarcian positive CIE was interrupted  
89 by the characteristic abrupt negative shift (to lower  $\delta^{13}\text{C}$ ) that occurred synchronously  
90 with the T-OAE (Jenkyns and Clayton, 1997). Important changes are documented  
91 among primary producers at the PI-To and across the T-OAE. Namely, a turnover in  
92 calcareous nannofossil communities is reported at the PI-To (Menini et al., 2019), while  
93 a significant decrease and temporary disappearance in calcareous nannofossil  
94 abundance is recorded across the T-OAE (Bucefalo Palliani et al., 2002; Mattioli et al.,  
95 2004b; Mattioli et al., 2008; Fraguas et al., 2012). During the T-OAE, primary  
96 productivity was solely sustained by phototrophic bacteria (Chlorobiaceae) (van de  
97 Schootbrugge et al., 2005) or by green algae (*Tasmanites*) (Bucefalo Palliani et al.,  
98 2002).

99 In the last decades several studies focused on the response of calcareous  
100 nannofossils to the Late Pliensbachian-Early Toarcian environmental perturbations in  
101 the Southern Tethys Ocean (Fig. 1), where several onshore marine sections provide  
102 excellent stratigraphic records of this time interval (e.g., Mattioli et al., 2004b; Mattioli  
103 et al., 2008; Fraguas et al., 2012; Casellato et al., 2015; Menini et al., 2019). Recent  
104 studies have focused on remote settings such as the Néquen Basin (Argentina) (Al-  
105 Suwaidi et al., 2016), Andean Basin (Fantasia et al., 2018) or Tibet (Wignall et al.,  
106 2006; Fu et al., 2016). However, calcareous nannofossils records in the northern  
107 Tethyan margin remain by now less studied. Mochras borehole, in the Cardigan Bay  
108 Basin (Wales), is the thickest complete Early Jurassic section, with a total thickness of  
109 1300 m for the Early Jurassic: this time interval is three times thicker at Mochras than  
110 coeval onshore sections (Hesselbo et al., 2013) and many sedimentological,  
111 geochemical and cyclostratigraphic data are available (e.g., Ruhl et al., 2016; Xu et  
112 al., 2018; Storm et al., 2020).

113 Here, we present new calcareous nannofossils data from the Mochras borehole in  
114 order to track changes in primary and carbonate production in response to  
115 paleoenvironmental changes across the Late Pliensbachian and Early Toarcian. To do  
116 this, we present nannofossil absolute abundance and fluxes and we compare them to  
117 available geochemical and sedimentological records. Ultimately, by comparing  
118 Mochras with other coeval sections, we discuss the relationship between  
119 paleoenvironmental changes and primary production across the Late Pliensbachian-  
120 Early Toarcian.

121

### 122 3. Geological setting

123

124 In the Early Jurassic the western Tethys consisted of shallow epicontinental basins  
125 extending between the Laurasian and African landmasses (Fig. 1). Several evidences  
126 point to consistent paleoclimatic and paleoceanographic differences between (~27-35  
127 °N) and the southern tropical margin (~17-23 °N). Water masses with distinctive  
128 properties have been interpreted for the two domains to explain the different ammonite  
129 faunas (Cecca and Macchioni, 2004 and references herein) and the dissimilar  
130 calcareous nannofossil assemblages (Bown, 1987; Mattioli et al., 2008). Evidences of  
131 more humid climate conditions in the northern margin opposed to a more arid climate  
132 in the southern part come from belemnite oxygen isotope composition, clay minerals

133 and fossil wood assemblages (van de Schootbrugge et al., 2005; Rosales et al., 2006;  
134 Dera et al., 2009; Philippe et al., 2017). Thus, the northern margin is characterized by  
135 siliciclastic deposits while the southern one is dominated by carbonates. Besides,  
136 paleoceanographic reconstructions show that the northern margin corresponded to the  
137 wide north European epicontinental shelf while the southern one comprised relatively  
138 shallow basins separated by large carbonate platforms (Bassoulet et al., 1993). In the  
139 Early Jurassic, Mochras borehole belonged to the Cardigan Bay Basin, at the southern  
140 end of the European epicontinental seaway that linked the north-western Tethys to the  
141 Boreal Sea (Fig. 1). The core covers some 27 Myr of Early Jurassic history, from the  
142 Hettangian to the Toarcian. It was drilled onshore by the British Geological Survey  
143 (BGS) and Arberys-coast University, between 1967 and 1969, on the Cardigan Bay  
144 coast, at Llamber, Gwynnedd, northwest Wales (Woodland, 1971; Gradstein et al.,  
145 2012; Hesselbo et al., 2013). The Lower Jurassic succession recovered at Mochras  
146 (~1300m) is much thicker than coeval onshore sections (Ruhl et al., 2016). All  
147 Pliensbachian and Toarcian ammonite zones and sub-zones are present at Mochras  
148 (Ivimey-Cook, 1971; Page, 2003; Simms et al., 2004; Copestake and Johnson, 2014).  
149 Here the ammonite zones and sub-zones are named by a typifying species (e.g  
150 *tenuicostatum* Zone). Calcareous nannofossils occur consistently throughout the core.  
151 Besides, belemnites, bivalves, brachiopods and benthic foraminifera occur regularly  
152 throughout the core and crinoid ossicles are locally common, but only up to the  
153 Pliensbachian. Macroscopic plant debris commonly occurs throughout the  
154 Pliensbachian and the Toarcian successions: their occurrence is coeval with levels rich  
155 in siliciclastic silt and sand, suggesting relatively close proximity to nearby landmasses  
156 (Cope, 1984). The predominant lithology characterized by dark grey mudstones and  
157 marl beds, alternated with pale grey limestone beds, suggests a relative open-marine  
158 sedimentary environment (Sellwood and Jenkyns, 1975).

159

#### 160 4. Materials and methods

161

162 Forty-seven samples for calcareous nannofossils were prepared following the method  
163 described by Beaufort et al., 2014, slightly modified here. A cover slide is weighted  
164 before and after a homogenous suspension of dried rock-powder and water  
165 (supersaturated with respect to CaCO<sub>3</sub> and with a basic pH) is let to settle on the cover

166 slides for 2 hours in a Petri-dish. After settling of the powder, water is carefully aspired  
167 with a water pump connected to a micro-pipette in order to avoid any turbulence in the  
168 Petri-dish. The residual water on the cover slide is dried, the cover slide is recovered  
169 and then attached on a microscope slide using Rhodopass resine. This method allows  
170 the quantification of absolute abundances of nannofossils per gram of rock (n/g), using  
171 the following formula:

$$x = \frac{n * l * h}{m * A}$$

172  
173 Where x is the absolute abundance value, n is the number of counted specimens in a  
174 slide, l is the length of the cover slide, h is the height of the cover slide, m is the mass  
175 of the weighted sample and A is the studied surface of the sample.

176 Fluxes are calculated by using the following formula:

$$F = X * AR * d$$

177  
178 where F is the flux (n/m<sup>2</sup>/yr); X is the absolute abundance of nannofossils (n/g); AR is  
179 the accumulation rates calculated on the basis of the age model of Ruhl et al., 2016  
180 for the Late Pliensbachian and new AR for the Early Toarcian, d (g/cm<sup>3</sup>) is the calcite  
181 density (d=2.71).

182 Sample richness is generally low at Mochras, so we did not count 300 nannofossils for  
183 each sample. We counted 200 calcareous nannofossils with a Leica DM750P  
184 microscope with a 1000X magnification. Counts of 200 specimens per sample provides  
185 us with a probability of ~10 % not to recover a rare species which has relative  
186 abundance of 1% in the total assemblage (Hay 1972). Depending of the richness a  
187 minimum of 50 up to 100 specimens has been counted in some samples. In 4 samples  
188 (820.55, 830.62, 832.61, 880.52m), less than 50 specimens were counted. Six  
189 samples are almost barren of calcareous nannofossils (5 specimens over 2 tranverses)  
190 and were excluded for the successive data treatment. Particularly, these samples  
191 produced artificial peaks in the relative abundance of some species as a consequence  
192 of closed-sum effects. However, they were scanned over 4 additional transverses in  
193 order to check the presence of biostratigraphically important species. Fatela and  
194 Taborda 2002 demonstrate that, for palaeoceanographic studies, counts of 100  
195 specimens have a satisfactory statistical reliability. Each sample was further scanned  
196 over two transects to detect rare but biostratigraphically important species. Also, we  
197 constructed rarefaction plots based on the method described by Krebs (1998) and  
198 Hammer et al., 2001. Through these graphs it is possible to evaluate the theoretical

199 diversity of samples with respect to a reference sample where species richness is  
200 higher. It is possible to estimate when sample size is significant. Namely, when the  
201 confidence interval of the tested samples is superimposed to the confidence interval  
202 of the reference sample the result can be considered as satisfactory.

203 The relative abundances of species expressed as percentages are calculated for  
204 *Schizosphaerella*, an *incertae sedis* but probably a dinoflagellate cyst (Bown, 1987),  
205 respectively to the total nannofossil counts (i.e., coccoliths plus *Schizosphaerella*),  
206 while the percentage of coccoliths is calculated with respect to the total coccoliths.  
207 Fatela and Taborda (2002) calculated the confidence interval for species with a  
208 proportion of 0.1 (i. e., 1 %) when counting 100 individuals. The confidence interval  
209 extends from 0.041 to 0.159 around the value of 1 %. This is the reason why in the  
210 rest of the manuscript we only discuss taxa representing more than 5 % in the  
211 assemblage.

212 Nannofossil preservation was investigated using a Phenom SEM G2 PRO; on the  
213 basis of the degree of etching and overgrowth (Roth et al., 1984), three classes are  
214 recognized: poor nannofossil assemblages if strong etching and overgrowth or  
215 fragmentation are observed; moderate and good when *Schizosphaerella*  
216 fragmentation is limited and delicate coccoliths still preserve intact structures. The  
217 nannofossil biostratigraphic record is compared to standard ammonite zones.

218 The nannofossil biostratigraphic record has been compared to the standard ammonite  
219 zones taking into account data available in the literature for the studied sections.  
220 Following Gradstein et al. (2012), the abbreviation FO (First Occurrence) is herein  
221 used for the first or stratigraphically lowest occurrence of a species in a section (or  
222 Base) and LO (Last Occurrence) for the last or stratigraphically highest occurrence  
223 of a species in a section (or Top).

224

225

226

## 227 5. Results

228

### 229 5.1. Biostratigraphy

230 Several first occurrences (FO) and some last occurrences (LO) are recorded across  
231 the Late Pliensbachian and the Early Toarcian. *Crepidolithus cavus* (868.32 m),



232 *Crepidolithus impontus* (872.36 m), *Zeugrhabdothus erectus* (868.32 m), *Lotharingius*  
233 *sigillatus* (884.45 m), *Lotharingius crucicentralis* (868.32 m), *Ethmorhabdus crucifer*  
234 (880.52 m) and *Ethmorhabdus gallicus* (870.53 m) appear in the Late Pliensbachian.  
235 Much of the FO are recorded around the PI-To boundary as previous studies observed  
236 in other sections (Mattioli et al., 2013; Menini et al., 2019): namely, *B. intermedium*  
237 (870.53 m), *Lotharingius velatus* (870.53 m), *Discorhabdus ignotus* (858.55 m), at the  
238 PI-To. The FO of *C. superbis* (842.62 m) is in the Early Toarcian, in the *tenuicostatum*  
239 zone. This a crucial moment for the evolutionary history of calcareous nannofossils  
240 since it represents the turnover murolith-coccoliths: placolith become increasingly  
241 more abundant in the Early Toarcian and will become the most dominant group of the  
242 Mesozoic (Bown, 1987; Menini et al., 2019). The FO of *Carinolithus poulhabronei*  
243 (822.55 m) is recorded across the T-OAE. In the *falciferum* zone we find the LO of *E.*  
244 *crucifer* and the genus *Watznaueria* appears (774.47 m).

245

## 246 5.2. Absolute abundance and flux

247

248 Total absolute abundance and flux are calculated by summing absolute abundance  
249 and flux values of all the counted species. At Mochras, absolute abundance and flux  
250 show the same trend ( $R^2=0.86$ ). Absolute abundance ranges from  $1E^6$  to  $150 E^6$   
251 and flux ranges from  $6E^6$  to  $1E^9$  (Fig. 2). An overall increasing trend is observed up  
252 in the section, with a peak in correspondence of the Pliensbachian-Toarcian boundary  
253 (PI-To), across the 2 ‰ negative excursion in  $\delta^{13}C_{org}$  defining the PI-To. Values are low  
254 from 884.45 m to 870.53 m ( $5E^6$  and  $50 E^6$  respectively) and start to increase at  
255 868.32 m ( $20 E^6$  and  $200 E^6$  respectively). At the PI-To we observe an abrupt peak  
256 in both absolute abundance and flux ( $140 E^6$  and  $1 E^9$ ).

257 Values decrease after the PI-To till up going down almost to 0 in some samples  
258 corresponding to the T-OAE (*exaratum* Subzone), defined on the base of the negative  
259 excursion of both carbonate and organic carbon (Katz et al., 2005; van de  
260 Schootbrugge et al., 2005; Xu et al., 2018). In the aftermath of the T-OAE absolute  
261 abundance and flux increase relatively to pre-T-OAE values but they are highly  
262 fluctuating, similarly to other localities (Mattioli et al., 2004b-2008; Menini et al., 2019).

263

## 264 5.3. Assemblages

265 Despite the presence of slight overgrowth, as observable on the basis of SEM pictures  
266 (Bown, 1987), coccoliths' fragile structures, such as spines in *Crucirhabdus primulus*  
267 and in *Parhadolithus liasicus*, are intact (This study; Bown, 1987) suggesting an overall  
268 good preservation relatively to other coeval sections. Generally Early Toarcian  
269 samples are richer than Late Pliensbachian ones. However, Toarcian samples that  
270 span the T-OAE present low richness and some are barren.

271 Calcareous nannofossil assemblages are dominated by *Schizosphaerella* spp.,  
272 *Lotharingius* spp., *Crepidolithus crassus* and *Similiscutum finchii* (Fig. 3). This is  
273 evidenced by both relative and absolute abundances. Other taxa, such as *P. liasicus*,  
274 *Crepidolithus* spp., *Bussonius* spp. ecc... are rarer, and usually do not overcome 5%.  
275 Here, we decided to separated small-size *Lotharingius* to large-size *Lotharingius*. *L.*  
276 *hauffii*, *L. frodoi* and *L. umbriensis* are grouped into "small-size *Lotharingius*". *L.*  
277 *crucicentralis*, *L. sigillatus* and *L. velatus* are included in "large-size *Lotharingius*". We  
278 refer to Menini et al., 2019 for the taxonomic concepts adopted here. Ferreira et al.,  
279 2017 show that *Lotharingius* spp. increase in size from the Upper Pliensbachian to the  
280 Upper Toarcian and this is related to paleoenvironmental factors. Given that species  
281 of the genus *Biscutum* and *Similiscutum* show the same trend in both relative and  
282 absolute abundance, we chose to group the whole family Biscutaceae.

283 We will subdivide the section analyzed here in three parts on the basis of trends in  
284 relative and absolute abundance and in the high-resolution  $\delta^{13}\text{C}_{\text{org}}$  isotopes record  
285 measured on organic matter (Xu et al., 2018; Storm et al., 2020) similarly to Mattioli et  
286 al., 2008

287 Then section is subdivided as follows:

288

- 289 1. Late Pliensbachian=> up to the PI-To (900.43- 866.42 m);
- 290 2. Lower Toarcian => from the PI-To to the T-OAE (864.59- 794.56 m);
- 291 3. Lower Toarcian=> recovery from the T-OAE (792.33-770.69 m)

292

- 293 1. The Late Pliensbachian corresponds here to the *spinatum* ammonite zone.  
294 Samples are generally poor in richness: assemblages are dominated by  
295 *Schizosphaerella* spp., small size-*Lotharingius* and Biscutaceae.  
296 *Schizosphaerella* spp. relative abundance varies from 30 to 50 %. The most  
297 abundant coccoliths are small-size *Lotharingius*, which represent 20 up to 40%  
298 of coccolith percentage. Biscutaceae are also abundant in the Late

299 Pliensbachian and range from 20% to 40 %. Despite of the elevated values of  
300 relative abundance, absolute abundance of these species is low from 884.45 m  
301 to 870. 53 m, where it never overcomes  $1 \text{ E}^6$ . Absolute abundance of  
302 *Schizosphaerella*, small *Lotharingius* and Biscutaceae start increase at 868.32  
303 m until 858.55 m where they reach in  $30 \text{ E}^6$  for *Schizosphaerella*,  $12 \text{ E}^6$  for  
304 small *Lotharingius* and  $20 \text{ E}^6$  for Biscutaceae. *Crucirhabdus primulus*, is locally  
305 abundant in the Late Pliensbachian (15-20%) but progressively decreases  
306 upward in the section. The PI-To is recognized on the basis of the negative  
307  $\delta^{13}\text{C}_{\text{org}}$  excursion at the boundary between the *spinatum* and the *tenuicostaum*  
308 ammonite zones (Xu et al., 2018; Storm et al., 2020; Fig. 3) All taxa show a  
309 peak in absolute abundances at the PI-To (858.55 m) and values are 4 times  
310 higher than in the Late Pliensbachian. However, this is not observed in relative  
311 abundances: *Schizosphaerella* spp. and Biscutaceae show a decrease followed  
312 by an increase across the PI-To while small-size *Lotharingius* gently increase  
313 across the PI-To. Also large-sized *Lotharingius* increase considerably in  
314 percentage across the PI-To but absolute abundance does not increase in this  
315 interval. However, from this moment large-size *Lotharingius* start to become  
316 significantly more abundant and relative abundance attain values up to 40%.

317

318 2. The negative shift of  $\delta^{13}\text{C}_{\text{org}}$  corresponding to the PI-To is followed by a gentle  
319 positive excursion (860.20-839.44 m) across the *tenuicostaum* zone that  
320 precedes the T-OAE (Fig. 3; Xu et al., 2018). *Schizosphaerella* spp. relative and  
321 absolute abundances progressively decrease at this stage, small-size  
322 *Lotharingius* and Biscutaceae are relatively constant, while *C. crassus* and  
323 large-size *Lotharingius* start to increase. Then,  $\delta^{13}\text{C}_{\text{org}}$  values show an abrupt  
324 negative shift of  $\sim -5\text{‰}$  ( $\sim 820$  m) across the *exaratum* subzone of *serpentinum*  
325 zone (Fig. 3) due to the T-OAE (e.g., Jenkyns et al., 1988; Xu et al., 2018).  
326 Absolute abundance of all taxa decrease at this point, attaining lowermost vales  
327 ( $\text{E}^6$ ). However relative abundances are different. *Schizosphaerella* spp. show  
328 a progressive decrease. The same is for Biscutaceae. Small-size *Lotharingius*  
329 relative abundances are more or less constant, while large-size ones show a  
330 progressive increase up in the section (Fig. 3a). Also, *C. crassus* shows an  
331 increase in abundance from the T-OAE up to the recovery, passing from  $3 \text{ E}^6$

332 at 808.38 m to 20 E<sup>6</sup> at 804.52 m (Fig. 3b). Across the T-OAE we observe a  
333 peak in the family Calyculaceae, which features *Calyculus* spp., *C. poulabronei*  
334 and *C. superbus*. The peak is more evident when looking at relative abundance:  
335 Calyculaceae are rare or absent before and after the T-OAE but here they attain  
336 values of more than 30%.

337

338 3. In the aftermath of the T-OAE (800.94-770.69 m),  $\delta^{13}\text{C}_{\text{org}}$  values return to pre-  
339 event ones. This is observed in both relative and absolute abundances. At this  
340 stage, the most abundant taxa are *C. crassus* and both small and large-size  
341 *Lotharingius* spp. (Fig. 3b). While relative abundance of small *Lotharingius*  
342 decrease, absolute one still increase in the aftermath of the T-OAE. Large-size  
343 *Lotharingius* increase in both relative and absolute abundance. This indicates  
344 that the increase in large-size *Lotharingius* is not counterbalanced by the  
345 decrease in small-sized ones. After the T-OAE, *C. crassus* and large-size  
346 *Lotharingius* continue to increase and reach values up to 60%. However, they  
347 show a fluctuating trend; namely, in samples where *C. crassus* is dominant,  
348 *Lotharingius* are rarer and viceversa. *Schizosphaerella* spp. and Biscutaceae  
349 show their lowest values here.

350

## 351 5. Discussion

352

### 353 5.1. Calcareous nannofossils bioevents: stratigraphic implications

354

355 Mochras is the thickest and one of the most-distal Lower Jurassic marine section  
356 available up to date (Hesselbo et al., 2003). This is also noticeable by relatively high  
357 (l) sedimentation intervals (on average 2.7 cm/kyrs for the studied interval; Ruhl et al.,  
358 2016; This work). Theoretically, it should be less affected by condensation problems,  
359 which have an impact on the ranking of the bioevents in several Tethyan sections  
360 (Menini et al., 2019). Calcareous nannofossils biostratigraphy for the whole Mochras  
361 borehole (Hettangian to Toarcian) was previously presented by Bown, 1987, who  
362 defined eight nannofossils zones and eleven subzones. The pivotal work by Bown,  
363 1987, slightly modified by Bown, 1988, allowed to refine the Early Jurassic calcareous  
364 nannofossil biostratigraphy in the north-Western Tethys and is still today one of the

365 standard schemes. However, recent advances as by more solid taxonomic concepts  
366 (Mattioli and Erba, 1999; Mattioli et al., 2013; Menini et al., 2019; Ferreira et al., 2019)  
367 allow us to achieve a higher-resolution than two-decades ago. Several first  
368 occurrences (FO) are reported around the Pliensbachian-Toarcian boundary, similarly  
369 to southern Tethyan settings (Mattioli et al., 2013; Menini et al., 2019; Ferreira et al.,  
370 2019). Also, placolith-coccoliths rapidly increase in abundance through the Late  
371 Pliensbachian-Early Toarcian as previously observed (Bown, 1987).

372 The lowest part of the section belongs to the CN zone NJ-5a, because of the presence  
373 of *Lotharingius hauffii* and the absence of *Crepidolithus cavus*. The FO of *C. cavus*  
374 marks the base of CN zone NJ-5b: this is recorded just before the onset of the negative  
375 excursion of the PI-To. We found this horizon at 868.32 m while Bown, 1987 found it  
376 at 866 m, or two meters above our record. The difference between our record and the  
377 one by Bown, 1987 can be easily explained by different sampling resolution. However,  
378 the taxonomy of this taxon is somehow problematic: Bown, 1987 consider *C. cavus*  
379 and *C. impontus* as synonyms while we consider them as the two distinct species  
380 (Menini et al., 2019). In our record, *C. impontus* occurs 2 m below *C. cavus* then,  
381 regardless of the taxonomic concept adopted, this does not impact the results since  
382 the two species occur almost simultaneously. The FO of *Carinolithus superbus* is a  
383 very distinct event at Mochras and marks the zone NJ-6: we found it at 842.62 m while  
384 Bown, 1987 found it at 824 m. This event is recorded across the positive carbon isotope  
385 excursion that follows the PI-To and precedes the T-OAE. Several papers have  
386 questioned the synchronism of this biohorizon in northern and in southern Tethys.  
387 Mattioli et al., 2004b show that the FO of *C. superbus* is just before the onset of the T-  
388 OAE and Menini et al., 2019 reported that is synchronous in both Tethyan and remote  
389 ones. While several studies focused on the southern Tethyan margin (e.g., Fraguas et  
390 al., 2012; Mattioli et al., 2008; Casellato et al., 2015), few data are available for the  
391 northern one. The FO of *C. superbus* at Mochras is also recorded across the positive  
392 carbon isotopes excursion, after the PI-To and before the T-OAE. This is coherent with  
393 other records coming from both Tethyan and remote sections. The FO of *C. superbus*  
394 reported by Bown, 1987 at 824 m coincides in our dataset with an acme of  
395 Calyculaceae during the T-OAE (Fig. 3). It is reasonable that, due to the rarity of this  
396 species when it firstly appears, Bown, 1987, placed the FO of this taxon in  
397 correspondence of this acme of Calyculaceae (Fig. 3b), where *C. superbus* suddenly  
398 attains ~15% and Calyculaceae reach 30 % in relative abundance.

399 Also, Bown, 1987 defines the NJ-7 at Mochras on the base of the FO of *Discorhabdus*  
400 *ignotus* but this has been lately replaced by the FO of *D. striatus*. (Bown, 1998).  
401 Previous studies evidenced that the FO of *D. ignotus* occurs at the Pliensbachian-  
402 Toarcian boundary (Mattioli et al., 2002; Mattioli et al., 2013; Bodin et al., 2016;  
403 Martinez et al., 2017; Menini et al., 2019) but these data mostly come from southern  
404 Tethyan sections. At Mochras, we find the FO of *D. ignotus* at 858.55 m, exactly across  
405 the PI-To.

406 The biostratigraphic marker defining the NJ-7 is the FO of *D. striatus*. We find the FO  
407 of *D. striatus* at 770.69 m depth, in the last samples that we analyzed. This is toward  
408 the end of the *falciferum* zone, as previously reported (Bown, 1987).

409

410 2) Total calcareous nannofossils absolute abundance and flux

411

412 Absolute abundance and flux are five times higher passing from the Pliensbachian to  
413 the Toarcian (Fig. 2). A similar increase has already been observed by other authors  
414 (Mattioli et al., 2004-2008; Menini et al., 2019) and this is probably due to an increase  
415 in primary productivity (Mattioli et al., 2008). An abrupt peak is observed in  
416 correspondence of the PI-To, which is difficult to explain in terms of enhanced primary  
417 productivity. The Late Pliensbachian is characterized by relatively cold sea-water  
418 temperatures (Morard et al., 2003; Suan et al., 2008a; Korte et al., 2011) and sea level  
419 experienced a prominent fall followed by a rapid transgression in the early Toarcian  
420 (e.g., Pittet et al., 2014). The alternation between regressions and transgressions gave  
421 rise to many condensation levels and/or hiatus in several localities (Menini et al., 2019)  
422 which could be at the basis of the observed peak in nannofossil absolute abundances  
423 and fluxes. Previous studies documented several episodes of fast regressions in the  
424 *polymorphum* zone and the quantification of nannofossil absolute abundance and flux  
425 allows to recognize condensed intervals, as aberrant peaks in these parameters are  
426 likely due to sediment starvation (Pittet et al., 2014; Menini et al., 2019). Here, we  
427 document the presence of condensed intervals at the PI-To in northern localities and  
428 we show that the fast transgression at the PI-To produced condensed intervals even  
429 in more expanded depositional settings, such as Mochras.

430 Both absolute abundance and flux collapse across the T-OAE (some samples are even  
431 barren) and recover in the aftermath of the event (Fig. 2), in agreement with previous  
432 studies in other Tethyan sections (Mattioli et al., 2008-2009). Size decrease of



433 *Schizosphaerella* spp. and Biscutaceae also support the crisis of pelagic environments  
434 (Mattioli et al., 2004a; Tremolada et al., 2005; Suan et al., 2008a; Mattioli et al., 2008-  
435 2009). Besides, shallow-water carbonate platforms recorded a dramatic crisis at the  
436 same time and this begun by the PI-To spanning the entire Early Jurassic (e.g.,  
437 Dromart et al., 1996; Blomeier and Reijmer, 1999; Mallarino et al., 2002 add reference  
438 papier emanuela 2009). The crisis of neritic environments started about 0.6 Ma before  
439 the biocalcification decrease in the pelagic realm, before the T-OAE (Suan et al.,  
440 2008b). At Mochras, nannofossil fluxes show the lowest values during the T-OAE (Fig.  
441 2) but values start to decrease well below the onset of the event (17 m below), in  
442 agreement with data from sections in the UK (Bucefalo-Palliani et al., 2002), N Spain  
443 (Tremolada et al., 2005), Portugal, Germany and Italy (Mattioli et al., 2004b-2008-  
444 2009; Casellato et al., 2015). This is also coherent with recent data coming from more  
445 remote settings, which point to a crisis of pelagic environments even if absolute  
446 abundances are not available (e.g., Fraguas et al., 2012; Bodin et al., 2016). We  
447 postulate that the T-OAE represents the acme of a longer trend difficulty of marine  
448 organisms to calcify that begun around the Pliensbachian-Toarcian boundary (PI-To  
449 event).

450 The marked negative excursion in  $\delta^{13}\text{C}$  associated with the T-OAE has been explained  
451 in several ways. Some authors inferred that this is the result of an injection of  $\text{CO}_2$  (with  
452 light isotope carbon) in the marine and atmospheric carbon reservoirs due to a sudden  
453 dissociation of large amounts of metastable methane hydrate from the seabed  
454 (Hesselbo et al., 2000; Beerling et al., 2002; Cohen et al., 2007). It seems that the  
455 release of methane occurred in pulses (Kemp et al., 2005). Alternatively, the input of  
456 isotopically light carbon from the release of thermogenic methane occurred because  
457 of magma intrusion of Gondwana coals by Toarcian aged Karoo-Ferrar dolerites  
458 (McElwain et al., 2005; Svensen et al., 2007). During the T-OAE, both mechanisms  
459 are consistent with elevated  $p\text{CO}_2$  (900-100 ppmv; Beerling et al., 2002; McElwain et  
460 al., 2005). Effectively elevated  $p\text{CO}_2$  could account for biocalcification crisis. Studies  
461 on modern corals show that calcification is hampered by elevated marine and  
462 atmospheric  $\text{CO}_2$  (Gattuso et al., 1998). However, studies on modern coccolithophores  
463 do not indicate a direct effect of increased  $p\text{CO}_2$  on calcification, since the response is  
464 species specific (Bollman, 1997; Hendiriks and Renaud, 2004; Iglesias-Rodriguez et  
465 al., 2008). An indirect role of increased  $p\text{CO}_2$  on nannofossils has also been  
466 demonstrated for PETM (Gibbs et al., 2016). The hypothesis that high  $p\text{CO}_2$  was

467 responsible for the nannofossils biocalcification crisis during the T-OAE has already  
468 been advanced by Mattioli et al., (2004b), Erba (2004) and Tremolada et al., (2005)  
469 and evidences exist that increased CO<sub>2</sub> levels were likely responsible for the drastic  
470 decrease in nannofossil fluxes across the Weissert OAE (Valanginian) and the OAE  
471 1a (Aptian) (Erba and Tremolada, 2004). As observed by Mattioli et al., 2009, this  
472 doesn't explain the reason why, for the T-OAE, the carbonate crisis affected earlier  
473 neritic environments than planktonic ones.

474 Blomeier and Rejimer, 1999 suggest that the demise of a carbonate platform in  
475 Morocco was due to an environmental deterioration in platform settings owing to either  
476 a nutrient input or a decrease in sea-surface temperature.

477 Several evidences indicate a climatic deterioration from the Pliensbachian to the  
478 Toarcian. Temperature decreased in various Tethyan settings (McArthur et al., 2000;  
479 Bailey et al., 2003; Rosales et al., 2004; Suan et al., 2008a; Gómez et al., 2008). The  
480 decrease in temperature likely caused sedimentary condensations and-or hiatus in  
481 many Tethyan settings that expanded till up the first Toarcian ammonite zone (Guex  
482 et al., 2001; Morard et al., 2003; Pittet et al., 2014). This was probably driven by  
483 glacioeustatic mechanisms (Guex et al., 2001; Morard et al., 2003; Pittet et al., 2014).  
484 Therefore, the crisis in neritic settings seems to be due to both cooling and nitrification  
485 of surface waters. Sea level low caused a reduction of space where carbonate  
486 platforms could develop. Then the crisis of carbonate platforms is not directly related  
487 to an increase in *p*CO<sub>2</sub> and the subsequent decrease in oceanic carbonate saturation  
488 state (Mattioli et al., 2009).

489 An increase in *p*CO<sub>2</sub> might have in turn caused ocean acidification, as suggested for  
490 the PETM (Zachos et al., 2005). The shallowing of the lysocline and the calcite  
491 compensation depth (CCD) during the T-OAE might be responsible for the observed  
492 demise in nannofossil abundance. If this is true for deep oceanic sites, as the one  
493 studied by Zachos et al., 2005 for the PETM, it must be noticed that all Early Jurassic  
494 sections belonged to epicontinental basins that were always above the CCD during the  
495 Early Jurassic (<200m). If we assume, as for the PETM, that the CCD shallowed of ~2  
496 km in open oceanic settings, it is improbable that Mochras and other Tethyan sections  
497 were above it during the event. Moreover, delicate coccoliths are always present during  
498 the event and this is at the odds with the hypothesis of dissolution.

499 So, we can ask ourselves if the low nannofossil fluxes during the T-OAE are directly  
500 related to an increase of *p*CO<sub>2</sub> and the subsequent sea-water carbonate saturation

501 decrease. Alternatively, the reduction in pelagic carbonate production was indirectly  
502 controlled by environmental changes induced by the  $p\text{CO}_2$  increase. Namely,  
503 increased hydrological cycle and the discharge of freshwater into the epicontinental  
504 basins of the western Tethys. The development of a more humid climate during the  
505 event might associated to an increase in sea water temperature from the second half  
506 of the *tenuicostatum* ammonite zone, could have favored a general sea level rise. This  
507 might have facilitated the connections between the Arctic Ocean and the western  
508 Tethys. Bjerrum et al., (2001) already discussed the southward flow of low-saline water  
509 masses from the Arctic Ocean over the Tethyan high-saline ones. This phenomenon  
510 might have then amplified the effect of a more humid climate, drastically reducing the  
511 surface water salinity (mostly in NW Tethys, that was connected to the Arctic Ocean  
512 through the Laurasian seaway). This is coherent with our data at Mochras, where low-  
513 salinity tolerant species show a peak in abundance during the T-OAE (see following  
514 section for details) while other species temporarily either disappear or drastically  
515 decrease in abundance.

516 It must be said that few modern coccolith species tolerate low-salinity environments  
517 (Bukry, 1974). Salinity can be an important factor controlling coccolith both abundance  
518 and size. Also, coccospheres with a reduced number of coccoliths are typical of Arctic  
519 and Subarctic regions where weakly saline waters form in response to seasonal melt  
520 water (Winterer et al., 1994).

521

### 522 3) Nannofossil assemblages across the Late Pliensbachian and the Early Toarcian

523

524 The Late Pliensbachian and Early Toarcian represent a significant acceleration in the  
525 evolution rate in the history of calcareous nannofossils (Bown et al., 2004). At Mochras,  
526 that values abruptly increase at the PI-To similarly to other northern and southern  
527 Tethyan sections (Mattioli et al., 2008; Fraguas et al., 2012; Ferreira et al., 2015;  
528 Menini et al., 2019). While the originations of placolith coccoliths are numerous in this  
529 time interval, there are not originations of muralith coccoliths. Biscutateae and  
530 *Lotharingius* spp. become dominant assemblage components in the aftermath of the  
531 PI-To. Then, across the T-OAE, *C. crassus* and large-size *Lotharingius* become  
532 dominant components.

533 Nannofossil assemblages change significantly across the early Toarcian CIE; as also  
534 suggested for other Tethyan localities (Mattioli et al., 2008) this parallels the long-term

535 (~2Ma) evolution of environmental conditions (Suan et al., 2008b). We exclude a  
536 control on differential preservation on the nannofossil trends observed, since  
537 preservation is overall good across the section. The only samples where signs of poor  
538 preservation are present were removed from the data set. Here we will discuss  
539 changes in nannofossils assemblages over the studied interval.

540

#### 541 *Pre-event*

542 Pre-event conditions correspond to the Late Pliensbachian and Lower Toarcian,  
543 including the PI-To CIE and the positive CIE in the aftermath of the PI-To. Assemblages  
544 are here dominated by *Schizosphaerella* spp., small-size *Lotharingius* and  
545 Biscutaceae, which are taxa with nutrient affinity (Mattioli et al., 2004a; Mattioli et al.,  
546 2008). Also, taxa with northern affinity (i.e., *C. primulus*, *P. liasicus*, *T. patulus*, *C.*  
547 *cavus*) are abundant in this interval (Bown, 1987; Mattioli et al., 2008). Therefore, this  
548 record can be interpreted in terms of the occurrence of cool surface waters associated  
549 with high productivity and fertility. Several evidences of relatively cool sea water  
550 temperature exist for the Tethys during this time. The Late Pliensbachian is interpreted  
551 as a cooling period (Morard et al., 2003; Suan et al., 2008a-b; Korte et al., 2011;  
552 Gómez et al., 2016). Oxygen isotopes measured on Late Pliensbachian belemnites  
553 rostra indicate sea-temperature of 12-13° in northern Spain (Rosales et al., 2004;  
554 Gómez et al., 2008) and brachiopod shells (Suan et al., 2008a) suggest temperature  
555 of 13-16° for bottom waters in the Lusitanian basin (Portugal). Also, evidences of a  
556 severe cooling event at that time come from fossil wood (Philippe and Thevenard,  
557 1996; Philippe et al., 2017). These authors show that *Xenoxylon*, a taxon adopted to  
558 cold, wet conditions, extended his distribution southward. Indirect proxies also suggest  
559 cold conditions at the time: the stomatal index measured on mesofossil leaves from  
560 the eastern Danish basin suggest low pCO<sub>2</sub> across the first Toarcian ammonite zone  
561 (*tenuicostatum*) (McElwain et al., 2005). Moreover, glendonites and dropstones in Late  
562 Pliensbachian sediments from high latitudes, suggest low temperature and continental  
563 ice (Price, 1999; Suan et al., 2015). Likely high sea water fertility happened at the time,  
564 since assemblages are dominated by schizospherellids and small-size coccoliths. This  
565 is in agreement with what observed in other settings (Mattioli et al., 2004b, Mattioli et  
566 al., 2008). A decoupling in *Schizosphaerella* spp. relative and absolute abundances is  
567 observed at the PI-To: while relative abundances suggest a decrease in

568 *Schizosphaerella* spp. across the PI-To, absolute abundances show a peak (Fig. 3).  
569 The decrease in *Schizosphaerella* spp. relative abundance is coherent with Tremolada  
570 et al., 2005 but, as stressed by Mattioli et al., 2008 and Menini et al., 2019, this result  
571 might be due to close-sum effects. A peak in absolute abundances of all species is  
572 observed at the PI-To as well as in the total absolute abundance as described in the  
573 previous chapter and this is probably due to condensation levels or hiatus. High  
574 surface water in this interval is also indicated by the occurrence of mesotrophic taxa  
575 such as Biscutaceae, in agreement with Mattioli and Pittet, 2002 and Tremolada et al.,  
576 2005. This is coherent with the  $\delta^{13}\text{C}$  records at Mochras by Xu et al., 2018 and Percival  
577 et al., 2016 and with the one of other sections (e.g., Hesselbo et al., 2007).

#### 578 T-OAE

579

580 In correspondence of the T-OAE, there is a remarkable peak in *Calyculaceae*, since  
581 they attain 30% of coccoliths. Absolute abundances and fluxes are the lowest in this  
582 interval similarly to what observed by Mattioli et al., 2008 at Dotternhausen (Germany).  
583 Mattioli et al., 2008 interpreted the peak of *Calyculaceae* in other Tethyan settings  
584 during the T-OAE as due to low salinity. Studies on dinoflagellates are in agreement  
585 with this both at Mochras (van de Schootbrugge et al., 2005) and in other Tethyan sites  
586 (Bucefalo-Palliani et al., 2002; Mattioli et al., 2004b). At Mochras, during the event, the  
587 primary productivity was solely sustained by prasinopythes (green algae) and in other  
588 sites it was both sustained by prasinopythes and Chlorobiaceae (phototrophic bacteria)  
589 (van de Schootbrugge et al., 2005). These organisms replaced nannofossils (Mattioli  
590 et al., 2008) and dinoflagellates during the event (Bucefalo-Palliani et al., 2002; van  
591 de Schootbrugge et al., 2005) and they can thrive in conditions of extremely low  
592 salinity. Few modern species can tolerate low-salinity ( $S < 15\text{-}20\text{ppt}$ ) environments  
593 (Paasche, 1968). Evidences of low salinity from the northern Tethyan margin is also  
594 supported by belemnite rostra data from both UK and German sections (after  
595 correction using Mg/Ca) (McArthur et al., 2000; Bailey et al., 2003) and from  
596 Dotternhausen (Germany) extremely low  $\delta^{18}\text{O}$  values of bulk sediment (Röhl et al.,  
597 2001; Schmid-Röhl et al., 2002).

598 Low surface water salinity during the event might be due to increased river inflow (Röhl  
599 et al., 2001) or southward flow of low density Arctic waters into the Tethys (Bjerrum et  
600 al., 2001). At Mochras, evidences of increased continental weathering during the T-

601 OAE also come from osmium isotopes ( $\delta^{187}\text{Os}$ ) (Percival et al., 2015-2016) and from  
602 elevated kaolinite/illite ratio (Xu et al., 2018). The low salinity might have produced  
603 stratification of surface waters, favoring anoxia (Farrimond et al., 1989; Prauss et al.,  
604 1991; Bucefalo-Palliani et al., 2002) that sometimes reached the photic zone. At  
605 Mochras, high pyrite concentrations and limited presence of the biomarkers  
606 gammacerane and isorenieritane in the sediment corresponding to the T-OAE, suggest  
607 transient photic zone euxinia and episodic anoxia at the seafloor (Xu et al., 2018).  
608 Intermittent anoxia could have further hampered nanofossils and dinoflagellate  
609 production. It is reasonable that salinity fluctuated significantly during the event and  
610 that when it approached “normal” conditions, a diverse nanofossils assemblage could  
611 develop.

612 If the photic zone was low saline and occasionally attained anoxic conditions this has  
613 a consequence on the interpretation of species of the family Calyculaceae, namely  
614 *Calyculus* spp., *C. superbus* and *C. poulabronei*. Bucefalo Palliani and Mattioli, 1998  
615 and Erba 2004 interpreted *Calyculus* as deep and intermediate dweller, respectively.  
616 More reasonably, it was a shallow dweller, tolerant to low salinity conditions and anoxia  
617 (Mattioli et al., 2008-2009; Clémence et al., 2015). The same for *Carinolithus*, in  
618 agreement with Clémence et al., 2015. It is reasonable that *Calyculus* and *Carinolithus*  
619 had similar palaeoecological affinities since *Carinolithus* evolved from *Calyculus* in the  
620 lower Toarcian (Mattioli et al., 1996). Besides, Calyculaceae closely resemble to  
621 modern coccolith *Umbellosphaera*. The species belonging to this genus, thrive in very  
622 shallow water (<80-100 m) in contexts of very low nitrate concentrations (Thierstein et  
623 al., 2004). *Umbellosphaera* is characterized by a “double-layered” coccosphere, with  
624 an extra cellular space that may serve to store nutrients or trap water (Young, 1994).  
625 Mattioli et al., 2008 state that the coccosphere of *Calyculus* might have functioned for  
626 similar purposes. Otherwise, it is also possible that the additional space served to  
627 reduce the overall hydrodynamic density of the organism by trapping water of relatively  
628 low density. This could have helped *Calyculus* to keep their position in proximity of the  
629 surface in presence of stratified waters.

630 This might also be true for *Carinolithus*, given that the structure of the two coccoliths  
631 is similar. *Carinolithus* is characterized by more developed vertical elements, and a  
632 progressive closing of the axial canal from *C. poulabronei* to *C. superbus* (Mattioli,  
633 1996). Given that the coccoliths of the genus *Carinolithus* present more developed  
634 vertical elements, the coccosphere might have been even further adapted to trap



635 water, store nutrients or ultimately reduce hydrodynamic density in low salinity  
636 conditions.

637 Site belonging to the southern Tethyan margin are characterized by high proportion of  
638 *Mitrolithus jansae* (Mattioli et al., 2008 and references herein) while it is nearly absent  
639 along the northern Tethyan margin. *M. jansae* presumably was a deep dweller (Mattioli  
640 and Pittet, 2004a; Mattioli et al., 2008; Casellato et al., 2015), that dominated over  
641 other coccoliths in times of stratification of the water column but when anoxia still did  
642 not reach the lower photic zone. It is possible that in northern settings anoxia expanded  
643 more frequently into the photic zone (Pancost et al., 2004). Alternatively, temperature  
644 or light penetration were not adequate, and irradiance was not sufficient to support the  
645 development of *M. jansae*. Modern coccolith species *Florisphaera profunda*, which is  
646 a deep dweller, exhibits a similar sharp decrease in abundance between 30° and 40°  
647 N in the Pacific (Okada and Honjio, 1973).

648

#### 649 *Post T-OAE*

650

651 After the CIE of the T-OAE, assemblages are dominated by *Lotharingius* and  
652 *Crepidolithus crassus*, a deep dweller (Bour et al., 2007; Mattioli et al., 2008). These  
653 observations are generally in agreement with what has already been observed by other  
654 authors in other both northern and southern Tethyan settings (e.g., Tremolada et al.,  
655 2005; Mattioli et al., 2008; Fraguas et al., 2012; Casellato et al., 2015). Namely, we  
656 observe successive pulses of *Lotharingius* and *C. crassus* and here these are  
657 interpreted in terms of gradual recovery to “normal” conditions, after the widespread  
658 eunoxia-anoxia. This could also be facilitated by more effective connections between  
659 the different basins due to the high sea level at the time (Pittet et al., 2014). Alongside  
660 with the increase in abundance, *Lotharingius* start to increase in size at the time  
661 (Ferreira et al., 2017). In the aftermath of the T-OAE, more stable conditions might  
662 have favored *Lotharingius* increase in size, as already observed for Cenozoic  
663 foraminifera and palaeoceanographic perturbations (Ferreira et al., 2017 and  
664 references herein)

665 *Lotharingius* probably dwelled in shallow water with high-moderate nutrient  
666 concentrations (Pittet and Mattioli, 2002; Mattioli and Pittet, 2004; Mattioli et al., 2008;  
667 Casellato et al., 2015) and the pulse of these species in the aftermath of the T-OAE  
668 signifies increased nutrient input to surface waters. Then, *C. crassus* definitely

669 dominates the assemblages in the aftermath of the T-OAE, in times of reduced species  
670 diversity. Given that *C. crassus* was a deep dweller (Bour et al., 2007; Mattioli et al.,  
671 2008), this might suggest a progressive deepening of anoxia and a restoration of the  
672 deep photic zone communities, in agreement with the recovery interval of marine  
673 invertebrates (Harries and Little, 1999) Absolute abundances and fluxes are elevated  
674 in this time interval (~100 E<sup>6</sup>) and this is coherent with the positive  $\delta^{13}\text{C}$  positive  
675 excursion of the late Early Toarcian (Jenkyns, 1988) also observed at Mochras (Xu et  
676 al., 2018). Accordingly, to literature data, this can be interpreted in terms of high  
677 productivity in the surface water of the western Tethys.

678 Also, taxa with northern affinity such as *P. liasicus*, *C. cavus* and *C. primulus* (Bown,  
679 1987; Mattioli et al., 2008) drastically decrease in abundance in this time interval at  
680 Mochras and this might be due to the rapid radiation of placolith coccoliths, such as  
681 *Lotharingius*. This phenomenon already started at the Pl-To event, where placolith-  
682 coccolith rapidly conquer the nannofossil assemblages (Menini et al., 2019). Perhaps  
683 more effective connections between western Tethys basins, coupled to a more  
684 greenhouse climate, facilitated the spread of placolith-coccoliths which increased both  
685 in abundance and in size. Ultimately, the favorable conditions for placolith-coccoliths  
686 might also be at the origin of the first occurrence of species of the genus *Watznaueria*,  
687 that will finally dominate the oceans for the rest of the Mesozoic era.

688

689 4) Comparison with an independent proxy: magnetostratigraphy and Karoo traps  
690 volcanism

691

692 Xu et al., 2018 published a magnetostratigraphic record of the entire Toarcian stage  
693 for the Mochras core. The Pliensbachian-Toarcian boundary is characterized by the  
694 inversion of the magnetic polarity from reverse to normal (T-R0-T-N1). The first two  
695 Toarcian ammonite zones (*tenuicostatum* and *serpentinum*) are characterized by two  
696 normal and two reverse chrons. Comas-Rengifo et al., 2010 studied  
697 magnetostratigraphy at the Almunacid de la Cuba section (Spain), located at a few  
698 kilometers from La Almunia section and high-resolution calcareous nannofossil data and  
699 C-isotopes stratigraphy exist for this section (Menini et al., 2019). Almunacid de la  
700 Cuba section has also been used in Rocha et al., 2016 as an additional section to  
701 define the Toarcian GSSP at Peniche (Portugal), since magnetostratigraphy did not  
702 provide satisfactory results at Peniche (see Rocha et al., 2016 for details). Xu et al.,

703 2018 show that there is a good correlation between Almunacid de la Cuba and  
704 Mochras magnetostratigraphic record: this provides us with an independent proxy to  
705 compare Tethyan sections to the Karoo Large Igneous Province reversed/normal  
706 polarity succession, and hence the possible projection of Karoo ages onto the PI-To  
707 (Fig. 4). The carbon cycle perturbations at the PI-To and in the Early Toarcian have  
708 been linked to the emplacement of Karoo traps and associated release of volcanogenic  
709 CO<sub>2</sub> and methane from biogenic sources and sub-seafloor clathrates (Duncan et al.  
710 1997; McElwain et al. 2005; Svensen et al. 2007; Percival et al. 2015, 2016). Increased  
711 sedimentary mercury concentrations at the PI-To and during the T-OAE further support  
712 enhanced volcanic activity at the time (Percival et al., 2015-2016). Across the PI-To  
713 CIE and the positive CIE just below the T-OAE, several nannofossil species show their  
714 first occurrence and this has been found in several Tethyan and remote settings  
715 (Menini et al., 2019). The most relevant for supraregional correlations are the first  
716 occurrence of *D. ignotus* across the PI-To CIE, and *C. superbus* across the positive C  
717 isotopes excursion preceding the T-OAE CIE (Fig. 4). Bio- and magnetostratigraphic  
718 correlation of the Pliensbachian-Toarcian boundary at Mochras and Almonacid De La  
719 Cuba, and consequent magnetostratigraphic correlation to the Karoo volcanic  
720 succession from the Lebombo volcanic rift margin and the Drakensberg Group in  
721 northern Lesotho, southern Africa, suggest that the three normal-polarity  
722 magnetozones there correspond to the N1 and N2 magnetozones in the Mochras core  
723 (Fig. 4; Riley et al. 2004; Comas-Rengifo et al. 2010; da Rocha et al. 2016). In all  
724 Tethyan sections, the FO of *D. ignotus* is recorded in correspondence of this inversion  
725 of the magnetic polarity (from reverse to normal) at the Pliensbachian-Toarcian  
726 boundary. This allows to correlate Tethyan sections to Karoo lavas and to project  
727 Karoo ages onto the FO of *D. ignotus*: <sup>40</sup>Ar/<sup>38</sup>Ar which provides an age of 182.7±0.8  
728 Ma for the Pliensbachian-Toarcian boundary (Duncan et al., 1997) and this age can be  
729 projected onto the FO of this species (Fig. 4). Similarly, the FO of *C. superbus*, is  
730 recorded in the middle of a normal chron in Tethyan sections (TN1 at Mochras, N3 at  
731 La Almunia) and this chron is also well represented at Karoo (Fig. 4). Radiometric ages  
732 of basalts belonging to this chron provide an age of 181.2 ±1.0 Ma. Menini et al., 2019  
733 have highlighted that the FO of *C. superbus* is synchronous in both tethyan and remote  
734 settings and, on the basis of radiometric ages and magnetostratigraphy, we can anchor  
735 this bioevent to the Karoo record.

736 Our age model for the Early Toarcian at Mochras, indicates that the timing between  
737 the FO of *D. ignotus* and *C. superbus* is approximately 770 kyrs, and this is coherent  
738 (within the error bars) with the results provided by radiometric ages. Previous studies  
739 suggested that the timing between the FO of these two taxon is either 500 in Morocco  
740 or 433 kyrs at Peniche (Martinez et al., 2017). A slightly longer interval at Mochras  
741 could be the result sedimentological artefacts, a primary difference between northern  
742 and southern tethyan sections or both factors. At Peniche, Pittet et al., 2014 discuss  
743 the presence of a hiatus near the FO of *C. superbus*. Moreover, the PI-To boundary in  
744 the Peniche section is condensed (Pittet et al., 2014; Martinez et al., 2017). Martinez  
745 et al., 2017 evidenced that at Foug Tillicht section some condensation levels exist  
746 from the FO of *D. ignotus* to the FO of *C. superbus*, affecting the timing between the  
747 events. Alternatively, differences could reflect the slight diachronous nature of these  
748 biohorizons from northern to southern Tethyan sections.

749 Being the thickest Lower Jurassic section, characterized by the highest sedimentation  
750 rates, we support the idea that longer timing between the FO of these taxa are due to  
751 the presence of condensation levels or hiatus, that in sections characterized by lower  
752 sedimentation rates (e.g., Peniche), lead to a more imprecise estimation of timings. In  
753 any case, at Mochras we evidenced the presence of condensation levels at the PI-To,  
754 meaning that sea-levels changes affected the stratigraphic record also in this locality.  
755 In any case, the correlation between Mochras, Almunacid de la Cuba (and in turn the  
756 GSSP at Peniche, Portugal) with Karoo lavas allows to unambiguously relate  
757 calcareous nannofossils events to magnetic chrons. Finally, the integration of high-  
758 resolution calcareous nannofossils biostratigraphy and magnetostratigraphy provide  
759 us with a powerful tool to link Late Pliensbachian-Early Toarcian environmental  
760 perturbations recorded in both northern and southern Tethyan sediments to the  
761 emplacement of the Karoo Large Igneous Province and to project Karoo ages onto the  
762 micropaleontological record.

763

## 764 6. Conclusions

765

766 We presented new calcareous nannofossils data from the Mochras borehole (Cardigan  
767 Bay Basin, UK), the thickest Lower Jurassic sections. The good preservation and  
768 abundance of nannofossils allows the establishment of a refined biostratigraphy in the  
769 northern Tethyan margin, which remains by now less studied than the southern one.

770 Thanks to the quantification nannofossil absolute abundance and fluxes we show that  
771 these organisms were very sensible to changes in paleoenvironmental conditions  
772 spanning the Late Pliensbachian and the Early Toarcian. This time interval saw the  
773 rise in abundance of placolith-coccoliths through the Pliensbachian-Toarcian  
774 boundary. During the T-OAE assemblages were typically dominated by Calyculaceae,  
775 which could sustain stressed environments. As previously reported, this time interval  
776 is a fundamental step in the evolution of this group of marine algae: large-size  
777 *Lotharingius* increased in abundance in the aftermath of the T-OAE as previously  
778 reported for other Tethyan sections. The correlation between Mochras, the GSSP in  
779 Peniche and La Almunia with Karoo lavas allows to unambiguously relate CN events  
780 to magnetic chrons and to finally link the environmental perturbations recorded in the  
781 western Tethys to Karoo volcanism.

## References

- Al-Suwaidi, A.H., Hesselbo, S.P., Damborenea, S.E., Manceñido, M.O., Jenkyns, H.C., Riccardi, A.C., Angelozzi, G.N., Baudin, F., 2016. The Toarcian Oceanic Anoxic Event (Early Jurassic) in the Neuquén Basin, Argentina: A Reassessment of Age and Carbon Isotope Stratigraphy. *The Journal of Geology*.
- Bailey, T. R., Y. Rosenthal, McArthur, J.M., van de Schootbrugge, B., Thirlwall M. F., 2003. Paleoceanographic changes of the late Pliensbachian- early Toarcian interval: A possible link to the genesis of an oceanic anoxic event, *Earth and Planetary Sciences Letters* 212, 307–320.
- Bassoulet, J.P., Elmi, S., Poisson, A., Cecca, F., Bellion, Y., Guiraud, R., Baudin, F., 1993. Mid Toarcian. In: Dercourt, J., Ricou, L.E., Vrielynck, B. (Eds.), *Atlas Tethys Paleoenvironmental Maps*, BEICIP-FRANLAB, Rueil-Malmaison. 63–80.
- Beaufort, L., Barbarin, N., Gally Y, 2014. Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature Protocols* 9, 633-642.
- Blomeier, D.P.G., Reijmer, J.J.G., 1999. Drowning of a lower Jurassic carbonate platform: Jbel Bou Dahar, High Atlas, Morocco. *Facies* 41, 81–110.
- Bodin, S., Krencker, F. N., Kothe, T., Hoffmann, R., Mattioli, E., Heimhofer, U., Kabiri, L., 2016. Perturbation of the carbon cycle during the late Pliensbachian - early Toarcian: New insight from high-resolution carbon isotope records in Morocco. *Journal of African Earth Sciences* 116, 89–104.
- Bour, I., Mattioli, E., Pittet, B., 2007. Nannofacies analysis as a tool to reconstruct paleoenvironmental changes during the Early Toarcian anoxic event. *Palaeogeography, Palaeoclimatology, Palaeoecology* 249(1–2), 58–79.
- Bown, P.R., 1987. Taxonomy, evolution and biostratigraphy of Late Triassic-early Jurassic calcareous nannofossils. *Special Papers in Paleontology* 38, 1–118.



- Bown, P.R., Cooper, M.K.E., 1998. Jurassic. In: Bown, P.R. (Ed), *Calcareous Nannofossil Biostratigraphy*, British Micropalaeontological Society Series. Chapman and Hall/Kluwer Academic Publishers, London, 86–131.
- Brazier, J. M., Suan, G., Tacail, T., Simon, L., Martin, J. E., Mattioli, E., and Balter, V., 2015. Calcium isotope evidence for dramatic increase of continental weathering during the Toarcian oceanic anoxic event (Early Jurassic). *Earth and Planetary Science Letters* 411, 164–176.
- Bucefalo Palliani, R. B., Cirilli S., Mattioli E., 1998. Influences of the relative sea level fluctuations on the primary productivity, an example from the early Toarcian Umbria-Marche basin (central Italy), *Palaeogeography, Palaeoclimatology and Paleoecology* 142, 33–50.
- Casellato, C.E., Erba, E., 2015. Calcareous nannofossil biostratigraphy and paleoceanography of the toarcian oceanic anoxic event at colle di sogno (Southern Alps, Northern Italy). *Rivista Italiana di Paleontologia e Stratigrafia* 121, 297–327.
- Cecca, F., Macchioni, F., 2004. The two Early Toarcian (Early Jurassic) extinction events in ammonoids. *Lethaia* 3, 35–56.
- Clémence, M. E., Gardin, S., Bartolini, A. 2015. New insights in the pattern and timing of the Early Jurassic calcareous nannofossil crisis. *Palaeogeography, Palaeoclimatology, Palaeoecology* 427, 100–108.
- Cohen, A. S., Coe, A. L., Harding, S. M., & Schwark, L. (2004). Osmium isotope evidence for the regulation of atmospheric CO<sub>2</sub> by continental weathering. *Geology*, 32(2), 157–160.
- Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Herrero, C., Osete, M. L., Palencia, A., 2010. A complementary section for the proposed Toarcian (Lower Jurassic) global stratotype: the Almonacid de la Cuba sections (Spain). *Stratigraphy and Geological Correlation* 18, 133–152.
- Cope, J.C.W., 1984. The Mesozoic history of Wales. *Proc. Geol. Assoc.* 95, 373–385.
- Copestake, P., Johnson, B., 2014. Lower Jurassic Foraminifera from the Llanbedr (Mochras Farm) Borehole, North Wales, UK. *Monograph of the Palaeontographical Society* 167.

- Dera, G., Neige, P., Dommergues, J. L., Brayard, A., 2011. Ammonite paleobiogeography during the Pliensbachian–Toarcian crisis (Early Jurassic) reflecting paleoclimate, eustasy, and extinctions. *Global and Planetary Change*, 78(3-4), 92–105.
- Dera, G., Pucéat, E., Pellenard, P., Neige, P., Delsate, D., Joachimski, M. M., et al., 2009. Water mass exchange and variations in seawater temperature in the NW Tethys during the Early Jurassic: evidence from neodymium and oxygen isotopes of fish teeth and belemnites. *Earth and Planetary Science Letters* 286(1–2), 198–207.
- Dromart, G., Allemand, P., Garcia, J.-P., Robin, C., 1996. Variation cyclique de la production carbonatée au Jurassique le long d'un transect Bourgogne-Ardèche, Est-France. *Bulletin de la Société Géologique de France* 167, 423–433.
- Duncan, R. A., Hooper, P. R., Rehacek, J., Marsh, J. S., Duncan, A. R., 1997. The timing and duration of the Karoo igneous event, southern Gondwana. *Journal of Geophysical Research* 102, 127–138.
- Erba, E., 2004. Calcareous nannofossils and Mesozoic oceanic anoxic events. *Marine Micropaleontology* 52 (1–4), 85–106.
- Fantasia, A., Föllmi, K. B., Adatte, T., Spangenberg, J. E., Montero-Serrano, J. C., 2018. The Early Toarcian oceanic anoxic event: Paleoenvironmental and paleoclimatic change across the Alpine Tethys (Switzerland). *Global and Planetary Change* 162, 53–68.
- Farrimond, P., G. Eglinton, and S. C. Brassel, 1989. Toarcian anoxic event in Europe: An organic geochemical study, *Marine and Petroleum Geology* 6, 136–147.
- Fatela, F., & Taborda, R., 2002. Confidence limits of species proportions in microfossil assemblages. *Marine Micropaleontology* 45(2), 169–174.
- Ferreira, J., Mattioli, E., Suchéras-Marx, B., Giraud, F., Duarte, L. V. et al., 2019. Western Tethys Early and Middle Jurassic calcareous nannofossil biostratigraphy. *Earth-Science Review* 197.
- Ferreira, J., Mattioli, E., van de Schootbrugge, B., 2017. Palaeoenvironmental vs. evolutionary control on size variation of coccoliths across the Lower-Middle Jurassic, *Paleogeography, Paleoclimatology, Paleoecology*. 465, 177–192.

- Fraguas, Á., Comas-Rengifo, M. J., Gómez, J. J., Goy, A., 2012. The calcareous nannofossil crisis in Northern Spain (Asturias province) linked to the Early Toarcian warming-driven mass extinction. *Marine Micropaleontology* 94–95, 58–71.
- Fu, X., Wang, J., Feng, X., Wang, D., Chen, W., Song, C., Zeng, S., 2016. Early Jurassic carbon-isotope excursion in the Qiangtang Basin (Tibet), the eastern Tethys: Implications for the Toarcian Oceanic anoxic event. *Chemical Geology* 442, 62–72.
- Gradstein, F. M., Ogg, J. G., Schmitz, M. B., Ogg, G. M., 2012. The geologic time scale.
- Hay, W.W., 1972. Probabilistic stratigraphy. *Eclogae Geologicae Helveticae* 65, 255–266.
- Hesselbo, S. P., Bjerrum, C. J., Hinnov, L. A., MacNiocaill, C., Miller, K. G., Riding, J. B., van de Schootbrugge, B., 2013. Mochras borehole revisited: a new global standard for Early Jurassic earth history.
- Hesselbo, S. P., Gröcke, D. R., Jenkyns, H. C., Bjerrum, C. J., Farrimond, P., Bell, H. S. M., Green, O. R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* 406(6794), 392–395.
- Hesselbo, S. P., Jenkyns, H. C., Duarte, L. V., & Oliveira, L. C. (2007). Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters* 253(3–4), 455–470.
- Hesselbo, S.P., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. *Proceedings of the Geologists' Association* 119, 19–34.
- Ivimey-Cook, H.C., 1971. Stratigraphical palaeontology of the Lower Jurassic of the Llanbedr (Mochras Farm) Borehole. In: Woodland, A.W. (Ed.), *The Llanbedr (Mochras Farm) Borehole*. Institute of Geological Sciences, 87–92.
- Izumi, K., Kemp, D. B., Itamiya, S., Inui, M., 2018. Sedimentary evidence for enhanced hydrological cycling in response to rapid carbon release during the early Toarcian oceanic anoxic event. *Earth and Planetary Science Letters* 481, 162–170.

- Jenkyns, H. C., 2010. Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems* 11(3).
- Jenkyns, H. C., Jones, C. E., Gröcke, D. R., Hesselbo, S. P., Parkinson, D. N., 2002. Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society* 159(4), 351–378.
- Jenkyns, H.C., 1988. The Early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. *Am. J. Sci.* 288, 101–151.
- Jenkyns, H.C., Clayton, C.J., 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology*, 44: 687–706.
- Katz, M. E., Wright, J. D., Miller, K. G., Cramer, B. S., Fennel, K., Falkowski, P. G., 2005. Biological overprint of the geological carbon cycle. *Marine Geology* 217(3-4), 323–338.
- Kemp, D. B., Coe, A. L., Cohen, A. S., & Weedon, G. P. (2011). Astronomical forcing and chronology of the early Toarcian (Early Jurassic) oceanic anoxic event in Yorkshire, UK. *Paleoceanography* 26(4).
- Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature* 437, 396–399.
- Korte, C. and Hesselbo, S. P., 2011. Shallow-marine carbon- and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic, *Paleoceanography* 26, PA4219.
- Little, C.T.S., Benton, M.J., 1995. Early Jurassic mass extinction: a global long term event. *Geology* 23, 495–498.
- Mallarino, G., Goldstein, R.H., Di Stefano, P., 2002. New approach for quantifying water depth applied to the enigma of drowning of carbonate platforms. *Geology* 30, 783–786.
- Martinez, M., Krencker, F.-N., Mattioli, E., Bodin, S., 2017. Orbital chronology of the Pliensbachian – Toarcian transition from the Central High Atlas Basin (Morocco). *Newsletters on Stratigraphy* 50(1), 47–69.
- Mattioli, E. 1996. New calcareous nannofossil species from the Early Jurassic of Tethys. *Rivista Italiana di Paleontologia e Stratigrafia* 102(3).

- Mattioli, E., Erba E., 1999. Synthesis of calcareous nannofossil events in tethyan lower and middle Jurassic successions. *Rivista Italiana di Paleontologia e Stratigrafia* 105, 343–376.
- Mattioli, E., Pittet, B., 2002. Contribution of calcareous nanoplankton to carbonate deposition: a new approach applied to the Lower Jurassic of central Italy. *Marine micropaleontology* 45(2), 175–190.
- Mattioli, E., Pittet, B., Palliani, R., Rohl, H.-J., Schmid-Rohl, A., Morettini, E., 2004a. Phytoplankton evidence for the timing and correlation of palaeoceanographical changes during the early Toarcian oceanic anoxic event (Early Jurassic). *Journal of the Geological Society* 161(4), 685–693.
- Mattioli, E., Pittet, B., Petitpierre, L., Mailliot, S., 2009. Dramatic decrease of pelagic carbonate production by nanoplankton across the Early Toarcian anoxic event (T-OAE). *Global and Planetary Change* 65(3–4), 134–145.
- Mattioli, E., Pittet, B., Suan, G., Mailliot, S., 2008. Calcareous nanoplankton changes across the early Toarcian oceanic anoxic event in the western Tethys. *Paleoceanography* 23(3), 1–17.
- Mattioli, E., Pittet, B., Young, J.R., Bown, P.R., 2004b. Biometric analysis of Pliensbachian-Toarcian (Lower Jurassic) coccoliths of the family Biscutaceae: intra- and interspecific variability versus palaeoenvironmental influence. *Marine Micropalaeontology* 52, 5–27.
- Mattioli, E., Plancq, J., Boussaha, M., Duarte, L.V., Pittet, B., 2013. Calcareous nannofossil biostratigraphy: new data from the Lower Jurassic of the Lusitanian Basin. *Comunicacoes Geologicas T. 100, 100 (Especial I)*, 69–76.
- McArthur, J. M., D. T. Donovan, M. F. Thirwall, B. W. Fouke, and D. Matthey, 2000. Strontium isotope profile of early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belmnite palaeotemperature, *Earth and Planetary Sciences Letters* 179, 269–285.
- McElwain, J.C., Wade-Murphy, J., Hesselbo, S.P., 2005. Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature* 435, 479–482.
- Menini, A., Mattioli, E., Spangenberg, J. E., Pittet, B., and Suan, G., 2019. New calcareous nannofossil and carbon isotope data for the Pliensbachian/Toarcian

boundary (Early Jurassic) in the western Tethys and their paleoenvironmental implications. *Newsletters on Stratigraphy*, 173–196.

- Morard, A., Guex, J., Bartolini, A., Morettini, E., De Wever, P., 2003. A new scenario for the Domerian - Toarcian transition. *Bull. Soc. géol. Fr.* 4, 351–356.
- Okada, H., and Honjo, S., 1973. The distribution of oceanic coccolithophorids in the Pacific, *Deep Sea Res. Oceanogr. Abstr.*, 20, 355– 374.
- Paasche, E., 1968. Biology and physiology of coccolithophorids, *Annual Review of Microbiology* 22, 71–86.
- Page, K.N., 2003. The Lower Jurassic of Europe: its subdivision and correlation. *Geological Survey of Denmark and Greenland* 1, 23–59.
- Palliani, R. B., Mattioli, E., Riding, J. B., 2002. The response of marine phytoplankton and sedimentary organic matter to the early Toarcian (Lower Jurassic) oceanic anoxic event in northern England. *Marine micropaleontology* 46(3–4), 223–245.
- Pancost, R. D., Crawford, N., Magness, S., Turner, A., Jenkyns, H. C., Maxwell, J. R., 2004. Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events, *Journal of the Geological Society of London* 161, 1–12.
- Percival, L. M. E., Witt, M. L. I., Mather, T. A., Hermoso, M., et al., 2015. Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo–Ferrar Large Igneous Province. *Earth and Planetary Science Letters* 428, 267–280.
- Percival, L.M.E., Cohen, A.S., Davies, M.K., Dickson, A.J., Hesselbo, S.P., Jenkyns, H.C., Leng, M.J., Mather, T.A., Storm, M.S., Xu, W., 2016. Osmium isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcan-ism and climate change. *Geology* 44, 759–762.
- Philippe, M., Pujalon, S., Suan, G., Mousset, S., Thévenard, F., Mattioli, E., 2017. The palaeolatitudinal distribution of fossil wood genera as a proxy for European Jurassic terrestrial climate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 466, 373 -381.
- Pittet, B., Suan, G., Lenoir, F., Duarte, L. V., Mattioli, E., 2014. Carbon isotope evidence for sedimentary discontinuities in the lower Toarcian of the Lusitanian



Basin (Portugal): Sea level change at the onset of the Oceanic Anoxic Event. *Sedimentary geology* 303, 1–14.

- Price, G. D., 1999. The evidence and implications of polar ice during the Mesozoic, *Earth-Sciences Reviews* 48, 183–210.
- Riley, T. R., Millar, I. L., Watkeys, M.K., Curtis, M. L., Leat, P.T., Klausen, M. B., Fanning, C. M., 2004. U–Pb zircon (SHRIMP) ages for the Lebombo rhyolites, South Africa: refining the duration of Karoo volcanism. *Journal of the Geological Society* 161(4), 547–550.
- Rocha, R. Mattioli, E., Duarte, L.V., Pittet, B., Elmi, S., Mouterde, R., Cabral, M.C., Comas-Rengifo, M.J., Gómez, J.J., Goy, A., Hesselbo, S.P., Jenkyns, H.C., Littler, K., Mailliot, S., Veiga de Oliveira, L.C., Osete, M.L., Perilli, N., Pinto, S., Ruget, C. and Suan, G., 2016. Base of the Toarcian Stage of the Lower Jurassic defined by the Global Boundary Stratotype Section and Point (GSSP) at the Peniche section (Portugal). *Episodes* 39, 460-481.
- Rohl, H. J., Schmid-Rohl, A., O. Frimmel, Wolfgang, A., Lorenz, S., 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: An oxygen-depleted ecosystem controlled by sea level and palaeoclimate, *Palaeogeography, Palaeoclimatology, Palaeoecology* 165, 27–52.
- Rosales, I., Quesada, S., Robles, S., 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque - Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 203, 253–275.
- Roth, P.H., 1984. Preservation of calcareous nannofossils and fine-grained carbonate particles in mid-Cretaceous sediments from the southern Angola Basin. In: Hay, W.W. (Ed.), *Initial Reports of Deep Sea Drilling Project 75*. U.S. Government Printing Office, Washington, 651–655.
- Ruhl, M., Hesselbo, S. P., Hinnov, L., Jenkyns, H. C., Xu, W., et al., 2016. Astronomical constraints on the duration of the Early Jurassic Pliensbachian Stage and global climatic fluctuations. *Earth and Planetary Science Letters* 455, 149–165.
- Schmid-Rohl, A., Rohl, H. J., O. Frimmel, W., A., Schwark L., 2002, *Palaeoenvironmental reconstruction of lower Toarcian epicontinental black*

shales (Posidonia Shale, SW Germany): Global versus regional control, *Geobios (Jodhpur India)* 35, 13–20.

- Sellwood, B.W., Jenkyns, H.C., 1975. Basins and swells and the evolution of an epeiric sea (Pliensbachian–Bajocian of Great Britain). *Journal of the Geological Society of London* 131, 373–388.
- Simms, M.J., Chidlaw, N., Morton, N., Page, K.N., 2004. *British Lower Jurassic Stratigraphy*. Geological Conservation Review Series 30. Joint Nature Conservation Committee, Peterborough.
- Storm, M. S., Hesselbo, S. P., Jenkyns, H. C., Ruhl, M., Ullmann, C. V., Xu, W. et al., 2020. Orbital pacing and secular evolution of the Early Jurassic carbon cycle. *Proceedings of the National Academy of Sciences* 117(8), 3974–3982.
- Suan, G., Mattioli, E., Pittet, B., Lécuyer, C., Suchéras-Marx, B., Duarte et al., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* 290 (3–4), 448–458.
- Suan, G., Mattioli, E., Pittet, B., Mailliot, S., Lécuyer, C., 2008a. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal, *Paleoceanography* 23, PA1202.
- Suan, G., Pittet, B., Bour, I., Mattioli, E., Duarte, L. V., Mailliot, S., 2008b. Duration of the Early Toarcian carbon isotope excursion deduced from spectral analysis : consequence for its possible causes. *Earth and Planetary Science Letters* 267(3–4), 666–679.
- Svensen, H., Planke, S., Chevallier, L., Malthé-Sorensen, A., Corfu, F., Jamtveit, B., 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global warming. *Earth and Planetary Sciences Letters* 256, 554–566.
- Thierstein, H. R., Cortès, M. Y., Haidar, A. T., 2004. Plankton community behaviour on ecological and evolutionary timescales: When models confront evidence, in *Coccolithophores From Molecular Processes to Global Impact*, edited by H. R. Thierstein and J. R. Young, 455–480.
- Tremolada, F., Van de Schootbrugge, B., & Erba, E. (2005). Early Jurassic schizosphaerellid crisis in Cantabria, Spain: implications for calcification rates and phytoplankton evolution across the Toarcian oceanic anoxic event. *Paleoceanography* 20(2).

- van de Schootbrugge, B., McArthur, J.M., Bailey, J.M., Rosenthal, Y., Wright, J.M., Miller, K.G., 2005, Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records, *Paleoceanography* 20.
- Wignall, P.B., Hallam, A., Newton, R.J., Sha, J.G., Reeves, E., Mattioli, E., Crowley, S., 2006. An eastern Tethyan (Tibetan) record of the Early Jurassic (Toarcian) mass extinction event. *Geobiology* 4, 179–190.
- Woodland, A. W., 1971. The Llanbedr (Mochras Farm) Borehole, Report 71/18, Institute of Geological Sciences.
- Xu, W., Ruhl, M., Jenkyns, H. C., Hesselbo, S. P., Riding, J. B., et al., 2017. Carbon sequestration in an expanded lake system during the Toarcian oceanic anoxic event. *Nature Geoscience* 10(2), 129-134.
- Xu, W., Ruhl, M., Jenkyns, H. C., Leng, M. J., Huggett, J. M., et al., 2018. Evolution of the Toarcian (Early Jurassic) carbon-cycle and global climatic controls on local sedimentary processes (Cardigan Bay Basin, UK). *Earth and Planetary Science Letters* 484, 396–411.
- Young, J. R., 1994. Functions of coccoliths, in *Coccolithophores*, edited by A. Winter and W. Siesser, 63–82.

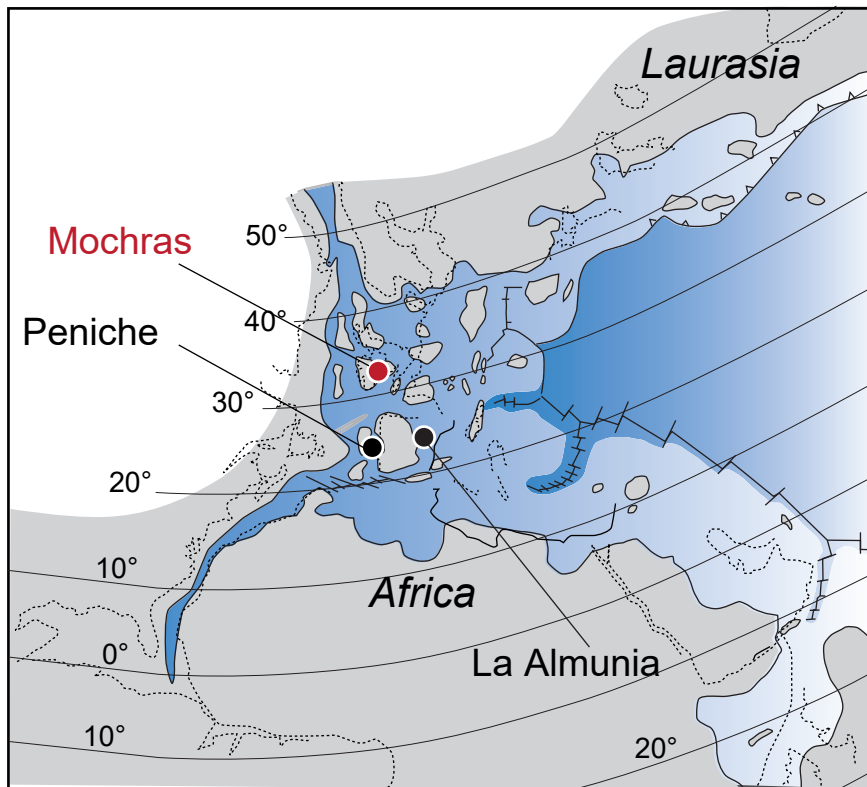


Figure 1. Paleoceanographic reconstruction of the western Tethys at about 183 Ma (after Bassoullet et al., 1993) showing the location of Mochras core and the two sections used for comparison. Mochras (Wales, UK) is located in the Northern Tethyan margin while La Almunia (Central Spain) is located in the Southern Tethyan margin. Peniche was located in the Lusitanian Basin, a N-S corridor in connexion with both Tethyan and NW European regions.

# Mochras

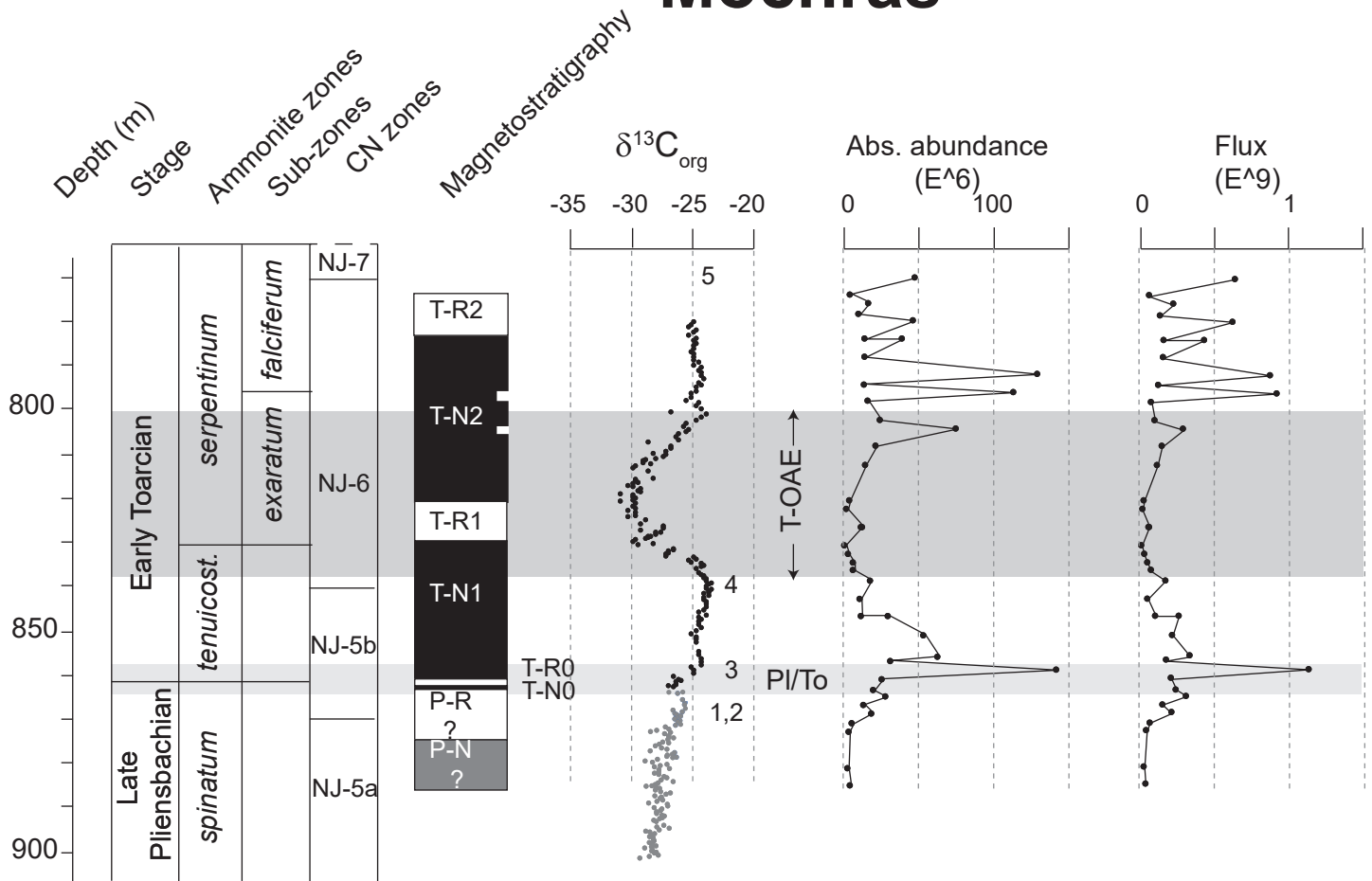


Figure 2. Absolute abundance of nannofossils per gram of rock and flux of nannofossils (nannofossils/m<sup>2</sup>/year). On the right, ammonite biostratigraphy (Tippan et al., 1994). Calcareous nannofossil biostratigraphy based on Bown, 1987 and Bown, 1998. First occurrences of biostratigraphically important species (1. *C. cavus*, 2. *Z. erectus*, 3. *D. ignotus*, 4. *C. superbus*, 5., *D. striatus*). Magnetostratigraphy after Xu et al., 2018.  $\delta^{13}\text{C}_{\text{org}}$  for the Lower Toarcian (black dots) after Xu et al., 2018 and for the Late Pliensbachian (grey dots) after Storm et al., 2020.

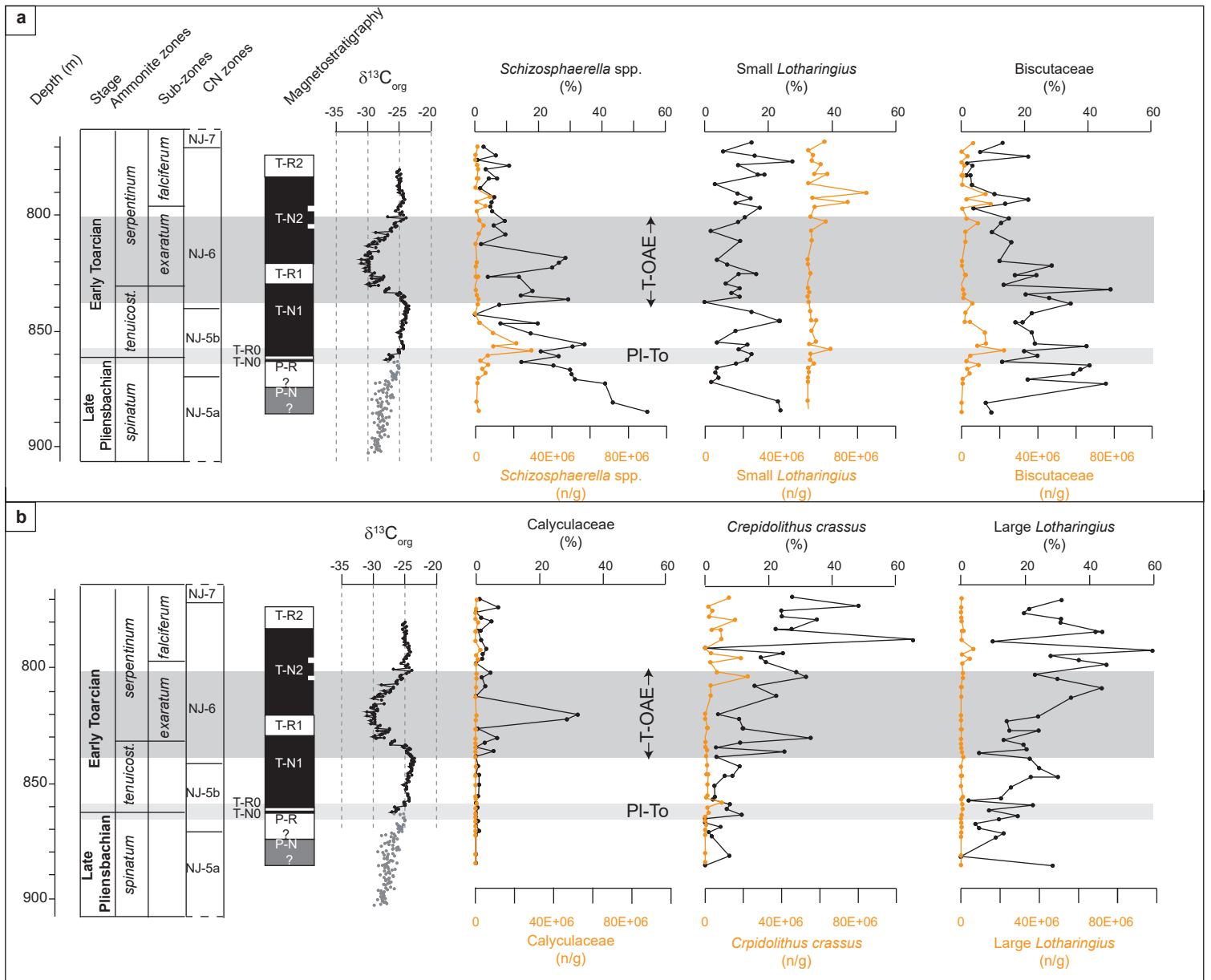


Figure 3. Relative and absolute abundance of main taxa. Ammonite biostratigraphy after Tappin et al., 1994. a., Nannofossil assemblages from the Late Pliensbachian and earliest Toarcian (*spinitum* to *tenuicostatum* ammonite zones, below the T-OAE). b., Nannofossil assemblages from the T-OAE and after the event (corresponding to *serpentinum* zone)



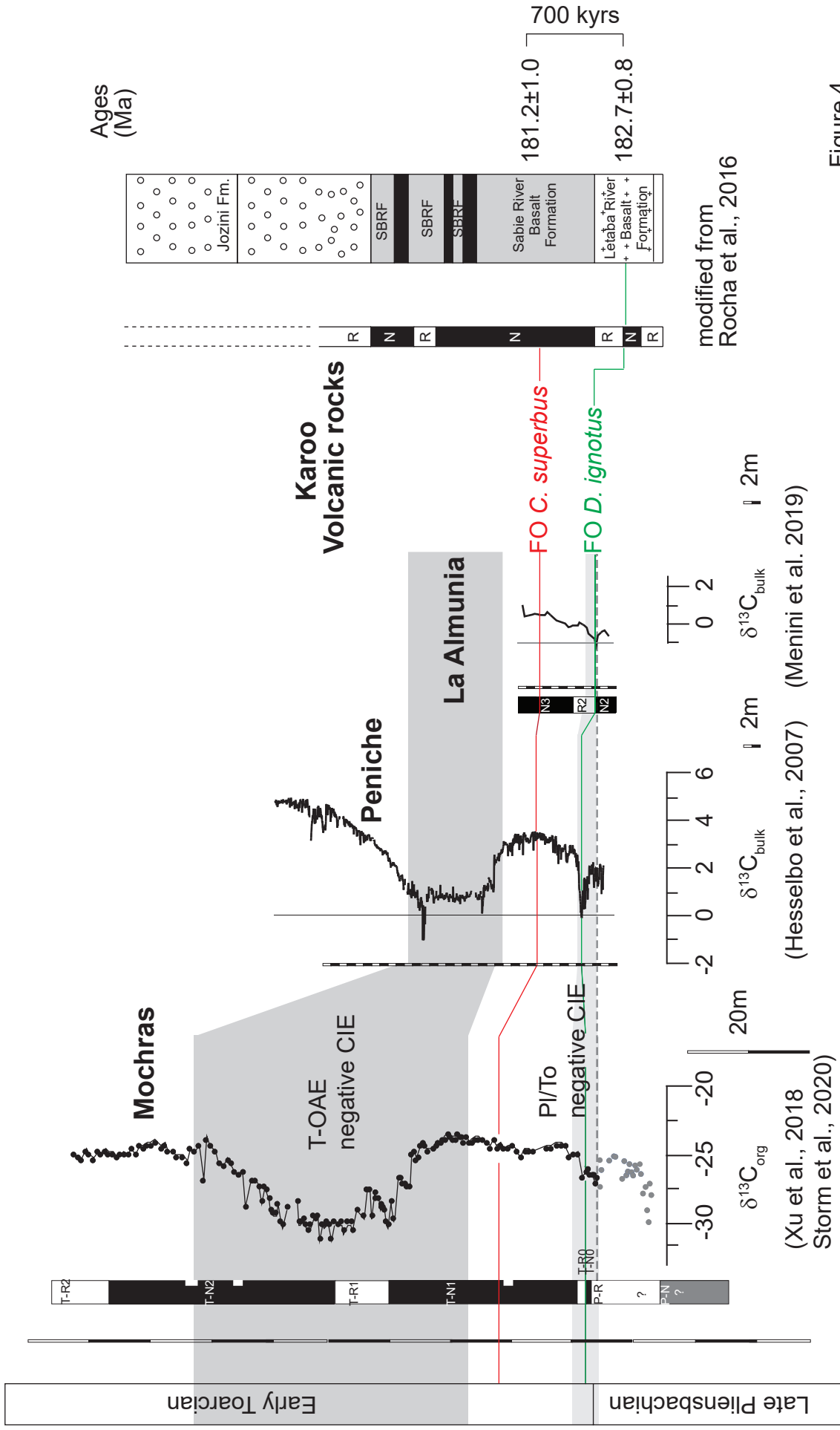


Figure 4

Figure 4. Correlation between Mochras (Wales, Cleveland Basin), Peniche (Portugal, Lusitanian Basin), La Almunia (Central Spain) and Karoo lavas. Magnetostratigraphy at La Almunia is from Almunacid de La Cuba section (see text for details). Litostratigraphy at Karoo is after Riley et al., 2004 Magnetostratigraphy at Karoo is after Hargreaves et al., 1997





## **Chapitre 3.2. Calcareous nannofossil response to PETM: a comparison between shelf and open-ocean settings.**

# 1 **Calcareous nanofossil response to PETM: a comparison between shelf and open-ocean** 2 **settings**

3

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## 16 **1. Introduction**

17 The Paleocene-Eocene transition is characterized by a brief but intense carbon isotope  
18 excursion (CIE) associated with a global warming of 5-7 °C (Kennet and Stott, 1991; Zachos  
19 et al., 2001). This transition is known as the Paleocene-Eocene Thermal Maximum (PETM).

20 The input of light carbon either from methane release or volcanism (Dickens et al., 1995, 1997;  
21 Dickson et al., 2005) led to enhanced  $p\text{CO}_2$  levels in the oceans, finally triggering ocean  
22 acidification (Penman et al., 2014; Babila et al., 2018) and the shoaling of the CCD (Kroon et  
23 al., 2004; Penman et al., 2016). Recent studies suggest that all these changes happened during  
24 a 405 kyrs eccentricity maximum (Zeebe and Lourens, 2009), and recent models estimated the  
25 duration of the event at ca. 200 kyrs (Rohl et al., 2000; Rohl et al., 2007). Benthic communities

26 suffered a dramatic extinction (Tjalsma and Lohmann, 1983; Thomas and Shackleton, 1996)  
27 and planktonic biota underwent a profound re-organization (e.g., Bralower et al., 1995; Kelly  
28 et al., 1996; Bralower et al., 2002; Gibbs et al., 2006b; Raffi et al., 2009).

29 Plankton assemblages are profoundly different in shelf or open-ocean sites. This pattern makes  
30 the interpretation on ecological preference of taxa difficult and sometimes contradictory from  
31 a paper to another. At open-ocean sites, the turnover which occurred during the PETM is  
32 thought to reflect warmer and nutrient-depleted conditions during the onset and peak of the  
33 event caused by thermally enhanced stratification (Kelly et al., 1998; Bralower, 2002).

34 However, in proximal sites, local conditions such as high precipitation rates and possible  
35 increase in storm events may have resulted in increased continental runoff that affected  
36 assemblage response to the PETM (Self-Trail et al., 2012). Previous studies showed that there  
37 is also an impact of paleotemperatures on the size of some taxa, such as *Discoaster*  
38 *multiradiatus*, that can be used to infer water mass stratification (Tremolada et al., 2008).

39 Geochemical and ~~other~~ biotic proxies at some of the ~~same~~ most studied oceanic sites and at  
40 shelf locations challenge the micropaleontological interpretations, as they preferentially support  
41 increased primary productivity as a consequence of intensified continental weathering and  
42 nutrient runoff (e.g., Thomas and Shackleton, 1996; Bains et al., 2000; Crouch et al., 2001;  
43 Stoll and Bains, 2003; Stoll et al., 2007b, c). Since elevated primary production, along with  
44 enhanced weathering, has been proposed as a major negative feedback of the carbon cycle  
45 perturbation after the onset of the PETM (Bains et al., 2000; Ravizza et al., 2001), it is critical  
46 to determine the global distribution of productivity at different stages of the event and thereby  
47 assess its role in carbon export and subsequent sequestration.

48 Calcareous nannofossils are exoskeletal microalgae and represent one of the most important  
49 sources of carbonate to deep-sea sediments. These organisms thriving in the upper photic zone  
50 are very sensitive to environmental parameters. The distribution of individual species in surface



51 waters is controlled by temperature, salinity, and, especially, availability of nutrients (e.g.,  
52 Winter et al., 1994). The paleoecology of extinct nannofossil species can be inferred from  
53 biogeography, paleoenvironmental proxy data, and comparison with extant taxa. Despite of  
54 limitations to these interpretations, calcareous nannofossils allow global productivity  
55 reconstruction since they are almost ubiquitous in the oceans.

56 So far, only a few open ocean sites with complete Paleocene/Eocene transitions and relatively  
57 well-preserved nannofossil assemblages have been studied in detail (Bralower, 2002;  
58 Tremolada and Bralower, 2004; Gibbs et al., 2006; Raffi et al., 2009), thus our knowledge of  
59 the response of calcareous nannofossils to the PETM remains partially unclear. Moreover,  
60 almost no data exist on nannofossil absolute abundance (nannofossils/grams of rock) or fluxes  
61 (per cm<sup>2</sup> and per year) and most of the paleoenvironmental interpretations are inferred from  
62 relative turnovers between species or genus, which do not represent effective changes in  
63 assemblage composition but only relative switchovers.

64 Here we present detailed nannofossil assemblage records of the PETM across disparate  
65 paleoceanographic settings (Fig. 1) in order to unravel global *versus* local environmental  
66 influences upon primary production during the PETM. We studied a proximal section  
67 (Kharouba, Tunisia), the South Eastern Atlantic Site ODP 1263 and a central gyre location in  
68 the Pacific Ocean (ODP Site 1209). All three studied sections display the C isotope anomaly,  
69 namely the negative excursion of carbon stable isotopes that characterizes the PETM (Kennet  
70 and Stott, 1991; Zachos et al., 2001). These records are compared to already published data  
71 from both proximal and distal localities, namely South Dover Bridge core (New Jersey Coastal  
72 Plain, SDB), ODP 690, ODP 1260, Cicogna section (North East Italy), Alamedilla (South  
73 Spain) and Tanzania Drilling Project core 14 (TDP14). Such a comparison should enable us to  
74 obtain a more comprehensive framework of calcareous nanoplankton distribution and of

75 ecological preferences of taxa across a major paleoceanographic event, and to discriminate  
76 between local *versus* global trends in assemblage changes.

77

## 78 **2. Materials and methods**

79

### 80 **2.1 Carbon isotope measurements**

81 Carbon isotope data are already available for Sites 1209 and 1263 (Penman et al., 2014; Zachos  
82 et al., 2005). We studied 37 samples of the Kharouba section for stable carbon isotopes  
83 measured on bulk rock carbonates ( $\delta^{13}\text{C}_{\text{bulk rock}}$ ). 25 samples were analysed at the Institute of  
84 Earth Surface Dynamics of the University of Lausanne, Switzerland (UNIL) and 12 were  
85 analysed at the Laboratoire de Géologie de Lyon (Université Lyon 1, LGL-TPE). At UNIL,  
86 sample powders were analysed using a Thermo Fisher Scientific Gas Bench II (Bremen,  
87 Germany) carbonate preparation device connected to a Delta Plus XL isotope ratio mass  
88 spectrometer that was operated in the continuous helium flow mode (Révész and Landwehr  
89 2002). At LGL-TPE, stable isotopes were determined using an autosampler MultiPrep™  
90 system coupled to a dual-inlet GV IsoPrime™ isotope ratio mass spectrometer (IRMS).

91 Samples with clear evidence of diagenetically neoformed or recrystallized carbonates (calcite  
92 or dolomite) were not analysed. For each sample, an aliquot of about 100–500  $\mu\text{g}$  (depending  
93 on the  $\text{CaCO}_3$  content) of bulk-rock samples was reacted with anhydrous oversaturated  
94 phosphoric acid at 90°C for 20 min. Carbon isotope compositions are quoted in the  $\delta$  notation  
95 in per mil (‰) relative to Vienna Pee Dee Belemnite standard (V-PDB). All samples were  
96 measured in duplicate and normalized to the V-PDB scales with an in-house working standard  
97 Carrara Marble (UNIL-CAM,  $\delta^{13}\text{C}_{\text{V-PDB}} = 2.05$ ; LGL-TPE-CAM,  $\delta^{13}\text{C}_{\text{V-PDB}} = 2.025$ ) and  
98 international reference standards (RMs) in each run. The  $\delta^{13}\text{C}$  values of the reference gas and  
99 the UNIL-CAM and LGL-TPE-CAM were normalized with the RMs NBS-19 limestone with

100  $\delta^{13}\text{C} = +1.95\text{‰}$ , NBS-18 carbonatite with  $\delta^{13}\text{C} = -5.04\text{‰}$ , and LSVEC lithium carbonate with  
101  $\delta^{13}\text{C} = -46.65\text{‰}$  (Brand et al., 2014). The repeatability and intermediate precision of the  
102 analyses ( $2\sigma$ ), monitored by replicate analyses of the laboratory standard UNIL-CAM and  
103 LGL-TPE-CAM and the RMs was better than  $\pm 0.05\text{‰}$ . The accuracy of the analyses was  
104 checked periodically through the analyses of the RMs.

105

## 106 **2.2 Calcareous nannofossils**

107 At Site 1209 (Fig. 1; Shatsky Rise, Tropical Pacific;  $32^{\circ}39.1'\text{N}$ ,  $158^{\circ}30.4'\text{E}$ , 2387 water depth,  
108 1900 paleodepth; Takeda and Kaiho, 2007), we studied 20 samples over 0.54 m transect  
109 spanning the PETM. The event lies in a  $\sim 25\text{-cm}$ -thick layer of clayey nannofossil ooze with a  
110 sharp basal contact and a gradational upper contact with underlying and overlying chalk,  
111 respectively (Fig. 2A). Samples were collected every 1-3 cm, with higher sampling rate across  
112 the PETM (1 cm).

113 At Site 1263 (Fig. 1; Walvis Ridge, Southern-East Atlantic;  $28^{\circ}32'\text{S}$ ;  $02^{\circ}47'\text{E}$ ; 2717 m water  
114 depth; 1500 m paleodepth; Zachos et al., 2004), we studied 26 samples over ca. 2 m transect  
115 across the PETM. The PETM onset is marked by a sharp contact between grayish brown ash-  
116 bearing clay above, and light gray nannofossil ooze below (Fig. 2B). Samples were collected  
117 every 5-10 cm, with higher sampling rate across the PETM (5 cm). Given higher sedimentation  
118 rates at Site 1263 relatively to Site 1209, we adopted a relatively coarser sampling resolution.  
119 However, because of paucity of material in the PETM core interval ( $\sim 10\text{ cm}$ ), this interval is  
120 undersampled. We analyzed the Hole 1263C between 333.61 and 335.15 rmcd, and Hole 1263D  
121 between 335.20 and 335.65 rmcd.

122 At Kharouba section (Fig.1; Tunisian Atlas) upper Paleocene to lower Eocene sediments  
123 outcrop over 30 meters and 51 samples were collected, selected as fresh and unaltered as  
124 possible and studied for their calcareous nannofossil content. The lower part of the section is

125 constituted by 10 meters of dark marls and continues with 20 meters of alternations of marls  
126 and calcareous marls (Fig. 2C). Samples were collected on average every 1 meter.  
127 All calcareous nannofossil slides were prepared following the settling method (Beaufort et al.,  
128 2014). A cover slide was weighted before and after the settling of a homogeneous suspension  
129 of dry bulk sediment and water supersaturated with respect to CaCO<sub>3</sub> for 4 hours in a Petri-dish.  
130 Water was carefully aspired with a water-pump connected to a micro-pipette to avoid any  
131 turbulence. After residual water drying, the cover slide was fixed on a microscope slide using  
132 Rhodopass B resin (Polyvinyl acetate). At least 500 specimens of calcareous nannofossils were  
133 counted for each sample with a Leica DM 750 P microscope with 1000X magnification. Each  
134 slide was further scanned over 10 transects (ca. 1500 FOV, 0.471 cm<sup>2</sup>) in order to detect the  
135 presence of rare species. Each slide was observed twice over a year in order to check  
136 consistency of the results. Five replicates per sample were studied at Site 1209 for absolute  
137 abundance in order to test statistical differences, thus average values with an error bar of (2 SD)  
138 were calculated.

139 Absolute nannofossil abundance per gram of sediment were calculated as follows:

140 
$$x = \frac{n*(l*h)}{m*A} \quad (1)$$

141 where  $x$  is the absolute abundance value,  $n$  is the number of counted specimens in a slide,  $l$   
142 is the length of the cover slide,  $h$  is the height of the cover slide,  $m$  is the mass of the weighted  
143 sample and  $A$  is the studied surface of the sample.

144 We calculated nannofossil accumulation rates (NAR) using the formula:

145 
$$NAR = X * AR * d \quad (2)$$

146 where  $NAR$  is in n/cm<sup>2</sup>/yr,  $X$  is the absolute abundance of nannofossils (n/g),  $AR$  is the  
147 accumulation rate (cm/ky),  $d$  is the dry bulk density of the sediment. The accumulation rate at  
148 Sites 1209 and 1263 has been calculated according to Menini et al. (submitted, 2020b). For  
149 Kharouba, we used the duration of 5 kyrs for the base of the section until the base of NP10

150 nannofossil zone, according to Zachos et al. (2005; calculated for Site 1263). For the core of  
151 the event and the recovery interval, we used the duration of the PE1 and PE2a nannofossil zones  
152 as defined by Menini et al. (submitted, 2020a), namely ~85 kyrs and ~15 kyrs respectively. The  
153 dry density of rock for Sites 1209 and 1263 was calculated according to the ship data (REFS);  
154 for Kharouba, as calcium carbonate measurements of samples showed they are mainly marls,  
155 we used the average value of 2.73 g/cm<sup>3</sup> provided for marls.

156 In order to compare our data with previous studies we generated relative abundance data for the  
157 three sections (Supplementary Material). The preservation was further investigated using a  
158 Phenom SEM G2 PRO microscope. In order to obtain a consistent dataset, only samples  
159 showing good preservation are retained for statistical analyses.

160 Principal components analysis (PCA) was applied to nannofossil assemblages on the entire  
161 dataset composed of samples from the 3 sections, and eventually to datasets of individual  
162 sections. This multivariate statistical method allows analysis of the entire nannofossils  
163 community, instead of changes in single taxa abundance. Also, this method permits a better  
164 interpretation of complex datasets and reduces a large data matrix composed of several variables  
165 to a small number of factors representing the main modes of variations (Beaufort and Heussner,  
166 2001).

167 PCA was computed with PAST 4.0 software (Hammer et al., 2001). The extraction method for  
168 eigenvalues was Orthotran/Varimax. We introduced the log<sub>2</sub> of relative abundance values in  
169 the matrix in order to reduce the influence of outliers. Some species (such as *Fasciculithus*  
170 *richardii*, *F. alanii*, *F. liliana*, *F. mitreus* and *F. tonii* or genera belonging to the family  
171 Zygodiscales) were grouped because they display abundance peaks in the same samples. Also,  
172 *Discoaster araneus* and *D. anartios* were grouped because both they co-occur in the same  
173 samples and they are interpreted as morphotypes of the same species (Bralower and Self-Trail,  
174 2016). The matrix consists of 13 to 18 taxa according to the different sections. Error bars in Fig.

175 3 represent lower and upper limits for 95% confidence intervals, using 9999 bootstrap  
176 replicates.

177 SIMPER (Similarity Percentage) was applied to counting data in order to test the degree of  
178 similarity between the sections we studied and already published sections. Detailed distribution  
179 charts were available in the literature for Alamedilla section in South Spain (Monechi et al.,  
180 2000), Cicogna in NE Italy (Agnini et al., 2016), Site 1260, central Atlantic off South America  
181 (Mutterlose et al., 2007), the TDP 14 core, Tanzania (Bown and Pearson, 2009), South Dover  
182 core in the mid-Atlantic Coastal Plain (Self-Trail et al., 2012), Site 690, Weddel Sea, South  
183 Atlantic (Bralower et al., 2002). Before applying SIMPER, a taxonomic revision was  
184 undertaken in order to make homogeneous the dataset. In this paper, the counting at the genus  
185 level was introduced in order to avoid eventual biases linked to different taxonomic concepts  
186 used in various works. SIMPER is a simple method for assessing which taxa are primarily  
187 responsible for an observed difference between groups of samples belonging to different  
188 sections. The overall significance of the difference has been assessed by ANOSIM. The Bray-  
189 Curtis similarity measure was used with SIMPER. Additionally, the hierarchical clustering was  
190 used to produce a dendrogram showing how data points (rows) can be clustered. Both SIMPER  
191 and cluster analysis were computed with PAST 4.0 software (Hammer et al., 2001).

192

### 193 **3. Results**

194

#### 195 **3.1 Depth definitions and PETM subdivision**

196 At both Site 1209 and 1263 we express our data relatively to the lithological contact of the  
197 PETM and carbon isotopes stratigraphy (Fig. 2A and B). We follow Zachos et al. (2005) in the  
198 definition on the PETM and we refer to pre-PETM below the carbon isotope excursion (CIE),  
199 to “core of the PETM” all through the  $\delta^{13}\text{C}$  CIE (-3‰) and to the recovery phase above it, where

200  $\delta^{13}\text{C}$  values recover to pre-PETM ones (Fig. 2A and B). At Kharouba, the lithology is constantly  
201 dominated by marls in this interval and no lithological contact exists for the basal Eocene. The  
202 base of the section is fixed at 0 m (Fig. 2C).

203 We express all the data at the same scale, in order to avoid visual erroneous interpretations.

204 In agreement to Zachos et al. (2005) and Röhl et al. (2007) we subdivide the PETM interval in  
205 pre-PETM, core of the PETM and recovery phase.

206

### 207 **3.2 Carbon isotopes**

208 At Site 1263, the  $\delta^{13}\text{C}_{\text{bulk rock}}$  curve of Paleocene-Eocene interval has been published by Zachos  
209 et al. (2005). At both sites 1209 and 1263, a prominent negative carbon excursion can be seen  
210 from  $\sim 3\text{‰}$  to  $\sim 0.2\text{‰}$  and from  $\sim 2\text{‰}$  to  $\sim -1\text{‰}$ , respectively (Fig. 2A and B). The  $\delta^{13}\text{C}_{\text{bulk rock}}$   
211 trend is the same as at Site 1209, but the values record a general offset towards more  
212 negative/positive values of  $\sim 0.8\text{‰}$ . We have measured the  $\delta^{13}\text{C}_{\text{bulk rock}}$  of 37 samples from the  
213 Kharouba section (Fig. 2C). From 0 to 1 m, values are stable and range from 0.8 to 0.9 ‰. At  
214 4.4 m values drastically decrease to  $-2.5\text{‰}$ , with a 2 ‰ negative excursion (Fig. 2C).  
215 Biostratigraphic and chemostratigraphic data allow us to recognize the onset of the PETM at  
216 1.1 m. Values stay low till up 4.4 m and recover at 6.2 m. These data are in agreement with  
217 previously published  $\delta^{13}\text{C}_{\text{bulk rock}}$  data for the PETM in both oceanic Sites 1209 (Colosimo et al.,  
218 2006; Penman et al., 2014; Menini et al., under revision) and 1263.

219

### 220 **3.3 Preservation and biostratigraphy**

221 At Site 1209, nannofossil preservation is good overall but it declines between 1 cm below and  
222 above the LC, as previously indicated by Bralower et al. (2014). Coccoliths in those samples  
223 are mostly affected by dissolution, consistently with the coeval maximum of nannofossil  
224 fragmentation, while *Discoaster* are slightly overgrown.



225 At Site 1263, SEM pictures reveal moderate to good preservation but increased dissolution is  
226 observed from 0 to 0.6 cm above the LC, as previously observed (Raffi et al., 2009). Although  
227 most of the coccoliths and nannoliths we observed in the slides as well in SEM are moderately  
228 to well preserved, etched and overgrown specimens coexist with fairly well preserved  
229 nannofossils in the same sample.

230 At Kharouba, nannofossil preservation is excellent throughout the section, and even the  
231 assemblages of the PETM interval include fragile coccoliths: delicate structures that are  
232 normally lacking in less well-preserved coeval material are present in Kharouba samples e.g.,  
233 holococcoliths (*Semihololithus*, *Holodiscolithus*, *Gladiolithus*) similarly to exceptional  
234 preserved sections of Tanzania (Bown 2005; Bown and Pearson, 2009).

235 At all the three localities, a typical and very rich late Paleocene and early Eocene calcareous  
236 nannofossil assemblage is recorded. The presence of *Discoaster multiradiatus* from the  
237 lowermost sample (- 0.13 m, at site 1209; -0.45 m, at site 1263; 0 m, at Kharouba) in the three  
238 sections allows us to recognize the NP9 zone of Martini (1971) and the CP8a subzone of Okada  
239 and Bukry (1980) (Fig. 2).

240 The first occurrence (FO) of *Tribrachiatus bramlettei* allows the recognition of the base of the  
241 NP10 at 0.02 m at 1209, at 0.97 m at Site 1263, and at 3 m at Kharouba. The FO of *Rhomboaster*  
242 *cuspis* or *R. calcitraba* allows the recognition of subzone CP8b (Okada and Bukry, 1980) in all  
243 the sections, namely at -0.03 m at 1209, at 0.12 m at 1263, and at 2.2 m at Kharouba.

244 At Kharouba, the FO of *Discoaster diastypus* is recorded at 13.2 m and it marks the CP9a of  
245 Okada and Bukry (1980). The section is dated to as CP9a from 13.2 to 28.2 m because of the  
246 absence of *Tribrachiatus contortus* until the uppermost studied sample (at 28.2 m). *D. diastypus*  
247 is absent at both 1263 and 1209, and the FO of this species is reported stratigraphically higher  
248 in these sections (Gibbs et al., 2006; Raffi et al., 2009).

249 The studied interval encompasses the zone CNP11 and CNE1 of Agnini et al. (2014) (Fig. 2).  
250 The last occurrence of *Fasciculithus richardii* group (0.17 m, site 1209; 0.97 m, site 1263; 13.2  
251 m, Kharouba) is recorded in the three sections across the recovery phase (Rohl et al., 2007) of  
252 the PETM.  
253 The cumulative graphs of the assemblage composition show as common trend the dominance  
254 of coccoliths over other nannofossils. However, *Fasciculithus* spp. are abundant at Sites 1209  
255 and 1263 in the pre-excursion interval and the core of the event while they are in low  
256 proportions at Kharouba. Also, *Zygrhablithus* spp. that are abundant starting from the core of  
257 the event and in the post-event interval at Sites 1209 and 1263 are rare at Kharouba. In this last  
258 section, small holococcoliths (*Gladiolithus flabellatus*, *Holodiscolithus* spp., *Semihololithus*  
259 *kanungoi*, *S. tentorium*, *S. biskayae*, *S. dimidius*) have small peaks just before and at the end of  
260 the PETM CIE (Fig. 2). The cumulative curves for the coccolith assemblage composition show  
261 a dominance in the three studied sites of *Coccolithus* spp. A major difference concerns  
262 *Ericsonia* spp., which is abundant at Site 1209 but absent or very rare at Site 1263 and  
263 Kharouba, respectively (Fig. 2).

264

### 265 **3.4 Absolute abundances and fluxes of calcareous nannofossils**

266 At Site 1209, absolute abundance decreases from  $4.5 \times 10^9$  to  $3.5 \times 10^9$  starting at -0.20 m up to  
267 the lithologic change corresponding to the PETM event (Fig. 4A). Minimum values are  
268 recorded ( $2 \times 10^9$ ) at 0.1 m. Values recover from 0.1 to 0.4 m up to  $3 \times 10^9$  but never attain pre-  
269 PETM records. One-way ANOVA test indicates that pre-PETM values are statistically different  
270 from the ones belonging to the core of the PETM and from those belonging to the recovery  
271 interval (Supplementary material). Fluxes measured as Nannofossil Accumulation Rates (NAR;  
272 number of specimens per square centimeter per year) overall match absolute abundance values.  
273 Overall values are very low, being in the range of 0 to  $0.05 \times 10^9$ .

274 At Site 1263 (Fig. 4B), absolute abundance is in the same order of magnitude as at Site 1209  
275 ( $E^9$ ) although values are slightly more fluctuating (Fig. 4). Values are about  $4 E^9$  in the  
276 interval below the PETM, then decrease down to  $\sim 2 E^9$  from - 0.2 m and stay low during core  
277 of the event (0.07 m to 0.57 m). A return to pre-PETM values is observed during the recovery  
278 phase (from 0.67 to 1.66). One-way ANOVA test indicates that pre-PETM values are  
279 statistically different than the ones belonging to the core of the PETM and from those belonging  
280 to the recovery interval (Supplementary material). NAR values well match absolute abundance.  
281 Overall values are quite low, being in the range of 0 to  $0.5 E^9$ .

282

283 At Kharouba absolute abundance values are lower respectively to ocean sites (Fig. 4C). Values  
284 are constant below the event from 0 to 3 m ( $0.1 E^9$ ). Despite a highly fluctuating trend, from  
285 3.2 to 28.2 m values show an almost 3-times increase. One-way ANOVA test indicates that  
286 values belonging to the recovery phase are statistically different with respect of those of pre-  
287 PETM and core of the event. NAR values are quite high compared to the oceanic sites, being  
288 in the range of 0 to  $50 E^9$ . NAR is relatively high in the pre-PETM interval, very low in the  
289 core of the event, and high again in the recovery interval and in the post-PETM. However, the  
290 sharp increase observed at  $\sim 7.5$ m might be an artifact due to the accumulation rate values used  
291 in this work.

292

### 293 **3.5 Principal Component Analysis**

294 Only species with a high sampling adequacy (that are recorded in a continuous way after their  
295 first occurrence) and having a loading higher than  $\pm 0.5$  on one of the extracted factors are  
296 considered here. Factors are regarded as significant only when they have a contribution to the  
297 variance higher than 10 %. First, we performed a PCA on the whole dataset from the three  
298 sections, then for each studied section separately.

299 Principal component analysis (PCA) performed on the whole dataset gives four main factors  
300 accounting for 79 % of total variance (Fig. 3A). The first factor (27 % of the variance) has an  
301 important positive loading of malformed *Discoaster*, *Rhomboaster* and *C. bownii*. The second  
302 factor (22 % of the variance) has strong negative loading of *Tribrachiatus bramlettei* opposed  
303 to *C. bownii*. The third factor (19 % of the variance) has strong loading of *Prinsius* and  
304 *Rhomboaster*. The fourth factor (11 % of the variance) has strong positive loading of  
305 *Thoracosphaera*.

306 For samples from Site 1209 when analyzed separately (Fig. 3B), three factors were extracted  
307 by PCA. The first one accounts 61 % of total variance and, similar to PCA applied to the whole  
308 dataset, has an important positive loading of malformed *Discoaster*, *Rhomboaster* and *C.*  
309 *bownii*. The second factor (13 % of total variance) has a strong loading for *T. bramlettei* like  
310 PCA applied to the whole dataset. The third factor (10 % of total variance) has a strong loading  
311 for *Thoracosphaera*, like the PC4 applied to the whole dataset.

312 At Site 1263 (Fig. 3C), PCA provides four factors. The first factor (43% of total variance) has  
313 a strong positive loading of malformed *Discoaster*, *Rhomboaster* and *C. bownii* like at Site  
314 1209, but at Site 1263 these are opposed to *Prinsius*. The second factor (43% of total variance)  
315 has a strong loading for *T. bramlettei* like at Site 1209 and PCA applied to the whole dataset,  
316 but here it is opposed to *Thoracosphaera*. At 1263, the third and fourth factor account both for  
317 10 % of total variance. PC4 has a strong positive loading for *Thoracosphaera* and compares to  
318 PC3 at both 1209 and Kharouba (see below). Here, *Thoracosphaera* is highly opposed to  
319 *Prinsius*.

320 The PCA at Kharouba (Fig. 3D) provides three factors representing 63 % of total variance. The  
321 second factor (22 % of total variance) has a strong (0.6) loading of malformed *Discoaster*,  
322 *Rhomboaster* and *C. bownii* like at both Site 1209 and 1263 but these are opposed to  
323 *Hornibrookina*, which is absent at both 1209 and 1263. The first factor (29 % of total variance)

324 has an important negative loading (-0.6) of *T. bramlettei* and it compares to the first PC factor  
325 at 1263 and 1209. Here, *T. bramlettei* it is opposed to *C. bownii* (like in PCA applied to the  
326 whole dataset) and *Prinsius*. The third factor displays negative (-0.5) loading for  
327 *Thoracosphaera*, but here this taxon is strongly opposed to *Hornibrookina*. This factor  
328 compares to PC3 of PCA applied to the whole dataset and of Site 1209, and to PC4 of Site  
329 1263.

330

### 331 **3.6 Stratigraphic changes in PCA scores**

332 PCA scores show some common stratigraphic features in the three sections, although the  
333 variance contribution of correlative factors is different in each section. Score values are  
334 generally more stable in open-ocean localities relatively to proximal ones. Namely, values are  
335 very stable at Site 1209, fluctuating at Site 1263, and highly fluctuating at Kharouba (Fig. 4A,  
336 B, C). In oceanic localities, we observe that the decrease of all factors begins well before the  
337 PETM and lithological change (Fig. 4A, B, C). At Kharouba, values are stable in the pre-PETM  
338 and highly fluctuate from the core of the PETM until the end of the recovery. It is worth noticing  
339 that even in the aftermath of the PETM values remain highly fluctuating at Kharouba.

340 The most striking similarity occurs between the first factor of oceanic sections (1209 and 1263)  
341 and the second one of Kharouba. These factors ~~begin to~~ display high positive values during the  
342 core of the PETM and persist at least until the end of the recovery phase (Fig. 4 A, B, C). At  
343 Site 1209, the first factor remains high until the last studied sample (0.42 m; Fig. 4A), while at  
344 Site 1263 and at Kharouba they decrease and are more fluctuating just above the end of the  
345 recovery phase (Fig. 4B, C). This is in perfect agreement with the fact that at Site 1209, the last  
346 studied sample belongs to the recovery phase (Fig. 4A), while at Site 1263 and at Kharouba the  
347 studied interval extends above the recovery phase. The most important taxa loading on these  
348 factors are *C. bownii*, malformed *Discoaster* and *Rhombaster*.

349 A decreasing trend is observed for PCA factors 2 at 1209 and 1263 and factor 1 at Kharouba  
350 respectively. Minimum values are recorded in the post-PETM. In all sections, the most  
351 important taxa loading on these factor is *T. bramlettei*. While at Site 1263 this taxon is strongly  
352 opposed to *Thoracosphaera* at Kharouba it is opposed to *Prinsius* and *C. bownii*.  
353 The third factor at Site 1209 and Kharouba and the fourth at 1263 present all high loading for  
354 *Thoracosphaera*. The stratigraphic pattern of this factor differs from open ocean localities to  
355 proximal ones. At Site 1209 is fluctuating in the pre-PETM but it is very stable during the core  
356 of the event, where it reaches highest values and is still very stable the recovery phase. At Site  
357 1263, albeit being less stable than at Site 1209, this factor displays higher values during the core  
358 of the event and is highly fluctuating in the post-PETM. Here, *Thoracosphaera* is strongly  
359 opposed to *Prinsius*. At Kharouba this factor is highly fluctuating. *Thoracosphaera* is here  
360 strongly opposed to *Hornibrookina*.

361

### 362 **3.7 SIMPER and cluster analysis used for comparisons between sites**

363 The similarities and dissimilarities between localities are evaluated by using multivariate  
364 analyses like SIMPER and cluster analysis applied to the three sections studied here and to six  
365 other sites used for comparison. The species accounting for the dissimilarities and their  
366 percentage contribution are also shown in the SIMPER graph. The percentages of similarity  
367 between localities are shown in the cluster analysis dendrogram. The results of SIMPER and  
368 cluster analysis show that *Coccolithus*, which is the most abundant species alongside with  
369 *Toweius*, is very abundant at Site 1263 as well as in the other localities, but at Site 690.  
370 Conversely, *Chiasmolithus* spp. are very abundant at Site 690. Also, *F. richardii* group is absent  
371 at Site 690, while it is very abundant at Site 1263 and other sites. This makes Site 690, which  
372 is located at high latitudes in the Southern Ocean, the most dissimilar location as far as  
373 calcareous nannofossils are concerned. *Ericsonia* spp. is very abundant at Site 1209, conversely

374 *Semihololithus*, which is interpreted as a holococcolith (Bown, 2005) is absent at Site 1209 (N  
375 Pacific gyre), but it is present only in proximal settings (TDP 14, Kharouba, Alamedilla). This  
376 peculiar assemblage composition makes Site 1209 very different from other localities. TDP 14,  
377 located in Tanzania, is also a quite peculiar site in which *Zygrhablithus* spp. is absent. This site  
378 is also known to be a sort of coccolith lagerstätt. The differences between Site 1263 and  
379 Kharouba section are mainly explained by the rarity of *Fasciculithus* spp. in this last location.  
380 Kharouba section is also different from Site 1260 because of the abundance of *Discoaster* spp.  
381 *Toweius* spp. is a very common taxon, its higher proportion at Kharouba explains the  
382 dissimilarity with respect to Alamedilla, in spite of the proximity between the two areas, and  
383 the similarity with respect to Atlantic sites, where *Toweius* is relatively more abundant than in  
384 Tethys or in the Pacific. The differences between Alamedilla (Spain) and Cicogna (Italy) are  
385 mainly explained by the more consistent presence of *Thoracosphaera* in this latter.

386

#### 387 **4. Discussion**

##### 388 **4.1 Preservation**

389 Before discussing trends in nannofossil assemblages, preservation issues potentially affecting  
390 assemblage composition have to be carefully considered. In fact, the PETM is classically  
391 considered as an event of shoaling of both lysocline and CCD inducing dissolution of delicate  
392 forms and, finally, diversity loss. The three studied sections were all deposited well above the  
393 CCD, and carbonate dissolution likely occurred a few centimeters around the lithological  
394 contact, as shown by a poor nannofossil preservation there also attested by previous studies  
395 (Bralower et al., 2014; Raffi et al., 2009). However, at Site 1209 nannofossil preservation is  
396 moderate to good unless the very thin interval across the LC, and slightly overgrowth  
397 *Discoaster* specimens are commonly observed in the studied samples, indicating that overall  
398 burial diagenesis was operating (Adelseck et al., 1973), but dissolution in the water column or



399 at the water/sediment interface were rather limited phenomena (unless around the LC interval).  
400 At Site 1263, poorly preserved coccoliths are observed in the same sample as pristinely  
401 preserved specimens of the same species. This peculiar pattern may indicate that a high-  
402 frequency (probably seasonal?) fluctuation in accumulation rate occurred at this location. In  
403 times of low accumulation rates, nannofossil assemblage was poorly preserved because of a  
404 longer exposure at the sediment/water interface (Schneidermann, 1977). Conversely, when  
405 sedimentary input was higher, nannofossils were rapidly buried and escaped to the corrosive  
406 action of waters at the sea-floor. At Kharouba, overall preservation is moderate-to-good likely  
407 due to the presence of clay minerals in marly lithologies, which inhibited corrosive water  
408 circulation more efficiently than in limestones. In fact, commonly the best preservation of  
409 nannofossils is recorded in marly lithologies (Thierstein and Roth, 1991). A common pattern in  
410 Kharouba samples is the presence of delicate holococcoliths, which also show abundance peaks  
411 just before and at the end of the PETM CIE. Holococcoliths would be easily dissolved if  
412 corrosive waters occurred or intense burial diagenesis. In synthesis, after carefully  
413 consideration of preservation issues, it seems likely that dissolution in the water column or at  
414 the water/sediment interface or within the sediment overall poorly impacted nannofossil  
415 assemblage composition, unless in discrete and stratigraphically circumscribed intervals.

416

#### 417 **4.2 Global *versus* local features**

418 The three studied sections were located in very different paleoceanographic settings during the  
419 late Paleocene and the early Eocene: while Sites 1209 and 1263 provide us with excellent  
420 records from tropical gyres in the Pacific and the Atlantic Ocean respectively (Bralower et al.,  
421 2002; Zachos et al., 2004), Kharouba section was located in a proximal setting in the southern  
422 Tethys (Karoui-Yaakoub et al., 2011). Although situated in a tropical gyre, Site 1263 was  
423 located on Walvis Ridge off Namibia coast. In the modern ocean, nutrient depleted tropical

424 gyres are characterized by very stable conditions (Milliman et al., 1993), contrarily to more  
425 unstable coastal localities, where the environmental parameters can undergo rapid changes.  
426 The ecology of calcareous nannofossils is inferred from their paleogeographic distributions;  
427 tropical species are thought to be adapted to warm-waters and high-latitude species to cold  
428 water, coastal species are adapted to eutrophic or unstable conditions and open-ocean species  
429 to oligotrophic environments (Haq and Loqmann, 1976; Gibbs et al., 2004; Bown and Pearson,  
430 2009). We discuss here similarities and differences in nannofossil assemblages between the  
431 three localities in order to track global *versus* local features in response to environmental  
432 perturbations across the PETM.

433 The most striking feature when comparing the three studied sites is that, although absolute  
434 abundances are in the same order of magnitude at Sites 1209 and 1263, and lower and quite  
435 steady at Kharouba, when taking fluxes into consideration the same trend is observed but with  
436 huge differences in the magnitude (Fig. 4). Kharouba records fluxes 3-to-4 orders of magnitude  
437 higher than at the oceanic sites. As general trend, both absolute abundance, fluxes and PCA  
438 scores show gradual and regular changes at Site 1209, are slightly more fluctuating at Site 1263  
439 and more irregularly fluctuating in the most coastal site (Kharouba), suggesting more unstable  
440 conditions there. Higher fluxes and more intensely fluctuating parameters at Kharouba may  
441 indicate that environmental conditions were more unstable there and that continent-delivered  
442 nutrients were in higher concentrations supporting a more vigorous nannoplankton  
443 productivity. Such an interpretation is further supported by the C-isotope trends, which although  
444 similarly record in the three sections the negative CIE related to PETM, display a very  
445 prominent offset. In fact at Site 1209, supposed to represent the most oligotrophic area, C-  
446 isotope values are comprised between 0 and 3 ‰, at Site 1263 between -1 and 2, and at  
447 Kharouba between -2.5 and 1. <sup>12</sup>C uptake by primary producers was therefore much more

448 efficient in the proximal Kharouba section than in the oceanic site and, especially, the Pacific  
449 gyre.

450 In all the sections, the change in absolute abundance and fluxes (i.e., the significant decrease)  
451 and in nannofossil assemblages as indicated by PCA factors slightly predates the onset of the  
452 PETM. This pattern may be linked to a differential diagenesis according to lithology. At Site  
453 1209, the lithology is constantly dominated by nannofossils oozes and CaCO<sub>3</sub> never goes below  
454 90 % even during the core of the PETM (Colosimo et al., 2006). This could explain why both  
455 absolute abundances, fluxes and PCA factors are very stable. At Site 1263, the onset of the  
456 PETM is marked by an increase in clay content and a decrease almost to 0 % in CaCO<sub>3</sub> (Zachos  
457 et al., 2005). However, no major shifts in absolute abundances, fluxes and PCA factors is  
458 observed, while both parameters start to vary before the PETM. At Kharouba, PCA values are  
459 very stable below the PETM, but during the PETM they become more fluctuating. PCA factors  
460 begin to fluctuate at 3.4 m, which is above the onset of the PETM, while fluxes are highly  
461 fluctuating from the recovery interval upsection. No lithological change is observed at  
462 Kharouba, since the lithology is always constituted by marls. Finally, different diagenetic or  
463 lithological conditions among the sections fail to explain increased fluctuating signals from  
464 open ocean localities to proximal ones.

465 In the three studied localities, environmental perturbations began before the PETM.-In the core  
466 of the PETM, an increase in factors characterized by strong loadings of malformed *Discoaster*,  
467 *Rhomboaster* and *C. bownii* is observed in all sections. Previous studies suggested that these  
468 taxa are restricted to the PETM interval and have an affinity for warm waters and oligotrophic  
469 environments (Bown and Pearson, 2009). Strongly oligotrophic conditions persisted in oceanic  
470 localities but in coastal environments, such as Kharouba, it is reasonable that increased nutrient  
471 influx and more humid conditions triggered more unstable conditions, as also suggested by  
472 mineralogical analyses (Karoui-Yaakoub et al., 2011). Bralower and Self-Trail (2016)

473 suggested that malformation of *Discoaster* across the PETM is due to a low saturation state of  
474 oceanic waters with respect to carbonates, proposing ocean acidification as the main cause.  
475 *Coccolithus bownii* has a peculiar morphology displaying a wider central area than other  
476 *Coccolithus* species and an overall smaller mass (see chapter 4). This feature would also be  
477 compatible with a low ocean saturation state of oceanic waters, but this remains highly  
478 speculative. Despite the ecological affinity of malformed *Discoaster*, *Rhombaster* and *C.*  
479 *bownii* cannot be unequivocally discerned because there are extinct taxa with no living  
480 counterpart, PCA results indicate a global pattern across all the Oceans and in disparate  
481 environmental conditions.

482 PC3 at 1209, PC4 at 1263 and PC3 at Kharouba are characterized by strong loadings of  
483 *Thoracosphaera*, a taxon adapted to nutrient-depleted environments in modern oceans (Vink et  
484 al., 2002). PC3 is very stable at Site 1209, particularly from the core of the PETM to the  
485 recovery (Fig. 4A) and this suggests very stable oligotrophic conditions across the event, in  
486 agreement to previous studies (Gibbs et al., 2006). At Site 1263, PC3 is more fluctuating and  
487 *Thoracosphaera* is opposed to *Prinsius* (Fig. 4B), a cold-water taxon adapted to eutrophic  
488 environments (Haq and Loqmann, 1976; Bown and Pearson, 2009; Self-Trail et al., 2012).

489 Previous studies showed that during the PETM, cold-water and eutrophic taxa (*Prinsius*,  
490 *Hoornibrookina*) are replaced by warm waters and oligotrophic species (*Thoracosphaera*, *C.*  
491 *bownii*; Gibbs et al., 2006; Self-Trail et al., 2012; Bown and Pearson, 2009). A direct  
492 temperature control explaining the response of *Prinsius* to the PETM is unlikely at both 1263  
493 and Kharouba, given that both localities were located in low-latitude contexts (Zachos et al.,  
494 2004; Karoui-Yaakoub et al., 2011). The strong opposition between oligotrophic-adapted taxa  
495 and eutrophic-ones suggests fluctuating nutrient conditions in these settings, that due to their  
496 proximity to emerged lands, were more prone to record shifting environmental conditions than  
497 Site 1209 situated in an oligotrophic gyre. Peaks in taxa indicative of cool and high-fertility

498 conditions suggest a relatively shallow nutricline and well mixed surface waters; conversely,  
499 peaks of taxa indicative of warm and low-fertility waters suggest a relatively deep nutricline  
500 and more stratified waters (Vink et al., 2002). Site 1263, shifted from oligotrophic to under  
501 more eutrophic conditions in the course of Paleogene, favoring the development of meso-  
502 eutrophic taxa (Bordiga et al., 2015). Then, alternating peaks of *Prinsius* and *Thoracosphaera*  
503 (PC4) suggest more unstable conditions compared to Site 1209 with alternating stratified and  
504 mixed waters.

505 At Kharouba, environmental conditions were even more unstable as indicated by higher  
506 fluxes, highly fluctuating absolute abundances and PCA factors (Fig. 4C). Here,  
507 *Thoracosphaera* is highly opposed to *Hornibrookina*. The similarity of their construction to  
508 specimens of the Cretaceous and Tertiary genus *Biscutum*, and their first occurrence  
509 immediately following the Cretaceous/Paleogene boundary, suggests that *Hornibrookina* may  
510 have evolved from *Biscutum*, a genus long thought to be indicative of high paleoproductivity  
511 (Watkins, 1989; Self-Trail et al., 2012). Thus, high fluctuating values of PC3 at Kharouba  
512 further support unstable conditions in this locality. In agreement to mineralogical analyses  
513 (Karoui-Yaakoub et al., 2011). Increased continental weathering due to more humid conditions  
514 favored eutrophic taxa, while during arid climatic phases (and reduced riverine nutrient  
515 discharge) oligotrophic taxa thrive.

516 PC2 at Site 1209 and 1263 and PC1 at Kharouba have strong loadings of *T. bramlettei*, pointing  
517 to a global trend across all oceans and different paleoenvironments. At Site 1263, PC2 markedly  
518 decreases at 0.97m, in correspondence of the appearance of *T. bramlettei* and at Kharouba PC1  
519 is constant below the appearance of *T. bramlettei* and starts to decrease at 3 m. Such an  
520 observation supports an evolutionary control on this factor. Even if at Site 1263 *T. bramlettei*  
521 is opposed to *Thoracosphaera* and at Kharouba it is opposed to *Prinsius*, the fact that at both  
522 localities these factors start to decrease in correspondence of the appearance of *T. bramlettei*

523 means that this is related to the emergence of the genus *Tribrachiatus*, that will thereafter evolve  
524 in the lower Eocene.

525

### 526 **4.3 Comparison with other sites**

527 The biogeographic patterns of Neogene calcareous nannofossils was already explored by Haq  
528 and Lohmann (1976) by using quantitative methods, namely Q-mode Varimax Factor and  
529 Oblique Factor Analyses. In this account, a quantification of similarities and dissimilarities of  
530 the sites we studied with respect to already published nannofossil data from various oceanic  
531 sites and proximal seas is attempted by using multivariate analyses. According to calcareous  
532 nannofossil assemblages, the most dissimilar section is Site 690 located in Antarctic waters.  
533 This pattern is also reported for modern assemblages that show a reduced diversity and a  
534 dominance of opportunistic species in sub-polar waters, where the limiting factors are the low-  
535 temperature and poor light availability in winter season, while surface waters are enriched in  
536 nutrients (Winter, 1994). Another locality which is very different from all the other settings is  
537 the TDP 14 core, located in Tanzania. This corresponds to a nannofossil lagerstätte, showing  
538 exceptionally well-preserved coccolith structures (Bown and Pearson, 2009). TDP 14 has some  
539 features typical of equatorial sites (e.g., the absence of *Zygrhablithus*) but, because of  
540 pronounced differences concerning the overall assemblage composition, this locality might  
541 correspond to a cul-de-sac, poorly connected with the open-ocean. Similarly, Alamedilla  
542 (Spain) and Cicogna (Italy) display nannofossil assemblages which are markedly different from  
543 the other oceanic sites, probably because of their proximal position with respect to emerged  
544 lands, and location in very restricted stretch of sea. Also, Site 1209 is fairly different from all  
545 the other sites, and this is probably due to its position within an oceanic gyre. There,  
546 oligotrophic conditions dominated and the gyre probably represented a physical barrier  
547 preventing mixing of waters with the rest of Pacific Ocean. Interestingly, Kharouba shows less

548 pronounced dissimilarities with Atlantic sites, which were located relatively close to emerged  
549 lands (namely, South Dover core, Sites 1260 and 1263), than with other Tethys settings (such  
550 as Alamedilla and Cicogna) in spite of geographic proximity. This pattern attests for the  
551 existence of effective oceanic connections between the south-western part of Tethys, where  
552 Kharouba is located, and the Atlantic Ocean. These novel results show that oceanic connections  
553 and surface circulation played a major control on upper Paleocene-lower Eocene calcareous  
554 nannofossil assemblage composition.

555

#### 556 **4.4 Comparison with other proxies**

557 The negative C-isotopes excursion at the PETM, despite its origin is still matter of debate  
558 (Dickens et al., 1995; Gutjahr et al., 2017), has been previously globally recorded and allows  
559 us to produce effective correlation of open ocean and proximal sections across different  
560 localities (Fig. 6; modified after Menini et al., submitted). Irrespectively of its source, the input  
561 of isotopically light carbon led to an increase of 5-8° C in seawater temperatures, as indicated  
562 by oxygen isotopes measured in planktonic and benthic foraminifera. Other  
563 paleothermometers such as the Mg/Ca ratio (Zachos et al., 2003; Penman et al., 2014) and  
564 TEX<sup>86</sup> (Suijs et al., 2007) confirm this pattern. Ultimately, excess *p*CO<sub>2</sub> lead to ocean  
565 acidification, as shown by boron isotopes (Penman et al., 2014; Penman et al., 2014; Babila et  
566 al., 2018). Enhanced continental weathering is thought to be the principal negative feedback  
567 responsible for the removal of the excess in *p*CO<sub>2</sub> and this is supported by both experimental  
568 data (Osmium isotopes; Ravizza et al., 2001) and models (Zeebe et al., 2012). The PETM is  
569 associated to perturbations in all the major geochemical cycles, and this prominently impacted  
570 on the response of marine ecosystems. All microfossils groups were affected by environmental  
571 perturbations induced by the PETM: calcareous nannofossils, living in the mixed-layer photic  
572 zone (uppermost 200 m in oceanic environment or lesser) were very sensitive to these changes.



573 In open-ocean localities (Fig. 6) dramatic decreases in absolute abundances and PCA are most  
574 probably related to reduced nutrient supply in the photic zone as a consequence of warming-  
575 driven oligotrophy (see above). Cold-water taxa decreased in abundance during the event and  
576 warm-water ones increased (Bralower et al., 2002; Gibbs et al., 2006; Self-Trail et al., 2012).  
577 However, some taxa (malformed *Discoaster*, *Rhombaster*, *Thoracosphaera*) took advantage  
578 of these stressful conditions in all localities and at all latitudes. In proximal localities,  
579 nannofossils assemblages suggest highly fluctuating trophic conditions from the PETM until  
580 the recovery (Fig. 6) and absolute abundances increased. Meso-eutrophic species flourished in  
581 times of enhanced nutrient discharge into the basins, in agreement with enhanced continental  
582 weathering during the event (Ravizza et al., 2001).

583 The environmental perturbations occurring along with the C-isotopes excursion of the PETM  
584 also affected other organisms, such as planktonic and benthic foraminifera and dinoflagellates.  
585 At both low and high latitudes, planktonic foraminifer assemblages shifted from cold-water  
586 taxa before the PETM to warm-water ones during the event, returning to pre-event conditions  
587 during the recovery phase (Clay Kelly et al., 2002; Petrizzo, 2007). Similar to nannofossils, the  
588 rapid diversification of planktonic foraminifer excursion taxa (Clay Kelly et al., 1996, 1998) is  
589 recorded in tropical localities, but these taxa are absent at high latitudes. Benthic foraminifera  
590 suffered a dramatic excursion at the base of the PETM and this is not only due to reduced  
591 carbonate preservation (Alegret et al., 2009). Another prominent example of biotic change  
592 associated with the onset of the PETM is recorded along continental margins, where sediment  
593 sequences from all latitudes contain high abundances of dinoflagellate cysts (dinocysts)  
594 belonging to the subtropical genus *Apectodinium* (e.g., Sluijs et al., 2006; Crouch et al., 2013).  
595 Previous studies have shown that a basic requirement for *Apectodinium* acme was high-  
596 temperature conditions, but it is also reasonably associated to meso-eutrophic conditions in  
597 proximal localities (Sluijs et al., 2007). However, our nannofossil data do not support this

598 hypothesis, namely reduced nannofossil fluxes during the event suggest decreased nannofossil  
599 production, while the flux increase in the recovery phase suggests enhanced nannofossil  
600 production and thereby nutrient supply in the aftermath of the PETM. However, pulses of  
601 eutrophic taxa, such as *Hornibrookina* and *Prinsius*, are observed in the proximal Kharouba  
602 section, suggesting that oligotrophy was sporadically interrupted because of continent-derived  
603 nutrient inputs. Previous studies have brought evidences that environmental perturbations  
604 preceded the light carbon injection (Sluijs et al., 2007; Frieling et al., 2019) and this is supported  
605 by our data, albeit the causes of early warming remain still uncertain.

606

## 607 **5. Conclusions**

608

609 The high-resolution study of calcareous nannofossil assemblages at three sections located in  
610 different paleoceanographic settings allowed us to track regional *versus* global features in  
611 response to the Paleocene Eocene Thermal Maximum. In both oceanic tropical oceanic  
612 localities from the Pacific and Atlantic oceans (Sites 120 and 1263) and in proximal settings  
613 Kharouba we show that changes in calcareous nannofossil assemblages predate the carbon  
614 isotopes excursion. PCA shows that the PETM interval is characterized by strong loadings of  
615 malformed *Discoaster*, *Rhomboaster* and *C. bownii* (excursion taxa). Despite of a global  
616 fingerprint, the three sections present some peculiarities as far as nannofossil assemblages are  
617 concerned and these are related to different paleoceanographic contexts.

618 At Site 1209, in the middle of a tropical gyre and far from emerged lands, very stable  
619 oligotrophic conditions characterize the PETM, as indicated by the consistent occurrence of  
620 *Thoracosphaera*, and the very low nannofossil fluxes. This locality was the less affected by  
621 environmental changes induced by the event and overall low productivity conditions are  
622 attested further by the positive offset of C-isotope values across the studied interval. At Site

623 1263, despite of the analogies with Site 1209, nannofossil assemblages record less stable  
624 conditions than at Site 1209. The proximity of emerged lands (Zachos et al., 2004) and the  
625 influence of upwelling (Bordiga et al., 2015) may explain the fluctuating trend from  
626 oligotrophic to eutrophic conditions at this site. At Kharouba, a proximal Tethys section,  
627 nannofossils assemblages indicate strongly fluctuating environments, namely an alternation of  
628 phases of stratification and mixing of surface waters. At this locality, PCA shows a strong  
629 opposition of eutrophic (*Hoornibrookina*) to oligotrophic (*Thoracosphaera*) taxa. This locality  
630 was also the most productive, as shown by very high nannofossil fluxes and negative overall  
631 offset of C-isotope values. Sporadic increased nutrient input also occurred during the PETM,  
632 as also pointed out by osmium isotopes (Ravizza et al., 2001), and modulated the response of  
633 nannofossils in proximal localities, which are more easily affected by changes in nutrient  
634 discharge because of their proximity to emerged lands.

635 An increase in nannofossil fluxes in all the studied localities during the recovery phase of the  
636 event suggests that primary productivity returned to pre-event levels. Recent studies on Barium  
637 isotopes evidenced that, in oceanic localities, export production either remained unchanged or  
638 decreased during the PETM (Bridgestock et al., 2019), before increasing during the recovery  
639 phase and this is coherent with our results. With this regard, calcareous nannofossil production,  
640 along with enhanced continental weathering and, to a more limited degree, increased organic  
641 carbon production and burial in shelf areas, likely contributed to CO<sub>2</sub> drawdown and ultimately  
642 climatic recovery in the aftermath of the PETM.

643

644

645 Figures captions

646

647 Figure 1. Fig. 1. Location of the three studied sections on a paleogeographic map at 56 Ma :  
648 (<http://www.odsn.de/odsn/services/paleomap/paleomap.html>): Kharouba section (Tunisia),  
649 Site 1209 (Shatsky Rise, Tropical Pacific), and Site 1263 (Walvis Ridge, South Eastern  
650 Atlantic). Location of the sites used for comparison is also shown: Site 690 (Southern Ocean)  
651 Site 1260 (Equatorial Atlantic), SDB (New Jersey), TDP 14 (Tanzania), Cicogna (North Italy),  
652 Alamedilla (Spain).

653

654 Figure 2. Cumulative graphic of main nannofossil genus for the three studied sections in  
655 function of depth. Horizontal scale is the same but vertical one is different because of important  
656 differences in the thickness between oceanic sites and Kharouba. Also, nannofossil  
657 biostratigraphy and lithostratigraphic column. Total assemblage composition (coccoliths,  
658 nannoliths) and coccolith assemblages for the three sections.

659

660 Figure 3. Principal components analysis loading plots. Only species with a high sampling  
661 adequacy and having a loading higher than  $\pm 0.5$  on one of the extracted factors are considered  
662 here. Factors are regarded as significant only when they have a contribution to the variance  
663 higher than 10 %. A; loading plot resulting from the PCA performed on the three studied  
664 sections.,B; loading plot resulting from the PCA performed on ODP Site 1209, C; ODP Site  
665 1263, D; Kharouba. Error bars represent lower and upper limits for 95% confidence intervals,  
666 using 9999 bootstrap replicates.

667

668 Figure 4. Stratigraphical evolution of PCA scores, absolute abundance (black) and NAR (grey)  
669 in function of depth against nannofossil biostratigraphy and carbon isotopes curve ( $\delta^{13}\text{C}$ ) in the  
670 three studied sections. Note that the vertical scale is different from a section to another. The  
671 correlative factors, i.e., those on which the same taxa load, are shown in the same order for the

672 three sections, irrespective of their variance values. The species with important loadings on the  
673 different factorial axes are reported.

674

675 Figure 5. Cluster analysis (right) and SIMPER analysis (left) applied on the three studied  
676 sections (Site 1209, 1263 and Kharouba) and 6 other sections that provide excellent  
677 stratigraphic records of the PETM calcareous nannofossils (See text for further details).

678

679 Figure 6. Synthesis of the main geochemical and biotic events occurring across the PETM  
680 relative to the  $\delta^{13}\text{C}$  bulk carbonate record (Alamedilla (red) Lu al. 1996, ODP 690 (grey) Bains  
681 et al. 1999, ODP 1209 (orange) Penman et al. 2014, ODP 1263 (light blue) Zachos et al. 2005,  
682 ODP 1260 (green) Mutterlose et al. 2007, Kharouba (brown), This work, South Dover (violet)  
683 Self Trail et al. 2012, Cicogna (black) Agnini et al. 2016). For TDP 14 (pink) we used  $\delta^{13}\text{C}_{\text{n-alkane}}$   
684 alkane record (isotopes of C-25, C-27, C-29 and C-31 alkanes), since  $\delta^{13}\text{C}_{\text{bulk carb}}$  did not  
685 provide satisfying results (Bown and Pearson 2009, Aze et al. 2014). Tie-points of the  
686  $\delta^{13}\text{C}_{\text{bulk carb}}$  at Site 690 as defined by Zachos et al. (2005) and Röhl et al. (2007) from -A to  
687 H are shown. Envelope curve of oxygen isotope records (extracted from the database of Cramer  
688 et al., 2009) from individual cores from the North Atlantic (ODP1051), and Southern Oceans  
689 (ODP690). Osmium isotopes record after Ravizza et al., 2001 at DSP Site 541. Planctonic  
690 foraminifera data after Petrizzo et al., 2008 (warm water=*Morozovella* spp., cold  
691 water=*Subbotina* spp.). Dynocists data after Sluijs et al., 2006. See text for details.

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## **Supplementary data**

### **3.4 Relative and absolute abundances of Nannofossils**

At Kharouba, placolith assemblages compose most of the assemblage: *Toweius* (30-50 %) and *Coccolithus* (30-40 %) are the most abundant genus. *Toweius serotinus* is particularly abundant from 5.3 to 7.6 m (15 %), across the recovery phase of the PETM. During the core of the PETM (from 0.9 m to 2.5 m) we observe increased abundances of *Hornibrookina* spp., *Coccolithus bownii*, *Discoaster araneus* and *D. anartios* and *Rhomboaster*. *Prinsius* spp. attain up 10 % in relative abundance before the event and become more scattered up in the section. *Cruciplacolithus* and *Chiasmolithus* never overcome 5 % in abundance. Nannoliths are mainly composed by *Fasciculithus* (10%), *Discoaster* (10 %) and *Sphenolithus* (10 %). *Fasciculithus* relative abundance drastically decreases to 1% at 14 m. *Zygrhablithus bijugatus* never overcomes 10 % but it increases up in the section starting at 12 m A peak (15 %) is observed at 15.2 m.

Absolute abundance of all genus is constant below the PETM for all genus values increase during the event at 3.2 m and remain high through the section until the last studied samples

721 (28.2 m). It is worth noticing that values decrease from 2.2 m to 3 m but this is not statistically  
722 significant, since one-way ANOVA indicates that only values belonging to the recovery interval  
723 are statistically different from the ones of the core and from the ones of the pre-PETM (Table  
724 S1).

725 *Coccolithus* and *Toweius* are the most abundant genera and account up to half of total absolute  
726 abundance. Values of each genus are stable below the PETM ( $60 \times 10^6$ ) and display a two-times  
727 increase at 3.2 m.

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729 *Coccolithus* abundance is constant ( $60 \times 10^6$ ) below the PETM. After the PETM values decrease to.  
730 *Prinsius* absolute abundance is higher below the PETM ( $20 \times 10^6$ ) until 3.2 m and then it  
731 gradually decreases.

732 Absolute abundance of *Discoaster* is constant from 0 to 3 m and from ( $20 \times 10^6$ ) and it displays  
733 a two-fold increase ( $40 \times 10^6$ ) at 3.2 m until the last studied sample.

734 Despite two peaks at 12.3 and 28.2 m, *Sphenolithus* absolute abundance is constant through  
735 the section ( $20 \times 10^6$ ). *Fasciculithus* absolute abundance are low at Kharouba in comparison to  
736 ODP 1209 and 1263. Maximum values are recorded during the core of the event at 3.4 m and  
737 then a gradual decrease is observed from 3.4 m to 14.2 m, where values drastically decrease  
738 to  $2 \times 10^6$  and will never recover.

739 At Site 1263 *Coccolithus* dominates the placolith-coccolith part of the assemblage (30-40 %)  
740 as well as *Toweius* (25 %). Small *Ericsonia* referred to as *E. orbis* (Bown et al., 2016) are  
741 present but never reach high abundance like at Site 1209. *Prinsius* are consistently present and  
742 account up to 2% of total assemblage. The rest of the assemblage is dominated by *Fasciculithus*  
743 (40 % to 5%), *Discoaster* (10 %) and *Sphenolithus* (10%). During the core of the PETM (from  
744 0 m to 0.47 m) we observe increased abundances of *Coccolithus bownii*, *Discoaster araneus* and  
745 *D. anartios* and *Rhomboaster*.



746 *Zygrhablithus* rapidly increases from 1 to 30 % at 0.57 m. At Site 1263 *Fasciculithus* increase  
747 in relative abundance from 10 % to 40 % from -0.45 m to 0.67m  
748 Afterwards (0.67 m), *Fasciculithus* decreases from 40 % to 5%, as previously observed (Raffi  
749 and De Bernardi, 2008; Raffi et al., 2009).

750 *Coccolithus* is the most abundant genus and it accounts up to half of total absolute abundance  
751 (Fig. 3) and values are stable across the PETM. *Toweius* is the second placolith most abundant  
752 genus at Site 1263 and neither displays changing in abundance. *Fasciculithus* absolute  
753 abundance increases from -0.45 m to 0.67 m, where they reach maximum values.

754 At the same time, *Zygrhablithus* spp. rapidly increases. Similarly, to Site 1209 *Sphenolithus*  
755 and *Discoaster* absolute abundance remain constant all through the event.

756 At site 1209, Placolith assemblages are dominated by *Coccolithus* (30-40 %) and *Ericsonia* (20  
757 %) accompanied by lower abundances of *Toweius* (10-15 %). *Ericsonia* rapidly decreases from  
758 40% to 10% at 0 cm above the PETM. During the core of the PETM (from -0.03 m to 0.07 m)  
759 we observe increased abundances of *Coccolithus bownii*, *Discoaster araneus* and *D. anartios*  
760 and *Rhomboaster*.

761 The rest of the assemblage is composed by *Fasciculithus* (40 % to 5%), *Discoaster* (10 %) and  
762 *Sphenolithus* (10%). *Zygrhablithus* rapidly increases from 1 to 20 % at 7 cm above the  
763 lithological contact. In parallel, *Fasciculithus* decreases from 40 % to 10%, as previously  
764 observed (Gibbs et al., 2006b).

765 *Coccolithus* is the most abundant genus and it accounts up to half of total absolute abundance  
766 (Fig. 3). Values are generally stable across the PETM except at the onset of the event, where  
767 absolute abundance show a distinct two-fold peak. *Ericsonia* is very abundant below the PETM  
768 but rapidly decreases starting from the onset of the event. Similarly, *Fasciculithus* decrease  
769 from the pre-PETM to the recovery phase but this is far less spectacular than the drastic decrease

770 in relative abundance. At the same time, *Zygrhablithus* spp. rapidly increase. Interestingly,  
771 *Sphenolithus* and *Discoaster* absolute abundance remain constant all through the event.

## References

- Agnini, C., Fornaciari, E., Raffi, I., Catanzariti, R., Pälike, H., Backman, J., Rio, D., 2014. Biozonation and biochronology of Paleogene calcareous nannofossils from low and middle latitudes. *Newsletters on Stratigraphy* 47, 131–181
- Alegret, L., Ortiz, S., and Molina, E., 2009. Extinction and recovery of benthic foraminifera across the Paleocene–Eocene Thermal Maximum at the Alamedilla section (Southern Spain). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 279(3–4), 186–200.
- Babila, T.L., Penman, D.E., Hönisch, B., Kelly, D.C., Bralower, T.J., Rosenthal, Y., Zachos, J.C., 2018. Capturing the global signature of surface ocean acidification during the Palaeocene–Eocene Thermal Maximum. *Philosophical Transactions A* 376.
- Bains, S., Norris, R. D., Cordfield, R. M., Faul, K. L., 2000. Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback. *Nature* 407, 171–174.
- Beaufort L., Barbarin, N., Gally Y., 2014. Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature protocols* 9(3), 633–642.
- Beaufort, L., Heussner, S., 2001. Seasonal dynamics of calcareous nannoplankton on a West European continental margin: The Bay of Biscay. *Marine Micropaleontology* 43(1–2), 27–55.
- Bown, P. R., 2005. Palaeogene calcareous nannofossils from the Kilwa and Lindi areas of coastal Tanzania (Tanzania Drilling Project 2003-4). *J. Nannoplankton Res.* 27 (1), 2005, 21–95.

- Bown, P. R., Pearson, P., 2009. Calcareous plankton evolution and the Paleocene/Eocene thermal maximum event: New evidence from Tanzania. *Marine Micropaleontology* 71, 60–70.
- Bralower, T., Clay Kelly, D., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L., Smith, G. S., 2014. Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum. *Earth and Planetary Sciences Letters* 401, 70–82.
- Bralower, T.J., 2002. Evidence of surface water oligotrophy during the Paleocene–Eocene Thermal Maximum: nanofossil assemblage data from Ocean Drilling Program Site 690 Maud Rise, Weddell Sea. *Paleoceanography* 17, 1–13.
- Bralower, T.J., Mutterlose, J., 1995. Calcareous nanofossil biostratigraphy of ODP Site 865, Allison Guyot, Central Pacific Ocean: a tropical Paleogene reference section. In: Winterer, E.L., Sager, W.W., Firth, J.V. (Eds.), *Proceedings of the Ocean Drilling Program. Scientific Results* 143, 31– 72.
- Bralower, T.J., Premoli Silva, I., Malone, M.J., et al., 2002. *Proc. ODP, Initial Reports.*, 198: College Station, TX (Ocean Drilling Program).
- Bralower, T.J., Self-Trail, J.M., 2016. Nannoplankton malformation during the Paleocene-Eocene Thermal Maximum and its paleoecological and paleoceanographic significance. *Paleoceanography* 31, 1423–1439.
- Brand, W. A., Coplen, T.B., Vogl, J., Rosner, M., Prohaska, T., 2014. Assessment of international reference materials for isotope-ratio analysis. *Pure and Applied Chemistry* 8866, 425–467.
- Colosimo, A.B., Bralower, T.J., Zachos, J.C., 2006. Evidence for lysocline shoaling at the Paleocene/Eocene thermal maximum on Shatsky rise, northwest Pacific. *Proceeding of the Ocean Drilling Program. Scientific Results* 198, 1–36.

- Crouch, E. M., Dickens, G. R., Brinkhuis, H., Aubry, M. P., Hollis, C. J., Rogers, K. M., and Visscher, H., 2003. The Apectodinium acme and terrestrial discharge during the Paleocene–Eocene thermal maximum: new palynological, geochemical and calcareous nannoplankton observations at Tawanui, New Zealand. *Palaeogeography, Palaeoclimatology, Palaeoecology* 194(4), 387–403.
- Crouch, E., Heilmann-Clausen, C., Brinkhuis H., Morgans H. E.G., Rogers K.M., Egger, H., Schmitz, B., 2001. Global dinoflagellate event associated with the late Paleocene thermal maximum. *Geology* 29(4), 315–318.
- Dickens, G.R., Castillo, M.M., Walker, J.G.C., 1997. A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate, *Geology* 25, 259–262.
- Dickens, G.R., O'Neil, J.R., Rea, D.K., Owen, R.M., 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* 10, 965–971
- Dickson, A.J., Cohen, A.S., Coe, A.L., Davies, M., Shcherbinina, E.A., Gavrillov, Y.O., 2015. Evidence for weathering and volcanism during the PETM from Arctic Ocean and Peri-Tethys osmium isotope records. *Palaeogeography, Palaeoclimatology, Palaeoecology* 438, 300–307.
- Frieling, J., Peterse, F., Lunt, D. J., Bohaty, S. M., Sinninghe Damsté, J. S., Reichert, G. J., Sluijs, A., 2019. Widespread warming before and elevated barium burial during the Paleocene-Eocene Thermal Maximum: Evidence for methane hydrate release ?. *Paleoceanography and paleoclimatology*, 34(4), 546–566.
- Gibbs, S., Shackleton, N., Young, J., 2004. Orbitally forced climate signals in mid-Pliocene nannofossil assemblages. *Marine Micropaleontology* 51(1–2), 39–56.

- Gibbs, S.J., Bralower, T.J., Bown, P.R., Zachos, J.C., Bybell, L.M., 2006. Shelf and open-ocean calcareous phytoplankton assemblages across the Paleocene–Eocene thermal maximum: implication for global productivity gradients. *Geology* 34 (4), 233–236.
- Hammer, Ø., Harper, D. A., Ryan, P. D., 2001. PAST: Paleontological statistics software package for education and data analysis. *Palaeontologia electronica*, 4(1), 9.
- Haq, B. U., Loqmann G. P., 1976. Early Cenozoic calcareous nannoplankton biogeography of the Atlantic ocean. *Marine Micropaleontology* 1, 119–194.
- Karoui-Yaakoub, N., M'barek-Jemaï, M. B., Cherni, R., 2011. Le passage Paléocène/Eocène au nord de la Tunisie (Jebel Kharouba): foraminifères planctoniques, minéralogie et environnement de dépôt. *Revue de Paléobiologie* 30(1), 105–121.
- Kelly, D. C., 2002. Response of Antarctic (ODP Site 690) planktonic foraminifera to the Paleocene–Eocene thermal maximum: faunal evidence for ocean/climate change. *Paleoceanography* 17(4), 23–1.
- Kelly, D.C., Bralower, T., J., Zachos, J.C., 1998. Evolutionary consequences of the latest Paleocene thermal maximum for tropical planktonic foraminifera. *Palaeogeography, Palaeoclimatology, Palaeoecology* 141, 139–161.
- Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* 353, 225–229.
- Martini, E., 1971. Standard Tertiary and Quaternary calcareous nannoplankton zonation. In: Farinacci, A., *Proceedings of the 2nd International Conference on Planktonic Microfossils* 2, 739–785.
- Milliman, J. D., 1993. Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state. *Global geochemical cycles* 7(4), 927–957.

- Okada, H., Bukry, K., 1980. Supplementary modification and introduction of code numbers to the low-latitude coccolith biostratigraphic zonation. *Marine Micropaleontology* 5, 321–325.
- Penman, D.E., Hönisch, B., Zeebe, R.E., Thomas, E., Zachos, J.C., 2014. Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* 29, 357–369.
- Penman, D.E., Turner, S.K., Sexton, P.F., Norris, R.D., Dickson, A.J., Boulila, S., Ridgwell, A., Zeebe, R.E., Zachos, J.C., Cameron, A., Westerhold, T., Röhl, U., 2016. An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene Thermal Maximum. *Nature Geoscience* 9, 575–580.
- Raffi, I., Backman, J., Zachos, J.C., Sluijs, A., 2009. The response of calcareous nannofossil assemblages to the Paleocene Eocene Thermal Maximum at the Walvis Ridge in the South Atlantic. *Marine Micropaleontology* 70, 201–212.
- Ravizza G., Norris R. N., Blusztajn J., Aubry M.P., 2001. An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering. *Paleoceanography and Paleoclimatology* 16(2), 155–163
- Révész, K., Landwehr, J.M., 2002.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic composition of  $\text{CaCO}_3$  measured by continuous flow isotope ratio mass spectrometry: statistical evaluation and verification by application to Devils Hole core DH-11 calcite. *Rapid Communications in Mass Spectrometry* 16, 2102–2114.
- Röhl, U., L. J. Abrams, 2000, High-resolution, downhole and non-destructive core measurements from Sites 999 and 1001 in the Caribbean Sea: Application to the late Paleocene thermal maximum, *Proceedings of the Ocean Drilling Program Sci. Results* 165, 191–203.



- Röhl, U., Westerhold, T., Bralower, T.J., Zachos, J.C., 2007. On the duration of the Paleocene–Eocene thermal maximum (PETM). *Geochemistry, Geophysics, Geosystems* 8
- Schneidermann, N., 1977. Selective dissolution of recent coccoliths in the Atlantic Ocean. In: Ramsay, A.T.S. (Ed.), *Oceanic Micropaleontology* 2, 1009–1053.
- Self-Trail, J. M., Powars, D. S., Watkins, D. K., Wandless, G., 2012. Calcareous nanofossil assemblage changes across the Paleocene-Eocene thermal maximum: Evidence from a shelf setting, *Marine Micropaleontology* 92–93, 61–80.
- Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S. M., John, C. M., Zachos, J. C. et al., 2007. Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature*, 450(7173), 1218–1221.
- Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H., Damsté, J. S. S., et al., 2006. Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature*, 441(7093), 610–613.
- Stoll, H. M., Bains, S., 2003. Coccolith Sr/Ca records of productivity during the Paleocene-Eocene thermal maximum from the Weddell Sea. *Paleoceanography* 18(2), 1–11.
- Stoll, H. M., Shimizu N., Archer D., Ziveri P., 2007. Coccolithophore productivity response to greenhouse event of the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 258, 192–206.
- Stoll, H. M., Shimizu N., Arevalos A., Matell N., Banasiak A, Zeren S., 2007. Insights on coccolith chemistry from a new ion probe method for analysis of individually picked coccoliths. *Geochemistry, Geophysics, Geosystems* 8 (6), 1–8.

- Takeda, K., Kaiho, K., 2007. Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 251, 175–197.
- Thierstein, H.R., Roth, P.H., 1991. Stable isotopic and carbonate cyclicality in Lower Cretaceous deep-sea sediments: Dominance of diagenetic effects. *Marine Geology* 97, 1–34.
- Thomas, E., Shackleton, N.J., 1996. The latest Paleocene benthic foraminiferal extinction and stable isotope anomalies. In: Knox, R.O., Corfield, R.M., Dunay, R.E. *Correlation of the Early Paleogene in Northwest Europe. Geological Society of London Special Publication* 101, 40–441.
- Tjalsma, R. C., Lohmann, G. P., 1983. Paleocene-Eocene bathyal and abyssal benthic foraminifera from the Atlantic Ocean. *Micropaleontology Special Publication* 4, 1–90.
- Tremolada, F., Bralower, T.J., 2004. Nannofossil assemblage fluctuations during the Paleocene-Eocene Thermal Maximum at Sites 213 (Indian Ocean) and 401 (North Atlantic Ocean): Palaeoceanographic implications. *Marine Micropaleontology* 52, 107–116.
- Vink, A., Brune, A., Höll, C., Zonneveld, K. A., Willems, H., 2002. On the response of calcareous dinoflagellates to oligotrophy and stratification of the upper water column in the equatorial Atlantic Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology* 178(1–2), 53–66.
- Winter, A., Siesser W.G., 2006. *Coccolithophores*. Cambridge University Press.
- Zachos, J.C., Kroon, D., Blum, P., Bowles, J., Gaillot, P., Hasegawa, T., Hathorne, E.C., Hodell, D. A., Kelly, D. C., Jung, J. H., Keller, S. M., Lee, Y. S., Leuschner, D. C., Lohmann, K. C., Lourens, L., Monechi, S., Nicolo, M., Raffi, I., Riesselman, C., Röhl, U., Schellenber, S. A., Schmidt, D., Slujis A., Thomas, D., Thomas, E., Vallius, H. ,

2004. Early Cenozoic extreme climates: the Walvis Ridge transect. Proceedings of the Ocean Drilling Program. Initial Reports 208.

- Zachos, J.C., Pagani, M., Sloan, L.C., Billups, K., Thomas, E., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* 292, 686–693.
- Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H., Kroon, D., 2005. Rapid acidification of the ocean during the Paleocene–Eocene thermal maximum. *Science* 308, 1611–1615.
- Zeebe, R.E., Lourens, L.J., 2019. Solar System chaos and the Paleocene–Eocene boundary age constrained by geology and astronomy. *Science* 365, 926–929.

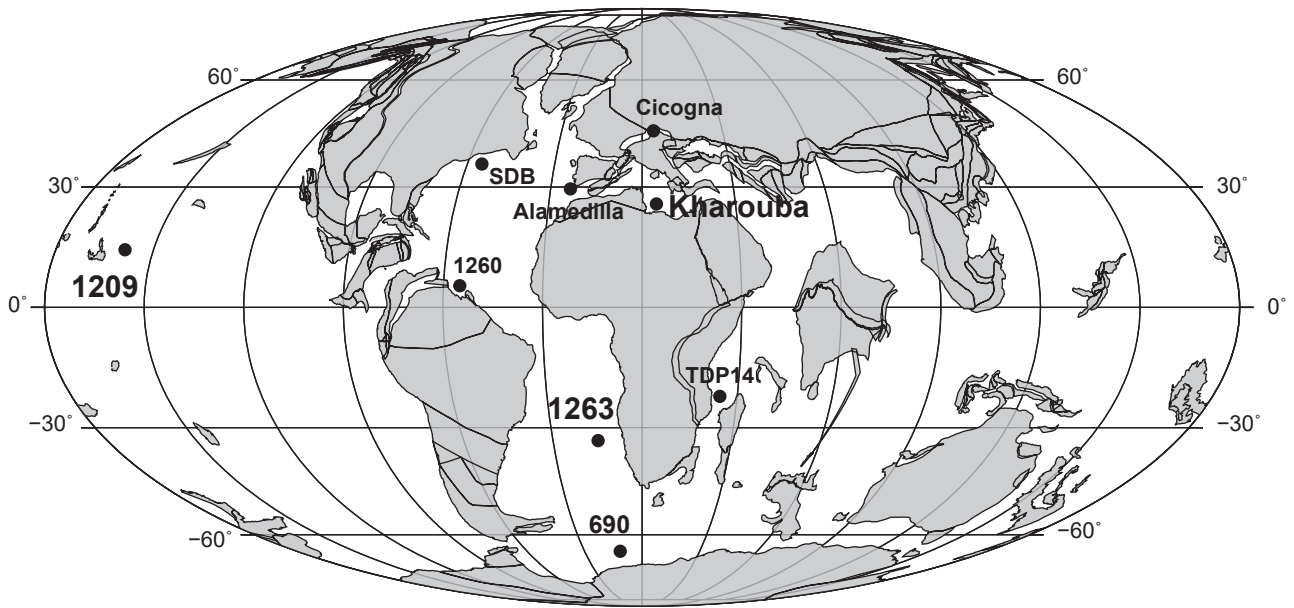


Figure 1. Location of the three studied sections on a paleogeographic map at 56 Ma : (<http://www.odsn.de/odsn/services/paleomap/paleomap.html>): Kharouba section (Tunisia), Site 1209 (Shatsky Rise, Tropical Pacific), and Site 1263 (Walvis Ridge, South Eastern Atlantic). Location of the sites used for comparison is also shown: Site 690 (Southern Ocean) Site 1260 (Equatorial Atlantic), SDB (New Jersey), TDP 14 (Tanzania), Cicogna (North Italy), Alamedilla (Spain).

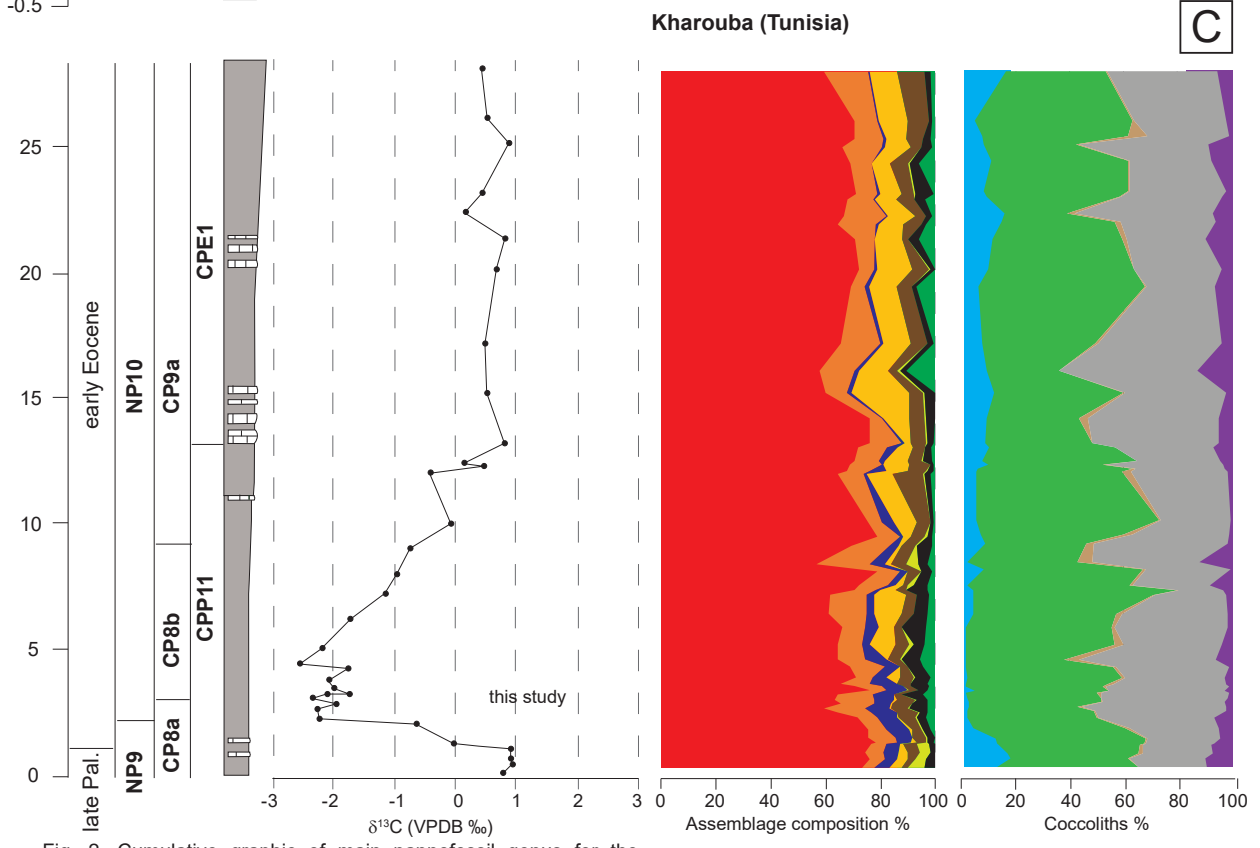
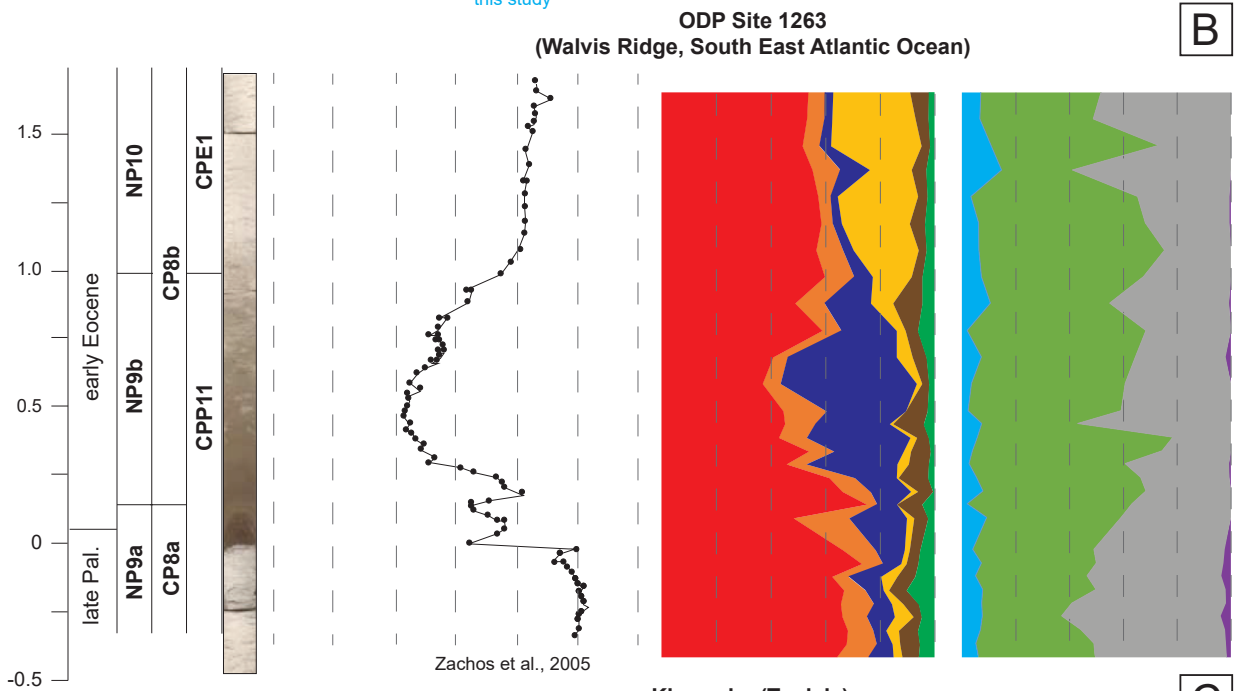
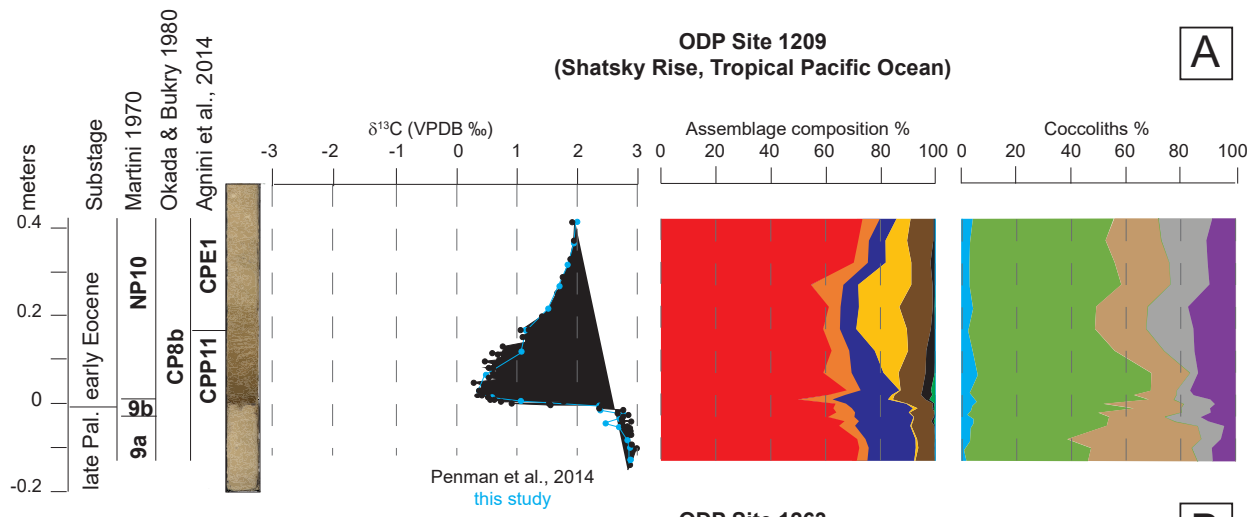


Fig. 2. Cumulative graphic of main nannofossil genus for the three studied sections in function of depth. Horizontal scale is the same but vertical one is different because of important differences in the thickness between oceanic sites and Kharouba. Also nannofossil biostratigraphy and lithostratigraphic column. Total assemblage composition (coccoliths, nanno-liths) and coccolith assemblages for the three sections.

- Cocoliths
- Discoaster
- Fasciculithus
- Zygrhablithus
- Sphenolithus
- Holococcoliths
- Other nannofossils
- Reworking
- Cruci+Chiasmo+Campylosphaera
- Coccolithus
- Ericsonia
- Toweius+Prinsius
- Other coccoliths

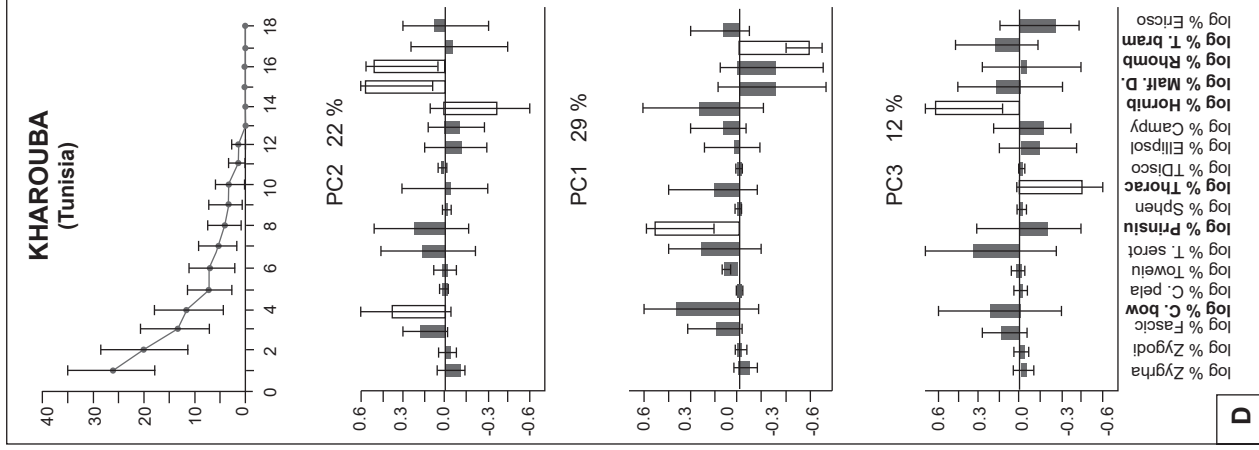
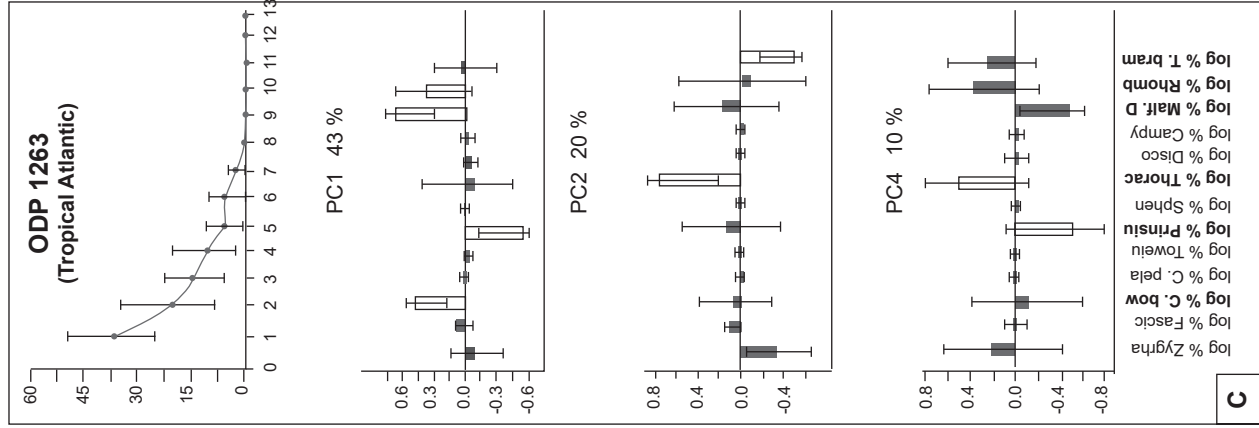
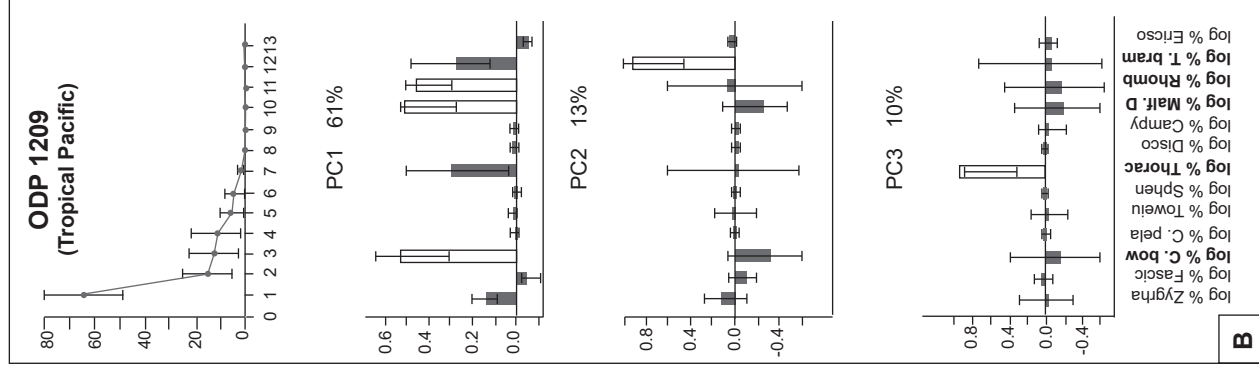
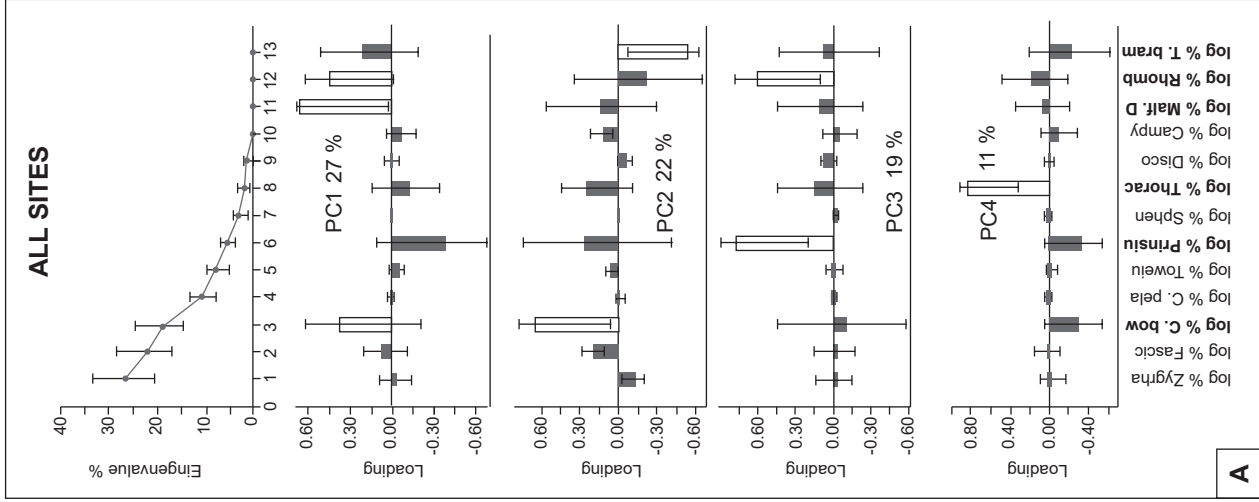


Fig.3. Principal components analysis loading plots. Only species with a high sampling adequacy and having a loading higher than  $\pm 0.5$  on one of the extracted factors are considered here. Factors are regarded as significant only when they have a contribution to the variance higher than 10 %. A; loading plot resulting from the PCA performed on the three studied sections, B; loading plot resulting from the PCA performed on ODP Site 1209, C; ODP Site 1263, D; Kharouba. Error bars represent lower and upper limits for 95% confidence intervals, using 9999 bootstrap

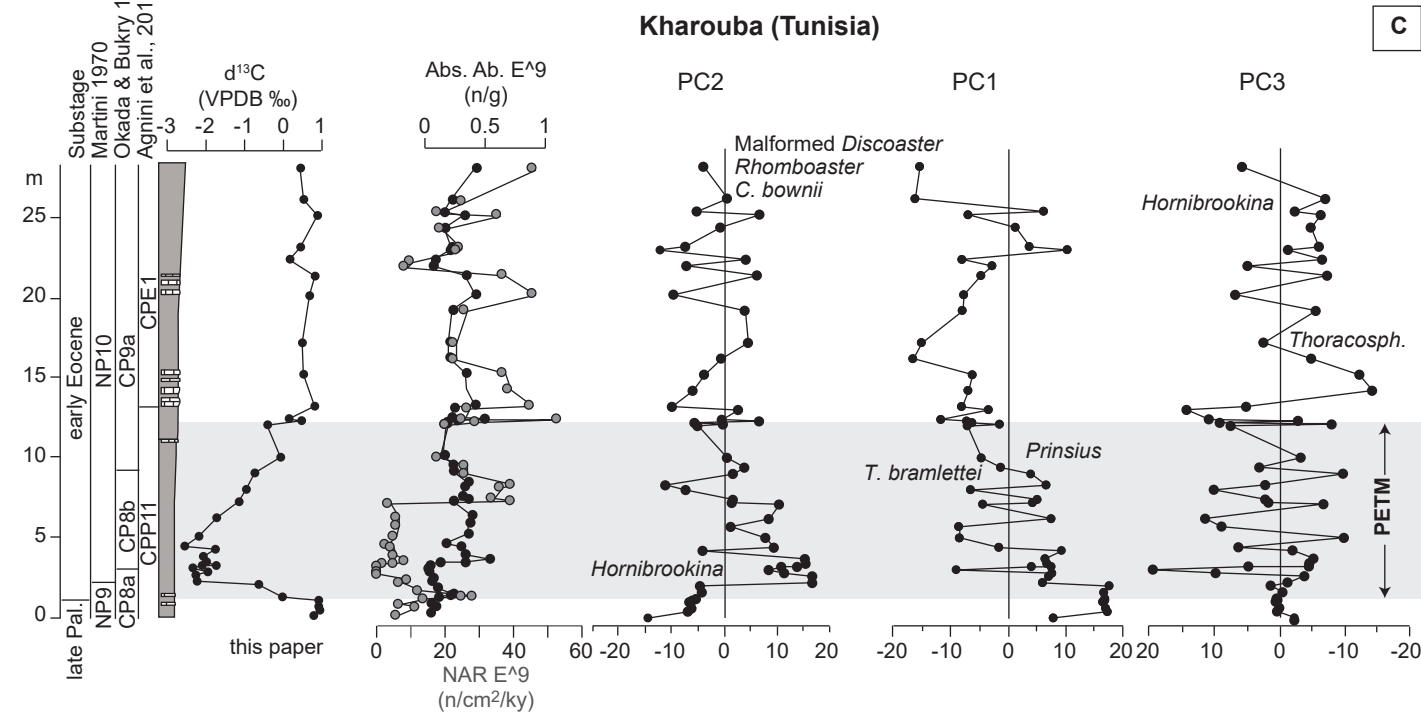
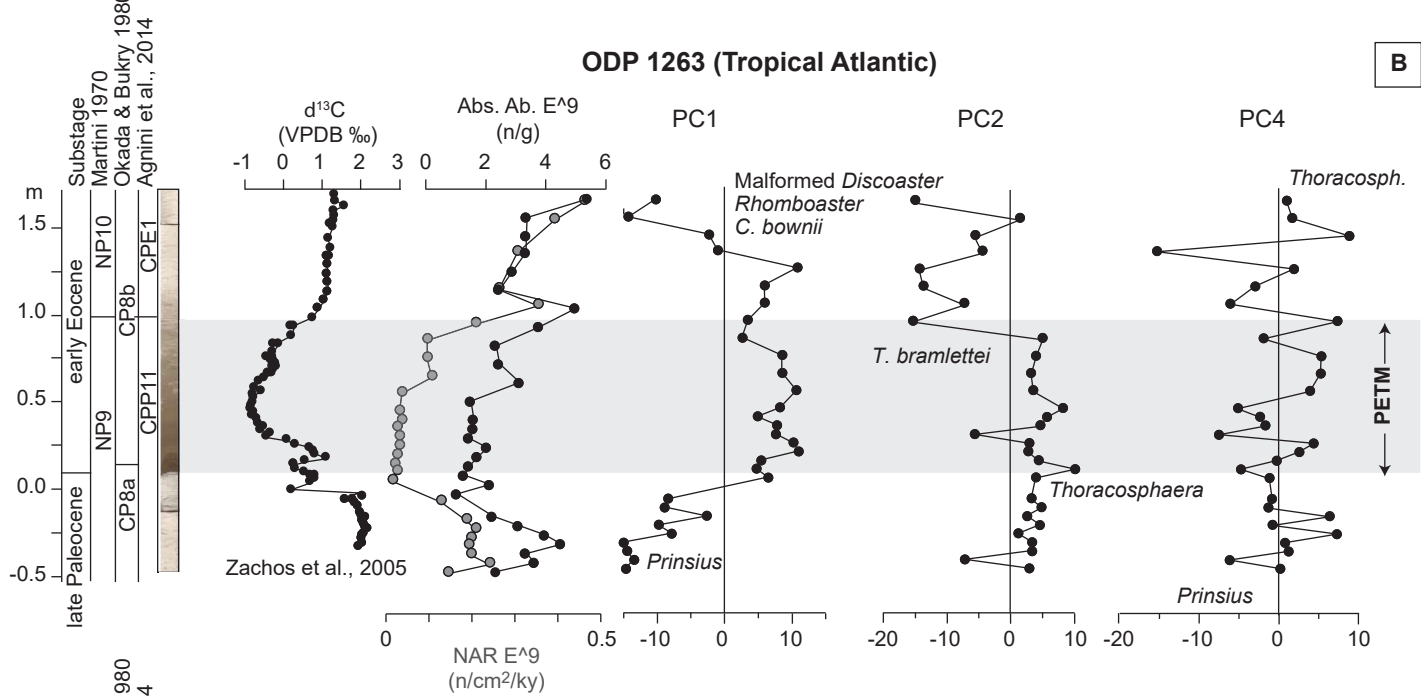
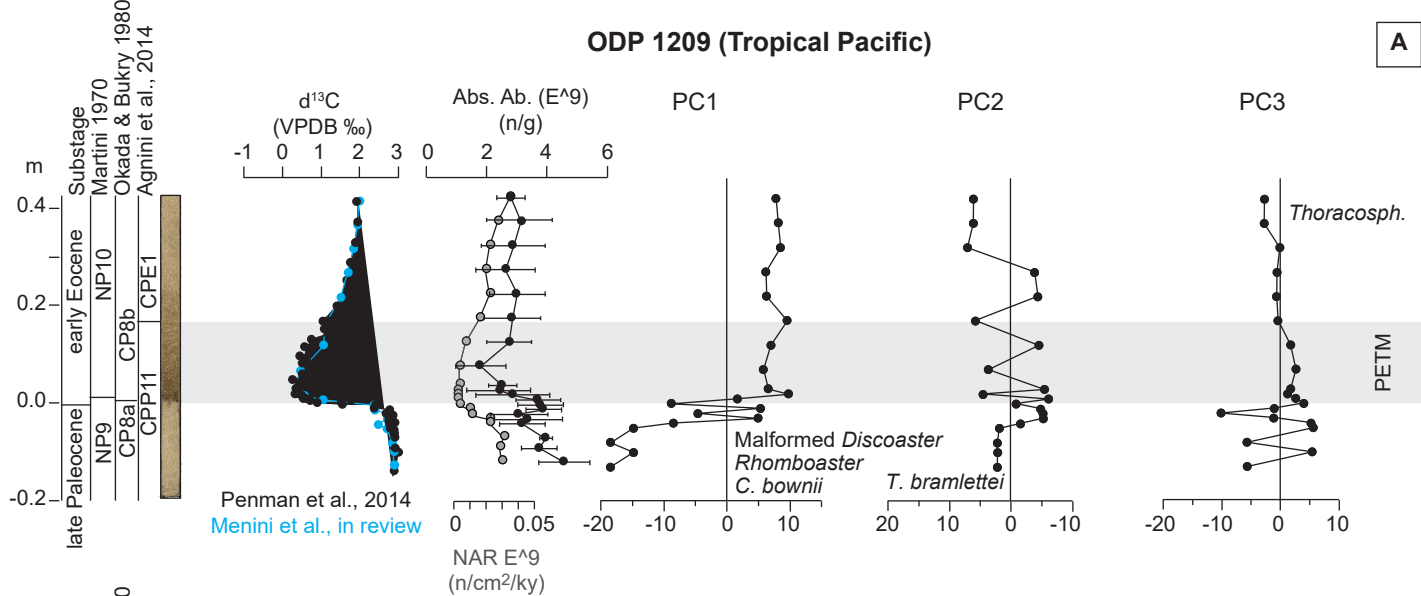
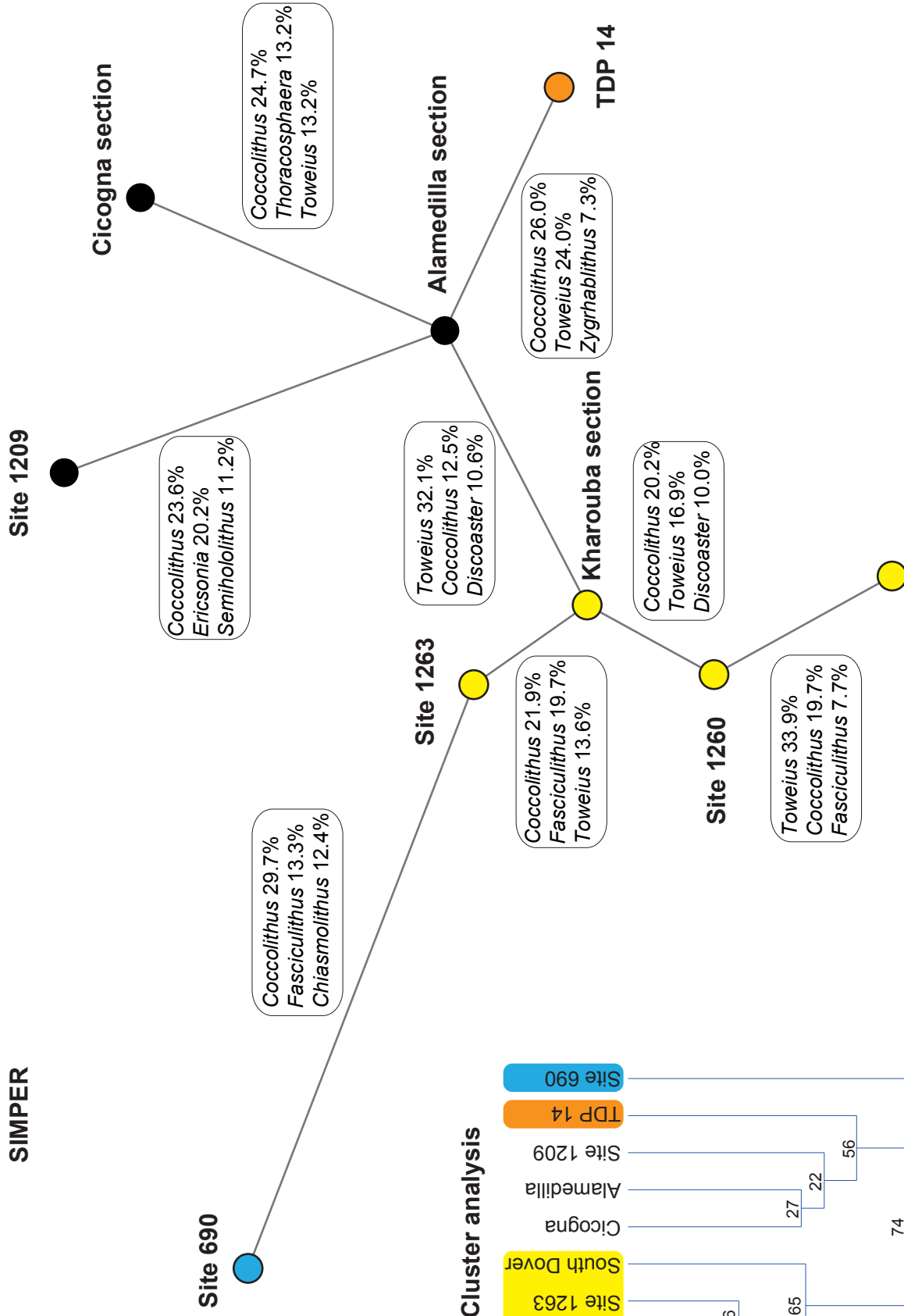


Figure 4. Stratigraphical evolution of PCA scores, absolute abundance (black) and NAR (grey) in function of depth against nannofossil biostratigraphy and carbon isotopes curve in the three studied sections. Note that the vertical scale is different from a section to another. The correlative factors, i.e., those on which the same taxa load, are shown in the same order for the three sections, irrespective of their variance values. The species with important loadings on the different factorial axes are reported.



**SIMPER**



**Cluster analysis**

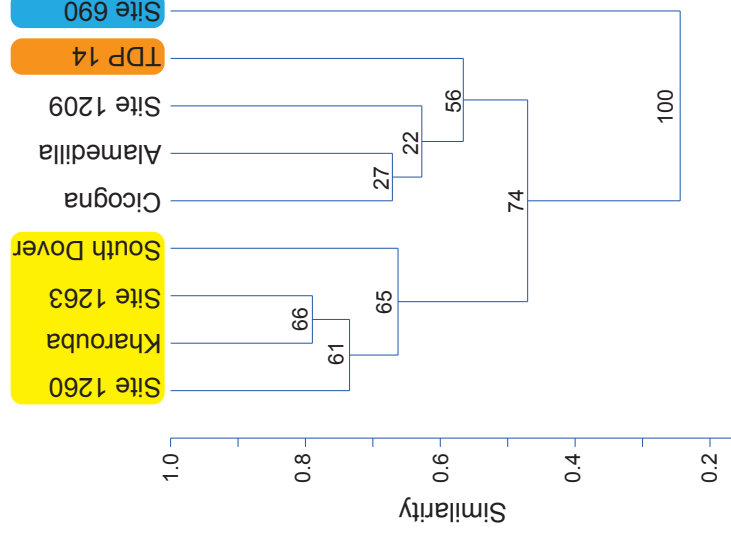


Figure 5. Cluster analysis (right) and SIMPER analysis (left) applied on the three studied sections (Site 1209, 1263 and Kharouba) and 6 other sections that provide excellent stratigraphic records of the PETM calcareous nannofossils .

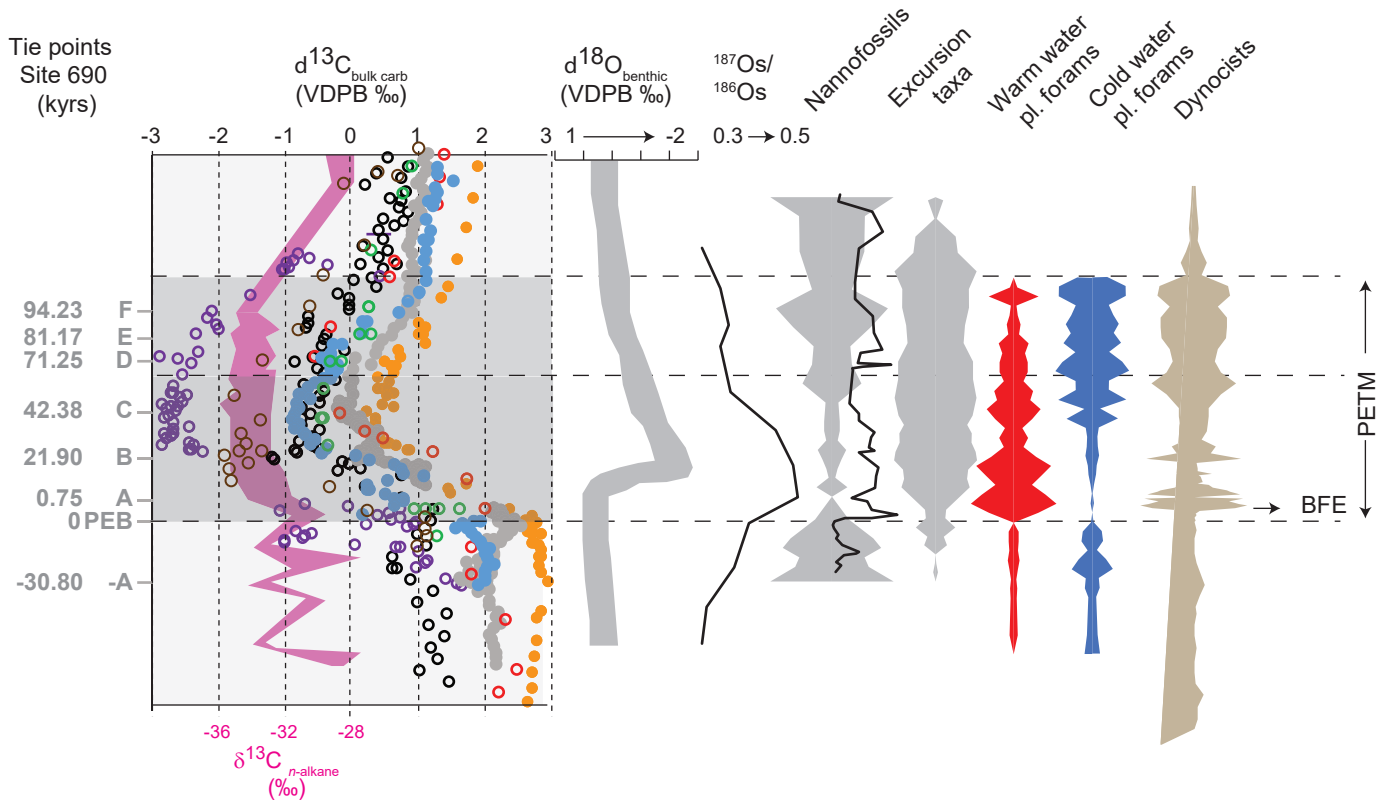


Figure 6. Synthesis of the main geochemical and biotic events occurring across the PETM relative to the  $\delta^{13}\text{C}_{\text{bulk carbonate}}$  record (Alamedilla (red) Lu et al. 1996, ODP 690 (grey) Bains et al. 1999, ODP 1209 (orange) Penman et al. 2014, ODP 1263 (light blue) Zachos et al. 2005, ODP 1260 (green) Mutterlose et al. 2007, Kharouba (brown), This work, South Dover (violet) Self Trail et al. 2012, Cicogna (black) Agnini et al. 2016). For TDP 14 (pink) we used  $\delta^{13}\text{C}_{\text{n-alkane}}$  record (isotopes of C-25, C-27, C-29 and C-31 alkanes), since  $\delta^{13}\text{C}_{\text{bulk carb}}$  did not provide satisfying results (Bown and Pearson 2009, Aze et al. 2014). Tie-points of the  $\delta^{13}\text{C}_{\text{bulk carb}}$  at Site 690 as defined by Zachos et al. (2005) and Röhl et al. (2007) from -A to H are shown. Envelope curve of oxygen isotope records (extracted from the database of Cramer et al., 2009) from individual cores from the North Atlantic (ODP1051), and Southern Oceans (ODP690). Osmium isotopes record after Ravizza et al., 2001 at DSP Site 541. Planctonic foraminifera data after Petrizzo et al., 2008 (warm water=*Morozovella* spp., cold water=*Subbotina* spp.). Dynocists data after Sluijs et al., 2006. See text for details.

<b>1209</b>					<b>A</b>					<b>1263</b>					<b>C</b>				
Test for equal means										Test for equal means									
	Sum of sqrs	df	Mean square	F	p (same)		Sum of sqrs	df	Mean square	F	p (same)		Sum of sqrs	df	Mean square	F	p (same)		
Between gro	3.08E+19	2	1.54E+19	19.9	4.02E-08	Between gro	2.01E+19	2	1.00E+19	17.87	1.14E-05	Between gro	2.01E+19	2	1.00E+19	17.87	1.14E-05		
Within group	8.65E+19	112	7.73E+17	Permutation p (n=99999)		Within group	1.52E+19	27	5.61E+17	Permutation p (n=99999)		Within group	1.52E+19	27	5.61E+17	Permutation p (n=99999)			
Total:	1.17E+20	114	1.00E-05			Total:	3.52E+19	29	4.00E-05			Total:	3.52E+19	29	4.00E-05				
Components of variance (only for random effects):										Components of variance (only for random effects):									
Var(group):	4.10E+17	Var(error):	7.73E+17	ICC:	0.346497	Var(group):	9.50E+17	Var(error):	5.61E+17	ICC:	0.62861	Var(group):	9.50E+17	Var(error):	5.61E+17	ICC:	0.62861		
omega2:	0.2474					omega2:	0.5293					omega2:	0.5293						
Levene's test p (same):	0.2017					Levene's test p (same):	0.08227					Levene's test p (same):	0.08227						
Levene's test p (same):	0.3046					Levene's test p (same):	0.1267					Levene's test p (same):	0.1267						
Welch F test in the case of unequal variances: F=20.13, df=48.22, p=4.409E-07										Welch F test in the case of unequal variances: F=29.58, df=14.62, p=7.255E-06									
					<b>B</b>										<b>D</b>				
	recovery	core	pre-petm				pre petm	Core	recovery				pre petm	Core	recovery				
recovery		0.8246	1.16E-07			pre petm		0.0001708	0.871			pre petm		0.0001708	0.871				
core	0.8375		0.0002514			core	6.719		2.24E-05			core	6.719		2.24E-05				
pre-petm	8.348	5.765				recovery	0.7097	7.796				recovery	0.7097	7.796					
					<b>E</b>										<b>F</b>				
Test for equal means										Test for equal means									
	Sum of sqrs	df	Mean square	F	p (same)		Sum of sqrs	df	Mean square	F	p (same)		Sum of sqrs	df	Mean square	F	p (same)		
Between gro	1.92E+17	2	9.62E+16	7.542	0.002007	Between gro	1.92E+17	2	9.62E+16	7.542	0.002007	Between gro	1.92E+17	2	9.62E+16	7.542	0.002007		
Within group	4.21E+17	33	1.28E+16	Permutation p (n=99999)		Within group	4.21E+17	33	1.28E+16	Permutation p (n=99999)		Within group	4.21E+17	33	1.28E+16	Permutation p (n=99999)			
Total:	6.13E+17	35	0.00203			Total:	6.13E+17	35	0.00203			Total:	6.13E+17	35	0.00203				
Components of variance (only for random effects):										Components of variance (only for random effects):									
Var(group):	8.14E+15	Var(error):	1.28E+16	ICC:	0.389581	Var(group):	8.14E+15	Var(error):	1.28E+16	ICC:	0.389581	Var(group):	8.14E+15	Var(error):	1.28E+16	ICC:	0.389581		
omega2:	0.2666					omega2:	0.2666					omega2:	0.2666						
Levene's test p (same):	0.03867					Levene's test p (same):	0.03867					Levene's test p (same):	0.03867						
Levene's test p (same):	0.1161					Levene's test p (same):	0.1161					Levene's test p (same):	0.1161						
Welch F test in the case of unequal variances: F=39.88, df=17.31, p=3.305E-07										Welch F test in the case of unequal variances: F=39.88, df=17.31, p=3.305E-07									

Table S1: One-way ANOVA applied on nannofossil absolute abundance for Site 1209, 1263 and Kharouba(A,C,E). In B,D,F the table of "post-hoc" pairwise comparisons, based on the Tukey-Kramer test. The Studentized Range Statistic Q is given in the lower left triangle of the array, and the probabilities p(equal) in the upper right.



# **Chapitre 4. Carbon cycle modulation by phytoplankton during the Paleocene-Eocene Thermal Maximum**

# 1 Carbon cycle modulation by phytoplankton during the Paleocene-Eocene 2 Thermal Maximum

3

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13

14 **The Paleocene Eocene Thermal Maximum (PETM, ~56 My ago), is considered as one of**  
15 **the best analogues for anthropogenic CO<sub>2</sub> emissions. Yet, the key negative feedbacks**  
16 **that removed the excess carbon during the PETM termination remain controversial.**  
17 **Higher deep-sea CaCO<sub>3</sub> saturation and burial due to enhanced silicate weathering are**  
18 **commonly accepted as the main driving processes. Alternatively, a CO<sub>2</sub>-induced drop in**  
19 **net algal CaCO<sub>3</sub> production could have triggered the alkalinity buildup and**  
20 **oversaturation, but this mechanism remains unsupported by proxy evidence. Here, we**  
21 **present a multiproxy study of tropical Pacific and Atlantic deep-sea records**  
22 **demonstrating that CaCO<sub>3</sub> burial recovered to pre-PETM levels about 30 000 years**  
23 **later than saturation. We attribute this decoupling to a dramatic (>60%) and sustained**  
24 **(>80 000 years) collapse in net CaCO<sub>3</sub> production due to warming-induced ocean**  
25 **stratification and lowered nutrient availability. Our records show that the resulting**  
26 **excess alkalinity was rapidly consumed when CaCO<sub>3</sub> production and burial eventually**  
27 **recovered, triggering a rapid and massive drawdown of both inorganic and organic**  
28 **carbon. Our findings elucidate some of the key biogeochemical mechanisms that drove**  
29 **the PETM recovery and emphasize the overlooked but crucial importance of biological**  
30 **thresholds in the regulation of past and ongoing events of greenhouse warming.**

31

32 Past greenhouse events, such as the PETM, provide deep geological insight into the critical  
33 biogeochemical consequences of ongoing anthropogenic CO<sub>2</sub> emissions. PETM marine

34 carbonates record a global 3-4‰ carbon isotope ( $\delta^{13}\text{C}$ ) negative excursion (CIE) coeval with  
35 a  $>5^\circ\text{C}$  temperature increase indicating the massive input of  $^{13}\text{C}$ -depleted carbon into the  
36 ocean-atmosphere system (Kennett and Stott, 1991; Zachos et al., 2003). The increase in  
37 atmospheric  $p\text{CO}_2$  led to a drastic drop in ocean  $p\text{H}$  and carbonate ion content  $[\text{CO}_3^{2-}]$   
38 (Penman et al., 2014; Babila et al., 2018). Such dramatic changes in ocean chemistry are  
39 reflected by widespread dissolution horizons in deep oceanic sediments, which record a  
40 global shoaling of the lysocline – the depth where  $[\text{CO}_3^{2-}]$  falls below calcite saturation – and  
41 of calcite compensation depth (CCD) – the depth where the dissolution becomes sufficiently  
42 rapid to exactly balance the calcite rain flux (Ridgwell and Zeebe, 2005; Zachos et al., 2005).  
43 Model simulations for the PETM suggest that the warming-induced increase in continental  
44 weathering favored a long-term (10-100 ky) increase in bicarbonate ion  $[\text{HCO}_3^-]$  ultimately  
45 leading to an overshoot of the lysocline and CCD, and enhanced  $\text{CO}_2$  drawdown (Penman et  
46 al., 2016).

47 Crucially, most previous simulations implicitly assumed constant  $\text{CaCO}_3$  production and  
48 export across the PETM (Dickens et al., 1997; Ridgwell, 2007; Zeebe et al., 2009), leaving  
49 seafloor dissolution/preservation of  $\text{CaCO}_3$  as the central oceanic carbon-cycle controlling  
50 feedback. In deep-sea sediments,  $\text{CaCO}_3$  export-flux is predominantly provided by calcareous  
51 phytoplankton (mainly coccolithophores), whose tiny ( $<30\ \mu\text{m}$ ) calcite remains form  
52 nanofossil ooze, and subordinately, by larger ( $>63\ \mu\text{m}$ ) shells of planktonic foraminifera.  
53 Previous studies of PETM nanofossils have shown that the drop of surface ocean  $p\text{H}$  and  
54  $[\text{CO}_3^{2-}]$  had little effects on both coastal- and open-ocean calcareous phytoplankton  
55 calcification (the ratio of inorganic carbon to photosynthetically derived organic carbon) and  
56 diversity (Gibbs et al., 2006b). However, changes in net open-ocean pelagic  $\text{CaCO}_3$   
57 production, despite their outstanding biogeochemical and ecological importance, remain  
58 virtually unconstrained by empirical data. The seldom attempts to constrain phytoplankton  
59 productivity using Sr/Ca ratios or Ba contents have proven controversial, due largely to the  
60 complex dependence of these proxies to several environmental forcing factors (Stoll and  
61 Bains, 2003; Ma et al., 2014; Bridgestock et al., 2019). Model simulations suggest that the  
62 input of  $>6500\ \text{Gt}$  of  $\text{CO}_2$  accompanied by a sustained 50% drop in net  $\text{CaCO}_3$  production  
63 could adequately reproduce  $\text{CaCO}_3$  depth transects at Walvis Ridge (S Atlantic)(Luo et al.,  
64 2016). Although yet unsupported by other quantitative evidence, such a drop in net  $\text{CaCO}_3$   
65 production implies, through a long term alkalinity buildup, a decoupling between  $\text{CaCO}_3$   
66 saturation and burial that should be detectable in PETM deep-sea sediments (Luo et al.,  
67 2016). By contrast,  $\text{CaCO}_3$  burial should closely track saturation if seafloor



68 dissolution/preservation of CaCO<sub>3</sub> was the central oceanic carbon-cycle controlling feedback  
69 (Zeebe, 2012). To test the importance of these two mechanisms, we reconstruct CaCO<sub>3</sub> burial  
70 and saturation across the PETM using nannofossil accumulation rates (NAR) and  
71 fragmentation from deep-ocean sediments recovered from Ocean Drilling Program (ODP)  
72 sites 1209 (Shatsky Rise, central Pacific) and 1263 (Walvis Ridge, South Atlantic). This  
73 approach is combined with new calcium isotope data ( $\delta^{44}\text{Ca}$ ) – a proxy for seawater saturation  
74 – and a comprehensive reassessment of previously published micropaleontological and  
75 geochemical data to constrain interactions between calcareous phytoplankton productivity,  
76 ocean chemistry and climate across the PETM.

77 Unlike all other previous PETM studies that used smear slides, we prepared the samples  
78 using standardized settling methods to robustly estimate the absolute abundances of  
79 individual particles per gram of rock. We then estimated sedimentation rates with an  
80 unprecedented ky-resolution based on helium isotope and CaCO<sub>3</sub> contents anchored to  
81 astronomical age models (Extended Data Fig. 1; methods) to infer nannofossil accumulation  
82 rates (NAR), the mass accumulation rates of the fine (MAR<sub>ff</sub>) and coarse (>63  $\mu\text{m}$ ) carbonate  
83 fractions (MAR<sub>cf</sub>), and that of abiogenic calcite particles (blades) (Fig. 1; Extended Data Fig.  
84 2). We estimated particle weight of the better-preserved nannofossils at Site 1209 using  
85 automated birefringence-based methods, combined with classical scanning electron and  
86 optical microscopy (see methods and Supplementary Information) and hence calculated  
87 nannofossil mass accumulation rates (MAR<sub>n</sub>). Our estimates indicate that the fine fraction  
88 CaCO<sub>3</sub> in the studied samples at Site 1209 contains an average proportion of >88 wt.%  
89 nannofossil calcite (Supplementary Information), whereas its accumulation rate (MAR<sub>ff</sub>) is  
90 highly correlated with NAR ( $R^2=0.99$ ;  $p<0.05$ ) and MAR<sub>n</sub> ( $R^2=0.98$ ;  $p<0.05$ ; Extended Data  
91 Table 1). Maximum Paleocene MAR<sub>ff</sub> values are > 5 times higher at Walvis Ridge (3.5  
92 g/cm<sup>2</sup>/ky) than at Shatsky Rise (0.6 g/cm<sup>2</sup>/ky), in remarkable consistency (in relative and  
93 absolute values) with modern export fluxes measured at equivalent sites (Milliman, 1993).  
94 Because of these very different background values, we thus only refer to the highest  
95 resolution changes in MAR<sub>ff</sub> relative to pre-PETM maximum values ( $\Delta\text{MAR}_{\text{ff}}$ ) to evaluate  
96 changes in nannofossil calcite accumulation (Supplementary Information). Despite these  
97 differences in absolute MAR<sub>ff</sub>, the two sites reveal strikingly similar trends in CaCO<sub>3</sub>  
98 accumulation. We find MAR<sub>ff</sub> at both sites fell dramatically by >80% across the CIE onset,  
99 stayed extremely low (<-50%) for ~80 ky, and rapidly returned to pre-excursion values only  
100 by +90-100 ky (Fig. 1). These patterns are largely insensitive to uncertainties of the age  
101 models (Extended data Fig. 2).

102 This >80ky-long phase of low nannofossil ooze burial can be directly compared to our new  
103 nannofossil fragmentation data. Nannofossil fragmentation varies inversely relative to CaCO<sub>3</sub>  
104 saturation (Beaufort et al., 2007) and directly tracks the dissolution of the dominant CaCO<sub>3</sub>  
105 component, unlike the fragmentation of foraminifera, which dissolve at shallower depths and  
106 constitute a subordinate fraction of studied sediments. These new data, together with our  
107  $\delta^{44}\text{Ca}$  data, calculated MAR<sub>cf</sub> data and available foraminiferal fragmentation (Petruzzo et al.  
108 2008), provide a coherent history of CaCO<sub>3</sub> saturation state at the two studied sites (Fig. 1).  
109 At both sites, CaCO<sub>3</sub> saturation dropped markedly across the CIE onset and therefore at least  
110 partly explains the unusually low MAR<sub>ff</sub> over the earliest ~30 ky of the event, as shown by  
111 coeval peaks in foraminifera and nannofossil fragmentation and lowest MAR<sub>cf</sub> (Phase I in  
112 Fig. 1). Similarly, the marked increase in nannofossil and foraminiferal fragmentation coeval  
113 with the decline in MAR<sub>cf</sub> and MAR<sub>ff</sub> starting -15 ky prior the CIE onset at Site 1209 likely  
114 indicates more intense postdepositional chemical erosion ('burndown') of latest Paleocene  
115 sediments exacerbated by low background accumulation rates in the Pacific gyre (Bralower et  
116 al., 2014). The coccolith lysocline recovered to pre-excursion values ~40 ky later in the  
117 Atlantic than in the Pacific (by +75 and +35 ky and at sites 1263 and 1209, respectively; Fig.  
118 1), consistent with the hypotheses of a second, >50 ky episode of carbon injection (phase II;  
119 Fig. 1) directly into the deep Atlantic (Zeebe et al., 2009). Such features could also indicate a  
120 southward spread of corrosive N Atlantic waters. The coeval episode of maximal surface  
121 water saturation at Site 1209 between + 50 and 90 ky is also supported by our new  $\delta^{44}\text{Ca}$   
122 measurements of the mixed-layer planktic foraminifera *Morozovella velascoensis* (Fig. 1).  
123 Previous studies have shown that calcite  $\delta^{44}\text{Ca}$  values mainly reflect global changes in  
124 seawater  $\delta^{44}\text{Ca}$  values, driven by the balance between weathering input or carbonate output,  
125 and changes in fractionation between seawater and calcite (Griffith et al., 2020). Because of  
126 the high Paleogene ocean [Ca] content, the marked positive peak toward higher  $\delta^{44}\text{Ca}$  values  
127 between +45 and +90 ky is too large and rapid to be explained by global changes in  $\delta^{44}\text{Ca}$  of  
128 seawater (Komar and Zeebe, 2011), thus pointing to diminished seawater-calcite  $\delta^{44}\text{Ca}$   
129 fractionation. Although our understanding of environmental factors controlling foraminiferal  
130 calcite  $\delta^{44}\text{Ca}$  fractionation is still in a state of flux (Griffith et al., 2020), culture experiments  
131 on inorganic (Lemarchand et al., 2004) and foraminiferal (Roberts et al., 2020) calcite  
132 indicate diminished fractionation with increasing CaCO<sub>3</sub> saturation and [CO<sub>3</sub><sup>2-</sup>]. Accordingly,  
133 and regardless of long-term changes in seawater  $\delta^{44}\text{Ca}$  values and uncertainties in absolute  
134 omega values (Supplementary information), our *M. velascoensis*  $\delta^{44}\text{Ca}$  record imply a marked

135 rise in surface water saturation between +45 and +90 ky, in excellent agreement with seafloor  
136 CaCO<sub>3</sub> saturation proxies (Fig. 1).

137 A remarkable aspect of our results is the low  $\Delta\text{MAR}_{\text{ff}}$  values ( $< -60\%$ ) recorded at Site  
138 1209 in the interval of maximum surface and seafloor CaCO<sub>3</sub> saturation between +45 and +90  
139 ky (Fig. 1). Although shorter-lived due to more prolonged seafloor dissolution, a similar  
140 mismatch is recorded at Site 1263. There,  $\Delta\text{MAR}_{\text{ff}}$  values are still  $<60\%$  lower than pre-  
141 PETM values by +80 ky, when nannofossil fragmentation recovers to pre-PETM values (Fig.  
142 1). This clear decoupling between CaCO<sub>3</sub> burial and saturation at the end of the PETM core in  
143 both the Pacific and Atlantic oceans is at odds with classical compensation models assuming  
144 a constant scaling between these two variables.

145 It could be argued that the low CaCO<sub>3</sub> burial recorded during episodes of high saturation  
146 was produced locally by the physical removal of CaCO<sub>3</sub> sediments. Winnowing the  
147 nannofossil fraction by ocean bottom currents has been for instance proposed as the cause of  
148 the anomalous rise of the foraminiferal coarse fraction at Site 1209 (Bralower et al., 2014).  
149 The relatively invariant trend of our  $\text{MAR}_{\text{cf}}$  estimates confirms that the rise in the  
150 foraminiferal fraction during the PETM at Site 1209 resulted from lower nannofossil dilution  
151 (Fig. 1). Nevertheless, our new data reveals no trend toward higher nannofossil weight across  
152 the PETM (Extended Data Fig. 3), and therefore does not support this hypothesis. As  
153 nannofossil ooze has the same density and size distribution as extraterrestrial <sup>3</sup>He-bearing  
154 interplanetary dust particles (Farley et al., 1997), another testable but previously overlooked  
155 consequence of the winnowing hypothesis is that bottom currents should have equally  
156 decreased the <sup>3</sup>He<sub>ET</sub> contents in the PETM interval. The large increase in <sup>3</sup>He<sub>ET</sub> contents  
157 recorded across the PETM and our age models clearly excludes this possibility  
158 (Supplementary Information).

159 Given the similarity of the deep-sea  $\Delta\text{MAR}_{\text{ff}}$  records from different oceans and  
160 hemispheres characterized by distinct bottom-water hydrodynamics, we therefore interpret the  
161 drastic decrease in nannofossil accumulation rates recorded at sites 1209 and 1263 as strong  
162 evidence for a sustained,  $> 80$  ky drop of net phytoplankton CaCO<sub>3</sub> export in tropical gyres  
163 during the PETM. In this regard, our new nannofossil weight estimates at Site 1209 reveal no  
164 noticeable changes across the PETM at Site 1209, indicating that nannofossil export fluxes  
165 rather than calcification drove the major drop in  $\text{MAR}_{\text{ff}}$  (Extended Data Fig. 3). This response  
166 contrasts strongly with the overwhelming influence of  $p\text{CO}_2$  levels and  $[\text{CO}_3^{2-}]$  on the weight  
167 of the dominant living family Noelarhabdaceae over the last 40 ky (Beaufort et al., 2011),  
168 likely translating fundamental differences in taxonomic composition between modern and

169 Paleogene coccolithophores as well as long-term evolutionary and ecological trends  
170 (Henderiks and Rickaby, 2007).

171 Importantly, several lines of evidence suggest that this decline in net export productivity  
172 was not confined to calcareous phytoplankton. The  $\Delta\text{MAR}_{\text{ff}}$  values at Site 1209 remarkably  
173 parallel changes in  $\delta^{13}\text{C}$  gradients between planktonic and benthic foraminifera (Extended  
174 Data Fig. 4). Minimal  $\delta^{13}\text{C}$  gradients during the PETM indicate diminished removal of  $^{13}\text{C}$ -  
175 depleted carbon by photosynthesis in superficial waters and are consistent with reduced  
176 organic carbon export and diminished productivity (Zachos et al., 2003; Tripathi and  
177 Elderfield, 2005). We rule out a decline in calcareous phytoplankton productivity as the main  
178 cause of this reduced  $\delta^{13}\text{C}$  gradient, because this group rarely exceeds 20% of phytoplankton  
179 carbon uptake in nutrient-depleted gyres (Poulton et al., 2007). Earth system modeling  
180 indicates that the similar 1-2 ‰ decrease in the vertical  $\delta^{13}\text{C}$  gradient recorded at the  
181 Cretaceous-Paleogene transition at Site 1209 requires a 50% reduction in total organic  
182 primary productivity (Henehan et al., 2019). At Site 1263, Ba isotopes and Ba/Al ratios  
183 (Bridgestock et al., 2019) also suggest parallel trends in primary organic and  $\text{CaCO}_3$   
184 productivity in the S Atlantic (Extended Data Fig. 4). These comparisons indicate that total  
185 organic productivity and calcareous phytoplankton productivity declined concomitantly and  
186 by the same order of magnitude in the tropical Pacific and S Atlantic gyres during the PETM.

187 Interestingly, our  $\text{MAR}_{\text{ff}}$  estimates at Site 1209 do correlate negatively with sea surface  
188 temperatures (SST) inferred from *M. velascoensis*  $\delta^{18}\text{O}$  ( $R^2= 0.53$ ;  $p<0.05$ ) and Mg/Ca ( $R^2=$   
189  $0.57$ ;  $p<0.05$ ) data, suggesting a strong climatic control (Extended Data Table 1). High  
190 (extra)tropical PETM SSTs ( $>35^\circ\text{C}$ ), which likely exceeded the upper physiological limits of  
191 most marine eukaryotes (Frieling et al., 2017), could explain the crash in both total and  
192  $\text{CaCO}_3$  productivity recorded at sites 1209 and 1263. Extreme warmth, however, appears less  
193 likely to explain the marked ( $>50\%$ ) and prolonged ( $>50$  ky) drop in  $\text{MAR}_{\text{ff}}$  recorded in the  
194 high latitude site 690 (Extended Data Fig. 2), where SST likely never exceeded  $20\text{-}25^\circ\text{C}$   
195 (Dunkley-Jones et al., 2013). More indirectly, modeling of the PETM warming produces,  
196 through higher SST and reduced latitudinal gradients (Frieling et al., 2017) enhanced surface  
197 ocean stratification, lower deep vertical mixing and upwelling of nutrients into surface waters,  
198 where photosynthesis occurs. Enhanced stratification is consistent with nannofossil  
199 assemblage at both sites 1209 and 1263, where shallow-dwellers typical of upwelled waters in  
200 the Late Paleocene are replaced by deep-water taxa that thrived in times of oligotrophy in  
201 surface waters during the PETM (Supplementary Information). Calcareous nannofossil

202 assemblages, also support thermally-induced stratification and overall oligotrophy in various  
203 oceanic sites (Bralower, 2002; Gibbs et al., 2010). Besides, *Thoracosphaera*, a calcareous  
204 dinoflagellate cyst generally used as an index of enhanced oligotrophy under stratified water  
205 conditions (Vink et al., 2002), is the only calcareous nannofossil investigated in this study  
206 showing an increase in absolute abundance and accumulation rate during the PETM at Site  
207 1209 (Fig. 1). We note that such evidence is not incompatible with meso-eutrophic  
208 nannofossil assemblages recorded in a few extra-tropical proximal sites, where increased  
209 continental runoff and higher nutrients availability may have locally fostered productivity  
210 (Gibbs et al., 2006b; Self-Trail et al., 2012). However, trophic conditions during the PETM  
211 are less obvious in other proximal sites from tropical paleolatitudes, with some sites recording  
212 a primary productivity crash in the core of the PETM as shown by dinoflagellates abundances  
213 (Frieling et al., 2017).

214 All together, these considerations strongly support thermally induced sluggish ocean  
215 circulation and stratification as the most likely trigger for the >60% decline in net CaCO<sub>3</sub>  
216 productivity recorded at sites 1209 and 1263 in the core of PETM. Model simulations show  
217 that a 50% drop in CaCO<sub>3</sub> export and burial would have led to a considerable build-up of  
218 [HCO<sub>3</sub><sup>-</sup>] and hence increased alkalinity in both surface and deep waters in the recovery  
219 interval (50-100 ky after the onset of the PETM) (Luo et al., 2016). Such a build-up of  
220 alkalinity and a reversal in saturation at +50 ky at Site 1209 is not only supported by our  
221 saturation reconstruction but also by the recent re-evaluation of Mg/Ca-δ<sup>18</sup>O records of *M.*  
222 *velascoensis* from Site 1209 using modern foraminiferal Mg/Ca sensitivity to dissolved  
223 inorganic carbon (DIC) (Holland et al., 2020). Accordingly, DIC, and by inference [HCO<sub>3</sub><sup>-</sup>],  
224 would have increased markedly between 50-100 ky (Holland et al., 2020). Given the existing  
225 pH and SST constraints from at Site 1209 (methods and supplementary information), these  
226 various records can be used to reconstruct the history of ocean carbon chemistry and hence  
227 constrain the role of phytoplankton productivity carbon cycle feedbacks across the PETM.  
228 These reconstructions imply a drastic rise in DIC and [HCO<sub>3</sub><sup>-</sup>] that is in excellent agreement  
229 with the Atlantic simulation of a 50% drop in net CaCO<sub>3</sub> export by Luo et al, 2016 but far  
230 exceeds their estimates for the Pacific Ocean, where CaCO<sub>3</sub> export was held identical to  
231 Paleocene values for most of the PETM. Our data thus not only strongly support the  
232 fundamental role of biological export in modulating the PETM carbon cycle suggested by  
233 their simulation, but further suggest that their conclusion should be extended to a much  
234 broader proportion of the ocean.



235 A complementary and crucial aspect of our reconstructions is that DIC and CaCO<sub>3</sub>  
236 saturation declined rapidly after 85 ky, implying a rapid and widespread episode of carbon  
237 burial. Enhanced carbon drawdown is consistent with the dramatic increase in  $\Delta\text{MAR}_{\text{ff}}$  at  
238 both sites and the large (>1000 ppm) drop  $p\text{CO}_2$  inferred from available records at Site 1209.  
239 As high alkalinity enhances atmospheric CO<sub>2</sub> absorption into the ocean (Feely et al., 2002),  
240 alkalinity buildup due to diminished CaCO<sub>3</sub> export represents a simple negative feedback  
241 process that could appropriately explain the rapid termination of the PETM. As more  
242 atmospheric CO<sub>2</sub> was absorbed, SST and stratification decreased, thus restoring nutrient  
243 availability and both net organic matter and CaCO<sub>3</sub> export, and eventually CaCO<sub>3</sub> burial in  
244 the vast, already oversaturated and deep-sea areas. In addition, it has been demonstrated that  
245 phytoplanktonic calcite act as ballast in fecal pellets and increases organic carbon fluxes to  
246 the ocean interior (Poulton et al., 2006), whereas higher CaCO<sub>3</sub> planktonic input increases  
247 sedimentation rates and accelerates organic carbon burial in the sediment column (Tyson,  
248 1995). The cooling-induced recovery of CaCO<sub>3</sub> export thus represents a simple and realistic  
249 mechanism to enhance the burial of <sup>13</sup>C-depleted carbon required to explain the puzzling and  
250 rapid rise in  $\delta^{13}\text{C}$  values evident in both continental and oceanic records (Bowen, 2013; Ma et  
251 al., 2014; van der Meulen et al., 2020).

252 The multiple lines of evidence presented here provide a strong case for ocean  
253 desertification in the tropical Pacific and Atlantic during the PETM, which elucidate some of  
254 the key biogeochemical mechanisms that likely facilitated its rapid termination. Further  
255 drilling of supra-lysoclinal oceanic sites is necessary to clarify the history of CaCO<sub>3</sub> export  
256 fluxes across the PETM onset, which is obscured by extensive dissolution in all available  
257 oceanic sites. Beyond the PETM, our findings bring empirical evidence that biocalcifying  
258 algae are not simple background players in a warming world but play a pivotal role by  
259 regulating or amplifying carbon cycle perturbations (Luo et al., 2016; Boudreau et al., 2018),  
260 as suggested for other extreme events of the Phanerozoic, such as the Toarcian Oceanic  
261 Anoxic Event (Mattioli et al., 2008) or the most dramatic K-Pg event (Henehan et al., 2019).  
262 Identifying such biological thresholds might also reveal crucial for the mitigation of  
263 anthropogenic CO<sub>2</sub> emissions.

264

## 265 **Methods**

### 266 **Samples and site selection**

267 The ODP sites 1209 and 1263 were selected for this study due to their central position  
268 within the extensive N Pacific and S Atlantic gyres. Due to their relatively shallow position

269 during PETM (respective paleo-water depths of 1900 m and 1500 m; Takeda and Kaiho,  
270 2007; Zachos et al., 2005), these two sites were minimally affected by dissolution compared  
271 to deeper nearby sites and benefit from some of the highest-resolution geochemical records  
272 available for deep-sea PETM sites (Colosimo et al., 2006; Zachos et al., 2005; Zachos et al.,  
273 2003; Tripathi and Elderfield, 2005; Westerhold et al., 2011). We collected samples with a 1 to  
274 5 cm spacing over 0.50 m recording the PETM in Hole 1209B and with 5-10 cm spacing over  
275 2 m in Hole 1263C/D (Supplementary Information).

276

277 **Absolute abundances of nannofossil and abiogenic particles.** All calcareous nannofossil  
278 slides were prepared following the settling method (Beaufort et al., 2014). A cover slide was  
279 weighted before and after the settling of a homogeneous suspension of dry bulk sediment and  
280 water supersaturated with respect to CaCO<sub>3</sub> for 4 hours in a Petri-dish. Water was carefully  
281 aspirated with a water pump connected to a micro-pipette to avoid any turbulence. After  
282 residual water drying, the cover slide was fixed on a microscope slide using Rhodopass B  
283 resin (Polyvinyl acetate). Nannofossil and abiogenic particles abundance were counted in a  
284 total of 30 Fields of View (FOV) for each sample with a Leica DM 750 P microscope with  
285 1000X magnification. The studied area is 0.00942 cm<sup>2</sup>. Five replicates per sample were  
286 studied at Site 1209. Absolute nannofossil abundance per gram of sediment were calculated  
287 using the formula:

$$288 \quad x = \frac{n*(l*h)}{m*A} \quad (1)$$

289

290 where  $x$  is the absolute abundance value,  $n$  is the number of counted specimens in a slide,  $l$   
291 is the length of the cover slide,  $h$  is the height of the cover slide,  $m$  is the mass of the weighted  
292 sample and  $A$  is the studied surface of the sample.

293

294 **Nannofossil fragmentation.** We consider a nannofossils as a fragment when it is less than  
295 half. Nannofossil fragmentation was calculated using the sum of whole nannofossil specimens  
296 and fragments counted in each sample as follows:

297

$$298 \quad \text{Nannofossil fragmentation} = \frac{\sum \text{fragments}}{\sum \text{fragments} + \sum \text{whole specimens}} \quad (2)$$

299

300 **Nannofossil and abiogenic particle weight.** Nannofossil weight was estimated at Site 1209  
301 following the method described by Beaufort et al., 2014. For each sample, >1000 images of



302 individual nanofossils were obtained using a fully automated polarizing microscope Leica  
303 DM6000B with an objective HCX PL APO 100/1.47, equipped with a SPOT Flex camera  
304 (Diagnostic Instrument) and a pair of circular polarizers, acquired using the Calciprobe macro  
305 with two LabView runtimes and treated with the automatic coccolith recognition system  
306 SYRACO (Beaufort and Dollfus, 2004) to separate nanofossils and abiogenic calcite  
307 particles. All images were inspected and some residual classification errors were corrected  
308 manually. The nanofossil images were then classified in 14 separate classes, on the basis of  
309 their shape, size and birefringence (Supplementary Information). This part of the process was  
310 done manually, since no automatic recognition is available yet for the studied time interval.  
311 For each sample, the surface and thickness of each nanofossil was measured in pixel (i.e.,  
312 brightness) on the obtained gray level images (100 images for each group) with ImageJ, with  
313 values ranging from 0 (black) to 255 (white). Nanofossil volume ( $V_p$ ) was calculated (voxel)  
314 by multiplying the measured area ( $A_p$ ) and the thickness ( $t_p$ ), as below, where “p” stands for  
315 pixel:

$$316 \quad V_p = A_p * t_p \quad (3)$$

317 These values were multiplied by 1.62  $\mu\text{m}$  (the maximum measureable thickness in this  
318 configuration) and divided by 255 (the maximum measureable pixel value with a 8 bit  
319 camera, see ref Beaufort et al., 2014 for further details).

$$320 \quad C = V_p * 1.62/255 \quad (4)$$

321 The obtained C value (voxel\* $\mu\text{m}$ ) was multiplied by the area of one pixel ( $S=0.0036 \mu\text{m}^2$  in  
322 our case) and by the density of calcite  $d=2.71 \text{ g/cm}^3$  to calculate the weight M (pg):

$$323 \quad M = C * S * d \quad (5)$$

324 For specimens belonging to *Fasciculithus* and *Discoaster* genera, this method allowed a  
325 robust assessment of the surface but systematically underestimated the lith thickness. A  
326 number of adjustments were thus necessary to obtain reliable results (Supplementary  
327 Information).

328 The weight of abiogenic calcite blades in each sample at Site 1209 was estimated using their  
329 thickness, length and width measured in SEM at 1550x magnification for all the studied  
330 samples (Supplementary Information).

331

332 **Age models.** Age models for ODP Site 1209 and Leg 208 sites at Walvis Ridge (including  
333 Site 1263) were developed assuming that sedimentation rates in these carbonate-rich sequence  
334 were predominantly controlled by changes in carbonate accumulation, either as changing net  
335 production or preservation (Supplementary Information). Sedimentation rates (SR) were  
336 calculated assuming the non-carbonate (i.e., terrigenous) fraction (NCF) flux and the  $^3\text{He}_{\text{ET}}$   
337 flux remained constant during the study interval (Supplementary Information) using the  
338 following equation:

339

$$340 \text{ SR} = F_X / ([X] * \rho) \text{ (6)}$$

341

342 where SR is the sedimentation rate in  $\text{m ky}^{-1}$ ,  $\rho$  the dry bulk density (DBD) in  $\text{g cm}^{-3}$ ,  $F_X$  is the  
343 flux of the considered component X in unit  $\text{cm}^{-2} \text{ky}^{-1}$ , and [X] its concentration per gram of  
344 sediment. DBD values were estimated at each site using the relationship between shipboard  
345 gamma-ray attenuation measurements and discrete DBD measurements (Marcantonio et al.,  
346 2009). For each site,  $F_X$  was iteratively adjusted to obtain a duration of  $94 \pm 1$  ky between  
347 carbon isotope inflexion points A (PETM onset) and F (Zachos et al., 2005). This duration  
348 was selected to facilitate comparisons with the widely used age model of Röhl et al. (2007)  
349 and is within error in line with the  $101 \pm 9$  ky duration constrained by most recent  
350 astronomical age models of expanded continental records of the Bighorn Basin (5 precession  
351 cycles; van der Meulen et al., 2020). The resulting  $F_X$  for each sedimentary component for  
352 each sites is given in Extended Data Fig. 1. The obtained relative changes in SR and age  
353 models assuming constant  $^3\text{He}$  and NCF fluxes show a high degree of self-consistency and  
354 appear much more realistic in terms of sedimentology than published astronomical age  
355 models for these sites (Supplementary Information).

356

357 **Accumulation rates.** We calculated nannofossil accumulation rates using the formula:

$$358 \text{ NAR} = X * \text{AR} * d \text{ (7)}$$

359 where NAR is the nannofossil accumulation rate ( $\text{n/m}^2/\text{yr}$ ), X is the absolute abundance of  
360 nannofossils ( $\text{n/g}$ ), AR is the accumulation rate ( $\text{cm/ky}$ ), d is the dry bulk density of the  
361 sediment (see Supplementary Information). Nannofossil mass accumulation rate was  
362 calculated using the formula as follows:

364

$$\text{MAR}_n = \sum \text{MAR}_x \text{ (8)}$$

363 where ( $\text{MAR}_n$ ;  $\text{g/cm}^2/\text{ky}$ )  $\text{MAR}_x$  is the MAR of every nannofossil class that we counted).

365 The  $MAR_x$  of each class was calculated as follows:

366

$$367 \quad MAR_x = NAR_x * weight(x) * AR * d \quad (9)$$

368

369 where  $NAR_x$  is the NAR of each class. The MAR of the fine fraction ( $MAR_{ff}$  (g/cm<sup>2</sup>/ky), was  
370 calculated using the formula:

371

$$372 \quad MAR_{ff} = CaCO3_{ff} * AR * d \quad (10),$$

373

374 where  $CaCO3_{ff}$  (wt %) is the weight percent calcium carbonate content of the fine fraction,  
375 AR is the accumulation rate (cm/ky) and d is the dry density of the sediment after Bralower et  
376 al., 2002 (ship data).

377 Similarly, we calculated the  $MAR_{cf}$ , which is the MAR of the coarse fraction.

378

$$379 \quad MAR_{cf} = CaCO3_{cf} * AR * d \quad (11)$$

380

381 **Calcareous particle contribution.** The mass of carbonate produced by nannofossils and  
382 calcite blades was calculated as follows:

383

$$384 \quad Mass \ CaCO3(i) = X(i) * m(i) \quad (12)$$

385 Where:

386

- 387 •  $Mass \ CaCO3(i)$ = Mass of  $CaCO3$  produced by every class (i) in gr per gr. of rock;
- 388 •  $X(i)$ =absolute abundance of (i) in number of nannofossils per gr. of rock;
- 389 •  $m(i)$ =mean of the weight of (i) in gr.

390

$$391 \quad \%CaCO3(i) = (Mass \ CaCO3(i)/CaCO3\%) * 100 \quad (13)$$

392 Where:

- 393 •  $\%CaCO3(i)$ =percentage of  $CaCO3$  produced by a class of nannofossils
- 394 •  $Mass \ CaCO3(i)$ =Mass of  $CaCO3$  produced by every class (i) in gr;
- 395 •  $CaCO3\%$ = % of  $CaCO3$  of each sample.

396

$$397 \quad \%CaCO3 \ (nanno) = \sum[\%CaCO3 \ (i)] \quad (14)$$

398 Where:

399

400 • %CaCO<sub>3</sub> (nanno)= percentage of CaCO<sub>3</sub> produced by nannofossils;

401 • %CaCO<sub>3</sub>(i)=percentage of CaCO<sub>3</sub> produced by a class (i).

402 **Stable calcium isotope measurements.** Washed sediment residuals from the study of  
403 Petrizzo, 2007 were dry-sieved and specimens of the photosymbiotic, surface-dwelling  
404 planktonic foraminiferal species *Morozovella velascoensis* were hand-picked from the size-  
405 fraction 250-355 µm. About 6 specimens per sample were necessary to supply sufficient  
406 calcium carbonate and to limit the effect of individual variation on the calcium isotope values.  
407 The specimens analyzed were free of sediment infilling or visible dissolution features. Careful  
408 observation of the shell ultrastructure of randomly selected specimens at high magnification  
409 (2000x) using a Phenom SEM G2 PRO confirmed the excellent preservation of the  
410 foraminifera. The specimens of *M. velascoensis* were further ultrasonically cleaned in  
411 distilled water, weighted and dissolved in subboiled distilled 1N HCl acid and processed  
412 through AG50X-W12 cation exchange resin in 1N HCl medium to dispose of sample matrix  
413 (i.e., phosphates, sulfates, alkali elements, and Mg). Ca and Sr fractions were collected in 6N  
414 HCl medium, and Ca fractions were separated from Sr by loading samples onto columns  
415 filled with Sr-specific resin (Eichrom Sr-Spec) in subboiled distilled 3N HNO<sub>3</sub> medium.  
416 Blanks for the whole procedure did not exceed 100 ng Ca (Tacail et al., 2017), i.e., about 200  
417 times smaller than the smallest processed Ca samples (about 20 µg). A standard-sample  
418 bracketing measurement method was used with the ICP Ca Lyon standard Tacail et al., 2014  
419 as bracketing standard. Measurements of all samples and standards were performed during  
420 two sessions in 2018 using a Neptune MC-ICP-MS at the Laboratoire de Géologie de Lyon.  
421 The  $\delta^{43/42}\text{Ca}$ - $\delta^{44/42}\text{Ca}$  values of all measured samples did not deviate statistically from the  
422 0.507 slope predicted by the linear approximation of exponential mass-dependent  
423 fractionation. If the calcium isotopic composition of standards is taken into account, the slope  
424 of the line is 0.5199. The measurements were systematically checked for long-term precision  
425 and accuracy using SRM1486 bone meal NIST secondary standard previously described and  
426 analyzed for Ca isotope compositions (Tacail et al., 2016, Heuser et al., 2011, Martin et al.,  
427 2015, Tacail et al., 2014, Heuser et al., 2016). SRM1486 yielded constant values across the  
428 six different analysis sessions, with an average  $\delta^{44/42}\text{Ca}$  value of  $-0.98 \pm 0.18\text{‰}$  (2 SE, n =  
429 30), in agreement with previously published values (as listed in Table S3), notably  $-1.03 \pm$   
430  $0.01\text{‰}$  (2 SE, n = 120) (Tacail et al., 2014). We also analyzed the commonly used SRM915b  
431 clinical-grade carbonate standards, and ICP1 Ca solution used as standard in former studies  
432 (Morgan et al., 2011, Channon et al., 2015). All measured  $\delta^{44/42}\text{Ca}$  values of standards and

433 previously published compositions are given for comparison in Table S3. Long-term external  
 434 precision was estimated using the SRM1486 standard and yields a 2 SD value of 0.12‰ for  
 435  $\delta^{44/42}\text{Ca}$  for 112 analyses, over the two sessions. Values of the  $\delta^{44/42}\text{Ca}$  Ca were converted into  
 436  $\delta^{44/40}\text{Ca}$  multiplying by mass fractionation ratio  $(1/m_{40}-1/m_{44})/(1/m_{42}-1/m_{44}) =$   
 437 2.099454809 (where  $m_x$  is the exact atomic mass of each calcium isotopes). All Ca isotope  
 438 compositions are expressed in per mil units, using the “delta” notation for the  $^{44}\text{Ca}/^{40}\text{Ca}$   
 439 isotope ratios defined as follows:

440

$$441 \delta^{44/40}\text{Ca} = \left( \frac{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}}{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{ICP Ca Lyon}}} - 1 \right) * 1000 \quad (15)$$

442 where  $(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}$  and  $(^{44}\text{Ca}/^{40}\text{Ca})_{\text{ICP Ca Lyon}}$  are Ca isotope abundance ratios measured in  
 443 sample and ICP Ca Lyon bracketing standard, respectively.

444 Calcium isotope values were expressed relative to SRM 915b and modern sea water to  
 445 compare with literature data. We converted  $\delta^{44/42}$  values relatively to ICP Ca Lyon standard in  
 446  $\delta^{44/42}$  relatively to 915b by adding 0.06. By multiplying by 2.1 (as expressed in the equation  
 447 above) we can convert it  $\delta^{44/40}$ . We added 0.72 to all values to express them relatively to 915a  
 448 and to express values relatively to modern sea water we subtracted 1.88 from values  
 449 expressed relatively to 915a (Griffith et al., 2008, 2015).

450 |

### 451 **Ocean carbonate chemistry reconstruction**

452 The carbonate system can be described by six fundamental parameters ( $[\text{CO}_3^{2-}]$ ,  $[\text{HCO}_3^-]$ ,  
 453 DIC, TA,  $p\text{CO}_2$ , and pH), but the knowledge of only two parameters along with T, S, and P,  
 454 allows the calculation of the four others using published dissociation constants (Zeebe, 2012).  
 455 For each considered level, we have thus estimated T using average *M. velascoensis*  $\delta^{18}\text{O}$   
 456 values (Zachos et al., 2003), a constant S of 37 salinity unit and P of 7 bar (assuming *M.*  
 457 *velascoensis* lived at depth of 70 m), in line with Penmann et al (2014). Carbonate chemistry  
 458 parameters were then calculated with the CO2syst calculator  
 459 (<https://www.nodc.noaa.gov/ocads/oceans/CO2SYS/co2rprt.html>) using dissociation  
 460 constants from Meherbach et al., 1973 refitted by Dickson and Millero, 1987 and  
 461 Uppstrom 1974 and applying three complementary approaches: 1)  $[\text{CO}_3^{2-}]$  were computed  
 462 from *M. velascoensis*  $\delta^{44}\text{Ca}$  values assuming an initial concentration of 80  $\mu\text{mol}/\text{kg}$  (Zeebe,  
 463 2012) and the highest end-member  $\delta^{11}\text{B}$ -derived pH of Penmann et al (2014) to infer all other  
 464 parameters (DIC, TA,  $p\text{CO}_2$  and  $[\text{HCO}_3^-]$ ); 2) DIC was computed from *M. velascoensis*

465 Mg/Ca-  $\delta^{18}\text{O}$  pairs assuming an initial concentration of 2200  $\mu\text{mol/kg}$  (Luo et al., 2016) and  
466 the highest end-member  $\delta^{11}\text{B}$ -derived pH of Penmann et al (2014) to infer  $[\text{CO}_3^{2-}]$ , TA,  $p\text{CO}_2$   
467 and  $[\text{HCO}_3^-]$ ; 3) pH and DIC were adjusted manually within proxy uncertainties to reproduce  
468 trends in saturation recorded at Site 1209 and calculate  $[\text{CO}_3^{2-}]$ , TA,  $p\text{CO}_2$  and  $[\text{HCO}_3^-]$ .

#### 469 **Extended data**

470

471 **Extended Data Fig. 1. Sedimentation rates across the PETM in key deep-sea sites. a,**  
472 Parameters used to derive the age models assuming a constant extraterrestrial helium ( $^3\text{He}_{\text{ET}}$ )  
473 flux or constant non-carbonate fraction (CNCF) flux and that the interval between carbon  
474 isotope inflexion points A and F was deposited within  $94 \pm 1$  ky (Rohl et al., 2007), consistent  
475 with the  $101 \pm 9$  ky duration produced for the same time interval by latest astronomical age  
476 models of expanded continental records (van der Meulen et al., 2020). The primary NCF,  
477  $\text{CaCO}_3$  and  $^3\text{He}_{\text{ET}}$  data used to derive these parameters are from Bralower et al. (2014); Farley  
478 and Eltgroth (2003); Griffith et al. (2015); Kelly et al. (2010); Murphy et al. (2010); Zachos et  
479 al. (2005). Note that the mean PETM  $^3\text{He}_{\text{ET}}$  flux calculated at Site 1209 is within error  
480 identical to the  $^3\text{He}_{\text{ET}}$  flux of  $5.9 \pm 0.9 \times 10^{-13} \text{ cm}^3\text{STPcm}^{-2}\text{ka}^{-1}$  calculated by Marcantonio et  
481 al. (2009) for a 800 ky-long upper Paleocene (-58 Ma) interval from the same site. **b-e,**  
482 Stratigraphic changes in sedimentation rates (SR) assuming constant fluxes of NCF (closed  
483 dots) and  $^3\text{He}_{\text{ET}}$  (open squares) for the N Pacific ODP Site 1209 (**b**), SE Atlantic ODP sites  
484 1263 (**c**) and 1266 (**d**), and S Ocean ODP Site 690 (**e**). The  $^3\text{He}_{\text{ET}}$ -derived SR values were  
485 smoothed using 3-point (Site 1209) or 5-point (Site 1266 and 690) running means to reduce  
486 the statistical effects of individual, outsized  $^3\text{He}_{\text{ET}}$ -bearing particles (Murphy et al., 2010).  
487 The green shaded band in **b-e** illustrates the PETM core interval as defined in **a**. PEB =  
488 Paleocene-Eocene boundary; ODP = Ocean Drilling Program.

489

490 **Extended Data Fig. 2. Carbonate sediment depositional dynamics across the PETM in**  
491 **selected deep oceanic sites. a-d,** reconstructions based on  $^3\text{He}_{\text{ET}}$ -inferred sedimentation rates;  
492 age models; **e-h,** reconstructions based on CNCF-inferred sedimentation rates; **a, e,** Bulk  
493 carbonate carbon isotope records (Kelly et al., 2005; Murphy et al., 2010; Penman et al.,  
494 2014; Takeda and Kaiho, 2007; Zachos et al., 2005). **b, f,** Changes in mass accumulation rates  
495 of fine fraction ( $\Delta\text{MAR}$  fine fraction) relative to pre-PETM maximum values. **c, g,** Mass  
496 accumulation rates of the coarse (foraminiferal) fraction. **d, h,** Nannofossil fragmentation.  
497 The primary coarse fraction data used to derive mass accumulation rates in **b-g** are from (  
498 Kelly et al., 2010; Kelly et al., 2005; Westerhold et al., 2018)



499

500 **Extended Data Fig. 3. Stable calcification rates of dominant nannofossil assemblages**  
501 **across the PETM at Site 1209.** Coccolith (**b-c**) and nannolith (**d-e**) weight for the most  
502 abundant genera at Site 1209B. Error bars reflect 2 standard error (2 SE).

503

504 **Extended Data Fig. 4. Organic and inorganic productivity across the PETM in deep-sea**  
505 **sites.**

506

507 **Extended Data Fig. 5.**  $\delta^{43/42}\text{Ca}$  on y-axis (per mil) as a function of  $\delta^{44/42}\text{Ca}$  on x-axis (per  
508 mil) relative to ICP Ca Lyon. Ca isotope composition falls on a line with a y axis intercept of  
509 0.0054 in the first graph and 0.0035 in the second one indistinguishable from theoretical 0‰  
510 intercept, and a slope of 0.5769 in the first graph and 0.05199 in the second one,  
511 indistinguishable from 0.507 predicted slope according to exponential law linear  
512 approximation of mass-dependent fractionation. Error bars correspond to average 2 SD  
513 precision on  $\delta^{44/42}\text{Ca}$  (per mil) and  $\delta^{43/42}\text{Ca}$  (per mil). Black dots are samples measured in this  
514 study; red dots are standards. The blue lines delimit the prediction interval, and the red lines  
515 corresponds to the 95% confidence interval on the regression line.

516

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522

523 **Author contributions.** AM and GS equally contributed to this paper in conceiving, writing  
524 and supervising the work. LB contributed in the data acquisition and interpretation of  
525 nannofossil mass. NP acquired nannofossils data at Site 1263 under the supervision of  
526 Alessandro Menini. JM and AH equally contributed in the acquisition of calcium isotopes  
527 data. FQ helped in the taxonomy of planktonic foraminifera and in the paleoecological  
528 interpretation. MRP provided the planktonic foraminifera samples for calcium isotopes  
529 analyses. KF provided previously unpublished  $\text{CaCO}_3$  and  $^3\text{He}$  data that were fundamental to  
530 develop the age model. EM contributed to the paleoceanographic interpretations of the PETM  
531 and to the coordination of this research.

532



533 **Materials & Correspondence.** Correspondence and requests for materials should be  
534 addressed to Alessandro Menini.

535

536 **Additional Information:** Supplementary Information is available for this paper.

537 Correspondence and requests for materials should be addressed to Alessandro Menini.

1 FO *C. bownii* 3 LO *B. supremus* 2 FO *D. araneus* 4 LO *F. richardii* group  
 —●— ODP Site 1263 —■— ODP Site 1209

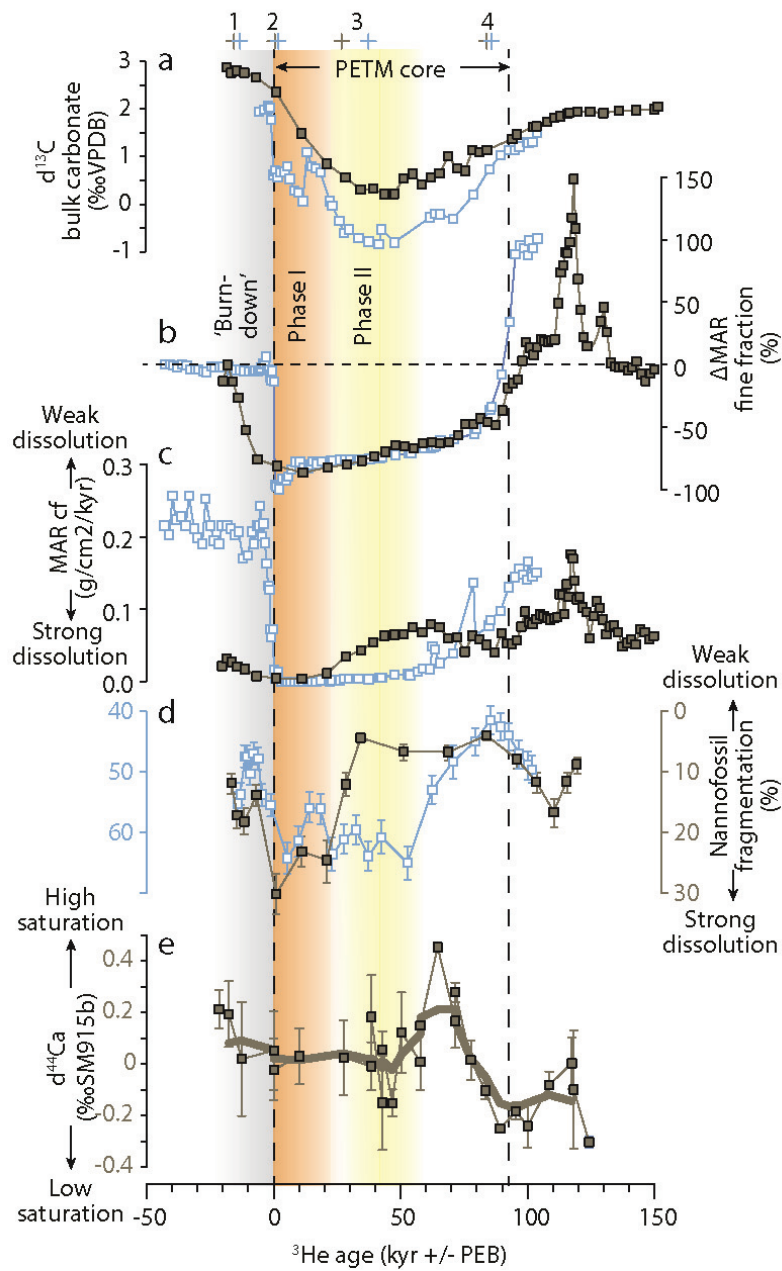
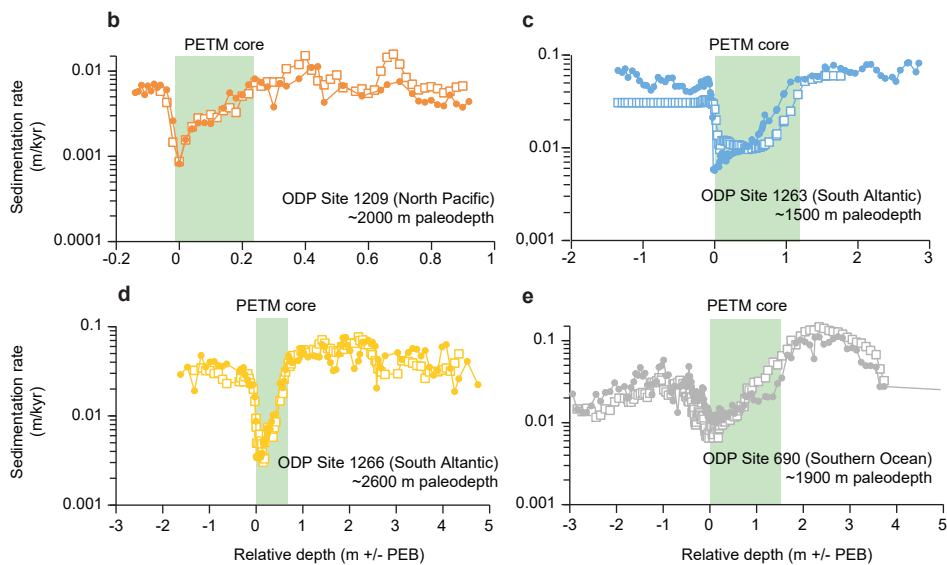


Figure 1. Synthesis of the main parameters discussed in the text for Site 1209 (Tropical Pacific) and 1263 (Tropical Atlantic). Age is expressed relatively to the PETM and reconstructions are based on  $^3\text{He}$ ET-inferred sedimentation rates. See main text for further details. a., Bulk carbonate carbon isotope records (Kelly et al., 2005; Murphy et al., 2010; Penman et al., 2014; Takeda and Kaiho, 2007; Zachos et al., 2005). b, Changes in mass accumulation rates of fine fraction ( $\Delta\text{MAR}$  fine fraction) relative to pre-PETM maximum values. c, Mass accumulation rates of the coarse (foraminiferal) fraction. d, Nannofossil fragmentation. e., Calcium isotopes. Error bars correspond to 2SD. The thick line corresponds to a 3-points average. The primary coarse fraction data used to derive mass accumulation rates in b-g are from (Kelly et al., 2010; Kelly et al., 2005; Westerhold et al., 2018)

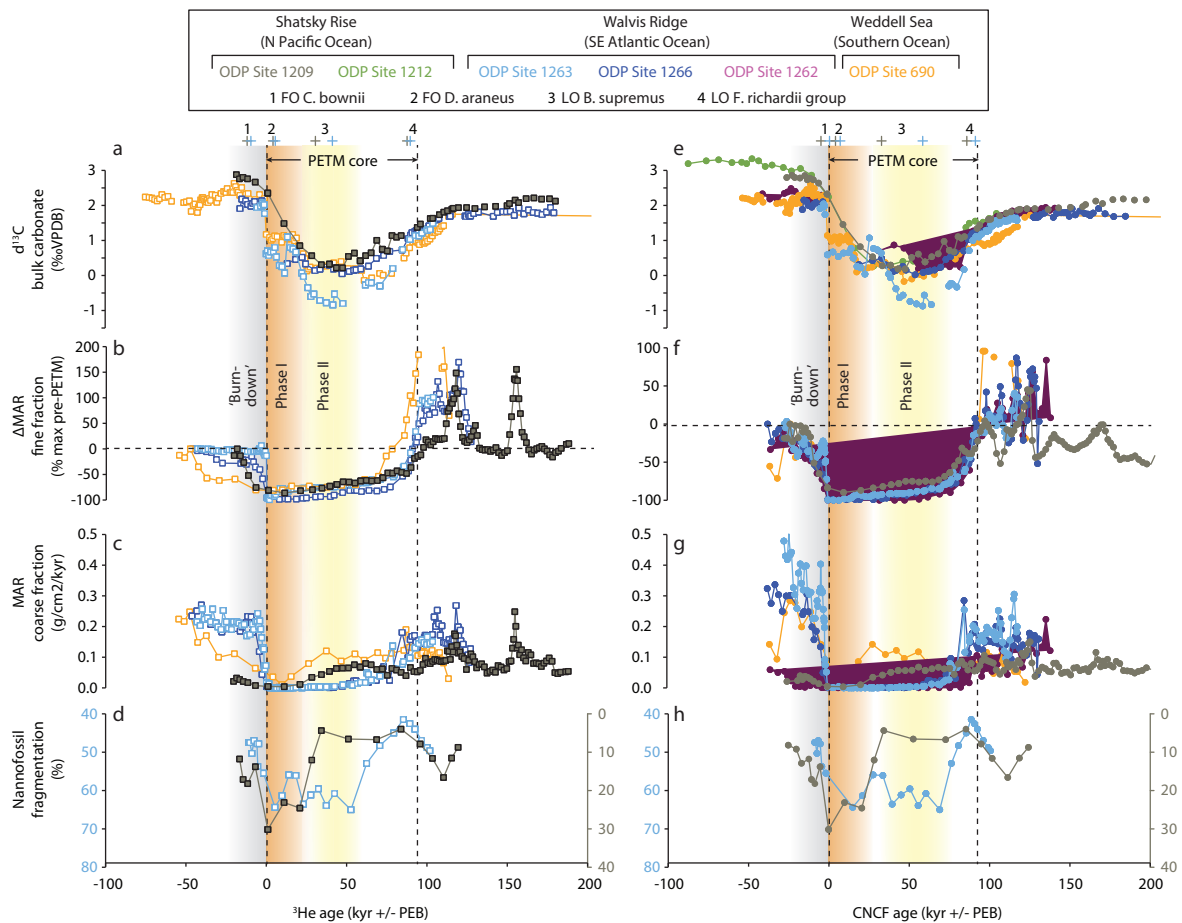
**a**

Site/age model	Component X	Methodology	$F_x$	$F_x$ units	PETM onset	Inflection point F
ODP Site 1209B/CNCF	NCF	Acid leaching	8.2	$\text{g cm}^{-2} \text{myr}^{-1}$	196.46 mbsf	196.23 mbsf
ODP Site 1209B/3He	$^3\text{He}_{\text{ET}}$	Noble gas mass spectrometry	5.2	$10^{-13} \text{cm}^3 \text{STPcm}^{-2} \text{kyr}^{-1}$	196.46 mbsf	196.23 mbsf
ODP Site 1263CD/CNCF	NCF	Coulometry	770.0	$\text{g cm}^{-2} \text{myr}^{-1}$	335.29 rmcd	334.11 rmcd
ODP Site 1263/3He	$^3\text{He}_{\text{ET}}$	Noble gas mass spectrometry	N/A*	N/A*	335.29 rmcd	334.11 rmcd
ODP Site 1266BC/CNCF	NCF	Acid leaching	450.0	$\text{g cm}^{-2} \text{myr}^{-1}$	306.77 rmcd	306.02 rmcd
ODP Site 1266BC/3He*	$^3\text{He}_{\text{ET}}$	Noble gas mass spectrometry	6.7	$10^{-13} \text{cm}^3 \text{STPcm}^{-2} \text{kyr}^{-1}$	306.77 rmcd	306.02 rmcd
ODP Site 690B/CNCF	NCF	Acid leaching	494.0	$\text{g cm}^{-2} \text{myr}^{-1}$	170.64 mbsf	169.1 mbsf
ODP Site 690B/3He	$^3\text{He}_{\text{ET}}$	Noble gas mass spectrometry	6.86	$10^{-13} \text{cm}^3 \text{STPcm}^{-2} \text{kyr}^{-1}$	170.64 mbsf	169.1 mbsf
ODP Site 1262A/CNCF	NCF	Coulometry	320.0	$\text{g cm}^{-2} \text{myr}^{-1}$	140.11 mbsf	139.71 mbsf
ODP Site 1212B/CNCF	NCF	Coulometry	20.7	$\text{g cm}^{-2} \text{myr}^{-2}$	79.92 mbsf	79.68 mbsf

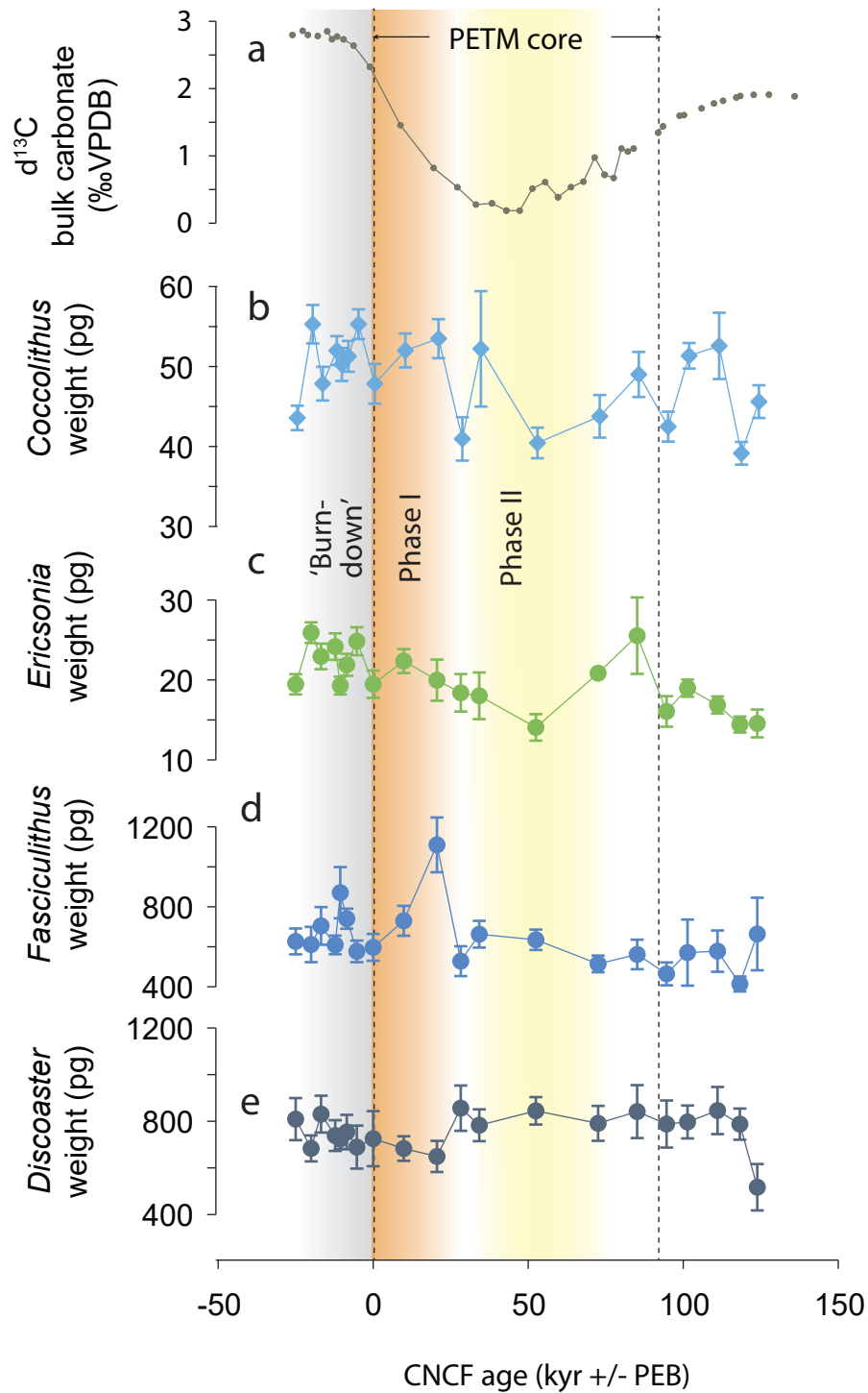
\* $^3\text{He}$  contents not published for ODP Site 1263.  $^3\text{He}$ -derived sedimentation rates of Ma et al. (2014) were multiplied by 1.55 to produce a duration of 94 kyr between the PETM onset and F.



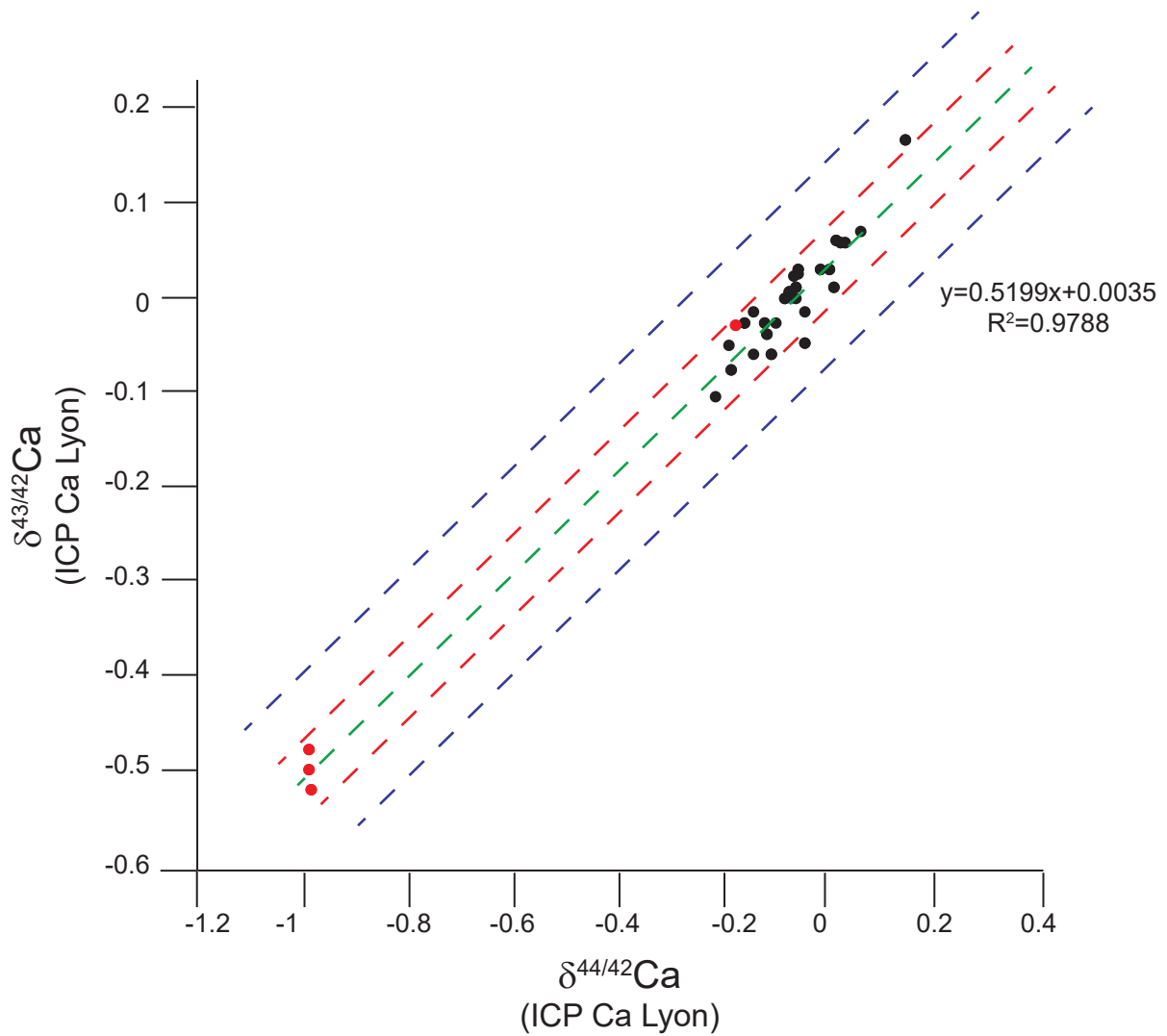
Extended Data Fig.1. Sedimentation rates across the PETM in key deep-sea sites. a, Parameters used to derive the age models assuming a constant extraterrestrial helium ( $^3\text{He}_{\text{ET}}$ ) flux or constant non-carbonate fraction (CNCF) flux and that the interval between carbon isotope inflexion points A and F was deposited within  $94 \pm 1$  ky (Rohl et al., 2007), consistent with the  $101 \pm 9$  ky duration produced for the same time interval by latest astronomical age models of expanded continental records (van der Meulen et al., 2020). The primary NCF,  $\text{CaCO}_3$  and  $^3\text{He}_{\text{ET}}$  data used to derive these parameters are from Bralower et al. (2014); Farley and Eltgroth (2003); Griffith et al. (2015); Kelly et al. (2010); Murphy et al. (2010); Zachos et al. (2005). Note that the mean PETM  $^3\text{He}_{\text{ET}}$  flux calculated at Site 1209 is within error identical to the  $^3\text{He}_{\text{ET}}$  flux of  $5.9 \pm 0.9 \times 10^{-13} \text{cm}^3 \text{STPcm}^{-2} \text{ka}^{-1}$  calculated by Marcantonio et al. (2009) for a 800 ky-long upper Paleocene (-58 Ma) interval from the same site. b-e, Stratigraphic changes in sedimentation rates (SR) assuming constant fluxes of NCF (closed dots) and  $^3\text{He}_{\text{ET}}$  (open squares) for the N Pacific ODP Site 1209 (b), SE Atlantic ODP sites 1263 (c) and 1266 (d), and S Ocean ODP Site 690 (e). The  $^3\text{He}_{\text{ET}}$ -derived SR values were smoothed using 3-point (Site 1209) or 5-point (Site 1266 and 690) running means to reduce the statistical effects of individual, outsized  $^3\text{He}_{\text{ET}}$ -bearing particles (Murphy et al., 2010). The green shaded band in b-e illustrates the PETM core interval as defined in a. PEB = Paleocene-Eocene boundary; ODP = Ocean Drilling Program.



Extended Data Fig. 2. Carbonate sediment depositional dynamics across the PETM in selected deep oceanic sites. a-d, reconstructions based on  $^3\text{HeET}$ -inferred sedimentation rates; age models; e-h, reconstructions based on CNCF-inferred sedimentation rates; a, e, Bulk carbonate carbon isotope records (Kelly et al., 2005; Murphy et al., 2010; Penman et al., 2014; Takeda and Kaiho, 2007; Zachos et al., 2005). b, f, Changes in mass accumulation rates of fine fraction ( $\Delta\text{MAR}$  fine fraction) relative to pre-PETM maximum values. c, g, Mass accumulation rates of the coarse (foraminiferal) fraction. d, h, Nannofossil fragmentation. The primary coarse fraction data used to derive mass accumulation rates in b-g are from ( Kelly et al., 2010; Kelly et al., 2005; Westerhold et al., 2018)



Extended Data Fig. 3. Stable calcification rates of dominant nannofossil assemblages across the PETM at Site 1209. Coccolith (b-c) and nannolith (d-e) weight for the most abundant genera at Site 1209B. Error bars reflect 2 standard error (2 SE).



Extended Data Fig. 5.  $\delta^{43/42}\text{Ca}$  on y-axis (per mil) as a function of  $\delta^{44/42}\text{Ca}$  on x-axis (per mil) relative to ICP Ca Lyon. Ca isotope composition falls on a line with a y axis intercept of 0.0054 in the first graph and 0.0035 in the second one indistinguishable from theoretical 0‰ intercept, and a slope of 0.5769 in the first graph and 0.05199 in the second one, indistinguishable from 0.507 predicted slope according to exponential law linear approximation of mass-dependent fractionation. Error bars correspond to average 2 SD precision on  $\delta^{44/42}\text{Ca}$  (per mil) and  $\delta^{43/42}\text{Ca}$  (per mil). Black dots are samples measured in this study; red dots are standards. The blue lines delimit the prediction interval, and the red lines corresponds to the 95% confidence interval on the regression line.

**a**

	Abs. Ab.	NAR	<i>Umbilicosphaera</i> weight	<i>Coccolithus</i> weight	<i>Fasciculithus</i> weight
F	2.685	20.76	4.143	2.359	3.106
p (same)	8.881E-04	2.295E-23	5.392E-09	7.520E-04	9.179E-06
	<i>Discoaster</i> weight	Calcite blades length	Calcite blades width	$\delta^{44}\text{Ca}$ (April 2018)	$\delta^{44}\text{Ca}$ (May 2018)
F	0.9389	6.793	3.439	4.117	5.41
p (same)	5.339E-01	3.073E-16	1.450E-06	1.567E-04	1.721E-03

**b**

	NAR-MARff	NAR-MARn	MARn-MARff	MARff-Mg/Ca	MARff-Mg/Ca-(M.vel)	MARff-Mg/Ca-(A.sol)	MARff-B/Ca-(M.vel)	MARff-B/Ca-(A.sol)	MARff-pH	<i>Thoracosphaera</i> abs.ab-pH	<i>Thoracosphaera</i> abs.ab-Mg/Ca
R	0.81	0.65	0.84	-0.85	-0.76	-0.76	0.51	0.82	0.70	-0.66	0.66
R <sup>2</sup>	0.65	0.43	0.71	0.72	0.57	0.57	0.26	0.68	0.49	0.43	0.43
p value	1.22E-06	1.52E-04	1.61E-04	2.98E-12	2.62E-09	1.35E-07	9.68E-06	4.71E-05	2.72E-03	5.45E-03	1.51E-02

**Extended Data Table 1. a.**, F and p(same) values after one way ANOVA test (See Methods) for Absolute Abundances, NAR, weight of *Umbilicosphaera*, *Coccolithus*, *Fasciculithus*, *Discoaster*, Calcite blades length and width and  $\delta^{44}\text{Ca}$  for the two sessions. **b.**, Pearson's R coefficient, R<sup>2</sup> and p(value) resulting from linear modeling to test correlation between all the parameters discussed in the main text. Data are for Site ODP 1209 (Shatsky Rise, Pacific Ocean).



# Supplementary information by Menini et al.

## 1. Samples

### 1.1. Site 1209

Sediment samples were obtained from across the PETM interval at Ocean Drilling Program (ODP) Site 1209 (Shatsky Rise, Central Pacific; 32° 39.1' N, 158° 30.4' E; 2387 m water depth; 1900 m paleodepth, Takeda and Kaiho, 2007). The position of the site relative to the PETM paleogeography has been reported in Bralower et al., 2002. Contrarily to the large majority of previous studies of the core 1209B-22H-1 from Site 1209 that used sediments from the working half, the samples we have analyzed for their nannofossil content have been collected from the archive half. Measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of these samples indicate that the working half has been offset downward by 25 mm relative to the archive half (Menini et al., submitted), consistent with the downward offset of 25 mm relative to the archive half during sampling mentioned in (Colosimo et al., 2006). The depths of the samples investigated in this study have therefore been shifted downward by a constant offset of 25 mm to facilitate comparisons with previously published datasets, and all sampling depths have been expressed relative to the main lithological change (i.e., 135 cm below the top of core 1209B-22H-1) to facilitate comparisons between records.

### 1.2. Site 1263

Sediment samples from Ocean Drilling Program (ODP) Site 1263 (Walvis Ridge, Southern-East Atlantic; 28°32'S; 02°47'E; 2717 m water depth; 1500 m paleodepth, Zachos et al., 2004) were also studied for comparison with ODP Site 1209. The position of the site relative to the PETM paleogeography has been reported in Zachos et al., 2004. In line with previous studies (Zachos et al., 2005; Kelly et al., 2010), we analyzed the Hole 1263C between 333.61 and 335.20 rmcd, and Hole 1263D between 335.20 and 335.65 rmcd. The PETM onset is marked by a sharp contact between grayish brown ash-bearing clay above and light gray nannofossil ooze below. Note that our record undersample the PETM onset and associated clay layer located between 335.20 and 335.30 rmcd, with the lowermost studied sample in the core 14H-2 at Hole 1263C being located 7 cm above the base of the clay layer and uppermost sample in the core D4H-1 at Hole 1263D being located 5 cm below the base of the clay layer.

## 34 2. Age models

### 35 2.1. Rationale

36 The Paleocene sediments of the considered sites at Shatsky Rise, Walvis Ridge and Maud  
37 Rise are overwhelmingly dominated (>85 wt%) by calcareous planktonic ooze, with  
38 subordinate amounts of terrigenous sediments, partly (Site 1263) to almost entirely (Site  
39 1209) supplied as windblown dust (Nicolo and Dickens, 2006; Woodard et al., 2011). The  
40 sediments at all sites contain no or negligible amounts (<<0.1%) of biogenic silica and  
41 organic carbon (Bralower et al., 2002)(Zachos et al., 2004). In sites where both NCF and  
42 extraterrestrial <sup>3</sup>He (<sup>3</sup>He<sub>ET</sub>) contents are available (sites 690, 1266, 1263 and 1209), their  
43 striking parallelism suggests a common controlling factor (Farley and Eltgroth, 2003; Murphy  
44 et al., 2010). Given the very different (extraterrestrial versus continental) sources and size  
45 distribution of these two components (Farley et al., 1997), the most parsimonious explanation  
46 is that both the NCF and <sup>3</sup>He<sub>ET</sub> fluxes remained fairly invariable across the PETM interval at  
47 each of these locations, and that their remarkable covariation reflects variable dilution by  
48 changing CaCO<sub>3</sub> accumulation, either through preservation or input. This conclusion is line  
49 with studies of Quaternary deep-sea sediments where SR largely depends on CaCO<sub>3</sub> fluxes in  
50 deep sea sediments. Assuming a constant flux for NCF and <sup>3</sup>He<sub>ET</sub> and knowing their  
51 concentrations, the sedimentation rate (SR) can be calculated using the equation:

52

$$53 \text{ SR} = F_X / ([X] * \rho)$$

54

55 where SR is the sedimentation rate in m ky<sup>-1</sup>,  $\rho$  the dry bulk density (DBD) in g cm<sup>-3</sup>,  $F_X$  is  
56 the flux of the considered component X in unit cm<sup>-2</sup> ky<sup>-1</sup>, and [X] its concentration per gram  
57 of sediment. DBD values were estimated at each site using the relationship between shipboard  
58 gamma-ray attenuation measurements and discrete DBD measurements (Marcantonio et al.,  
59 2009). Most previous attempts to infer SR using this method calculated <sup>3</sup>He<sub>ET</sub> fluxes using a  
60 calibration interval for which astronomical age models were also available (Farley and  
61 Eltgroth, 2003; Murphy et al., 2010). Nevertheless, this approach is limited by the  
62 uncertainties associated with duration estimates of the calibration interval (Sluijs et al., 2007),  
63 a condition that certainly explains why the PETM duration obtained using this method vary  
64 significantly between the considered sites (Murphy et al., 2010).

65 We have thus considered an alternative approach, in which the interval between carbon  
66 isotope inflexion points A (marking the PETM onset) and F, a readily identifiable and widely  
67 used segment of the PETM (van der Meulen et al., 2020; Zachos et al., 2005; Zeebe and

68 Lourens, 2019) is considered of equal duration in all sites, and have then calculated  $F_x$   
69 iteratively at each site. This methodology does not provide an independent estimate of the  
70 PETM duration, but has the advantage of capturing changes in SR relative to a self-consistent  
71 temporal scale for all sites. A similar approach assuming a constant NCF sedimentation rate  
72 over a defined interval was used by Stap et al. (2009) to derive an age model for the ETM2-  
73 H2 interval at Walvis Ridge. The most notable difference is that their model relies on NCF  
74 sedimentation rates (i.e., thickness/time) rather than fluxes (mass/area/time), and hence  
75 neglects the influence of changes in DBD. Because DBD values may vary by a factor of 2  
76 between some levels of the Paleocene-Eocene interval at Walvis Ridge, this caveat might  
77 explain why the manual adjustment of NCF rates through space and time was required to  
78 obtain a self-consistent temporal scale for the different sites.

79 To facilitate comparisons with the widely used age model of Röhl et al. (2007), we have  
80 calibrated our age models assuming that the A-F interval (Zachos et al., 2005) was deposited  
81 within  $94 \pm 1$  ky. This estimate is indeed statistically indistinguishable from the  $101 \pm 9$  ky  
82 duration constrained by the most recent astronomical age model (5 precession cycles) of  
83 expanded continental records of the Bighorn Basin (van der Meulen et al., 2020), where the  
84 A-F segment is well defined and cycle counting is facilitated by the absence of dissolution-  
85 induced condensation.

86 Recent astronomical tuning of Walvis Ridge records suggests that the A-F interval might  
87 comprise two short eccentricity cycles and lasted  $170 \pm 30$  ky (Zeebe and Lourens, 2019), i.e.,  
88 almost twice the duration used in our models. This revised duration would imply that the  $\sim 7.5$   
89 m sedimentary cycles well expressed in the Bighorn Basin correspond to obliquity cycles  
90 rather than precession; precession would correspond to the  $\sim 3.5$  m cycles currently attributed  
91 to half-precession (van der Meulen et al., 2020; Westerhold et al., 2018b). If confirmed by  
92 independent evidence, the upper estimate would roughly double the relative ages of all  
93 samples in our reconstructions, but would leave the relative changes in SR values unaffected.  
94 Because SR is the major term in the determination of  $MAR_{ff}$  and  $MAR_n$ , we are therefore  
95 confident that the major and long-lived drop in nannofossil accumulation evident from our  
96 reconstructions will be resilient to possible future adjustments of the PETM duration.

97

## 98 2.2. Shatsky Rise

99 The approach described above was used to develop a new detailed age model for sites  
100 1209 and 1212. This was done using a comprehensive reexamination of published  
101 sedimentological and geochemical records including bulk sediment, benthic and planktonic

102 foraminifera  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data (Griffith et al., 2015; Penman et al., 2014; Tripathi and  
103 Elderfield, 2005; Westerhold et al., 2011; Zachos et al., 2003), carbonate contents (Colosimo  
104 et al., 2006; Griffith et al., 2015; Zachos et al., 2003), XRF data (Westerhold et al., 2018a),  
105 helium isotopes and the non-carbonate fraction (Bralower et al., 2014). No detailed  
106 astrochronology exists for the PETM interval at Shatsky Rise, as obliquity and precession-  
107 related cycles are not obvious due to low sedimentation rate (SR) and bioturbational  
108 smoothing (Westerhold et al., 2018a; Westerhold et al., 2008). Changes in NCF in the  
109 carbonate-rich ( $\text{CaCO}_3 >90$  wt%) sediment from Site 1209B match very well smoothed  
110 extraterrestrial  $^3\text{He}$  ( $^3\text{He}_{\text{ET}}$ ) contents across the Paleocene-Eocene transition. As argued above,  
111 the repeated and parallel increases in NCF and  $^3\text{He}_{\text{ET}}$  most likely reflect episodes of decreased  
112 sedimentation rates, either resulting from decreased carbonate input or increased carbonate  
113 dissolution, as previously suggested for Fe counts at Site 1209 (Westerhold et al., 2018a).  
114 Variable  $\text{CaCO}_3$  dilution as the main controlling factor of sedimentation rates at Shatsky Rise  
115 across the PETM is also supported by parallel increases in ichthyolith (i.e., fish remains)  
116 (Tomczik et al., 2015) and Fe counts in core 1209C-11H (Westerhold et al., 2018a).

117 Because the stratigraphic position of inflection F at Site 1209 was insufficiently  
118 constrained by the relatively low resolution bulk carbonate  $\delta^{13}\text{C}$  records, its position was  
119 further refined using the core 9H-5 in Hole B of ODP Site 1212. There, the higher resolution  
120 bulk carbonate  $\delta^{13}\text{C}$  record (Griffith et al., 2015) unambiguously shows it occurs at 79.68  
121 mbsf. The correlation between these two sites and the position of point F at Site 1209 (at  
122 196.23 mbsf, i.e., 22 cm above the main lithological change) was then determined using  $\delta^{18}\text{O}$   
123 and  $\delta^{13}\text{C}$  records from both sites, which show a remarkable match in our NCF-derived age  
124 models. A notable implication of our age of these age models is that they imply a more than  
125 twofold increase in NCF fluxes from Site 1209 to Site 1212 (Extended Data Fig. 1). We are  
126 not aware of any independent data that would support such a dramatic increase in terrigenous  
127 fluxes with depth at Shatsky Rise. We note, however, that the NCF values obtained at Site  
128 1209 using coulometry (Colosimo et al., 2006; Zachos et al., 2003) are much more scattered  
129 and are offset by about 4% to higher values relative to those obtained using acid digestion  
130 (Bralower et al., 2014). As NCF values are derived from coulometric methods at Site 1212  
131 and acid leaching at Site 1212, we therefore attribute these large differences in reconstructed  
132 NCF values to methodological biases rather than to much higher terrigenous fluxes in the  
133 deeper site.

134 The developed age models assuming constant NCF and  $^3\text{He}_{\text{ET}}$  fluxes reveal very similar  
135 changes in SR throughout the study interval (Extended Data Fig. 1). These trends in SR are

136 also broadly similar to those estimated for Site 1209 using biohorizon- and stable isotope-  
137 based correlations with astronomically-tuned records of southeast Atlantic ODP Site 1262  
138 (Bralower et al., 2014; Kaiho et al., 2006; Penman et al., 2014; Westerhold et al., 2011;  
139 Westerhold et al., 2018a; Westerhold et al., 2008) (Penman et al., 2014; Westerhold et al.,  
140 2018a), which all point to extreme condensation in the PETM interval. Due to the relatively  
141 low number of available tie points, however, these SR were inherently of low resolution  
142 (hence showing step-like patterns) compared to our new age models, which allow a more  
143 realistic reconstruction of mass accumulation rates at this site.

144

## 145 2.2. Walvis Ridge

146 As with ODP sites 1266, 1209 and 690, NCF- and  $^3\text{He}_{\text{ET}}$ -derived SR at Site 1263 show a  
147 striking similarity across the PETM (Extended Data Fig. 1). We note that these SR and the  
148 resulting MAR derived from our age models provide an internal consistency among the  
149 Walvis Ridge sites across the PETM much higher than that implied by precession cycle  
150 counts at this location (Röhl et al., 2007; Westerhold et al., 2018b). Crucially, maxima in  
151 these precession-based SR and MARff occur at a variable position during the PETM  
152 recovery, while they are synchronous in both NCF- and  $^3\text{He}_{\text{ET}}$ -derived age models. Similarly,  
153 the recovery of MARff occurs abruptly and near-synchronously at the PETM core termination  
154 in our NCF- and  $^3\text{He}_{\text{ET}}$ -derived reconstructions, whereas its position appears far more variable  
155 in precession-based records. We thus suggest that a robust cycle count across the PETM at  
156 Walvis Ridge has been compromised by severe dissolution (and condensation), and we hence  
157 discarded the implied SR for our flux reconstructions.

158 Our age models imply a two-fold decrease in NCF fluxes from the shallowest Site 1263 to  
159 the deepest Site 1262 (Extended Data Fig. 1). Unlike data from Shatsky Rise, the  $\text{CaCO}_3$  data  
160 from these two sites were obtained using the same method and device (Zachos et al., 2004,  
161 2005) so that the spatial difference in NCF fluxes reconstructed here cannot be attributed to  
162 methodological biases. Such a preferential accumulation of terrigenous material in shallower  
163 sites, however, fully agrees with the long-term Paleogene NCF fluxes recorded at Shatsky  
164 Rise (Zachos et al., 2004) and with the terrigenous accumulation rates estimated by Stap et  
165 al., (2009) for the ETM2 interval.

166

## 167 **3. Nature, weight and accumulation rates of carbonate components at Site 1209**

168

169 *Calcareous nannofossils*

170 The studied nannofossil assemblages at ODP Site 1209 are diverse and generally well  
171 preserved, in agreement with previous studies (Gibbs et al., 2006a, b). Nannofossil  
172 assemblages are typical of Late Paleocene-Early Eocene (Plate 1) and these are mainly  
173 constituted of *Coccolithus* spp., *Toweius* spp., *Fasciculithus* spp., *Discoaster* spp., and  
174 *Zygrhablithus bijugatus*.

175 The preservation of the studied nannofossil assemblages across the PETM at 1209 was  
176 further investigated using a Phenom SEM G2 PRO microscope (Menini et al. under review).  
177 SEM pictures reveal a slight decline in nannofossil preservation between 1 cm below and  
178 above the PETM (-3 kyrs and 16.58 kyrs) from the onset of the event, as previously suggested  
179 by Bralower et al., 2014. Coccoliths in those samples are mostly affected by dissolution,  
180 consistently with the coeval maximum of nannofossil fragmentation.

181 Some previous studies of PETM calcareous nannofossil presented abundances using  
182 nannofossils/mm<sup>2</sup> of the slide, but these invariably used standard smear slides that are far less  
183 homogenous in terms of concentration of nannofossils per field of view. The settling method  
184 used in our study allows the sediment to settle homogeneously on the cover-slide without any  
185 turbulence, so that the number of nannofossils is comparable in different fields of view  
186 allowing a more rigorous calculation of nannofossils per gram of rock.

187

#### 188 *Nannofossil weight*

189 We estimated nannofossil weight at ODP Site 1209 following the method described by  
190 Beaufort et al., 2014. This method allows the estimate of the thickness of calcite (t) using its  
191 birefringence (Dn) and its color in grey-level (GL) in cross-polarized light. This is possible  
192 since a linear relationship exists between the thickness of a crystal (t in nm) and the  
193 retardation ( $\Gamma$ ), which represents the difference between the fast ray and the slow ray  
194 produced along the light path within a crystal. Calcareous nannofossil test is made of calcite,  
195 and its birefringence is  $Dn = -0.172$ . For further details, we refer to Beaufort et al., 2014, where  
196 all the optical theory is exhaustively explained.

197 The nannofossil images obtained using the automated microscope and automatic  
198 recognition system SYRACO were classified into 14 separate classes based on the shape, size  
199 and birefringence of the nannofossils. The acronyms of the 14 created classes along with the  
200 description of the nannofossils featured in each class are listed in Table S1.

201

202

203



Class	Corresponding nannofossils
BAR	<i>Fasciculithus</i> Top-Bottom View, <i>Z. bijugatus</i> base, <i>Sphenolithus</i> spp.
CHI	Specimens with a “chi” or a “cross” structure in the central area: <i>Chiasmolithus</i> spp., <i>Cruciplacolithus</i> spp.
CLA	High birefringence specimens, elliptical in shape: <i>Neocrepidolithus</i> , <i>Z. sigmoides</i>
COC	<i>Coccolithus</i> spp., <i>Prinsius</i> spp., <i>Toweius</i> spp.
DIS	<i>Discoaster</i> spp., <i>Biantolithus</i> spp.
GEP	Low birefringence specimens, elliptical in shape: <i>Calcidiscus</i> spp., <i>Craticullithus</i> spp., <i>Campylosphaera</i> spp.
LAN	<i>Fasciculithus</i> spp.
PON	<i>Ellipsolithus</i> spp., <i>Pontosphaera</i> spp.
RIE	Particles other than nannofossil
SPS	Broken specimens
THO	<i>Thoracosphaera</i> spp., a calcareous dinocyst
UMB	Low birefringence specimens, circular in shape: <i>Ericsonia</i> spp., <i>Umbilicosphaera</i> spp.
ZYG	<i>Zygrhablithus bijugatus</i>
BRA	<i>Braarudosphaera</i> spp.

204

205 Table S1: The different classes created on the basis of shape, birefringence and size of nannofossils.

206

207 The estimated weights of the different classes were compared to that of previous studies.

208 The length range of the coccoliths of *Coccolithus* at Site 1209 (6-14 $\mu$ m), one of the main

209 carbonate producers in the studied interval, is slightly wider but in the range of that

210 documented (10-12  $\mu$ m) for this genus in modern and Holocene sediments (Young and Ziveri,

211 2000; Beaufort and Heussner, 2001; Cubillos et al., 2012). The estimated weight of

212 *Coccolithus* coccoliths in our PETM samples (~50 pg), however, is 3 to 6 times lower than

213 that estimated for modern *C. pelagicus* (> ~150 pg) studied by Beaufort and Heussner, 2001

214 and Holocene *C. pelagicus* (~300 pg) studied by Cubillos et al., 2012. This difference is

215 largely attributable to the lower thickness of *Coccolithus* in our material (0.41  $\mu$ m, as checked

216 under SEM) compared to that reported by Cubillos et al., 2012 for Holocene samples (1.18

217  $\mu$ m). In fact, PETM *Coccolithus* are constituted by *C. pelagicus* and *C. bownii*, the latter

218 being associated with the PETM and dominating the assemblages across the event (Jiang and

219 Wise, 2007). *C. bownii* was described by Jiang and Wise, 2007 as a medium to large broadly

220 elliptical to subcircular *Coccolithus* with a broad, open central area and with a simplified tube

221 structure making the coccolith thinner. Our SEM analyses indicate that several of the

222 investigated *Coccolithus* species generally have a very open central area and a very reduced

223 proximal shield, both characters reducing the coccolith mass, and we refer to these as



224 belonging to *Coccolithus bownii*. In summary, these considerations indicate that the PETM  
225 *Coccolithus* coccoliths were consistently far thinner and lighter than that of living and  
226 Holocene representatives, in line with the conclusions of previous studies (Cubillos et al.,  
227 2012).

228 The birefringence method might not provide reliable estimates of the thickness of  
229 specimens belonging to *Discoaster* spp. and *Fasciculithus* spp., which are very thick. We  
230 have thus measured the thickness of at least 30 specimens for each of these genera in SEM to  
231 reevaluate their thickness and eventually correct the automatically acquired values. The  
232 birefringence method cannot be correctly applied to *Discoaster* spp. because these are non-  
233 birefringent in plan-view (Fig. 4, Young, 1992). The surface of *Discoaster* nannofossils was  
234 thus measured in pixel for every automatically taken picture in optical microscope and  
235 multiplied by the thickness of 2  $\mu\text{m}$  calculated by repeated SEM measurements to better  
236 estimate their volume and weight.

237 The very thick *Fasciculithus* spp. (3-5  $\mu\text{m}$ ) produces high-birefringence colors that hamper  
238 the use of grey level images for estimating their thickness (Fig. 5; Beaufort et al., 2014). As  
239 for *Discoaster* spp., the surface of *Fasciculithus* was estimated using their basal views in  
240 automatically taken pictures and multiplied by the thickness 4.5  $\mu\text{m}$  determined by repeated  
241 measurements under SEM.

242 The obtained nannofossil masses do not show substantial change across the PETM. This  
243 record is intriguing in comparison to living coccolithophores. Variations in mass of  
244 Noellharbaceae, which dominate living coccolithophore assemblages from 50 Ma onwards,  
245 has been previously correlated to increased  $p\text{CO}_2$  levels and reduced  $\text{CO}_3^{2-}$  concentrations in  
246 surface waters (Beaufort et al., 2011). Late Paleocene-Early Eocene oceans were dominated  
247 by Coccolithaceae and nannoliths (*Fasciculithus* spp., *Discoaster* spp.), which likely thrived  
248 under  $p\text{CO}_2$  levels higher than today. In all oceans at different latitudes, the most abundant  
249 taxon during the PETM is *Coccolithus* (e.g. Bralower et al., 2002; Gibbs et al., 2006 a; Agnini  
250 et al., 2007; Raffi et al., 2009). *C. pelagicus* is still present in modern oceans but it is  
251 restricted to high latitudes, where dissolved  $\text{CO}_2$  is higher relatively to low-latitudes settings.  
252 Thus, it seems like PETM nannofossil masses were relatively “insensitive” to enhanced  $p\text{CO}_2$   
253 levels, likely because the main species originated during, and were better adapted to, high  
254 carbon dioxide levels (Henderiks and Rickaby, 2007).

255

256 *Abiogenic calcite* (*'calcite blades'*)

257 Calcite blades (CB) constitute an intriguing but substantial part of pelagic carbonates  
258 preserved at ODP Site 1209 (Colosimo et al., 2006; Stoll et al., 2007c; Bralower et al., 2014).  
259 CB are prismatic calcite crystals of micrometric size, the same order of magnitude as  
260 nannofossils. Bralower et al. (2014; citing Gibbs et al., 2006a but not found in their paper or  
261 dataset) and Stoll et al (2007c) provided semi-qualitative estimate of their abundance at Site  
262 1209. Their data show a distinct peak within the PETM interval, but their record show some  
263 noticeable differences, hampering detailed comparison with our data.

264 We have quantified the shape and absolute abundance of calcite blades at Site 1209 both in  
265 optical microscope (1000x magnification) and SEM using the same samples investigated for  
266 nannofossils. Their absolute abundance (n/g) and CBAR (calcite blades accumulation rate)  
267 ( $n/m^2/yr$ ) were determined using the methodology described above for nannofossils. Their  
268 length and width were systematically measured in SEM using 30 specimens/sample at 1550x  
269 magnification for all the studied samples. We calculated the volume of all the calcite blades as  
270 follows:

$$CBv = l * w * t$$

271  
272  
273  
274 where  $l$  is the length ( $\mu m$ ),  $w$  is the width ( $\mu m$ ) and  $t$  is the thickness ( $\mu m$ ). We measured  
275 calcite blades thickness on the basis of SEM pictures, where we can observe their geometry in  
276 3D. CB weight was thus estimated by multiplying their volume by the calcite density ( $2.71$   
277  $g/cm^3$ ).

278 CBAR, absolute abundances and flux are an order of magnitude lower than those of  
279 coccoliths ( $E^8$ ). However, a five-fold increase in both abundances and CBAR is documented  
280 5 cm above the onset of the PETM, i.e., 50 kyrs after the onset of the event in our preferred  
281 age model. We performed ANOVA to compare the mean values of the CB absolute  
282 abundance across the event. This test provides us a statistical tool to infer that the average  
283 values are statistically different in the core of the event and its aftermath with respect to the  
284 intervals below and above, since the null hypothesis is not verified. We do not observe any  
285 statistically significant change in the size of calcite blades.

286  
287 Previous studies interpreted CB as diagenetic minerals that precipitated within the sediment,  
288 possibly as a consequence of high Ca and carbonate ion contents resulting from dissolution  
289 (Bralower et al., 2014). Their precipitation would have taken place once carbonate saturation  
290 recovered (Bralower et al., 2014). Their Sr/Ca ratios are almost an order of magnitude lower

291 than coeval nannofossils (Stoll et al 2007) and foraminifera (Zachos et al., 2003) and support  
292 an abiotic origin. However, precipitation in the sediment would rather result in xenomorphic  
293 crystals (cement) showing continuity with grains. Precipitation within pore space seems at the  
294 odds with their prismatic shape and their occurrence as isolated crystals without apparent  
295 contact with a specific type of particle.

296 Kozdon et al. (2013) showed SEM image with 10–15  $\mu\text{m}$  sized blade-shaped diagenetic  
297 crystallites protruding from pustular muricae of planktic foraminiferal (*M. velascoensis*) for  
298 site 865. These are coalesced atop the chamber tips. Pustular biogenic mounds on the surface  
299 of morozovellid and acarininid shells might serve as nucleation sites for cementation.  
300 Colosimo et al. (2006) also show blade-shaped crystallites that seem detached from the  
301 ‘mounds’ of planktic foraminifers. However, the shape of CB measured in this paper poorly  
302 resemble to the cemented blades on planktonic foraminifera pustulae, because they are perfect  
303 elongated rhombohedra, with sharply truncated surfaces on both sites of the blade, whilst the  
304 cemented crystals on foraminifer pustules have rather an acicular shape.

305 We alternatively suggest that these CB precipitated near the sediment/water interface in  
306 seawater or porewaters, once saturation levels recovered (Stoll et al., 2007c; Dedert et al.,  
307 2012). We note that CB absolute abundances and % in mass of carbonate are the highest in  
308 the interval where minimum foraminiferal and nannofossil fragmentation occurred and  $\text{MAR}_{\text{ff}}$   
309 is low, there they reach their largest sizes. Hence, these comparisons support the idea that  
310 their precipitation was induced by higher  $\text{CaCO}_3$  saturation state in times where primary and  
311 carbonate productivity was still low because of enhanced surface seawater stratification.

312

### 313 *Estimates of the contribution of different components to pelagic carbonate production*

314 Nanofossils are reported as the main component of the bulk sediment of the studied  
315 samples at ODP Site 1209 (70-80% in weight) while planktonic foraminifera only account for  
316 10-20% in weight (Bralower et al., 2014). In order to more precisely quantify the pelagic  
317 carbonate accumulation, we calculated the mass of carbonate produced by every component,  
318 namely nannofossils, planktonic foraminifera and calcite blades.

319 The mass of nannofossil and authigenic (CB) calcite and can be calculated as follows:

320

$$321 \quad m\text{CaCO}_3(i) = X(i) * m(i)$$

322

323 where  $mCaCO_3(i)$  is the mass of  $CaCO_3$  produced by every class ( $i$ ) in gr per gr. of rock,  $X(i)$   
324 is the absolute abundance of ( $i$ ) in number of particles per gr of rock,  $m(i)$  is the mean of the  
325 weight of ( $i$ ) in gr.

326 We can calculate the percentage of  $CaCO_3$  produced by a class of nannofossils (See section 3)  
327 using the following formula:

328

$$329 \quad \%CaCO_3(i) = (mCaCO_3(i)/CaCO_3\%) * 100$$

330

331 where  $mCaCO_3(i)$  is the mass of  $CaCO_3$  produced by every class ( $i$ ) in gr and  
332  $CaCO_3\%$  is the percentage of  $CaCO_3$  of each sample.

333 The percentage of  $CaCO_3$  produced by nannofossils is calculated as follows:

334

$$335 \quad \%CaCO_3 (nanno) = \sum [\%CaCO_3 (i)]$$

336

337 where  $\%CaCO_3(i)$  is the percentage of  $CaCO_3$  produced by a class ( $i$ ).

338 This calculation shows that nannofossil calcite compose the bulk of the sediments at Site  
339 1209 and are the main contributors to the fine-fraction (4-10  $\mu$ m), in agreement with previous  
340 studies (Extended Data Fig. 2, Bralower et al., 2014). Planktonic foraminifera, which  
341 basically constitute the coarse-fraction (> 63  $\mu$ m), account up to 10-15 % of the mass of  
342 carbonate. Calcite blades account up to ~12 % of bulk  $CaCO_3$  during the PETM.

343

#### 344 **4. Nature and accumulation rates of carbonate components at Site 1263**

345

346 Calcareous nannofossils assemblages at Site 1263 were previously studied by Raffi et al.,  
347 2009. However, they only report nannofossils/ $mm^2$  of the slide while we studied absolute  
348 abundances (n/g) using the settling technique, then we calculated nannofossil accumulation  
349 rate (NAR) as detailed in the method section.

350 Late Paleocene and Early Eocene samples are constituted by nannofossil ooze and chalky  
351 nannofossil ooze. Nannofossils compose the bulk of the  $CaCO_3$  fraction of the studied  
352 samples (90-95 wt. %) while the coarse fraction (>63  $\mu$ m), which is almost entirely  
353 constituted by planktonic foraminifera, is overall lower than 10% in weight (Kelly et al.,  
354 2010). Planktonic foraminifera fragmentation is nearly 100% during the core of the PETM  
355 and in its aftermath.

Site	Hole	Core	Section	Top Interval (cm)	Bottom Interval (cm)	Depth (mbsf)	Height above LC	Age (ky)	Nanno Abs. Ab. (n/g)	SD (n/g)	SR 3he 1209 smoothed 3pt update PETM onset m/ky	Age 3he 3pt ave ky +/- PEB	SR CNCF interpolated 1209 m/ky	Age CNCF 1209 ky +/- PEB	nanno frag. 1209 %	NAR 3he min 1209 n/cm2/ky	NAR 3he mean 1209 n/cm2/ky	NAR 3he max 1209	NAR CNCF n/cm2/ky	Dry Bulk Density g/cm3	MAR ff CNCF 1209 g/cm2/kyr
1209	B	22	1	90	91	196.03	0.42	149.72	2.83E+09	4.81E+08	1.00E-02	1.19E+02	1.09E-02	123.88	8.73E+00	2.77E+07	3.34E+07	3.90E+07	3.62E+07	1.18E+00	1.14E+00
1209	B	22	1	95	96	196.08	0.37	140.47	3.17E+09	1.09E+09	1.13E-02	1.15E+02	7.57E-03	118.26	1.15E+01	2.78E+07	4.23E+07	5.68E+07	2.83E+07	1.18E+00	7.92E-01
1209	B	22	1	100	101	196.13	0.32	128.93	2.90E+09	1.06E+09	7.28E-03	1.09E+02	7.08E-03	111.06	1.66E+01	1.57E+07	2.47E+07	3.37E+07	2.40E+07	1.17E+00	7.32E-01
1209	B	22	1	105	105	196.18	0.27	118.54	2.65E+09	9.94E+08	6.87E-03	1.03E+02	6.81E-03	101.39	1.16E+01	1.34E+07	2.15E+07	2.96E+07	2.13E+07	1.18E+00	7.07E-01
1209	B	22	1	110	111	196.23	0.22	108.34	3.02E+09	9.25E+08	5.28E-03	9.49E+01	6.80E-03	94.62	7.85E+00	1.30E+07	1.87E+07	2.44E+07	2.41E+07	1.17E+00	7.12E-01
1209	B	22	1	115	116	196.28	0.17	93.60	2.87E+09	9.49E+08	3.40E-03	8.30E+01	5.08E-03	85.14	3.98E+00	7.66E+06	1.14E+07	1.52E+07	1.71E+07	1.17E+00	5.07E-01
1209	B	22	1	120	121	196.33	0.12	77.33	2.77E+09	7.51E+08	2.78E-03	6.78E+01	2.90E-03	72.54	6.73E+00	6.23E+06	8.55E+06	1.09E+07	8.91E+06	1.11E+00	2.48E-01
1209	B	22	1	125	126	196.38	0.07	57.65	1.82E+09	8.29E+08	2.71E-03	5.01E+01	2.43E-03	52.47	6.57E+00	2.93E+06	5.39E+06	7.86E+06	4.84E+06	1.10E+00	1.97E-01
1209	B	22	1	129	130	196.42	0.03	37.62	2.55E+09	4.64E+08	1.84E-03	3.33E+01	1.80E-03	34.22	4.37E+00	4.16E+06	5.08E+06	6.00E+06	4.97E+06	1.08E+00	1.43E-01
1209	B	22	1	130	131	196.43	0.02	29.52	2.42E+09	1.06E+09	1.52E-03	2.74E+01	1.54E-03	28.24	1.20E+01	2.31E+06	4.11E+06	5.90E+06	4.18E+06	1.12E+00	1.28E-01
1209	B	22	1	131	132	196.44	0.01	16.59	2.89E+09	1.22E+09	1.18E-03	2.00E+01	1.06E-03	20.57	2.46E+01	2.26E+06	3.91E+06	5.56E+06	3.52E+06	1.15E+00	1.03E-01
1209	B	22	1	132	133	196.45	0.00	0.00	3.73E+09	7.36E+08	8.46E-04	1.01E+01	8.04E-04	9.86	2.31E+01	2.96E+06	3.68E+06	4.41E+06	3.50E+06	1.17E+00	8.19E-02
1209	B	22	1	133	134	196.46	-0.01	-3.48	3.81E+09	7.55E+08	1.14E-03	0.00E+00	1.23E-03	0.00	3.01E+01	4.04E+06	5.04E+06	6.04E+06	5.44E+06	1.17E+00	1.29E-01
1209	B	22	1	134	135	196.47	-0.02	-5.90	3.92E+09	5.88E+08	1.43E-03	-7.81E+00	2.57E-03	-5.27	1.38E+01	5.51E+06	6.48E+06	7.45E+06	1.17E+07	1.16E+00	2.76E-01
1209	B	22	1	135	136	196.48	-0.03	-8.09	3.09E+09	9.58E+08	2.80E-03	-1.25E+01	3.60E-03	-8.51	1.82E+01	6.92E+06	1.00E+07	1.31E+07	1.29E+07	1.16E+00	3.86E-01
1209	B	22	1	136	137	196.49	-0.04	-9.89	3.40E+09	1.14E+09	4.17E-03	-1.54E+01	5.94E-03	-10.61	1.71E+01	1.10E+07	1.66E+07	2.22E+07	2.36E+07	1.17E+00	6.56E-01
1209	B	22	1	137	138	196.50	-0.05	-11.48	3.21E+09	7.60E+08	4.90E-03	-1.76E+01	6.32E-03	-12.24	1.18E+01	1.41E+07	1.85E+07	2.29E+07	2.38E+07	1.18E+00	6.97E-01
1209	B	22	1	140	141	196.53	-0.08	-17.10	3.99E+09	2.02E+08			6.94E-03	-16.82	1.29E+01				3.28E+07	1.18E+00	7.71E-01
1209	B	22	1	142	143	196.55	-0.10	-21.20	3.77E+09	5.93E+08			6.59E-03	-20.02	9.19E+00				2.95E+07	1.18E+00	7.73E-01
1209	B	2	1	145	146	196.58	-0.13	-27.70	4.60E+09	8.43E+08			5.68E-03	-25.00	8.17E+00				3.10E+07	1.18E+00	6.43E-01

Table S2: Compilation of all the data presented in this paper for both Site 1209 and 1263

3He MAR nanno mean	SD 3He MAR nanno mean	MARn 3He min 1209	MARn 3He max 1209	Thoracosphaera Abs. Ab. spp.	CB Abs. Ab.	CB L	SD	CB W	SD	Nannofossil fragmentation	CaCO3 nanno	SR 3He 1209 3pt ave	Dry Bulk Density	Age 3He 3pt ave	MARff 3He 3ptave 1209	ΔMARff 3He 3ptave 1209	MARff 3He 3ptave 1209	MARct 3He 3ptave 1209	SR CNCF interpolated 1209	Age CNCF 1209	Age composite 1209	SD composite age	MAR ct CNCF 1209	
g/cm2/kyr	g/cm2/kyr	g/cm2/kyr	g/cm2/kyr	(n/g)	(n/g)	(μm)	(μm)	(μm)	(μm)	(%)	%	m/ky	g/cm3	ky +/- PEB	g/cm2/ky	g/cm2/ky	g/cm2/ky	g/cm2/ky	m/kyr	kyr +/- PEB	kyr +/- PEB	kyr	g/cm2/kyr	
8.35E-01	1.42E-01	6.93E-01	9.77E-01	2.44E+07	1.13E+08	6.40	2.79	2.66	0.98	8.73	70.80	0.01	1.18	118.56	1.05	68.43	0.12	0.01	0.01	123.88	121.22	3.76	0.13	
9.61E-01	3.30E-01	6.32E-01	1.29E+00	1.98E+07	1.79E+08	7.26	3.30	3.17	1.88	11.53	72.06	0.01	1.18	114.54	1.18	88.96	0.14	0.01	0.01	118.26	116.40	2.63	0.09	
7.55E-01	2.75E-01	4.80E-01	1.03E+00	1.28E+08	4.04E+08	7.81	2.79	3.67	1.92	16.59	88.65	0.01	1.17	109.49	0.75	20.22	0.09	0.01	0.01	111.06	110.27	1.11	0.09	
7.11E-01	2.67E-01	4.45E-01	9.78E-01	4.76E+07	1.24E+08	6.46	2.11	2.93	0.96	11.61	87.67	0.01	1.18	102.56	0.71	13.99	0.09	0.01	0.01	101.39	101.97	0.83	0.09	
4.73E-01	1.45E-01	3.29E-01	6.18E-01	7.77E+07	1.14E+08	8.48	2.92	3.21	1.08	7.85	76.61	0.00	1.17	94.89	0.55	-11.74	0.06	0.01	0.01	94.62	94.76	0.20	0.08	
3.18E-01	1.05E-01	2.13E-01	4.23E-01	7.21E+07	9.51E+08	12.38	3.69	4.68	1.72	3.98	79.89	0.00	1.17	82.96	0.34	-45.76	0.05	0.01	0.01	85.14	84.05	1.54	0.08	
1.89E-01	5.12E-02	1.38E-01	2.40E-01	6.14E+07	1.46E+09	11.83	4.81	4.36	1.75	6.73	61.18	0.00	1.11	67.81	0.24	-61.97	0.06	0.00	0.00	72.54	70.18	3.35	0.07	
1.88E-01	8.57E-02	1.02E-01	2.73E-01	1.06E+08	1.10E+09	11.91	5.21	4.16	2.14	6.57	63.23	0.00	1.10	50.15	0.22	-64.81	0.07	0.00	0.00	52.47	51.31	1.64	0.06	
1.42E-01	2.58E-02	1.16E-01	1.67E-01	1.17E+08	1.69E+09	11.64	5.25	4.14	2.20	4.37	71.17	0.00	1.08	33.32	0.15	-76.71	0.04	0.00	0.00	34.22	33.77	0.64	0.04	
1.25E-01	5.45E-02	7.03E-02	1.79E-01	8.54E+07	1.10E+09	10.88	3.03	4.07	1.50	12.05	73.39	0.00	1.12	27.36	0.13	-79.85	0.04	0.00	0.00	28.24	27.80	0.62	0.04	
1.15E-01	4.86E-02	6.64E-02	1.64E-01	3.62E+07	8.02E+08	9.16	1.97	3.36	1.17	24.57	85.00	0.00	1.15	19.95	0.11	-81.74	0.01	0.00	0.00	20.57	20.26	0.44	0.01	
9.48E-02	1.87E-02	7.61E-02	1.13E-01	1.39E+07	4.75E+08	8.58	3.63	3.79	1.70	23.13	96.01	0.00	1.17	10.09	0.09	-86.24	0.01	0.00	0.00	9.86	9.97	0.17	0.00	
1.22E-01	2.41E-02	9.77E-02	1.46E-01	1.45E+08	7.65E+08	9.05	4.72	3.12	1.41	30.15	92.04	0.00	1.17	0.00	0.12	-80.85	0.00	0.00	0.00	0.00	0.00	0.00	0.01	
1.59E-01	2.38E-02	1.35E-01	1.83E-01	0.00E+00	4.09E+08	5.83	1.81	2.98	1.10	13.80	95.98	0.00	1.16	-7.81	0.15	-75.57	0.01	0.00	0.00	-5.27	-6.54	1.80	0.01	
3.04E-01	9.40E-02	2.10E-01	3.97E-01	5.22E+07	5.17E+08	9.52	5.02	3.42	1.35	18.21	93.59	0.00	1.16	-12.55	0.30	-52.05	0.02	0.00	0.00	-8.51	-10.53	2.85	0.02	
4.36E-01	1.47E-01	2.89E-01	5.83E-01	2.19E+07	1.16E+09	9.08	3.70	3.61	1.51	17.11	89.49	0.00	1.17	-15.42	0.46	-26.47	0.02	0.01	0.01	-10.61	-13.01	3.40	0.03	
4.70E-01	1.11E-01	3.59E-01	5.81E-01	7.43E+07	6.70E+08	9.12	3.46	2.58	1.21	11.78	81.61	0.00	1.18	-17.62	0.54	-13.49	0.03	0.01	0.01	-12.24	-14.93	3.81	0.04	
				0.00E+00	7.11E+08	10.30	3.76	3.85	2.13	12.88	85.03		1.18						0.01	0.01	-16.82	-20.19	4.77	0.04
				5.12E+07	7.12E+08	8.94	2.49	3.03	0.80	9.19	93.33		1.18						0.01	0.01	-20.02	-23.86	5.43	
				0.00E+00	5.86E+08	8.26	2.43	3.29	1.55	8.17	91.13		1.18						0.01	0.01	-25.00	-29.45	6.29	0.02

MAR ff CNCF 1209	MAR ff composite 1209	Coccolithus	Coc 1SE	Ericsonia	Fri 1SE	Fasciculithus	Fasc 1SE	Discoaster	Dis 1SD
g/cm2/kyr	g/cm2/kyr	(pg)	(pg)	(pg)	(pg)	(pg)	(pg)	(pg)	(pg)
1.14	1.10	45.61	2.05	14.56	1.74	663.98	181.55	517.18	99.37
0.79	0.99	39.15	1.42	14.43	1.00	413.81	37.39	787.75	66.82
0.73	0.74	52.58	4.15	16.87	1.07	578.17	103.3	845.98	100.98
0.71	0.71	51.35	1.59	18.97	1.07	570.94	165.32	797.09	70.47
0.71	0.63	42.48	1.87	16.06	1.91	464.44	57.22	788.15	100.9
0.51	0.42	49.01	2.82	25.54	4.78	561.69	73.89	841.51	113.39
0.25	0.24	43.77	2.66	20.85	0.00	514.40	41.63	791.07	74.85
0.20	0.21	40.45	1.91	14.06	1.66	635.03	50.95	844.82	58.86
0.14	0.14	52.21	7.22	18.02	2.91	662.85	66.89	782.92	68.24
0.13	0.13	40.95	2.71	18.39	2.34	528.06	74.72	856.2	97.1
0.10	0.11	53.49	2.44	19.98	2.57	1109.80	136.91	649.27	66.67
0.08	0.08	52.01	2.11	22.36	1.50	729.90	74.78	683.09	52.69
0.13	0.12	47.84	2.48	19.47	1.71	597.11	67.2	725.45	118.09
0.28	0.21	55.29	1.86	24.84	1.75	577.06	54.05	689.25	92.2
0.39	0.34	51.27	1.93	21.90	1.37	740.39	50.22	753.93	73.7
0.66	0.56	50.26	2.06	19.29	1.11	870.60	128.13	723.87	42.61
0.70	0.62	51.99	1.81	24.17	1.66	609.35	46.58	738.67	65.98
0.77	0.77	47.86	2.10	22.94	1.60	704.45	94.19	830.61	79.05
0.77		55.29	2.40	25.91	1.30	611.27	88.24	683.7	55.7
0.64		43.57	1.52	19.46	1.27	626.87	64.64	809.24	90.17



Depth	Height above lithological change	Age 3He 3pt ave	Age CNCF 1209	Age composite 1209	d42Ca ICP Lyon	1SD	Date	d44/42Ca915b	SD	d44/40Ca915b	SD	d44/40Ca915a	SD	reconstructed SW/915b	SD	reconstructed SW/sw
196.04	0.41	117.67	122.92	120.30	-0.11	0.11	april 2018	-0.05	0.17	-0.10	0.36	0.62	1.08	1.92	-0.80	0.04
196.05	0.40	116.93	121.88	119.41	-0.06	0.05	april 2018	0.00	0.11	0.00	0.23	0.72	0.95	2.02	-0.93	0.14
196.23	0.22	94.89	94.62	94.76	-0.15	0.02	april 2018	-0.09	0.08	-0.18	0.16	0.54	0.88	1.84	-1.00	-0.04
196.28	0.17	82.96	85.14	84.05	-0.11	0.01	april 2018	-0.05	0.07	-0.10	0.16	0.62	0.88	1.92	-1.00	0.04
196.32	0.13	71.24	75.76	73.50	0.07	0.02	april 2018	0.13	0.08	0.28	0.16	1.00	0.88	2.30	-1.00	0.42
196.34	0.11	64.29	68.91	66.60	0.16	0.00	april 2018	0.22	0.06	0.45	0.13	1.17	0.85	2.47	-1.03	0.59
196.36	0.09	57.48	60.72	59.10	0.01	0.00	april 2018	0.00	0.11	0.01	0.23	0.73	0.95	2.03	-0.93	0.15
196.38	0.07	50.15	52.47	51.31	0.00	0.07	april 2018	0.06	0.13	0.12	0.28	0.84	1.00	2.14	-0.88	0.26
196.40	0.05	42.63	44.05	43.34	-0.03	0.03	april 2018	0.03	0.09	0.06	0.20	0.78	0.92	2.08	-0.96	0.20
196.41	0.04	38.30	39.39	38.85	0.03	0.08	april 2018	0.09	0.14	0.18	0.29	0.90	1.01	2.20	-0.87	0.32
196.43	0.02	27.36	28.24	27.80	-0.05	0.07	april 2018	0.01	0.13	0.03	0.27	0.75	0.99	2.05	-0.89	0.17
196.45	0.00	10.09	9.86	9.97	-0.05	0.05	april 2018	0.01	0.11	0.03	0.23	0.75	0.95	2.05	-0.93	0.17
196.46	-0.01	0.00	0.00	0.00	-0.07	0.06	april 2018	-0.01	0.12	-0.02	0.25	0.70	0.97	2.00	-0.91	0.12
196.48	-0.03	-12.55	-8.51	-10.53	-0.05	0.11	april 2018	0.01	0.17	0.02	0.35	0.74	1.07	2.04	-0.81	0.16
196.50	-0.05	-17.62	-12.24	-14.93	0.03	0.06	april 2032	0.09	0.12	0.19	0.25	0.91	0.97	2.21	-0.91	0.33
196.52	-0.07	-21.46	-15.31	-18.38	0.04	0.04	april 2018	0.10	0.10	0.21	0.20	0.93	0.92	2.23	-0.96	0.35
195.99	0.46	123.68	128.79	126.23	-0.20	0.01	may 2018	-0.14	0.07	-0.30	0.15	0.42	0.87	1.72	-1.01	-0.16
196.14	0.31	108.11	109.38	108.75	-0.10	0.02	may 2018	-0.04	0.08	-0.08	0.18	0.64	0.90	1.94	-0.98	0.06
196.20	0.25	99.56	98.62	99.09	-0.17	0.04	may 2018	-0.11	0.10	-0.24	0.21	0.48	0.93	1.78	-0.95	-0.10
196.26	0.19	88.76	89.24	89.00	-0.18	0.00	may 2018	-0.12	0.06	-0.25	0.13	0.47	0.85	1.77	-1.03	-0.11
196.30	0.15	77.29	81.21	79.25	-0.05	0.04	may 2018	0.01	0.10	0.02	0.20	0.74	0.92	2.04	-0.96	0.16
196.32	0.13	71.24	75.79	73.52	0.02	0.05	may 2018	0.08	0.11	0.17	0.23	0.89	0.95	2.19	-0.93	0.31
196.39	0.06	46.48	48.35	47.42	-0.13	0.02	may 2018	-0.07	0.08	-0.15	0.18	0.57	0.90	1.87	-0.98	-0.01
196.40	0.05	42.63	44.02	43.33	-0.13	0.09	may 2018	-0.07	0.15	-0.15	0.31	0.57	1.03	1.87	-0.85	-0.01
196.41	0.04	38.30	39.39	38.85	-0.06	0.04	may 2018	0.00	0.11	-0.01	0.23	0.71	0.95	2.01	-0.93	0.13
196.46	-0.01	0.00	0.00	0.00	-0.04	0.07	may 2018	0.02	0.13	0.05	0.28	0.77	1.00	2.07	-0.88	0.19
196.58	-0.13	-33.89	-25.00	-29.45	-0.09	0.00	may 2018	-0.03	0.06	-0.07	0.13	0.65	0.85	1.95	-1.03	0.07

Site	Hole	Core	Section	Top interval	Bottom interval	Rmcd	Depth to LC	CNCF Age	3He age	CNCF SR
1263	C	14	1A	129	130	333.61	1.66	100.51	101.81	0.08
1263	C	14	1A	139	140	333.71	1.56	99.17	100.14	0.07
1263	C	14	1A	149	150	333.81	1.46	97.39	98.09	0.06
1263	C	14	2A	09	10	333.90	1.37	96.03	96.66	0.06
1263	C	14	2A	29	30	334.10	1.17	92.46	92.55	0.05
1263	C	14	2A	39	40	334.20	1.07	90.57	89.34	0.05
1263	C	14	2A	49	50	334.30	0.97	88.57	85.29	0.04
1263	C	14	2A	59	60	334.40	0.87	85.47	79.36	0.03
1263	C	14	2A	69	70	334.50	0.77	80.61	70.65	0.02
1263	C	14	2A	79	80	334.60	0.67	76.22	62.50	0.02
1263	C	14	2A	89	90	334.70	0.57	68.97	52.68	0.01
1263	C	14	2A	99	100	334.80	0.47	60.35	42.45	0.01
1263	C	14	2A	104	105	334.85	0.42	55.52	37.32	0.01
1263	C	14	2A	109	110	334.90	0.37	50.41	32.42	0.01
1263	C	14	2A	114	115	334.95	0.32	44.91	27.73	0.01
1263	C	14	2A	119	120	335.00	0.27	39.36	23.05	0.01
1263	C	14	2A	124	125	335.05	0.22	33.55	18.42	0.01
1263	C	14	2A	129	130	335.10	0.17	27.51	14.03	0.01
1263	C	14	2A	134	135	335.15	0.12	20.83	9.81	0.01
1263	C	14	2A	139	140	335.20	0.07	14.78	5.39	0.01
1263	D	4	1A	72	73	335.32	-0.05	-1.42	-1.00	0.04
1263	D	4	1A	82	84	335.42	-0.15	-3.46	-4.12	0.05
1263	D	4	1A	87	88	335.47	-0.20	-4.47	-5.71	0.05
1263	D	4	1A	92	93	335.52	-0.25	-6.04	-7.99	0.04
1263	D	4	1A	97	98.00	335.57	-0.30	-6.51	-8.64	0.04
1263	D	4	2A	02	03	335.62	-0.35	-7.73	-10.27	0.04
1263	D	4	2A	07	08	335.67	-0.40	-9.22	-12.22	0.04
1263	D	4	2A	12	13	335.72	-0.45	-10.37	-13.85	0.05

3He sed rate (cm/ky)	density (g/cm3)	Abs. Abundance	NAR CNCF (g/cm2/ky)	NAR 3He (g/cm2/ky)
0.06	1.27	4.73E+09	4.68E+08	3.61E+08
0.06	1.32	4.25E+09	4.00E+08	3.36E+08
0.06	1.37			
0.05	1.43	3.66E+09	3.11E+08	2.86E+08
0.04	1.45	3.37E+09	2.67E+08	1.83E+08
0.02	1.52	4.66E+09	3.62E+08	1.75E+08
0.02	1.44	3.85E+09	2.15E+08	1.09E+08
0.01	1.59	2.52E+09	1.04E+08	5.65E+07
0.01	1.68	3.05E+09	1.00E+08	5.93E+07
0.01	1.66	4.05E+09	1.14E+08	7.09E+07
0.01	1.75	2.24E+09	4.49E+07	3.90E+07
0.01	1.72	2.10E+09	3.79E+07	3.47E+07
0.01	1.66	2.57E+09	4.47E+07	4.23E+07
0.01	1.70	2.10E+09	3.29E+07	3.76E+07
0.01	1.70	2.66E+09	4.06E+07	4.82E+07
0.01	1.68	2.46E+09	3.65E+07	4.43E+07
0.01	1.69	2.32E+09	3.30E+07	4.30E+07
0.01	1.63	2.06E+09	2.63E+07	3.93E+07
0.01	1.65	2.56E+09	3.44E+07	5.07E+07
0.01	1.53	1.96E+09	2.11E+07	2.87E+07
0.03	1.34	2.66E+09	1.32E+08	1.09E+08
0.03	1.35	3.11E+09	1.93E+08	1.36E+08
0.03	1.35	3.42E+09	2.14E+08	1.42E+08
0.03	1.33	3.41E+09	2.02E+08	1.39E+08
0.03	1.29	3.66E+09	1.99E+08	1.45E+08
0.03	1.29	3.92E+09	2.02E+08	1.55E+08
0.03	1.29	4.70E+09	2.47E+08	1.86E+08
0.03	0.84	3.89E+09	1.50E+08	9.99E+07

MARn CNCF (g/cm2/kyrs)	$\lambda_n$ 3He (g/cm2/kyrs)
9.14	7.03
9.44	7.94
0.00	0.00
7.53	6.92
5.97	4.10
8.00	3.87
4.39	2.24
2.84	1.54
2.08	1.23
2.31	1.43
1.22	1.06
0.99	0.91
0.87	0.83
0.83	0.95
0.92	1.09
0.82	1.00
0.47	0.61
0.38	0.57
0.45	0.66
0.38	0.52
2.38	1.96
4.94	3.48
4.93	3.27
3.82	2.62
4.30	3.14
3.14	2.41
4.26	3.20
3.03	2.01

356 The studied nannofossil assemblages are fairly diverse in the studied interval at Site 1263.  
357 The preservation of calcareous nannofossils is reported to be moderate to good, but the 6-cm  
358 interval from 335.27 to 335.21 rmcd (base of the CIE) shows evidence for dissolution (Raffi  
359 et al. 2009). Although most of the coccoliths and nannoliths we observed in the new slides as  
360 well in SEM (Phenom SEM G2 PRO microscope) are moderately to well preserved, strongly  
361 etched specimens coexist in the same sample. This record is indicative of a fluctuating  
362 accumulation rate. In times of reduced sediment accumulation, nannofossils were longer  
363 exposed to corrosive conditions at the water-sediment interface. Such conditions likely  
364 alternated with higher sedimentation rate inducing a more rapid nannofossil burial and better  
365 preservation. Nannofossil fragmentation is consistently higher at Site 1263 than at Site 1209,  
366 varying between 35% and 65% (in the core of the PETM).

367

## 368 **5. Calcium isotopes at Site 1209**

### 369 5.1. Sampling and methodology

370 The calcium isotope composition of carbonate sediments and fossils has been proposed as  
371 a tool for reconstructing the variations in Ca cycling in the geological past (e.g., De La Rocha  
372 and DePaolo, 2000; Farkaš et al., 2007a; Griffith et al., 2008a; Blättler et al., 2011, 2012;  
373 Fantle and Tipper, 2014). As species-specific  $\delta^{44/40}\text{Ca}$  fractionation effects have been reported  
374 in planktonic foraminifera, (Griffith et al., 2008; Kisakureh et al., 2011), we have restricted  
375 our analyses to the species *Morozovella velascoensis*, a photosymbiotic, surface dwelling  
376 species that occupied oligotrophic settings at low and middle latitudes during the Late  
377 Paleocene and the earliest Eocene (Norris et al., 1996, Kelly et al. 1996, Quillévéré et al.,  
378 2001). This species is very abundant at Site 1209 (Petrizzo, 2007-2008) and dominates  
379 planktonic foraminifera assemblages across the PETM. Foraminifera were carefully selected:  
380 cement-filled specimens were carefully avoided.

381 The samples were carefully ultrasonicated to further eliminate any trace of diagenetic  
382 cements. After several tests, we found that six specimens per sample are needed for Ca  
383 isotope analyses. This corresponds to ~0.1 mg of calcite. The chemical processing of samples  
384 follows the technique described in Tacail et al., 2014 and consists of a chemical-  
385 chromatography. Every sample was dissolved in subboiled distilled 1N HCl acid and  
386 processed through AG50X-W12 cation exchange resin in 1N HCl medium to dispose of  
387 sample matrix (i.e., phosphates, sulfates, alkali elements, and Mg). Ca and Sr fractions were  
388 collected in 6N HCl medium. Ca fractions were then separated from Sr by loading samples  
389 onto columns filled with Sr-specific resin (Eichrom Sr-Spec) in subboiled distilled 3N HNO<sub>3</sub>

390 medium. Blanks for the whole procedure did not exceed 100 ng Ca (Tacail et al., 2014). This  
391 is 200 times smaller than the smallest processed Ca samples (about 20 µg) and should not  
392 affect the measured isotopic compositions beyond the measurement precision.

393 A standard-sample bracketing measurement method was used with the ICP Ca Lyon standard  
394 (Tacail et al., 2014) as bracketing standard. Measurements of all samples and standards were  
395 performed during two sessions in 2018. The  $\delta^{43/42}\text{Ca}$ - $\delta^{44/42}\text{Ca}$  values of all measured materials  
396 show an excellent positive correlation, with a slope close to the 0.507 slope predicted by the  
397 linear approximation of exponential mass-dependent fractionation. If the calcium isotopic  
398 composition of standards is taken into account, the slope of the line is 0.5199.

399 The measurements were systematically checked for long-term precision and accuracy  
400 using SRM1486 bone meal NIST secondary standard previously described and analyzed for  
401 Ca isotope compositions (Tacail et al., 2016; Martin et al., 2015, Tacail et al., 2014).  
402 SRM1486 yielded constant values across the six different analysis sessions, with an average  
403  $\delta^{44/42}\text{Ca}$  value of  $-0.98 \pm 0.18 \text{ ‰}$  (2 SE,  $n = 30$ ), in agreement with previously published  
404 values (as listed in Table S4), notably  $-1.03 \pm 0.01 \text{ ‰}$  (2 SE,  $n = 120$ ) (Tacail et al., 2016).  
405 We also analyzed the commonly used SRM915b clinical-grade carbonate standards, and ICP1  
406 Ca solution used as standard in former studies (Morgan et al., 2012; Channon et al., 2015,).  
407 All measured  $\delta^{44/42}\text{Ca}$  values of standards and previously published compositions are given  
408 for comparison in Table S3. Long-term external precision was estimated using the SRM1486  
409 standard and yields a 2 SD value of 0.12‰ for  $\delta^{44/42}\text{Ca}$  for 112 analyses, over the two  
410 sessions. Values of the  $\delta^{44/42}\text{Ca}$  can be converted into  $\delta^{44/40}\text{Ca}$  multiplying by mass  
411 fractionation ratio  $(1/m_{40}-1/m_{44})/(1/m_{42}-1/m_{44}) = 2.099454809$  (where  $m_x$  is the exact  
412 atomic mass of each calcium isotopes). All Ca isotope compositions are expressed in per mil  
413 units, using the “delta” notation for the  $^{44}\text{Ca}/^{40}\text{Ca}$  isotope ratios defined as follows:

$$414 \quad \delta^{44/40}\text{Ca} = \left( \frac{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}}{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{ICP Ca Lyon}}} - 1 \right) * 1000$$

415 where  $(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}$  and  $(^{44}\text{Ca}/^{40}\text{Ca})_{\text{ICP Ca Lyon}}$  are Ca isotope abundance ratios measured  
416 in sample and ICP Ca Lyon bracketing standard, respectively. The accuracy and long-term  
417 precision of analyses was checked periodically through the analyses of SRM1486 bone meal  
418 NIST standard.

419  
420  
421  
422

Standard	Source	n	$\delta^{44/42}\text{Ca}$ ‰; $\pm$ 2SD relative to ICP Ca Lyon
SRM1486 (cow bone meal)	This study (April 2018)	2	-0.97 $\pm$ 0.00
	This study (April 2018)	10	-0.97 $\pm$ 0.16
	This study (May 2018)	10	-0.96 $\pm$ 0.18
	Tacail et al., 2017	147	-1.03 $\pm$ 0.12
	Tacail et al., 2014	17	-0.96 $\pm$ 0.14
	Tacail et al., 2016	120	-1.03 $\pm$ 0.13
	Martin et al., 2015	37	-1.04 $\pm$ 0.11
SRM915b (Ca carbonate)	This study (May 2018)	3	-0.16 $\pm$ 0.03
	Tacail et al., 2017	4	-0.16 $\pm$ 0.04
	Tacail et al., 2014	11	-0.12 $\pm$ 0.07
	Tacail et al., 2016	4	-0.14 $\pm$ 0.06
	Martin et al., 2015	13	-0.15 $\pm$ 0.11

423

424 Table S3.  $\delta^{44/42}\text{Ca}$  values of standards as measured in this study (in per mil relative to ICP Ca Lyon standard)  
425 compared with previously published values.

426

427 We performed ANOVA to compare the means of  $\delta^{44/42}\text{Ca}$  isotopic data (Extended Data  
428 Table 1). This test provides us with a statistical tool to confidentially assess that the means are  
429 statistically different each-others, since the null hypothesis is not verified.

430

431 5.2. Likely causes of changes in calcium isotope values

432 5.2.1. Diagenesis

433 A previous study of the PETM in Pacific Ocean sites attributed much of variability in the  
434 bulk carbonate  $\delta^{44}\text{Ca}$  record to secondary calcite precipitation (Griffith et al., 2015). Evidence  
435 for pervasive, secondary overgrowth in planktonic foraminifera across the PETM does exist  
436 in the Pacific Ocean at ODP Site 865 in the form of  $\mu\text{m}$ -sized calcite blades precipitated along  
437 the foraminiferal muricae and specimens partially or entirely cemented with 100-500  $\mu\text{m}$   
438 calcite crystallites (Edgar et al., 2015; Kozdon et al., 2013). Although no comparable  
439 crystallites have been documented at Site 1209, the frosty texture of foraminifera points to a  
440 certain degree of secondary overgrowth (Colosimo et al., 2006), which could have increased  
441  $\delta^{44}\text{Ca}$  values substantially (Griffith et al., 2015). Because Sr contents of abiogenic calcite are



442 around an order of magnitude lower than that of biogenic material, even slightly higher  
443 secondary overgrowth should be reflected by substantially lower Sr/Ca ratio (Kozdon et al.,  
444 2013; Stoll et al., 2007c). The invariant Sr/Ca record of *Morozovella velascoensis* at Site 1209  
445 (Zachos et al., 2003) suggests that secondary calcite overgrowth, if any, has been relatively  
446 uniform over the studied time interval. As argued for the boron isotope composition of this  
447 species from the same site (Babila et al., 2018), this strongly suggests that relative changes in  
448 *Morozovella velascoensis*  $\delta^{44}\text{Ca}$  composition were preserved.

#### 449 5.2.2. Secular changes in seawater $\delta^{44}\text{Ca}$ values

450 Assuming it is mostly primary, our  $\delta^{44}\text{Ca}$  record should reflect changes in  $\delta^{44}\text{Ca}$  of  
451 seawater and isotope fractionation of the calcifying organism (Griffith et al., 2008a; Fantle,  
452 2010; Blättler et al., 2011, 2012; Fantle and Tipper, 2014). One notable feature likely  
453 resulting from the first option is the long-term, 0.2 permil decrease of  $\delta^{44}\text{Ca}$  values recorded  
454 between 0 and 100 kyr at Site 1209. This change is consistent both in magnitude and duration  
455 with a warming-induced increase in continental weathering and riverine,  $^{44}\text{Ca}$ -depleted Ca  
456 input to the ocean. Modeling indicates this process should have increased oceanic Ca contents  
457 and decreased  $\delta^{44}\text{Ca}$  values, with global seawater lowest values predicted around 100 kyr  
458 after the PETM onset (Komar and Zeebe, 2011, 2016), in excellent agreement with the lowest  
459  $\delta^{44}\text{Ca}$  values recorded by our data at Site 1209. This increase in weathering at the PETM  
460 onset is corroborated by a coeval shift to more radiogenic Os values in several sites (Dickson  
461 et al., 2015). The PETM  $\delta^{44}\text{Ca}$  and Os records bear strong similarities with those of the  
462 Toarcian Oceanic Anoxic Event (Brazier et al., 2015), for which osmium and calcium  
463 isotopes also point to increased continental weathering (Ravizza, 2001, Dickson, 2015). More  
464 quantitatively, however, the magnitude of the PETM decrease in  $\delta^{44}\text{Ca}$  values recorded  
465 between 0 and 100 kyr at Site 1209 exceeds previous model-predictions (Komar and Zeebe,  
466 2011). Simulations involving relatively small increase in weathering due to the input of 4500  
467 Pg of carbon indicate that such  $\delta^{44}\text{Ca}$  changes should be less than 0.05‰, i.e., below standard  
468 measurement uncertainty (Komar and Zeebe, 2011). Nevertheless, carbon emissions have  
469 been revised upward since then using boron isotope constraints to more than 10,000 Pg  
470 (Gutjahr et al., 2017; Penman and Zachos, 2018). Modeling of >10,000 PgC input over 100  
471 kyr for end-Permian conditions produces a larger, 0.1‰ shift in  $\delta^{44}\text{Ca}$  values, which is still  
472 lower than that suggested by our data. Seawater  $\delta^{44}\text{Ca}$  values could have been further lowered  
473 by a slowing down of the biological carbon pump (Komar and Zeebe, 2016), as suggested by  
474 our data from Site 1209. Although changes in calcium isotope fractionation might have been  
475 involved as well (see below), our new data invalidate previous simulations suggesting that the

476 PETM perturbation was insufficient to impact the calcium isotope budget and supports  
477 higher-end estimates of carbon input during the PETM.

478

### 479 5.2.3. Changes in calcium isotope fractionation

480 Because of the long residence time of Ca (~1 Ma; Berner and Berner, 1996) relative to the  
481 ocean mixing time in the global ocean, more rapid (<100 kyr) and larger changes in global  
482 seawater  $\delta^{44}\text{Ca}$  are very unlikely. This is particularly true for the Paleocene-Eocene interval  
483 during which Ca content was almost twice higher than today. The 0.5 permil positive  
484 excursion recorded between 50 and 100 kyr at Site 1209 can thus hardly be explained by a  
485 global change in seawater  $\delta^{44}\text{Ca}$  unless invoking the combination of unrealistically large  
486 swings of calcium input or burial and unidentified and highly fractionated sources. This  
487 positive peak recorded between + 50 and + 100 kyrs thus requires changes in foraminiferal  
488 calcium isotope fractionation, as suggested by the absence of such a large shift in the bulk  
489 carbonate record of the nearby ODP Site 1212 Griffith et al., 2015). The bulk sediment  $\delta^{44}\text{Ca}$   
490 values should indeed mainly reflect that of nannofossils, which according to our calculations  
491 overwhelmingly dominate the bulk carbonate at Shatsky Rise. Modern experiments suggest  
492 that coccolithophore and foraminifera possess very different calcium incorporation pathways  
493 and hence their calcium isotope fractionations are likely controlled by different mechanisms.  
494 We note however that such differences between and within these two groups cannot be taken  
495 into account when dealing only with  $\delta^{44}\text{Ca}$  values of the bulk sediment, which is necessarily a  
496 complex mixture of different nannofossil and foraminiferal species as well as secondary  
497 calcite particles such as the blades present in Site 1209.

498 Several parameters might influence calcium isotope fractionation of planktonic  
499 foraminifera shells (Fantle and Tipper, 2014), including calcification rate, growth rate,  
500 temperature (Gussone et al., 2003; Sime et al., 2005), salinity and seawater carbonate  
501 chemistry (Kisakureh et al., 2011). The measured  $\delta^{44/40}\text{Ca}$  values show no correlation with  
502 previously published size estimates (Petrizzo et al., 2008) and Sr/Ca contents (Zachos et al.,  
503 2003) for this genus and, paleotemperature proxies such as  $\delta^{18}\text{O}$  and Mg/Ca (Zachos et al.,  
504 2003; Tripathi and Elderfield, 2005). Changes in seawater carbonate chemistry thus appears the  
505 most likely cause of this large positive peak recorded between + 50 and + 100 kyrs. The  
506 interval recording this positive  $\delta^{44/40}\text{Ca}$  excursion records higher seafloor carbonate  
507 oversaturation, as suggested by lowest foraminiferal and nannofossil fragmentation and  
508 highest CB abundance. According to theoretical calculations of Nielsen et al. (2012),

509 however, such a phase of diminished calcium isotope fractionation should reflect higher  
510 seawater  $[Ca]/[CO_3^{2-}]$  ratio. Because large and abrupt changes in  $[Ca]$  would require  
511 unrealistic large swings in input and burial fluxes (see above), highest  $\delta^{44/40}Ca$  values would  
512 point to minimal  $[CO_3^{2-}]$  at +80 kyrs. This is at odds with most model simulations indicating  
513 that  $[CO_3^{2-}]$  decreased markedly due to massive CO<sub>2</sub> input at the onset of the PETM and  
514 increased afterwards due to higher riverine input (Komar and Zeebe, 2011). This mismatch  
515 suggests that  $\delta^{44/40}Ca$  fractionation was somehow largely decoupled from  $[CO_3^{2-}]$  values  
516 during the PETM. Alternatively,  $\delta^{44/40}Ca$  fractionation could have increased with  $[HCO_3^-]$   
517 rather than with  $[CO_3^{2-}]$ . In both field and experimental studies, the influence of this major  
518 parameter on foraminiferal calcium isotope fractionation has been seldom tested, because it is  
519 classically inversely proportional to  $[CO_3^{2-}]$  in modern oceans (refs). On geological  
520 timescales, however, the two parameters might be somehow decoupled. Different models  
521 simulate relatively invariant  $[HCO_3^-]$  at the PETM onset followed by a steady distinct rise to  
522 maximum values some 80 kyrs afterwards resulting from higher riverine input and lower  
523 calcite burial (Komar and Zeebe, 2011; Luo et al., 2016). Importantly, bicarbonate ion levels  
524 decrease slowly in the model of Komar and Zeebe (2011) where carbonate export is held  
525 constant. In the model of Luo et al., 2016, a long-lived 50% decrease Accordingly, the  
526 decrease to lower  $\delta^{44/40}Ca$  values between + 80 kyr and 100 kyrs would imply a rapid  
527 superficial  $[HCO_3^-]$  decrease, in line with coeval rapid rise of calcite export flux suggested by  
528 our MAR<sub>ff</sub> data.

529

530 **Statistical treatment of data.** We performed statistical treatment of data using the software  
531 PAST 3.25. We performed One-way ANOVA (ANalysis Of VAriance) on NAR, nannofossil  
532 weight, calcite blades length and width and  $\delta^{44}Ca$  separately, in order to test that the observed  
533 stratigraphic trends are statistically significant. One-way ANOVA is a statistical method for  
534 testing the null hypothesis that several univariate samples are taken from populations with the  
535 same mean. The samples are assumed to be close to normally distributed and have similar  
536 variances.

537 The test statistic F is computed as

538

$$539 \quad F = MS_{bg} / MS_{wg}$$

540 Where  $MS_{bg}$  is the mean square between groups and  $MS_{wg}$  is the mean square within  
541 groups. The p value is based on F with degrees of freedom between groups ( $df_{bg}$ ) and and

542 degrees of freedom within groups ( $df_{wg}$ ; Hammer et al., 2001). This test allows us to  
543 confidentially assess that the mean values are statistically different each-others, since the null  
544 hypothesis is not verified. For NAR, calcite blades length and width and  $\delta^{44}\text{Ca}$ , “F value” is  
545 always much higher than 1 and p-value is always  $<0.05$ . We also analyzed for the same  
546 parameters the table of "post-hoc" pairwise comparisons, based on the Tukey-Kramer test.  
547 This test shows us that the “P-equal” values of pre-PETM and post-PETM respect to PETM  
548 values are very small. This means that the mean values of pre-PETM and post-PETM samples  
549 respectively to PETM ones are statistically different. For nannofossil weight, “F value” is  
550 around 1 and p-value is systematically  $<0.05$ . However, Tukey-Kramer test indicates that “P-  
551 equal” values of pre-PETM and post-PETM relative to PETM values are large thus we cannot  
552 reject the null-hypothesis. This means that no statistically significant weight differences do  
553 exist between samples. (See Extended Data Table 1)

554 We also tested a linear model to NAR,  $\text{MAR}_{ff}$ ,  $\text{MAR}_n$  to test correlation with temperature and  
555  $p\text{H}$ , as recorded by Mg/Ca ratio and  $\delta^{11}\text{B}$  isotope values, respectively and excluding samples  
556 belonging to the dissolution interval. Inclusion of the samples corresponding to the  
557 dissolution interval has negligible effect on the correlation between the different parameters.  
558 NAR and  $\text{MAR}_n$  show a good and significant correlation ( $R^2=0.65$ ,  $p<0.05$  at Site 1209;  
559  $R^2=0.57$ ,  $p<0.05$  at 1263), as well as  $\text{MAR}_n$  and  $\text{MAR}_{ff}$  (e.g., site 1209;  $R^2=0.70$ ,  $p<=0.05$ ).  
560  $\text{MAR}_{ff}$  at Site 1209 correlates positively with  $p\text{H}$  ( $R^2=0.59$ ,  $p<<0.05$ ) but is better correlated  
561 with Mg/Ca ( $R^2=0.72$ ,  $p<0.05$ ). At Site 1209,  $\text{MAR}_{ff}$  correlates very poorly with B/Ca  
562 ( $R^2=0.02$ ,  $p>0.05$ ).

563 Thus, we calculated the correlation between  $\text{MAR}_{ff}$ , Mg/Ca and B/Ca for *M. velascoensis* and  
564 for *A. soldadoensis*. For both species, both Mg/Ca and B/Ca are well correlated to  $\text{MAR}_{ff}$  (*A.*  
565 *soldadoensis* B/Ca  $R^2=0.77$ ,  $p<0.05$ ; Mg/Ca  $R^2= 0.57$ ,  $p<0.05$  - *M. velascoensis* B/Ca  
566  $R^2=0.51$ ,  $p<0.05$ ; Mg/Ca  $R^2= 0.57$ ,  $p<0.05$ ). This is not only in agreement with the  
567 temperature dependence of the measured Mg/Ca values but also with evidences of strong  
568 species-specific B/Ca dependence on calcification temperature.

569 *Thoracosphaera* absolute abundance does positively correlate to Mg/Ca and to  $p\text{H}$  as  
570 measured from boron isotopes at Site 1209 ( $R^2=0.43$ ,  $p<0.05$ ). However, *Thoracosphaera*  
571 percentage shows highest correlation with Mg/Ca ( $R^2=0.63$ ,  $p<0.05$ ) than to  $p\text{H}$  ( $r^2=0.50$ ,  
572  $p>0.05$ ). (See Extended Data Table 1)

## References

- Agnini, C., Fornaciari, E., Rio, D., Tateo, F., Backman, J., Giusberti, L., 2007. Responses of calcareous nannofossil assemblages, mineralogy and geochemistry to the environmental perturbations across the Paleocene/Eocene boundary in the Venetian Pre-Alps. *Marine Micropaleontology* 63(1–2), 19–38.
- Agnini, C., Spofforth, D. J., Dickens et al., 2016. Stable isotope and calcareous nannofossil assemblage record of the late Paleocene and early Eocene (Cicogna section). *Climate of the Past* (4), 883–909.
- Babila, T.L., Penman, D.E., Hönisch, B., Kelly, D.C., Bralower, T.J., Rosenthal, Y., Zachos, J.C., 2018. Capturing the global signature of surface ocean acidification during the Palaeocene–Eocene Thermal Maximum. *Philosophical Transactions A* 376.
- Beaufort L., Barbarin, N., Gally Y., 2014. Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature protocols* 9(3), 633–642.
- Beaufort, L., Dollfus, D., 2004. Automatic recognition of coccoliths by dynamical neural networks. *Marine Micropaleontology* 51(1–2), 57–73.
- Beaufort, L., Heussner, S. 2001. Seasonal dynamics of calcareous nanoplankton on a West European continental margin: the Bay of Biscay. *Marine Micropaleontology*, 43(1-2), 27–55.
- Beaufort, L., Probert, I., Buchet, N., 2007. Effects of acidification and primary production on coccolith weight: Implications for carbonate transfer from the surface to the deep ocean. *Geochemistry, Geophysics, Geosystems*, 8(8).
- Beaufort, L., Probert, I., de Garidel-Thoron et al., 2011. Sensitivity of coccolithophores to carbonate chemistry and ocean acidification. *Nature*, 476(7358), 80–83.
- Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall, New Jersey. 376 pp.
- Blättler, C. L., Henderson, G. M., & Jenkyns, H. C. (2012). Explaining the Phanerozoic Ca isotope history of seawater. *Geology* 40(9), 843–846.
- Blättler, C. L., Jenkyns, H. C., Reynard, L. M., & Henderson, G. M. 2011. Significant increases in global weathering during Oceanic Anoxic Events 1a and 2 indicated by calcium isotopes. *Earth and Planetary Science Letters* 309(1-2), 77–88.
- Boudreau, B. P., Middelburg, J. J., & Luo, Y. (2018). The role of calcification in carbonate

- compensation. *Nature Geoscience*, 11(12), 894–900.
- Bowen, G. J., 2013. Up in smoke: A role for organic carbon feedbacks in Paleogene hyperthermals. *Global and Planetary Change* 109, 18–29
  - Bralower, T., Premoli Silva, I., Malone, M., 2002. Leg 198, Proceedings of the Ocean Drilling Program: Initial reports, 148.
  - Bralower, T.J., 2002. Evidence of surface water oligotrophy during the Paleocene–Eocene Thermal Maximum: nanofossil assemblage data from Ocean Drilling Program Site 690 Maud Rise, Weddell Sea. *Paleoceanography* 17, 1–13.
  - Bralower, T.J., Kelly, D.C., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L., Smith, G.J., 2014. Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters* 401, 70–82.
  - Bralower, T.J., Kelly, D.C., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L., Smith, G.J., 2014. Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters* 401, 70–82.
  - Bralower, T.J., Premoli Silva, I., Malone, M.J., et al., 2002. Proc. ODP, Initial Reports., 198: College Station, TX (Ocean Drilling Program).
  - Brazier, J. M., Suan, G., Tacail, T., Simon, L., Martin, J. E., Mattioli, E., Balter, V., 2015. Calcium isotope evidence for dramatic increase of continental weathering during the Toarcian oceanic anoxic event (Early Jurassic). *Earth and Planetary Science Letters* 411, 164–176.
  - Bridgestock, L., Hsieh, Y. T., Porcelli, D., & Henderson, G. M. (2019). Increased export production during recovery from the Paleocene–Eocene thermal maximum constrained by sedimentary Ba isotopes. *Earth and Planetary Science Letters*, 510, 53-63.
  - Channon, M. B., Gordon, G. W., Morgan, J. L., Skulan, J. L., Smith, S. M., Anbar, A. D., 2015. Using natural, stable calcium isotopes of human blood to detect and monitor changes in bone mineral balance. *Bone*, 77, 69-74.
  - Colosimo, A.B., Bralower, T.J., Zachos, J.C., 2006. Evidence for lysocline shoaling at the Paleocene/Eocene thermal maximum on Shatsky rise, northwest Pacific. *Proceeding of the Ocean Drilling Program. Scientific Results* 198, 1–36.
  - Colosimo, A.B., Bralower, T.J., Zachos, J.C., 2006. Evidence for lysocline shoaling at the Paleocene/Eocene thermal maximum on Shatsky Rise, northwest Pacific, *Proceedings of the Ocean Drilling Program: Scientific Results*. Texas A & M University.
  - Cubillos, J. C., Henderiks, J., Beaufort, L., Howard, W. R., Hallegraeff, G. M., 2012. Reconstructing calcification in ancient coccolithophores: Individual coccolith weight and



- morphology of *Coccolithus pelagicus* (sensu lato). *Marine Micropaleontology* 92 29–39.
- De La Rocha, C.L., De Paolo, D.J., 2000. Isotopic Evidence for Variations in the Marine Calcium Cycle Over the Cenozoic. *Science* 289, 1176–1178
  - Dickens, G.R., Castillo, M.M., Walker, J.G.C., 1997. A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate, *Geology* 25, 259–262.
  - Dickens, G.R., O'Neil, J.R., Rea, D.K., Owen, R.M., 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* 10, 965–971
  - Dickson, *Journal of Chemical Thermodynamics* 22, 113–127, 1990.
  - Dickson, A. J., Cohen, A. S., Coe, A. L., Davies, M., Shcherbinina, E. A., & Gavrilov, Y. O., 2015. Evidence for weathering and volcanism during the PETM from Arctic Ocean and Peri-Tethys osmium isotope records. *Palaeogeography, Palaeoclimatology, Palaeoecology* 438, 300–307.
  - Edgar, K. M., Anagnostou, E., Pearson, P. N., & Foster, G. L., 2015. Assessing the impact of diagenesis on  $\delta^{11}\text{B}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite. *Geochimica et Cosmochimica Acta* 166, 189–209.
  - Fantle, M. S., Tipper, E. T., 2014. Calcium isotopes in the global biogeochemical Ca cycle: implications for development of a Ca isotope proxy. *Earth-Science Reviews*, 129, 148–177.
  - Farkaš, J., Böhm, F., Wallmann, K., Blenkinsop, J., Eisenhauer, A., van Geldern, R., Munnecke, A., Voigt, S., Veizer, J., 2007a. Calcium isotope record of Phanerozoic oceans: implications for chemical evolution of seawater and its causative mechanisms. *Geochim. Cosmochim. Acta* 71, 5117–5134.
  - Farley, K. A., Love, S. G., Patterson, D. B., 1997. Atmospheric entry heating and helium retentivity of interplanetary dust particles. *Geochimica et Cosmochimica Acta*, 61(11), 2309–2316.
  - Farley, K.A., Eltgroth, S.F., 2003. An alternative age model for the Paleocene–Eocene thermal maximum using extraterrestrial  $^3\text{He}$ . *Earth and Planetary Science Letters* 208, 135–148.
  - Farley, K.A., Love, S.G., Patterson, D.B., 1997. Atmospheric entry heating and helium retentivity of interplanetary dust particles. *Geochimica et Cosmochimica Acta* 61, 2309–2316.
  - Frieling, J., Gebhardt, H., Huber et al., 2017. Extreme warmth and heat-stressed plankton in the tropics during the Paleocene-Eocene Thermal Maximum. *Science advances* 3(3),



e1600891.

- Gibbs, S. J., Stoll, H. M., Bown, P. R., Bralower, T. J., 2010. Ocean acidification and surface water carbonate production across the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters* 295(3–4), 583–592.
- Gibbs, S.J., Bralower, T.J., Bown, P.R., Zachos, J.C., Bybell, L.M., 2006. Shelf and open-ocean calcareous phytoplankton assemblages across the Paleocene–Eocene thermal maximum: implication for global productivity gradients. *Geology* 34 (4), 233–236.
- Griffith, E. M., Fantle, M. S., Eisenhauer, A., Paytan, A., Bullen, T. D., 2015. Effects of ocean acidification on the marine calcium isotope record at the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 419, 81–92.
- Griffith, E. M., Paytan, A., Caldeira, K., Bullen, T. D., Thomas, E., 2008. A dynamic marine calcium cycle during the past 28 million years. *Science* 322(5908), 1671–1674.
- Griffith, E. M., Schauble, E. A., Bullen, T. D., & Paytan, A., 2008. Characterization of calcium isotopes in natural and synthetic barite. *Geochimica et Cosmochimica Acta*, 72(23) 5641–5658.
- Griffith, E. M., Schmitt, A. D., Andrews, M. G., & Fantle, M. S. (2020). Elucidating modern geochemical cycles at local, regional, and global scales using calcium isotopes. *Chemical Geology*, 534, 119445.
- Griffith, E.M., Fantle, M.S., Eisenhauer, A., Paytan, A., Bullen, T.D., 2015. Effects of ocean acidification on the marine calcium isotope record at the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 419, 81–92.
- Griffith, E.M., Fantle, M.S., Eisenhauer, A., Paytan, A., Bullen, T.D., 2015. Effects of ocean acidification on the marine calcium isotope record at the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 419, 81–92.
- Griffith, E.M., Paytan, A., Kozdon, R., Eisenhauer, A., Ravelo, A.C., 2008. Influences on the fractionation of calcium isotopes in planktonic foraminifera. *Earth and Planetary Sciences Letters* 268, 124–136.
- Gussone, N., Eisenhauer, A., Heuser, A., et al., 2003. Model for kinetic effects on calcium isotope fractionation ( $\delta^{44}\text{Ca}$ ) in inorganic aragonite and cultured planktonic foraminifera. *Geochimica et Cosmochimica Acta*, 67(7), 1375–1382.
- Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälike, H., ... & Foster, G. L., 2017. Very large release of mostly volcanic carbon during the Palaeocene–Eocene Thermal Maximum. *Nature* 548(7669), 573–577.
- Henderiks, J., Rickaby, R. E., 2007. A coccolithophore concept for constraining the

Cenozoic carbon cycle. *Biogeosciences* 4, 323–329.

- Henehan, M. J., Ridgwell, A., Thomas, E., Zhang et al., 2019. Rapid ocean acidification and protracted Earth system recovery followed the end-Cretaceous Chicxulub impact. *Proceedings of the National Academy of Sciences* 116(45), 22500–22504.
- Heuser, A., Eisenhauer, A., Scholz-Ahrens, K. E., & Schrezenmeir, J., 2016. Biological fractionation of stable Ca isotopes in Göttingen minipigs as a physiological model for Ca homeostasis in humans. *Isotopes in environmental and health studies* 52(6) 633-648.
- Holland, K., Branson, O., Haynes, L. L. et al., 2020. Constraining multiple controls on planktic foraminifera Mg/Ca. *Geochimica et Cosmochimica Acta* 273 116–136.
- Jiang, S., Wise Jr, S. W., 2007. Taxonomic note: A new *Coccolithus* species that thrived during the Paleocene/Eocene Thermal Maximum. *Journal of Nannoplankton Research* 29, 88–91.
- Jones, T. D., Lunt, D. J., Schmidt, D. N., Ridgwell, A., Sluijs, A., Valdes, P. J., & Maslin, M., 2013. Climate model and proxy data constraints on ocean warming across the Paleocene–Eocene Thermal Maximum. *Earth-Science Reviews* 125 123–145.
- Kaiho, K., Takeda, K., Petrizzo, M.R., Zachos, J.C., 2006. Anomalous shifts in tropical Pacific planktonic and benthic foraminiferal test size during the Paleocene–Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 237, 456–464.
- Kelly, C. D., Bralower, T. J., Zachos, J. C., Silva, I. P., Thomas, E., 1996. Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum. *Geology* 24(5), 423–426.
- Kelly, D. C., Zachos, J. C., Bralower, T. J., Schellenberg, S. A., 2005. Enhanced terrestrial weathering/runoff and surface ocean carbonate production during the recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography* 20(4).
- Kelly, D.C., Nielsen, T.M.J., McCarren, H.K., Zachos, J.C., Röhl, U., 2010. Spatiotemporal patterns of carbonate sedimentation in the South Atlantic: Implications for carbon cycling during the Paleocene–Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 293, 30–40.
- Kelly, D.C., Zachos, J.C., Bralower, T.J., Schellenberg, S.A., 2005. Enhanced terrestrial weathering/runoff and surface ocean carbonate production during the recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography* 20.
- Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* 353, 225–229.
- Kısakürek, B., Eisenhauer, A., Böhm, F., Hathorne, E. C., Erez, J., 2011. Controls on

- calcium isotope fractionation in cultured planktic foraminifera, *Globigerinoides ruber* and *Globigerinella siphonifera*. *Geochimica et Cosmochimica Acta* 75(2), 427–443.
- Komar, N., Zeebe, R. E., 2011. Oceanic calcium changes from enhanced weathering during the Paleocene-Eocene thermal maximum: No effect on calcium-based proxies. *Paleoceanography*, 26(3).
  - Komar, N., Zeebe, R. E., 2016. Calcium and calcium isotope changes during carbon cycle perturbations at the end-Permian. *Paleoceanography* 31(1), 115–130.
  - Kozdon, R., Kelly, D. C., Kitajima, K., Strickland, A., Fournelle, J. H., & Valley, J. W., 2013. In situ  $\delta^{18}\text{O}$  and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene-Eocene thermal maximum. *Paleoceanography*, 28(3), 517–528.
  - Lemarchand, D., Wasserburg, G. J., Papanastassiou, D. A., 2004. Rate-controlled calcium isotope fractionation in synthetic calcite. *Geochimica et cosmochimica acta*, 68(22), 4665–4678.
  - Luo, Y., Boudreau, B. P., Dickens, G. R., Sluijs, A., & Middelburg, J. J. (2016). An alternative model for  $\text{CaCO}_3$  over-shooting during the PETM: biological carbonate compensation. *Earth and Planetary Science Letters*, 453, 223–233.
  - Ma, Z., Gray, E., Thomas, E., Murphy, B., Zachos, J., & Paytan, A. (2014). Carbon sequestration during the Palaeocene–Eocene Thermal Maximum by an efficient biological pump. *Nature Geoscience* 7(5), 382–388.
  - Marcantonio, F., Thomas, D.J., Woodard, S., McGee, D., Winckler, G., 2009. Extraterrestrial  $^3\text{He}$  in Paleocene sediments from Shatsky Rise: Constraints on sedimentation rate variability. *Earth and Planetary Science Letters* 287, 24–30.
  - Marcantonio, F., Thomas, D.J., Woodard, S., McGee, D., Winckler, G., 2009. Extraterrestrial  $^3\text{He}$  in Paleocene sediments from Shatsky Rise: Constraints on sedimentation rate variability. *Earth and Planetary Science Letters* 287, 24–30.
  - Martin, J.E., Tacail, T., Adnet, S., Girard, C., Balter, V., 2015. Calcium isotopes reveal the trophic position of extant and fossil elasmobranchs. *Chemical Geology* 415, 118–125.
  - Mattioli, E., Pittet, B., Suan, G., Mailliot, S. 2008. Calcareous nannoplankton changes across the early Toarcian oceanic anoxic event in the western Tethys. *Paleoceanography* 23(3).
  - Mehrbach, C., Culberson, C. H., Hawley, J. E., & Pytkowicz, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure 1. *Limnology and oceanography* 18(6), 897–907.
  - Milliman, J. D., 1993. Production and accumulation of calcium carbonate in the ocean:

budget of a nonsteady state. *Global geochemical cycles* 7(4), 927–957.

- Morgan, J. L., Skulan, J. L., Gordon, G. W., Romaniello, S. J., Smith, S. M., & Anbar, A. D., 2012. Rapidly assessing changes in bone mineral balance using natural stable calcium isotopes. *Proceedings of the National Academy of Sciences* 109(25), 9989-9994.47.
- Murphy, B.H., Farley, K.A., Zachos, J.C., 2010. An extraterrestrial <sup>3</sup>He-based timescale for the Paleocene–Eocene thermal maximum (PETM) from Walvis Ridge, IODP Site 1266. *Geochimica et Cosmochimica Acta* 74, 5098–5108.
- Murphy, B.H., Farley, K.A., Zachos, J.C., 2010. An extraterrestrial <sup>3</sup>He-based timescale for the Paleocene–Eocene thermal maximum (PETM) from Walvis Ridge, IODP Site 1266. *Geochimica et Cosmochimica Acta* 74, 5098–5108.
- Nicolo, M.J., Dickens, G.R., 2006. Data Report: Terrigenous Grain-Size Distributions at Sites 1263 and 1267: Testing the Applicability of Leg 208 Sediments for Eolian Analysis, in: Kroon, D., Zachos, J.C., Richter, C. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results Volume 208*, College Station, TX 1–13.
- Nielsen, L. C., Druhan, J. L., Yang, W., Brown, S. T., DePaolo, D. J., 2012. Calcium isotopes as tracers of biogeochemical processes. In *Handbook of environmental isotope geochemistry*, 105–124. Springer, Berlin, Heidelberg.
- Norris, R. D., 1996. Symbiosis as an evolutionary innovation in the radiation of Paleocene planktic foraminifera. *Paleobiology*, 461–480.
- Penman, D. E., Zachos, J. C., 2018. New constraints on massive carbon release and recovery processes during the Paleocene-Eocene Thermal Maximum. *Environmental Research Letters* 13(10), 105008.
- Penman, D.E., Hönisch, B., Zeebe, R.E., Thomas, E., Zachos, J.C., 2014. Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* 29, 2014 PA002621.
- Penman, D.E., Turner, S.K., Sexton, P.F., Norris, R.D., Dickson, A.J., Boulila, S., Ridgwell, A., Zeebe, R.E., Zachos, J.C., Cameron, A., Westerhold, T., Röhl, U., 2016. An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene Thermal Maximum. *Nature Geoscience* 9, 575–580.
- Petrizzo, M. R., 2007. The onset of the Paleocene–Eocene Thermal Maximum (PETM) at Sites 1209 and 1210 (Shatsky Rise, Pacific Ocean) as recorded by planktonic foraminifera. *Marine Micropaleontology* 63(3–4), 187–200.
- Petrizzo, M. R., Leoni, G., Speijer, R. P., De Bernardi, B., & Felletti, F. (2008). Dissolution susceptibility of some Paleogene planktonic foraminifera from ODP site 1209 (Shatsky Rise,

- Pacific Ocean). *The Journal of Foraminiferal Research*, 38(4), 357–371.
- Poulton, A. J., Sanders, R., Holligan, P. M., Stinchcombe, M. C., Adey, T. R., Brown, L., Chamberlain, K., 2006 Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean. *Global Biogeochemical Cycles* 20(4).
  - Quillévéré, F., Norris, R. D., Moussa, I., Berggren, W. A., 2001. Role of photosymbiosis and biogeography in the diversification of early Paleogene acarininids (planktonic foraminifera). *Paleobiology* 27(2), 311–326.
  - Ravizza, G., Norris, R. N., Blusztajn, J., Aubry, M. P., 2001. An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering. *Paleoceanography* 16(2), 155–163.
  - Ridgwell, A. (2007). Interpreting transient carbonate compensation depth changes by marine sediment core modeling. *Paleoceanography*, 22(4).
  - Ridgwell, A., Zeebe, R. E., 2005. The role of the global carbonate cycle in the regulation and evolution of the Earth system. *Earth and Planetary Science Letters*, 234(3–4), 299–315.
  - Roberts, J., Kaczmarek, K., Skinner, L.C., Bijma J., Bradbury, H., Turchyn A.V., Misra, S., Lithium Isotopes in Benthic Foraminifera, *GCA* 2020.
  - Röhl, U., Westerhold, T., Bralower, T.J., Zachos, J.C., 2007. On the duration of the Paleocene–Eocene thermal maximum (PETM). *Geochemistry, Geophysics, Geosystems* 8.
  - Self-Trail, J. M., Powars, D. S., Watkins, D. K., Wandless, G., 2012. Calcareous nannofossil assemblage changes across the Paleocene-Eocene thermal maximum: Evidence from a shelf setting, *Marine Micropaleontology* 92–93, 61–80.
  - Sime, N. G., Christina, L., Galy, A., 2005. Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera. *Earth and Planetary Science Letters* 232(1–2), 51–66.
  - Sluijs, A., Bowen, G., Brinkhuis, H., Lourens, L., Thomas, E., 2007. The Palaeocene-Eocene Thermal Maximum super greenhouse: biotic and geochemical signatures, age models and mechanisms of global change. *Deep Time Perspectives on Climate Change: Marrying the Signal From Computer Models and Biological Proxies*, 323–347.
  - Stap, L., Sluijs, A., Thomas, E., Lourens, L., 2009. Patterns and magnitude of deep sea carbonate dissolution during Eocene Thermal Maximum 2 and H2, Walvis Ridge, southeastern Atlantic Ocean. *Paleoceanography* 24.
  - Stoll, H. M., Bains, S., 2003. Coccolith Sr/Ca records of productivity during the Paleocene-Eocene thermal maximum from the Weddell Sea. *Paleoceanography* 18(2), 1–11.
  - Stoll, H., Shimizu, N., Arevalos, A., Matell, N., Banasiak, A., Zeren, S., 2007. Insights on

- coccolith chemistry from a new ion probe method for analysis of individually picked coccoliths. *Geochemistry, Geophysics, Geosystems*, 8(6).
- Tacail T, Albalat E, Télouk P, Balter V., 2014. A simplified protocol for measurement of Ca isotopes in biological samples. *J. Anal. At.Spectrom.* 29,5 29–535.
  - Tacail, T., Télouk, P., Balter, V., 2016. Precise analysis of calcium stable isotope variations in biological apatites using laser ablation MC-ICPMS. *Journal of Analytical Atomic Spectrometry* 31(1), 152–162.
  - Tacail, T., Thivichon-Prince, B., Martin, J. E., Charles, C., Viriot, L., Balter, V., 2017. Assessing human weaning practices with calcium isotopes in tooth enamel. *Proceedings of the National Academy of Sciences* 114(24), 6268–6273.
  - Takeda, K., Kaiho, K., 2007. Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 251, 175–197.
  - Takeda, K., Kaiho, K., 2007. Faunal turnovers in central Pacific benthic foraminifera during the Paleocene–Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 251, 175–197.
  - Tripathi, A., Elderfield, H., 2005. Deep-sea temperature and circulation changes at the Paleocene-Eocene thermal maximum. *Science*, 308(5730), 1894–1898.
  - Tripathi, A., Elderfield, H., 2005. Deep-Sea Temperature and Circulation Changes at the Paleocene-Eocene Thermal Maximum. *Science* 308, 1894–1898.
  - Tyson, R. V., 1995. Abundance of organic matter in sediments: TOC, hydrodynamic equivalence, dilution and flux effects. In *Sedimentary organic matter*. 81–118. Springer, Dordrecht.
  - Uppstrom, L. R. (1974). The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep Sea Research* 21, 161–162.
  - van der Meulen, B., Gingerich, P. D., Lourens, L. J., Meijer, N., van Broekhuizen, S., van Ginneken, S., Abels, H. A., 2020. Carbon isotope and mammal recovery from extreme greenhouse warming at the Paleocene–Eocene boundary in astronomically-calibrated fluvial strata, Bighorn Basin, Wyoming, USA. *Earth and Planetary Science Letters* 534, 116044.
  - van der Meulen, B., Gingerich, P.D., Lourens, L.J., Meijer, N., van Broekhuizen, S., van Ginneken, S., Abels, H.A., 2020. Carbon isotope and mammal recovery from extreme greenhouse warming at the Paleocene–Eocene boundary in astronomically-calibrated fluvial strata, Bighorn Basin, Wyoming, USA. *Earth and Planetary Science Letters* 534, 116044.
  - Vink, A., Brune, A., Höll, C., Zonneveld, K. A., Willems, H., 2002. On the response of



- calcareous dinoflagellates to oligotrophy and stratification of the upper water column in the equatorial Atlantic Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology* 178(1–2), 53–66.
- Westerhold, T., Röhl, U., Donner, B., McCarren, H. K., Zachos, J. C., 2011. A complete high-resolution Paleocene benthic stable isotope record for the central Pacific (ODP Site 1209). *Paleoceanography* 26(2).
  - Westerhold, T., Röhl, U., Donner, B., McCarren, H.K., Zachos, J.C., 2011. A complete high-resolution Paleocene benthic stable isotope record for the central Pacific (ODP Site 1209). *Paleoceanography* 26.
  - Westerhold, T., Röhl, U., Donner, B., Zachos, J. C., 2018. Global extent of early Eocene hyperthermal events: A new Pacific benthic foraminiferal isotope record from Shatsky Rise (ODP Site 1209). *Paleoceanography and Paleoclimatology* 33(6), 626–642.
  - Westerhold, T., Röhl, U., Donner, B., Zachos, J.C., 2018. Global Extent of Early Eocene Hyperthermal Events: A New Pacific Benthic Foraminiferal Isotope Record From Shatsky Rise (ODP Site 1209). *Paleoceanography and Paleoclimatology* 33, 626–642.
  - Westerhold, T., Röhl, U., Donner, B., Zachos, J.C., 2018a. Global Extent of Early Eocene Hyperthermal Events: A New Pacific Benthic Foraminiferal Isotope Record From Shatsky Rise (ODP Site 1209). *Paleoceanography and Paleoclimatology* 33, 626–642.
  - Westerhold, T., Röhl, U., Raffi, I., Fornaciari, E., Monechi, S., Reale, V., Bowles, J., Evans, H.F., 2008. Astronomical calibration of the Paleocene time. *Palaeogeography, Palaeoclimatology, Palaeoecology* 257 377–403.
  - Westerhold, T., Röhl, U., Wilkens, R.H., Gingerich, P.D., Clyde, W.C., Wing, S.L., Bowen, G.J., Kraus, M.J., 2018b. Synchronizing early Eocene deep-sea and continental records – cyclostratigraphic age models for the Bighorn Basin Coring Project drill cores. *Clim. Past* 14, 303–319.
  - Woodard, S.C., Thomas, D.J., Hovan, S., Röhl, U., Westerhold, T., 2011. Evidence for orbital forcing of dust accumulation during the early Paleogene greenhouse. *Geochemistry, Geophysics, Geosystems* 12.
  - Young, J. R. (1992). The description and analysis of coccolith structure. *Nannoplankton Research*. Hamrsmid B, Young JR (eds) ZPZ, Knihovnicna, 35–71.
  - Young, J. R., Ziveri, P., 2000. Calculation of coccolith volume and its use in calibration of carbonate flux estimates. *Deep sea research Part II: Topical studies in oceanography*, 47(9-11), 1679–1700.
  - Zachos, J. C., Dickens, G. R., Zeebe, R. E., 2008. An early Cenozoic perspective on



greenhouse warming and carbon-cycle dynamics. *Nature*, 451(7176), 279–283.

- Zachos, J.C., Kroon, D., Blum, P., Bowles, J., Gaillardet, P., Hasegawa, T., Hathorne, E.C., Hodell, D. A., Kelly, D. C., Jung, J. H., Keller, S. M., Lee, Y. S., Leuschner, D. C., Lohmann, K. C., Lourens, L., Monechi, S., Nicolo, M., Raffi, I., Riesselman, C., Röhl, U., Schellenber, S. A., Schmidt, D., Sluijs A., Thomas, D., Thomas, E., Vallius, H. , 2004. Early Cenozoic extreme climates: the Walvis Ridge transect. *Proceedings of the Ocean Drilling Program. Initial Reports* 208.
- Zachos, J.C., Rohl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H., Kroon, D., 2005. Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science* 308, 1611–1615.
- Zeebe, R. E. (2012). History of seawater carbonate chemistry, atmospheric CO<sub>2</sub>, and ocean acidification. *Annual Review of Earth and Planetary Sciences*, 40(141), 2012.
- Zeebe, R. E., Zachos, J. C., Dickens, G. R., 2009. Carbon dioxide forcing alone insufficient to explain Palaeocene–Eocene Thermal Maximum warming. *Nature Geoscience*, 2(8), 576–580.



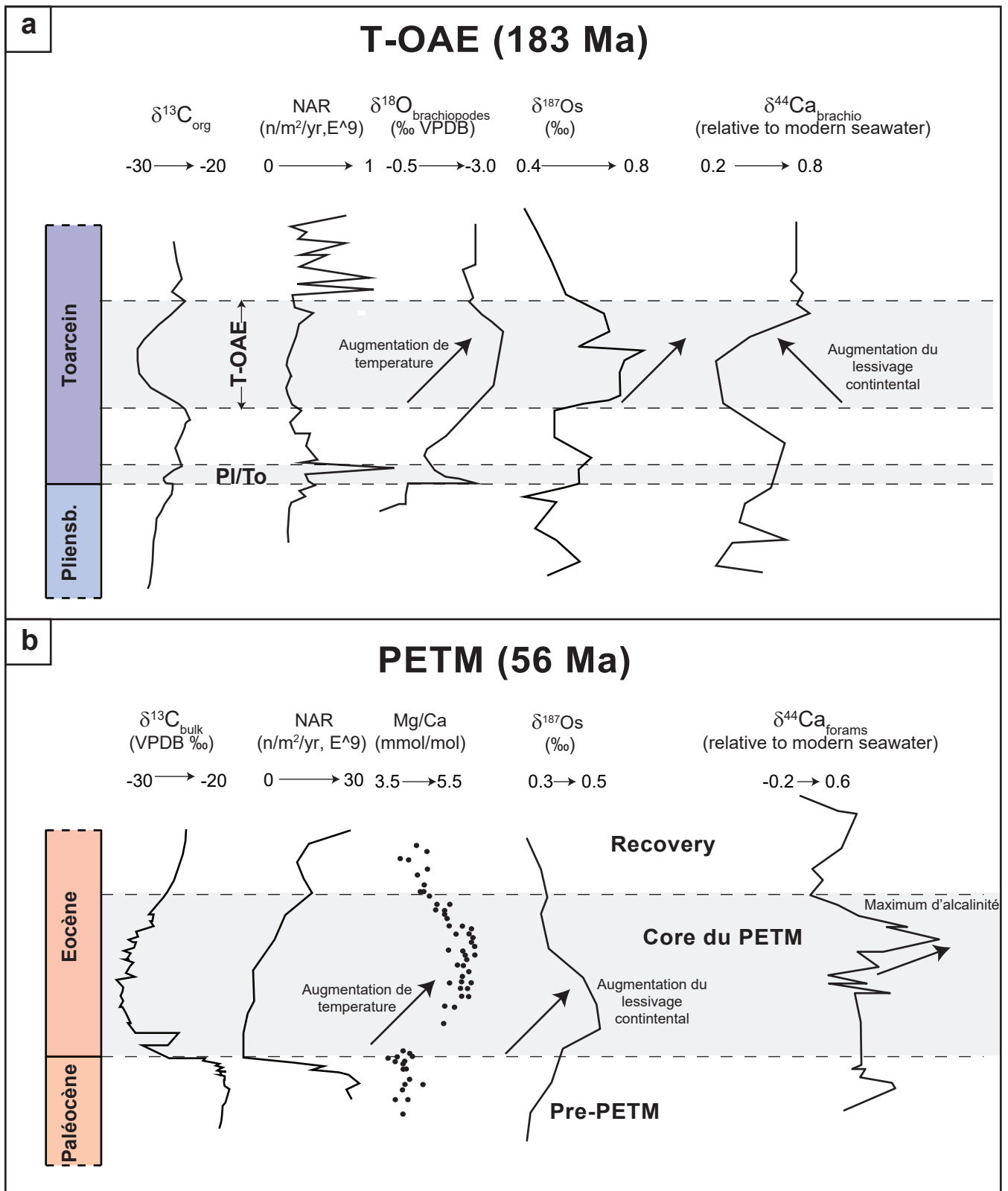
## Chapitre 5: Conclusions et synthèse

## Conclusion et synthèse

Dans les précédents chapitres du manuscrit j'ai discuté des deux intervalles de temps individuellement. L'objectif de ce dernier chapitre est de comparer les deux intervalles de temps par rapport à la réponse des nanofossiles calcaires.

### 1. Biostratigraphie

Les deux chapitres de biostratigraphie m'ont permis de mettre en évidence que 1) : les biozonations standards (Bown, 1987 ; Bown 1998 ; Mattioli et Erba, 1999 ; Martini 197 ; Okada et Bukry, 1980) ne fournissent pas une résolution suffisante pour étudier des évènements de quelque centaines de milliers d'année de durée ; 2) : il est nécessaire d'avoir une biostratigraphie à très haute résolution pour étudier des évènements tels que le PETM et les deux évènements (PI/To et T-OAE) au Pliensbachien-Toarcien. Les données biostratigraphiques ont été représentés par rapport à la courbe des isotopes stables du carbone ( $\delta^{13}\text{C}$ ). Pour le Pliensbachien-Toarcien, j'ai pu mettre en évidence qu'il y a un épisode majeur d'apparitions autour de la limite Pliensbachien-Toarcien, contrairement au T-OAE qui ne représente ni un épisode de diversification ni d'extinction pour les nanofossiles. Ceci est en partie lié à l'augmentation des placolithes, qui domineront les assemblages pour le reste Mésozoïque et Cénozoïque et en partie liés à des condensations dans plusieurs bassins de la Tethys autour de la limite. Pour le PETM, j'ai pu mettre en évidence que le record sédimentaire a une influence majeure sur l'ordre des évènements. Similairement au Pliensbachien-Toarcien, la présence de discontinuités à la limite explique certaines différences d'une localité à l'autre. Cependant, il existe un certain degré de diachronisme, affectant également les marques biostratigraphiques utilisées dans les zonations standards. La limite Paléocène-Eocène est caractérisée par plusieurs origines et extinctions, à différence de la limite Pliensbachien Toarcien. De même, l'on enregistre des changements au sein des communautés des nanofossiles calcaires. Certains de ces événements, jamais pris en compte dans les biozonations antérieures, se sont avérés cohérents, avec un degré de diachronisme moindre que les marqueurs biostratigraphiques utilisés précédemment. Finalement j'obtiens un nouveau schéma de biozonation à haute résolution avec une résolution moyenne de 50-100 kyrs par zone. De plus, je corrèle les événements



**Fig. 1.** Figure de synthèse de comparaison entre les deux cas d'études discutés dans ce manuscrit: l'événement anoxique du Toarcien (a; T-OAE) et le Maximum thermique à la limite Paléocène-Eocène (b; PETM). Pour les deux événements la courbe des isotopes stables du carbone mesurés sur la matière organique totale pour le T-OAE ( $\delta^{13}\text{C}_{\text{org}}$ ) et sur roche totale pour le PETM ( $\delta^{13}\text{C}_{\text{bulk}}$ ) et le NAR provenant des forages Mochras pour le T-OAE et du site 1209 (Pacifique Equatorial) pour le PETM. Le  $\delta^{18}\text{O}_{\text{brachiopodes}}$  mesurés sur des coquilles de brachiopodes d'après Suan et al. 2008 à Peniche (Bassin Lusitanien, Portugal). Le rapport Mg/Ca mesuré sur des coquilles de l'espèce *Morozovella velascoensis* d'après Penman et al., 2014 au site 1209. Le  $\delta^{187}\text{Os}$  mesurés sur roche totale d'après Percival et al., 2016 pour le T-OAE à Mochras et d'après Ravizza et al., 2001 pour le PETM. Le  $\delta^{44}\text{Ca}_{\text{forams}}$  mesuré sur des coquilles de l'espèce *Morozovella velascoensis* au site 1209 provient de ce travail (PETM) Le  $\delta^{44}\text{Ca}_{\text{brachiopodes}}$  mesuré sur des coquilles de brachiopodes à Peniche d'après Suan et al., 2008.

biostratigraphiques et les nouvelles zones aux différentes phases caractérisant l'excursion négative des isotopes du carbone définissant la limite Paléocène-Éocène.

## 2. Est-ce le PETM un évènement océanique anoxique ? Indices provenant des assemblages à nanofossiles calcaires

Malgré plusieurs auteurs se soient intéressés à ces deux épisodes de profonds changements environnementaux et ont mis en évidence des aspects similaires entre le T-OAE et le PETM (Cohen et al., 2007), la comparaison entre les changements biotiques au sein des communautés planctoniques ça n'a jamais été faite auparavant. Il est nécessaire de préciser que les assemblages du Jurassique Inferieur sont totalement différentes de celles du Paléogène (Bown, 1998). Cependant, malgré le fait que la différence au sein des assemblages est due au chemin évolutif des nanofossiles, la réponse et leur sensibilité aux changements paleoenvironnementaux restent analogues au cours des temps géologiques. Cela nous permet donc de comparer ces deux évènements, séparés par 130 Ma d'histoire de la Terre, en s'appuyant sur le fait qu'ils présentent déjà de nombreuses similitudes. Pour cela, ils sont les candidats parfaits pour cette étude (Fig.1a,b).

Comme pour le T-OAE, le PETM a été caractérisée par changements au sein des communautés marines, y compris les nanofossiles, et une excursion négative majeure des isotopes du carbone dans les réservoirs de carbone marins et continentaux (par exemple, Koch et al., 1992 ; Schouten et al., 2007). Des travaux récents ont souligné des similitudes, notamment le réchauffement climatique et un lessivage continentale plus efficace (Cohen et al., 2007 ; Hesselbo et al., 2007). Bien que ce ne soit pas aussi clair que pour le T-OAE, des conditions d'hypoxie généralisée (Remmelzwaal et al., 2019) atteignant parfois des conditions d'anoxie au moins en proximité des plateformes continentales (Nicolo et al., 2010), pourraient avoir également marqué le PETM (Sluijs et al., 2006, 2008, 2014). Pour cela, certains auteurs parlent d'un « évènement océanique anoxique naissant » (e.g., Cohen et al., 2007). Les deux évènements peuvent être liés de manière causale, les deux étant associé à un apport massif de carbone appauvri en  $^{13}\text{C}$  (Dickens et al. 1995, 1997 ; Hesselbo et al. 2000 ; Svensen et al., 2007). Sur la base des résultats collecté pendant ce travail de thèse,

on peut conclure que les enregistrements qui nous fournissent les nanofossiles au T-OAE et au PETM présentent des similitudes et des différences.

Sur la base d'assemblages de nanofossiles, ainsi que de données provenant des foraminifères planctoniques et benthiques et les dinoflagellés, des travaux récents suggèrent que les conditions trophiques étaient profondément différentes dans les zones proximales et dans les zones distales pendant le PETM (Bralower, 2002 ; Tremolada et Bralower, 2004 ; Gibbs et al., 2006b). Similairement au T-OAE, des pics en abondance relative et absolue de taxons indiquant des eaux froides et une fécondité élevée (*Prinsius*, *Hornibrookina*, *Biscutum*, *Chiasmolithus*) sont observées dans les sédiments pélagiques (Site 1209, 1263) et proximaux (e.g., Kharouba, Tunisie) déposés avant le PETM. Ces taxons sont remplacés par des taxons d'eaux chaudes, ce qui indique également des conditions plus oligotrophes dans les eaux de surface. Inversement, l'on enregistre un pic des taxons adaptés à des eaux de surface moins salines durant le T-OAE (Calyculaceae). Dans les deux cas, les assemblages de nanofossiles indiquent une stratification des masses d'eau. Pendant le PETM, la stratification était plus marquée dans les zones océaniques, comme indiquée par les assemblages et par l'analyse en composante principales (ACP). En particulier, le score factoriel qui est contrôlé par *Thoracosphaera*, est particulièrement stable pendant le PETM dans les gyres océaniques (Site, 1209) alors que dans les zones proximales les conditions étaient beaucoup plus fluctuantes. Dans ces zones, les assemblages à nanofossiles montrent une alternance entre des conditions plutôt mésotrophes et des conditions oligotrophes. Cependant, l'ACP montre aussi que l'intervalle du PETM est caractérisé par *Discoaster* malformées, *Rhomboaster* et *Coccolithus bownii* (taxons d'excursion) ce qui est un trait commun du PETM indépendamment de l'environnement de dépôt, en plein accord avec les données de littérature (e.g., Bralower et Self-Trail., 2016). Au PETM, on observe un effondrement spectaculaire (>60 %) et durable (>80 000 ans) de la production nette de CaCO<sub>3</sub> dans l'océan Atlantique et Pacifique en milieu tropical en raison de la stratification des océans induite par le réchauffement et de la diminution de la disponibilité des nutriments. Nos enregistrements montrent que l'excès d'alcalinité qui en résulte, suggéré par les données de fragmentation des nanofossiles ainsi que par les isotopes du calcium, a été rapidement consommé lorsque la production et l'enfouissement du CaCO<sub>3</sub> ont repris, déclenchant un stockage rapide et massif du carbone inorganique et organique. En revanche, dans les zones



proximales l'on enregistre une disponibilité accrue des nutriments. La différence de productivité entre les zones proximales et distales pendant le PETM ressemble quelque peu les variations observées entre le marge nord et sud de la Téthys à travers le T-OAE. Cependant, ces variations, dans le contexte de la paléogéographie toarcienne, se peuvent probablement traduire en un contraste entre un climat humide le long de la marge nord et conditions plus arides aux paléolatitudes tropicales, plutôt qu'en terme de distance par rapport aux continents et, ainsi, aux sources de nutriments. Un apport important et rapide de CO<sub>2</sub> dans l'océan devrait produire une chute du pH de l'eau de mer et entrainer ainsi une remontée de la profondeur de compensation des carbonates (CCD). C'est certainement le cas pour le PETM, car comme en témoigne la dissolution généralisée des carbonates des fonds marins (e.g., Zachos et al., 2005 ; Zeebe, 2012 ; Penman et al., 2014. Penman et al., 2016). Une baisse du pH de l'eau de mer pendant la T-OAE a été évoquée par Tremolada et al., 2005 pour expliquer les enregistrements de sédiments dans le Bassin de Cantabrie (nord de l'Espagne). Ici, l'intervalle correspondant à l'événement (T-OAE) est stérile en nanofossiles calcaires. Toutefois, il faut noter que ce bassin et d'autres bassins épicontinentaux de la Téthys occidentale étaient très peu profondes (moins de 200 m selon Bjerrum et al. (2001), et un telle montée de la CCD semble peu probable. Alternativement, on propose que les milieux du nord-ouest de Téthys, plus proche de la Laurasian Seaway, enregistrent des conditions environnementales peu favorables au nanofossiles calcaires. En effet, similairement aux observations de Tremolada et al., 2005, les nanofossiles sont absents dans des sédiments déposés pendant le T-OAE dans le forage de Brown Moor (nord de l'Angleterre ; Bucefalo Palliani et al., 2002). Les données provenant du forage Mochras (Pays de Galle) montrent des résultats très similaires pendant, car l'abondance absolue et le flux de nanofossiles diminuent brutalement pendant le T-OAE.

En particulier, le  $\delta^{13}\text{C}$  au PETM suggère un gradient vers des valeurs plus négatives en passant du Site 1209 à Kharouba : ceci pourrait indiquer une productivité globalement faible au niveau de la gyre océanique (Site 1209) et progressivement plus forte dans le proximal (Kharouba ; Fig. 4, chapitre 3.1). C'est intéressant également pour ce qui concerne les NAR : plus forts dans les trois sites avant l'événement, puis faibles dans le *core* et forts à nouveau dans la phase de recovery. Comme pour le

d<sup>13</sup>C, les flux les plus faibles (productivité globalement faible) au 1209 et 4 ordres de grandeurs plus forte à Kharouba. On observe exactement la même chose au Toarcien. Finalement, l'étude des taux d'accumulation des nanofossiles (NAR) montre que aussi bien pour le PETM que pour le T-OAE il existe une différence de 4 ordre de grandeurs entre les sites le plus oligotrophes (e.g., ODP 1209 pour le PETM, Grèce au T-OAE : Kafousia et al., 2011) et les sites les plus proximaux, caractérisés par des conditions plus mesotrophes (e.g., Kharouba au PETM et Brown Moore Borehole, Angleterre).

Comme le PETM, le T-OAE est un événement hyperthermique (réchauffement climatique global) et plusieurs indices suggèrent une meilleure efficacité du lessivage continentale. Lors de chaque événement, la distribution de la production carbonatée par les nanofossiles varie considérablement entre les sites étudiés, probablement en raison de l'hydrographie et la proximité des continents. La dissolution généralisée des carbonates pélagiques observés pour le PETM ne sont pas connus pour le T-OAE, peut-être en raison de la rareté des coupes du Jurassique Inferieur déposées en eau profonde. Des recherches futures devraient se focaliser sur les coupe du Toarcian qui présentent des sédiments d'eaux profondes, comme celles de sud-ouest du Japon (Hori, 1997).

### 3. Causes probables des modifications des valeurs isotopiques du calcium

La composition isotopique du calcium des sédiments carbonatés et des fossiles a été proposée comme outil pour reconstituer les variations du cycle du calcium dans le passé géologique (e.g., De La Rocha et DePaolo, 2000 ; Farkaš et al., 2007a ; Griffith et al., 2008a ; Blättler et al., 2011, 2012 ; Fantle et Tipper, 2014). Comme des effets de fractionnement spécifiques à l'espèce  $\delta^{44/40}\text{Ca}$  existent chez les foraminifères planctoniques, (Griffith et al., 2008 ; Kisakureh et al, 2011), nous avons limité nos analyses à l'espèce *Morozovella velascoensis*, une espèce photosymbiotique vivant en surface et qui occupait des milieux oligotrophes aux basses et moyennes latitudes pendant le Paléocène supérieur et l'Éocène inférieur (Norris et al., 1996, Kelly et al. 1996, Quillévéré et al., 2001). Cette espèce est très abondante au site 1209 (Petruzzo, 2007-2008) et domine les assemblages de foraminifères planctoniques au PETM

### 3.1. Diagenèse

Une étude précédente sur le PETM sur des sites de l'océan Pacifique attribuait une grande partie de la variabilité de l'enregistrement du  $\delta^{44}\text{Ca}$  mesurés sur roche totale à la précipitation de calcite secondaire (Griffith et al., 2015). Des preuves de précipitation de calcite secondaire sur les coquilles des foraminifères planctoniques pendant le PETM existent dans l'océan Pacifique au site ODP 865 sous la forme de bâtonnets de calcite de taille micrométriques précipités le long des *muricae* des foraminifères et de spécimens partiellement ou entièrement cimentés avec des cristallites de calcite de 100-500  $\mu\text{m}$  de longueur (Edgar et al., 2015 ; Kozdon et al., 2013). Bien que la présence de cristallites comparables n'ait pas été documentée au site 1209, la texture givrée (*frosty*) des foraminifères indique un certain degré de précipitation secondaire (Colosimo et al., 2006), qui pourrait avoir augmenté considérablement les valeurs de  $\delta^{44}\text{Ca}$  (Griffith et al., 2015). Comme la teneur en Sr de la calcite abiogène est inférieure d'environ un ordre de grandeur à celle de la calcite biogène, une surcroissance secondaire (même légèrement plus importante) devrait se traduire par un rapport Sr/Ca nettement plus faible (Kozdon et al., 2013 ; Stoll et al., 2007c). Le rapport Sr/Ca invariant de *Morozovella velascoensis* au site 1209 (Zachos et al., 2003) suggère que la croissance secondaire de calcite, si elle existe, a été relativement uniforme sur l'intervalle de temps étudié. Comme le suggère la composition isotopique du Bore de cette espèce au même site (Babila et al., 2018), il est raisonnable que les changements relatifs de la composition de *Morozovella velascoensis*  $\delta^{44}\text{Ca}$  ont été préservés.

### 3.2. Changements séculaires dans l'eau de mer $\delta^{44}\text{Ca}$

En supposant qu'il soit principalement primaire, notre enregistrement du  $\delta^{44}\text{Ca}$  devrait refléter les changements dans  $\delta^{44}\text{Ca}$  de l'eau de mer et le fractionnement isotopique des organismes calcifiant (Griffith et al., 2008a ; Fantle, 2010 ; Blättler et al., 2011, 2012 ; Fantle et Tipper, 2014). Une caractéristique notable résultant probablement de la première option est la diminution à long terme, de 0,2 ‰, des valeurs de  $\delta^{44}\text{Ca}$  enregistrées entre 0 et 100 kyr au site 1209. Ce changement est cohérent à la fois en termes d'ampleur et de durée avec une augmentation du lessivage continental induite par le réchauffement, en favorisant l'apport de calcium isotopiquement appauvri dans l'océan.

Les modèles indiquent que ce processus devrait avoir augmenté la teneur en Ca de l'océan et diminué les valeurs de  $\delta^{44}\text{Ca}$ , les valeurs les plus faibles de l'eau de mer étant prévues autour de 100 kyr après le début du PETM (Komar et Zeebe, 2011, 2016), en excellent accord avec les valeurs les plus faibles de  $\delta^{44}\text{Ca}$  enregistrées par nos données au 1209. Cette augmentation de l'altération au début du PETM est corroborée par un changement contemporain vers des valeurs de l'osmium plus radiogènes et cela dans plusieurs sites (Dickson et al., 2015). Les données du  $\delta^{44}\text{Ca}$  du PETM et les valeurs de l'osmium présentent de fortes similitudes avec celles de l'événement océanique anoxique de Toarcian (Brazier et al., 2015), pour lequel les isotopes de l'osmium et du calcium indiquent également une augmentation de l'altération continentale (Ravizza, 2001, Dickson, 2015). Plus quantitativement, cependant, l'ampleur de la diminution du PETM dans les valeurs de  $\delta^{44}\text{Ca}$  enregistrés entre 0 et 100 kyr au site 1209 est supérieure aux prédictions proposées par les modèles précédents (Komar et Zeebe, 2011). Les simulations impliquant une augmentation relativement faible de l'altération continentale due à l'apport de 4500 Pg de carbone, indiquent que ces changements de  $\delta^{44}\text{Ca}$  devraient être inférieurs à 0,05‰, c'est-à-dire inférieurs à l'incertitude de mesure standard (Komar et Zeebe, 2011). Néanmoins, les émissions de carbone ont été révisées à la hausse en utilisant les isotopes du bore (plus de 10 000 Pg ; Gutjahr et al., 2017 ; Penman et Zachos, 2018). La modélisation d'un apport de plus de 10 000 PgC sur 100 kyr pour les conditions à la limite Permo-Trias produit un décalage plus important, de 0,1‰, des valeurs de  $\delta^{44}\text{Ca}$ , qui reste inférieur à celui suggéré par nos données. Les valeurs de  $\delta^{44}\text{Ca}$  pour l'eau de mer auraient pu être encore plus faibles par un ralentissement de la pompe biologique du carbone (Komar et Zeebe, 2016), comme le suggèrent nos données du site 1209. Bien que des changements dans le fractionnement des isotopes de calcium aient pu également être impliqués (voir ci-dessous), nos nouvelles données invalident les simulations précédentes suggérant que la perturbation du PETM était insuffisante pour avoir un impact sur le budget des isotopes de calcium et soutiennent des estimations plus élevées de l'apport de carbone pendant le PETM.

### 3.3. Changements dans le fractionnement des isotopes de calcium

En raison de la longue durée de résidence du Ca ( $\sim 1$  Ma ; Berner et Berner, 1996) par rapport au temps de mélange dans l'océan global, des changements plus rapides ( $< 100$  kyr) et plus importants dans l'eau de mer mondiale  $\delta^{44}\text{Ca}$  sont très peu

probables. Cela est particulièrement vrai pour l'intervalle Paléocène-Eocène pendant lequel la teneur en Ca était presque deux fois plus élevée qu'aujourd'hui. L'excursion positive de 0,5 ‰ enregistrée entre 50 et 100 kyr au site 1209 peut donc être difficilement expliquée par un changement global de l'eau de mer en  $\delta^{44}\text{Ca}$ , à moins d'invoquer la combinaison de fluctuations irréalistes de l'apport ou de l'enfouissement de calcium et de sources non identifiées et fortement fractionnées. Ce pic positif enregistré entre + 50 et + 100 kyrs nécessite donc des changements dans le fractionnement des isotopes de calcium chez les foraminifères, comme le suggère l'absence d'un tel changement dans l'enregistrement de roche totale au voisin site ODP 1212 (Griffith et al., 2015). Les valeurs de  $\delta^{44}\text{Ca}$  mesurées sur roche totale devraient en effet refléter principalement celles des nanofossiles, qui, selon nos calculs, dominant largement le pourcentage de carbonate à Shatsky Rise. Les expériences modernes suggèrent que les coccolithophores et les foraminifères possèdent des voies d'incorporation du calcium très différentes et donc que leurs fractionnements en isotopes de calcium sont probablement contrôlés par des mécanismes différents. Nous notons cependant que de telles différences entre et au sein de ces deux groupes ne peuvent être prises en compte lorsqu'on traite uniquement des valeurs  $\delta^{44}\text{Ca}$  mesurés sur roche totale, qui est nécessairement un mélange complexe de différentes espèces nanofossiles et foraminifères ainsi que de particules de calcite secondaires telles que les lamelles (*calcite blades*) présentes au site 1209.

Plusieurs paramètres pourraient influencer le fractionnement des isotopes de calcium des coquilles de foraminifères planctoniques (Fantle et Tipper, 2014), notamment le taux de calcification, le taux de croissance, la température (Gussone et al., 2003 ; Sime et al., 2005), la salinité et la chimie des carbonates d'eau de mer (Kisakureh et al., 2011). Les valeurs mesurées de  $\delta^{44/40}\text{Ca}$  ne montrent aucune corrélation avec les estimations de taille publiées précédemment (Petruzzo et al., 2008) et les teneurs en Sr/Ca (Zachos et al., 2003) pour ce genre et, les indicateurs de paléotempérature tels que le  $\delta^{18}\text{O}$  et le Mg/Ca (Zachos et al., 2003 ; Tripathi et Elderfield, 2005). Les changements de la chimie des carbonates de l'eau de mer semblent donc être la cause la plus probable du pic positif enregistré entre + 50 et + 100 kyrs. L'intervalle enregistrant cette excursion positive de  $\delta^{44/40}\text{Ca}$  enregistre une sursaturation plus importante des carbonates du fond marin, comme le suggèrent la plus faible

fragmentation des foraminifères et des nanofossiles et la plus forte abondance de *calcite blades*. Cependant, selon les calculs théoriques de Nielsen et al. (2012), une telle phase de fractionnement réduit des isotopes de calcium devrait refléter un rapport  $[Ca]/[CO_3^{2-}]$  plus élevé de l'eau de mer. Étant donné que des changements importants et brusques du  $[Ca]$  nécessiteraient des variations importantes et irréalistes des flux d'entrée et d'enfouissement (voir ci-dessus), les valeurs les plus élevées de  $\delta^{44/40}Ca$  indiqueraient un taux minimal de  $[CO_3^{2-}]$  à +80 kyrs. Ceci est en contradiction avec la plupart des simulations de modèles qui indiquent que le  $[CO_3^{2-}]$  a diminué de manière significative en raison d'un apport massif de  $CO_2$  au début du PETM et a augmenté par la suite en raison d'un apport fluvial plus important (Komar et Zeebe, 2011). Ce décalage suggère que le fractionnement  $\delta^{44/40}Ca$  était en quelque sorte largement découplé des valeurs  $[CO_3^{2-}]$  pendant le PETM. Par ailleurs, le fractionnement  $\delta^{44/40}Ca$  aurait pu augmenter avec le  $[HCO_3^-]$  plutôt qu'avec le  $[CO_3^{2-}]$ . Dans les études de terrain et expérimentales, l'influence de ce paramètre majeur sur le fractionnement des isotopes de calcium foraminifères a rarement été testée, car il est classiquement inversement proportionnel au  $[CO_3^{2-}]$  dans les océans modernes. Cependant, à l'échelle des temps géologiques, les deux paramètres pourraient être d'une manière ou d'une autre découplés. Différents modèles simulent un  $[HCO_3^-]$  relativement invariant au début du PETM, suivi d'une augmentation constante et distincte jusqu'à des valeurs maximales d'environ 80 kyrs par la suite, résultant d'un apport fluvial plus important et d'un enfouissement de calcite plus faible (Komar et Zeebe, 2011 ; Luo et al., 2016). Il est important de noter que les niveaux d'ions bicarbonate diminuent lentement dans le modèle de Komar et Zeebe (2011) où l'exportation de carbonate est maintenue constante. Dans le modèle de Luo et al, 2016, on observe une diminution de 50% à long terme. En conséquence, la diminution vers des valeurs inférieures de  $\delta^{44/40}Ca$  entre + 80 kyr et 100 kyrs impliquerait une diminution superficielle rapide  $[HCO_3^-]$ , en accord avec l'augmentation rapide du flux d'exportation de calcite suggérée par nos données MAR<sub>ff</sub>.

#### 4. Perspectives

Dans ce travail de thèse je me suis concentré sur l'étude de deux événements marqués par des profondes perturbations du cycle d carbone, une hausse de températures de au moins 5-6°C en moyenne (Zachos et al., 2004 ; Suan et al., 2008a) et un changement dans la chimie des océans, au moins au PETM associé à une réduction du pH de 0.3 unités (Penman et al., 2014 ; Babila et al., 2018).

Pour valider le modèle de compensation biologique proposé et étendre ces conclusions, il est nécessaire d'appliquer la même approche sur d'autres événements comparables au PETM et au T-OAE. Un intervalle qui mériterait d'être investigué est l'Eocène Inferieur, entre 57 Ma et 54 Ma, car de nombreux événements d'acidification de plus faible amplitude que le PETM sont enregistrés dans les sédiments océaniques. Du Pacifique et de l'Atlantique. L'étude combinée des taux de fragmentation et d'accumulation des restes de phytoplancton calcaire (NAR), des taux d'accumulation en masse de la fraction fine ( $< 63 \mu\text{m}$  ;  $\text{MAR}_{\text{ff}}$ ) et des isotopes du calcium pourrait permettre de répondre à deux questions scientifiques fondamentales:

1) comment l'export de carbonate a-t-il varié lors d'épisodes moins intenses de réchauffement et d'acidification de l'océan ;

2) ces épisodes sont-ils systématiquement associés à des changements de saturation de la calcite des eaux superficielles et profondes, ou existe-t-il des effets de seuil ? Cette étude permettrait de reconstruire très finement l'export carbonaté et la saturation en calcite sur un intervalle de plusieurs millions d'années afin de mieux contraindre le couplage entre la biologie et la chimie des océans.

Les résultats présentés dans cette thèse montrent qu'il y a un lien étroit mais variable temporellement entre biologie et chimie des océans : il est nécessaire de valider ces hypothèses sur d'autres événements moins extrêmes et potentiellement moins affectés par des problèmes de dissolution et de préservation.

Finalement, ces résultats permettront de déterminer l'importance respective des modèles existant et de mieux comprendre le rôle de la compensation chimique et biologique pendant l'Anthropocène.





## Bibliographie

- Adelseck, C.G., Geehan, G.W., Roth, P.H., 1973. Experimental evidence for the selective dissolution and overgrowth of calcareous nannofossils during diagenesis. *Geological Society of America Bulletin* 84, 2755–2762.
- Agnini, C., Fornaciari, E., Raffi, I., Catanzariti, R., Pälike, H., Backman, J., Rio, D., 2014. Biozonation and biochronology of Paleogene calcareous nannofossils from low and middle latitudes. *Newsletters on Stratigraphy* 47, 131–181
- Agnini, C., Fornaciari, E., Rio, D., Tateo, F., Backman, J., Giusberti, L., 2007. Responses of calcareous nannofossil assemblages, mineralogy and geochemistry to the environmental perturbations across the Paleocene/Eocene boundary in the Venetian Pre-Alps. *Marine Micropaleontology* 63(1–2), 19–38.
- Agnini, C., Muttoni, G., Kent, D. V., Rio, D., 2006. Eocene biostratigraphy and magnetic stratigraphy from Possagno, Italy: The calcareous nannofossil response to climate variability. *Earth and Planetary Science Letters* 241, 815–830.
- Agnini, C., Spofforth, D. J., Dickens et al., 2016. Stable isotope and calcareous nannofossil assemblage record of the late Paleocene and early Eocene (Cicogna section). *Climate of the Past* (4), 883–909.
- Alegret, L., Ortiz, S., and Molina, E., 2009. Extinction and recovery of benthic foraminifera across the Paleocene–Eocene Thermal Maximum at the Alamedilla section (Southern Spain). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 279(3–4), 186–200.
- Ali, J. R., Kent, D. V., Hailwood, E. A., 2000. Magnetostratigraphic reinvestigation of the Palaeocene/Eocene boundary interval in Hole 690B, Maud Rise, Antarctica. *Geophysical Journal International* 141(3), 639–646.
- Al-Suwaidi, A.H., Hesselbo, S.P., Damborenea, S.E., Manceñido, M.O., Jenkyns, H.C., Riccardi, A.C., Angelozzi, G.N., Baudin, F., 2016. The Toarcian Oceanic Anoxic Event (Early Jurassic) in the Neuquén Basin, Argentina: A Reassessment of Age and Carbon Isotope Stratigraphy. *The Journal of Geology*.
- Angori, E., Monechi, S., 1995. High-resolution calcareous nannofossils biostratigraphy across the Paleocene/Eocene boundary at Caravaca (southern Spain). *Israel Journal of Earth Sciences* 44, 197– 206.

- Arias, C.F., 1991. Las asociaciones de ostrácodos del Domeriense superior y Toarciense inferior de la Cordillera Ibérica. *Coloquios de Paleontología* 43, 79–99.
- Arias, C.F., 1995. Los ostrácodos del Toarciense inferior en la Cordillera Ibérica. Ph. D. Thesis. Fac. C. Geológicas. Univ. Complutense Madrid, Spain.
- Aubry, M.-P., 1995. Towards an upper Paleocene–lower Eocene high resolution stratigraphy based on calcareous nannofossils stratigraphy. *Israel Journal of Earth Sciences* 44, 239–253.
- Aubry, M.-P., 1998. Early Paleogene calcareous nannoplankton evolution: a tale of climatic amelioration. In: Aubry, M.-P., Lucas, S., Berggren, W.A. (Eds.), *Late Paleocene and Early Eocene Climatic and Biotic Evolution*. Columbia University Press, New York, 158–203
- Aubry, M.-P., 1999. Late Paleocene–early Eocene sedimentary history in western Cuba: implications for the LPTM and for regional tectonic history. *Micropaleontology* 45, 5–18.
- Aubry, M.-P., 2001. Provincialism in the photic zone during the LPTM. In: Ash, A., Wing, Abstract Volume, Powell, S. (Eds.), *Climate and Biota of the Early Paleogene*. International Meeting, p. 6
- Aubry, M.P., Cramer, B.S., Miller, K.G., Wright, J.D., Kent, D. V., Olsson, R.K., 2000. Late Paleocene event chronology: Unconformities, not diachrony. *Bulletin de la Société. Geologique de France* 171 (3), 367–378
- Aze, T., Pearson, P.N., Dickson, A.J., Badger, M.P.S.S., Bown, P.R., Pancost, R.D., Gibbs, S.J., Huber, B.T., Leng, M.J., Coe, A.L., Cohen, A.S., Foster, G.L., 2014. Extreme warming of tropical waters during the Paleocene-Eocene thermal maximum. *Geology* 42 (9),739–742
- Babila, T.L., Penman, D.E., Hönisch, B., Kelly, D.C., Bralower, T.J., Rosenthal, Y., Zachos, J.C., 2018. Capturing the global signature of surface ocean acidification during the Palaeocene–Eocene Thermal Maximum. *Philosophical Transactions A* 376.
- Bailey, T. R., Y. Rosenthal, McArthur, J.M., van de Schootbrugge, B., Thirlwall M. F., 2003. Paleoceanographic changes of the late Pliensbachian- early Toarcian interval: A possible link to the genesis of an oceanic anoxic event, *Earth and Planetary Sciences Letters* 212, 307–320.

- Bains, S., Norris, R. D., Corfield, R. M., Faul, K. L., 2000. Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback. *Nature* 407, 171–174.
- Bains, S., R. Corfield, M., Norris, R. D., 1999. Mechanisms of climate warming at the end of the Paleocene, *Science* 285, 724–727.
- Bassoullet, J.P., Elmi, S., Poisson, A., Cecca, F., Bellion, Y., Guiraud, R., Baudin, F., 1993. Mid Toarcian. In: Dercourt, J., Ricou, L.E., Vrielynck, B. (Eds.), *Atlas Tethys Paleoenvironmental Maps*, BEICIP-FRANLAB, Rueil-Malmaison. 63–80.
- Beaufort, L., Barbarin, N., Gally, Y., 2014. Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths. *Nature Protocols* 9 (3), 633–642
- Beaufort, L., Heussner, S., 2001. Seasonal dynamics of calcareous nannoplankton on a West European continental margin: The Bay of Biscay. *Marine Micropaleontology* 43(1–2), 27–55.
- Beaufort, L., Probert, I., Buchet, N., 2007. Effects of acidification and primary production on coccolith weight: Implications for carbonate transfer from the surface to the deep ocean. *Geochemistry, Geophysics, Geosystems*, 8(8).
- Beaufort, L., Probert, I., de Garidel-Thoron et al., 2011. Sensitivity of coccolithophores to carbonate chemistry and ocean acidification. *Nature*, 476(7358), 80–83.
- Bécaud, M., 2002. Le Toarcien de la bordure sud et sud-est du Massif armoricain (Deux-Sèvres et Vendée). *Le naturaliste vendéen* 2, 3-33.
- Bécaud, M., 2005. Ammonites peu connues du Toarcien inférieur du sud-ouest de la Vendée. *Le naturaliste vendéen* 5, 45-48.
- Bécaud, M., 2006. Les Hildoceratidae (Ammonitina) du Toarcien de la bordure sud et sud est du Massif armoricain (France). *Docum. Lab. Géologie Lyon* 162, 1-148.
- Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall, New Jersey. 376 pp.
- Billard, C., Inouye, I., 2004. What is new in coccolithophore biology?. In *Coccolithophores* (pp. 1-29). Springer, Berlin, Heidelberg.

- Blair, S., Watkins, D. K., 2009. High-resolution calcareous nannofossil biostratigraphy for the Coniacian/Santonian Stage boundary, Western Interior Basin. *Cretaceous Research* 30, 367–384.
- Blättler, C. L., Henderson, G. M., Jenkyns, H. C., 2012. Explaining the Phanerozoic Ca isotope history of seawater. *Geology* 40(9), 843–846.
- Blättler, C. L., Jenkyns, H. C., Reynard, L. M., & Henderson, G. M., 2011. Significant increases in global weathering during Oceanic Anoxic Events 1a and 2 indicated by calcium isotopes. *Earth and Planetary Science Letters* 309(1-2), 77–88.
- Blomeier, D.P.G., Reijmer, J.J.G., 1999. Drowning of a lower Jurassic carbonate platform: Jbel Bou Dahar, High Atlas, Morocco. *Facies* 41, 81–110. <sup>[L]</sup><sub>SEP</sub>
- Bodin, S., Krencker, F. N., Kothe, T., Hoffmann, R., Mattioli, E., Heimhofer, U., Kabiri, L., 2016. Perturbation of the carbon cycle during the late Pliensbachian - early Toarcian: New insight from high-resolution carbon isotope records in Morocco. *Journal of African Earth Sciences*, 116, 89–104. <https://doi.org/10.1016/j.jafrearsci.2015.12.018>
- Bodin, S., Mattioli, E., Fröhlich, S., Marshall, J. D., Boutib, L., Lahsini, S., and Redfern, J., 2010, Documentation of Early Toarcian (Jurassic) carbon isotope negative shifts and nutrient changes along the Northern Gondwana margin (High Atlas, Morocco): palaeoenvironmental implications: *Palaeogeog.*, *Palaeoclim.*, *Palaeoecol.* 297, 377–390.
- Boomer, I., Lord, A.R., Page, K.N., Bown, P.R., Lowry, F.M.D., Riding, J.B., 2009. The biostratigraphy of the Upper Pliensbachian–Toarcian (Lower Jurassic) sequence at Ilminster, Somerset. *Journal of Micropalaeontology* 28, 67–85.
- Boudreau, B. P., Middelburg, J. J., & Luo, Y. (2018). The role of calcification in carbonate compensation. *Nature Geoscience*, 11(12), 894–900.
- Bour, I., Mattioli, E., Pittet, B., 2007. Nannofacies analysis as a tool to reconstruct paleoenvironmental changes during the Early Toarcian anoxic event. *Palaeogeography, Palaeoclimatology, Palaeoecology* 249(1–2), 58–79.
- Bowen, G. J., 2013. Up in smoke: A role for organic carbon feedbacks in Paleogene hyperthermals. *Global and Planetary Change* 109, 18–29

- Bown, P. R., 2005a. Palaeogene calcareous nannofossils from the Kilwa and Lindi areas of coastal Tanzania (Tanzania Drilling Project 2003-4). *J. Nanoplankton Res.* 27 (1), 2005, 21–95.
- Bown, P. R., 2010. Calcareous nannofossils from the Paleocene/Eocene Thermal Maximum interval of southern Tanzania (TDP Site 14). *Journal of Nanoplankton Research.* 31(1), 11–38.
- Bown, P. R., Dunkley Jones, T., 2006. New Paleogene calcareous nannofossil taxa from coastal Tanzania: Tanzania Drilling Project Sites 11 to 14. *Journal of Nanoplankton Research* 28 (1), 17–34.
- Bown, P. R., Pearson, P., 2009. Calcareous plankton evolution and the Paleocene/Eocene thermal maximum event: New evidence from Tanzania. *Marine Micropaleontology* 71, 60–70.
- Bown, P.R., 1987. Taxonomy, evolution and biostratigraphy of Late Triassic-early Jurassic calcareous nannofossils. *Special Papers in Paleontology* 38, 1–118.
- Bown, P.R., 2005b. Cenozoic calcareous nannofossils biostratigraphy, ODP Leg 198 Site 1208 (Shatsky Rise, northwest Pacific Ocean). In Bralower, T.J., Premoli Silva, I., and Malone, M.J. *Proceedings of the Ocean Drilling Program. Scientific Results* 198, 1– 44.
- Bown, P.R., 2016. Paleocene calcareous nannofossils from Tanzania (TDP sites 19, 27 and 38). *J. Nanoplankton Res.* The calcareous nannofossil genus *Ericsonia* in the upper Paleocene 149 36 (1), 1–32.
- Bown, P.R., Cooper, M.K.E., 1998. Jurassic. In: Bown, P.R. (Ed), *Calcareous Nannofossil Biostratigraphy*, British Micropalaeontological Society Series. Chapman and Hall/Kluwer Academic Publishers, London, 86–131.
- Bralower, T., Clay Kelly, D., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L., Smith, G. S., 2014. Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum. *Earth and Planetary Sciences Letters* 401, 70–82.
- Bralower, T.J., 2002. Evidence of surface water oligotrophy during the Paleocene–Eocene Thermal Maximum: nannofossil assemblage data from Ocean Drilling Program Site 690 Maud Rise, Weddell Sea. *Paleoceanography* 17, 1–13.
- Bralower, T.J., Kelly, D.C., Gibbs, S., Farley, K., Eccles, L., Lindemann, T.L.,

- Smith, G.J., 2014. Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters* 401, 70–82.
- Bralower, T.J., Mutterlose, J., 1995. Calcareous nannofossil biostratigraphy of ODP Site 865, Allison Guyot, Central Pacific Ocean: a tropical Paleogene reference section. In: Winterer, E.L., Sager, W.W., Firth, J.V. (Eds.), *Proceedings of the Ocean Drilling Program. Scientific Results* 143, 31– 72.
  - Bralower, T.J., Premoli Silva, I., Malone, M.J., et al., 2002. *Proc. ODP, Initial Reports.*, 198: College Station, TX (Ocean Drilling Program).
  - Bralower, T.J., Self-Trail, J.M., 2016. Nannoplankton malformation during the Paleocene-Eocene Thermal Maximum and its paleoecological and paleoceanographic significance. *Paleoceanography* 31, 1423–1439.
  - Bramlette, M. N., Sullivan, F. R., 1961. Coccolithophorids and related nannoplankton of the early Tertiary in California. *Micropaleontology*, 129-188.
  - Brand, W. A., Coplen, T.B., Vogl, J., Rosner, M., Prohaska, T., 2014. Assessment of international reference materials for isotope-ratio analysis. *Pure and Applied Chemistry* 86, 425–467.
  - Brazier, J. M., Suan, G., Tacail, T., Simon, L., Martin, J. E., Mattioli, E., Balter, V., 2015. Calcium isotope evidence for dramatic increase of continental weathering during the Toarcian oceanic anoxic event (Early Jurassic). *Earth and Planetary Science Letters* 411, 164–176.
  - Bridgestock, L., Hsieh, Y. T., Porcelli, D., & Henderson, G. M. (2019). Increased export production during recovery from the Paleocene–Eocene thermal maximum constrained by sedimentary Ba isotopes. *Earth and Planetary Science Letters*, 510, 53-63.
  - Bucefalo Palliani, R. B., Cirilli S., Mattioli E., 1998. Influences of the relative sea level fluctuations on the primary productivity, an example from the early Toarcian Umbria-Marche basin (central Italy), *Palaeogeography, Palaeoclimatology and Paleoecology* 142, 33–50.
  - Bukry, D., 1973. Low-latitude coccolith biostratigraphic zonation. In: Edgar, N.T., Saunders, J.B., et al. *Initial Reports of the Deep Sea Drilling Project* 15. U.S. Government Printing Office, Washington, 685–703.



- Bukry, D., 1975. Coccolith and silicoflagellate stratigraphy, northwestern Pacific Ocean, Deep Sea Drilling Project Leg 32. In: Larson, R.L., Moberly, R., et al. Initial Reports of the Deep Sea Drilling Project 32. U.S. Government Printing Office, Washington, 677– 701.
- Bybell, L.M., Self-Trail, J.M., 1995. Evolutionary, biostratigraphic, and taxonomic study of calcareous nannofossils from a continuous Paleocene-Eocene boundary section in New Jersey. US Geological Survey Professional Paper 1554.
- Bybell, L.M., Self-Trail, J.M., 1997. Late Paleocene and early Eocene calcareous nannofossils from three boreholes in an onshore-offshore transect from New Jersey to the Atlantic Continental Rise. Proceedings of the Ocean Drilling Program. Scientific results 150, 91–110.
- Caldeira, K., Wickett, M. E., 2005 Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *Journal of Geophysical Research: Oceans* 110(C9).
- Cande, S.C., Kent, D.V., 1995. Revised calibration of the geomagnetic polarity timescale for the Late Cretaceous and Cenozoic. *Journal of Geophysical Research* 100, 6093– 6095.
- Casellato, C.E., Erba, E., 2015. Calcareous nannofossil biostratigraphy and paleoceanography of the toarcian oceanic anoxic event at colle di sogno (Southern Alps, Northern Italy). *Rivista Italiana di Paleontologia e Stratigrafia* 121, 297–327.
- Cecca, F., Macchioni, F., 2004. The two Early Toarcian (Early Jurassic ) extinction events in ammonoids. *Lethaia* 3, 35-56.
- Channon, M. B., Gordon, G. W., Morgan, J. L., Skulan, J. L., Smith, S. M., Anbar, A. D., 2015. Using natural, stable calcium isotopes of human blood to detect and monitor changes in bone mineral balance. *Bone*, 77, 69-74.
- Clémence, M. E., Gardin, S., Bartolini, A. 2015. New insights in the pattern and timing of the Early Jurassic calcareous nannofossil crisis. *Palaeogeography, Palaeoclimatology, Palaeoecology* 427, 100–108.
- Cohen, A. S., Coe, A. L., Harding, S. M., Schwark, L., 2004. Osmium isotope evidence for the regulation of atmospheric CO<sub>2</sub> by continental weathering. *Geology*, 32(2), 157–160.

- Cohen, A. S., Coe, A. L., Kemp, D. B., 2007. The Late Palaeocene–Early Eocene and Toarcian (Early Jurassic) carbon isotope excursions: a comparison of their time scales, associated environmental changes, causes and consequences. *Journal of the Geological Society* 164(6), 1093–1108.
- Colosimo, A.B., Bralower, T.J., Zachos, J.C., 2006. Evidence for lysocline shoaling at the Paleocene/Eocene thermal maximum on Shatsky rise, northwest Pacific. *Proceeding of the Ocean Drilling Program. Scientific Results* 198, 1–36.
- Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Herrero, C., Osete, M. L., Palencia, A., 2010. A complementary section for the proposed Toarcian (Lower Jurassic) global stratotype: the Almonacid de la Cuba sections (Spain). *Stratigraphy and Geological Correlation* 18, 133–152.
- Comas-Rengifo, M. J., Gómez, J. J., Goy, A., Herrero, C., Perilli, N., Rodrigo, A., 1999. El Jurásico Inferior en la sección de Almonacid de la Cuba (Sector central de la Cordillera Ibérica), Zaragoza, España. *Cuad. Geol. Ibér.* 25, 27-57.
- Cope, J.C.W., 1984. The Mesozoic history of Wales. *Proc. Geol. Assoc.* 95, 373–385.
- Copestake, P., Johnson, B., 2014. Lower Jurassic Foraminifera from the Llanbedr (Mochras Farm) Borehole, North Wales, UK. *Monograph of the Palaeontographical Society* 167.
- Courtinat, B., Pittet, B., Mattioli, E., Rio, M., 2007. Marine microplankton and calcareous nannofossil palaeoecology of the Toarcian stratotype. *Geobios* 40, 785–800.
- Crouch, E. M., Dickens, G. R., Brinkhuis, H., Aubry, M. P., Hollis, C. J., Rogers, K. M., and Visscher, H., 2003. The Apectodinium acme and terrestrial discharge during the Paleocene–Eocene thermal maximum: new palynological, geochemical and calcareous nannoplankton observations at Tawanui, New Zealand. *Palaeogeography, Palaeoclimatology, Palaeoecology* 194(4), 387–403.
- Crouch, E., Heilmann-Clausen, C., Brinkhuis H., Morgans H. E.G., Rogers K.M., Egger, H., Schmitz, B., 2001. Global dinoflagellate event associated with the late Paleocene thermal maximum. *Geology* 29(4), 315–318.
- Cubillos, J. C., Henderiks, J., Beaufort, L., Howard, W. R., Hallegraeff, G. M., 2012. Reconstructing calcification in ancient coccolithophores: Individual coccolith weight and morphology of *Coccolithus pelagicus* (sensu lato). *Marine*

Micropaleontology 92, 29–39.

- Dallanave, E., Agnini, C., Muttoni, G., Rio, D., 2009. Magneto-biostratigraphy of the Cicogna section (Italy): Implications for the late Paleocene-early Eocene time scale. *Earth and Planetary Science Letters* 285, 39–51.
- De La Rocha, C.L., De Paolo, D.J., 2000. Isotopic Evidence for Variations in the Marine Calcium Cycle Over the Cenozoic. *Science* 289, 1176–1178
- Dera, G., Neige, P., Dommergues, J. L., Brayard, A., 2011. Ammonite paleobiogeography during the Pliensbachian–Toarcian crisis (Early Jurassic) reflecting paleoclimate, eustasy, and extinctions. *Global and Planetary Change*, 78(3-4), 92–105.
- Dera, G., Pellenard, P., Neige, P., Deconinck, J.-F., Pucéat, E., Dommergues, J.-L., 2009. Distribution of clay minerals in Early Jurassic Peritethyan seas: Palaeoclimatic significance inferred from multiproxy comparisons. *Palaeogeography, Palaeoclimatology, Palaeoecology* 271, 39–51.
- Dera, G., Pucéat, E., Pellenard, P., Neige, P., Delsate, D., Joachimski, M. M., et al., 2009. Water mass exchange and variations in seawater temperature in the NW Tethys during the Early Jurassic: evidence from neodymium and oxygen isotopes of fish teeth and belemnites. *Earth and Planetary Science Letters* 286(1–2), 198–207.
- Dickens, G.R., Castillo, M.M., Walker, J.G.C., 1997. A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate, *Geology* 25, 259–262.
- Dickens, G.R., O'Neil, J.R., Rea, D.K., Owen, R.M., 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* 10, 965–971
- Dickson, *Journal of Chemical Thermodynamics* 22,113–127, 1990.
- Dickson, A. J., Cohen, A. S., Coe, A. L., Davies, M., Shcherbinina, E. A., & Gavrillov, Y. O., 2015. Evidence for weathering and volcanism during the PETM from Arctic Ocean and Peri-Tethys osmium isotope records. *Palaeogeography, Palaeoclimatology, Palaeoecology* 438, 300–307.
- Dickson, A. G., Millero, F. J., 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Research Part A. Oceanographic Research Papers* 34(10), 1733–1743.

- Dromart, G., Allemand, P., Garcia, J.-P., Robin, C., 1996. Variation cyclique de la production carbonatée au Jurassique le long d'un transect Bourgogne-Ardèche, Est-France. *Bull. Soc. Géol. Fr.* 167, 423–433.
- Duncan, R. A., Hooper, P. R., Rehacek, J., Marsh, J. S., Ducan, A. R., 1997. The timing and duration of the Karoo igneous sevend, southern Gondwana. *Journal of Geophysical Research* 102, 127–138.
- Edgar, K. M., Anagnostou, E., Pearson, P. N., & Foster, G. L., 2015. Assessing the impact of diagenesis on  $\delta^{11}\text{B}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite. *Geochimica et Cosmochimica Acta* 166, 189–209.
- Elmi, S., 2007. Pliensbachian/Toarcian boundary: the proposed GSSP of Peniche (Portugal). *Ciências da Terra (UNL)* 16, 7-16.
- Elmi, S., Rulleau, L., Gabilly, J., Mouterde, R., 1997. Ammonites: Toarcien. In: Cariou, E., Hantzpergue, P. (Eds.), *Biostratigraphie du Jurassique ouest-européen et méditerranéen: Zonations parallèles et distribution des invertébrés et microfossiles*. Groupe Français d'Étude du Jurassique. *Bulletin du Centre de Recherches, Elf Exploration Production*, 17, pp. 25-36 + 120-125.
- Erba, E., 2004. Calcareous nannofossils and Mesozoic oceanic anoxic events. *Marine Micropaleontology* 52 (1–4), 85–106.
- Erbacher, J., Mosher, D.C., Malone, Berti, D., Bice, K. L., Bostock, H., Jürgen Brumsack, H., Danelian, T., Glatz, C., Heidersdorf, F., Henderiks, J., Janecek, T., Junium, C., Le Callonec, L., MacLeod, K., Meyers, P. A., Mutterlose, J., Nishi, H., Norris, R., Ogg, J. G., O'Regan, M., Rea, B., Sexton, P., Sturt, H., Suganuma, Y., Thurow, J.W., Wilson, P. A., Wise, S. W., 2004. Demerara rise: equatorial cretaceous and Paleogene paleoceanographic transect, Western Atlantic (Leg 207, Sites 1257–1261). *Proceedings of the Ocean Drilling Program 207*, 1–89.
- Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C., 2008 . Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65(3), 414-432.
- Fantasia, A., Föllmi, K. B., Adatte, T., Spangenberg, J. E., Montero-Serrano, J. C., 2018. The Early Toarcian oceanic anoxic event: Paleoenvironmental and paleoclimatic change across the Alpine Tethys (Switzerland). *Global and Planetary Change*, 162, 53–68.
- Fantle, M. S., Tipper, E. T., 2014. Calcium isotopes in the global biogeochemical

- Ca cycle: implications for development of a Ca isotope proxy. *Earth-Science Reviews*, 129, 148–177.
- Farkaš, J., Böhm, F., Wallmann, K., Blenkinsop, J., Eisenhauer, A., van Geldern, R., Munnecke, A., Voigt, S., Veizer, J., 2007a. Calcium isotope record of Phanerozoic oceans: implications for chemical evolution of seawater and its causative mechanisms. *Geochim. Cosmochim. Acta* 71, 5117–5134.
  - Farley, K. A., Love, S. G., Patterson, D. B., 1997. Atmospheric entry heating and helium retentivity of interplanetary dust particles. *Geochimica et Cosmochimica Acta*, 61(11), 2309–2316.
  - Farley, K.A., Eltgroth, S.F., 2003. An alternative age model for the Paleocene–Eocene thermal maximum using extraterrestrial <sup>3</sup>He. *Earth and Planetary Science Letters* 208, 135–148.
  - Farley, K.A., Love, S.G., Patterson, D.B., 1997. Atmospheric entry heating and helium retentivity of interplanetary dust particles. *Geochimica et Cosmochimica Acta* 61, 2309–2316.
  - Farrimond, P., G. Eglinton, and S. C. Brassel, 1989. Toarcian anoxic event in Europe: An organic geochemical study, *Marine and Petroleum Geology* 6, 136–147.
  - Fatela, F., Taborda, R., 2002. Confidence limits of species proportions in microfossil assemblages. *Marine Micropaleontology* 45(2), 169–174.
  - Ferreira, J., Mattioli, E., Pittet, B., Cachão, Spangenberg, J.E., 2015. Palaeoecological insights on Toarcian and lower Aalenian calcareous nanofossils from the Lusitanian Basin (Portugal). *Paleogeography, Paleoclimatology, Paleoecology* 436, 245-262.
  - Ferreira, J., Mattioli, E., Suchéras-Marx, B., Giraud, F., Duarte, L., V., Pitter, B., Hassler, A., Spangenberg, J., 2019. Western Tethys Early and Middle Jurassic calcareous nanofossils biostratigraphy. *Earth-Science Reviews* 197, 1–19.
  - Ferreira, J., Mattioli, E., van de Schootbrugge, B., 2017. Palaeoenvironmental vs. evolutionary control on size variation of coccoliths across the Lower-Middle Jurassic, *Paleogeography, Paleoclimatology, Paleoecology*. 465, 177–192.
  - Fraguas, Á., Comas-Rengifo, M. J., Gómez, J. J., Goy, A., 2012. The calcareous nanofossil crisis in Northern Spain (Asturias province) linked to the Early

- Toarcian warming-driven mass extinction. *Marine Micropaleontology* 94–95, 58–71.
- Fraguas, Á., Comas-Rengifo, M. J., Gómez, J. J., Goy, A., 2012. The calcareous nannofossil crisis in Northern Spain (Asturias province) linked to the Early Toarcian warming-driven mass extinction. *Marine Micropaleontology* 94–95, 58–71.
  - Fraguas, Á., Erba, E., 2010. Biometric analyses as a tool for the differentiation of two coccolith species of the genus *Crepidolithus* (Pliensbachian, Lower Jurassic) in the Basque-Cantabrian Basin (Northern Spain). *Marine Micropaleontology* 77, 125–136.
  - Frieling, J., Gebhardt, H., Huber et al., 2017. Extreme warmth and heat-stressed plankton in the tropics during the Paleocene-Eocene Thermal Maximum. *Science advances* 3(3), e1600891.
  - Frieling, J., Peterse, F., Lunt, D. J., Bohaty, S. M., Sinninghe Damsté, J. S., Reichart, G. J., Sluijs, A., 2019. Widespread warming before and elevated barium burial during the Paleocene-Eocene Thermal Maximum: Evidence for methane hydrate release ?. *Paleoceanography and paleoclimatology*, 34(4), 546–566.
  - Fu, X., Wang, J., Feng, X., Wang, D., Chen, W., Song, C., Zeng, S., 2016. Early Jurassic carbon-isotope excursion in the Qiangtang Basin (Tibet), the eastern Tethys: Implications for the Toarcian Oceanic anoxic event. *Chemical Geology* 442, 62–72.
  - Fu, X., Wang, J., Feng, X., Wang, D., Chen, W., Song, C., Zeng, S., 2016. Early Jurassic carbon-isotope excursion in the Qiangtang Basin (Tibet), the eastern Tethys: Implications for the Toarcian Oceanic anoxic event. *Chemical Geology* 442, 62–72.
  - Gabilly J., 1976. Le Toarcien à Thouars et dans le Centre-Ouest de la France. *Biostratigraphie. Évolution de la faune (Harpoceratinae - Hildoceratinae)*; collection: Comité français de Stratigraphie - Les stratotypes français, vol. 3. Paris, éd. du CNRS, 217 p.
  - Gabilly, J., 1964. Stratigraphie et limite de l'étage Toarcien Thouars et dans les régions voisines. *Coll. Jurassique, Luxembourg (1962). C. R. Mém. Inst. Grand Duc., Sect. Sci. Nat. Phys. Math., pp. 193-201.*

- Gabilly, J., 1973. Le Toarcien du Poitou. Biostratigraphie de la région du stratotype. Évolution des Hildocerataceae (Ammonitina) (Doctoral dissertation), Poitiers, 546 p.
- Garzarella, A., Raffi, I., 2018. Taxonomy and evolutionary relationships within the calcareous nannofossil genus *Ericsonia* in the upper Paleocene. *Rivista Italiana di Paleontologia e Stratigrafia* 124 (1), 129–150.
- Gautier, F., Mousterde, R., 1964. Stratigraphie - lacunes et irrégularités des dépôts à la limite du Jurassique inférieur et du jurassique moyen de la bordure nord des chaînes ibériques (Espagne). *Comptes rendus hebdomadaires des séances de l'académie des sciences* 258, 3064.
- Geisen, M., Bollmann, J., Herrle, J.O., Mutterlose, J., Young, J.R., 1999. Calibration of the random settling technique for calculation of absolute abundances of calcareous nanoplankton. *Micropaleontology* 45, 437– 442.
- Gibbs, S. J., Stoll, H. M., Bown, P. R., Bralower, T. J., 2010. Ocean acidification and surface water carbonate production across the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters* 295(3–4), 583–592.
- Gibbs, S., Shackleton, N., Young, J., 2004. Orbitally forced climate signals in mid-Pliocene nannofossil assemblages. *Marine Micropaleontology* 51(1–2), 39–56.
- Gibbs, S.J., Bralower, T.J., Bown, P.R., Zachos, J.C., Bybell, L.M., 2006a. Shelf and open-ocean calcareous phytoplankton assemblages across the Paleocene–Eocene thermal maximum: implication for global productivity gradients. *Geology* 34 (4), 233–236.
- Gibbs, S.J., Bralower, T.J., Bown, P.R., Zachos, J.C., Bybell, L.M., 2006b. Shelf and open-ocean calcareous phytoplankton assemblages across the Paleocene–Eocene thermal maximum: implication for global productivity gradients. *Geology* 34 (4), 233–236.
- Gibbs, S. J., Bown, P. R., Ridgwell et al., 2016. Ocean warming, not acidification, controlled coccolithophore response during past greenhouse climate change. *Geology* 44(1), 59-62.
- Gómez, J. J., Comas – Rengifo, M. J., Goy, A., 2016. Palaeoclimatic oscillations in the Pliensbachian (Early Jurassic) of the Asturian Basin (Northern Spain). *Clim. Past*, 12, 1199–1214.



- Gómez, J. J., Goy, A., Canales, M. L., 2008. Seawater temperature and carbon isotope variations in belemnites linked to mass extinction during the Toarcian (Early Jurassic) in Central and Northern Spain. Comparison with other European sections. *Palaeogeography Palaeoclimatology Palaeoecology* 258, 28–58.
- Goy, A., Martínez, G., 1990. Biozonacion del Toarciense en el área de La Almunia de Doña Godina-Ricla (Sector Central de la Cordillera Ibérica). *Cuadernos Geología Ibérica* 14, 9–44.
- Gradstein, F. M., Ogg, J. G., Schmitz, M. B., Ogg, G. M., 2012. The geologic time scale.
- Griffith, E. M., Fantle, M. S., Eisenhauer, A., Paytan, A., Bullen, T. D., 2015. Effects of ocean acidification on the marine calcium isotope record at the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 419, 81–92.
- Griffith, E. M., Paytan, A., Caldeira, K., Bullen, T. D., Thomas, E., 2008a. A dynamic marine calcium cycle during the past 28 million years. *Science* 322(5908), 1671–1674.
- Griffith, E. M., Schauble, E. A., Bullen, T. D., & Paytan, A., 2008b. Characterization of calcium isotopes in natural and synthetic barite. *Geochimica et Cosmochimica Acta*, 72(23) 5641–5658.
- Griffith, E. M., Schmitt, A. D., Andrews, M. G., Fantle, M. S., 2020. Elucidating modern geochemical cycles at local, regional, and global scales using calcium isotopes. *Chemical Geology*, 534, 119445.
- Griffith, E.M., Paytan, A., Kozdon, R., Eisenhauer, A., Ravelo, A.C., 2008. Influences on the fractionation of calcium isotopes in planktonic foraminifera. *Earth and Planetary Sciences Letters* 268, 124–136.
- Gussone, N., Eisenhauer, A., Heuser, A., et al., 2003. Model for kinetic effects on calcium isotope fractionation ( $\delta^{44}\text{Ca}$ ) in inorganic aragonite and cultured planktonic foraminifera. *Geochimica et Cosmochimica Acta*, 67(7), 1375–1382.
- Gutjahr, M., Ridgwell, A., Sexton, P. F., et al., 2017. Very large release of mostly volcanic carbon during the Palaeocene–Eocene Thermal Maximum. *Nature* 548(7669), 573–577.

- Hammer, Ø., Harper, D. A., Ryan, P. D., 2001. PAST: Paleontological statistics software package for education and data analysis. *Palaeontologia electronica*, 4(1), 9.
- Handley, L., Pearson, P., McMillan, I.K., Pancost, R.D., 2008. Large terrestrial and marine carbon and hydrogen isotope excursions in a new Paleocene/Eocene boundary section from Tanzania. *Earth and Planetary Science Letters* 275, 17–25.
- Haq, B. U., Loqmann G. P., 1976. Early Cenozoic calcareous nannoplankton biogeography of the Atlantic ocean. *Marine Micropaleontology* 1, 119–194.
- Hay, W.W., 1972. Probabilistic stratigraphy. *Eclogae Geologicae Helveticae* 65, 255–266.
- Hay, W.W., 1972. Probabilistic stratigraphy. *Eclogae Geologicae Helveticae* 65, 255–266.
- Henderiks, J., Rickaby, R. E., 2007. A coccolithophore concept for constraining the Cenozoic carbon cycle. *Biogeosciences* 4, 323–329.
- Henehan, M. J., Ridgwell, A., Thomas, E., Zhang et al., 2019. Rapid ocean acidification and protracted Earth system recovery followed the end-Cretaceous Chicxulub impact. *Proceedings of the National Academy of Sciences* 116(45), 22500–22504.
- Hermoso, M., Minoletti, F., Rickaby, R.E.M., Hesselbo, S.P., Baudin, F., Jenkyns, H.C., 2012. Dynamics of a stepped carbon-isotope excursion: Ultra high-resolution study of Early Toarcian environmental change. *Earth and Planetary Science Letters* 319–320, 45–54.
- Herrero, C., 1992. Los foraminífero del Toarciense inferior de la Cordillera Ibérica. Tesis Doctoral, Facultad de Ciencias Geológicas, Universidad Complutense de Madrid, 523 pp.
- Hesselbo, S. P., Bjerrum, C. J., Hinnov, L. A., MacNiocaill, C., Miller, K. G., Riding, J. B., van de Schootbrugge, B., 2013. Mochras borehole revisited: a new global standard for Early Jurassic earth history.
- Hesselbo, S. P., Gröcke, D. R., Jenkyns, H. C., Bjerrum, C. J., Farrimond, P., Bell, H. S. M., Green, O. R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* 406(6794), 392–395.

- Hesselbo, S. P., Jenkyns, H. C., Duarte, L. V., Oliveira, L. C. 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters* 253(3–4), 455–470.
- Hesselbo, S.P., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. *Proceedings of the Geologists' Association* 119, 19–34.
- Hesselbo, S.P., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. *Proceedings of the Geologists' Association*, 119, 19–34.
- Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., Oliveira, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth Planet. Sci. Lett.* 253, 455–470.
- Heuser, A., Eisenhauer, A., Scholz-Ahrens, K. E., & Schrezenmeir, J, 2016. Biological fractionation of stable Ca isotopes in Göttingen minipigs as a physiological model for Ca homeostasis in humans. *Isotopes in environmental and health studies* 52(6) 633-648.
- Holland, K., Branson, O., Haynes, L. L. et al., 2020. Constraining multiple controls on planktic foraminifera Mg/Ca. *Geochimica et Cosmochimica Acta* 273 116–136.
- Hori, R. S., 1997. The Toarcian radiolarian event in bedded cherts from southwestern Japan, *Marine Micropaleontology* 30, 159 – 169.
- Houghton, J. T., 2001. *Climate Change 2001: The Scientific Basis*.
- Huang, C., Hesselbo, S. P., 2014. Pacing of the Toarcian Oceanic Anoxic Event (Early Jurassic) from astronomical correlation of marine sections. *Gondwana Research*, 25, 1348–1356.
- Iglesias-Rodriguez, M. D., Halloran, P. R., Rickaby et al., 2008. Phytoplankton calcification in a high-CO<sub>2</sub> world. *Science* 320(5874), 336-340.
- Ivimey-Cook, H.C., 1971. Stratigraphical palaeontology of the Lower Jurassic of the Llanbedr (Mochras Farm) Borehole. In: Woodland, A.W. (Ed.), *The Llanbedr (Mochras Farm) Borehole*. Institute of Geological Sciences, 87–92.
- Izumi, K., Kemp, D. B., Itamiya, S., & Inui, M. (2018). Sedimentary evidence for enhanced hydrological cycling in response to rapid carbon release during the

- early Toarcian oceanic anoxic event. *Earth and Planetary Science Letters* 481, 162–170.
- Jenkyns, H. C. (2010). Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems* 11(3).
  - Jenkyns, H. C., Jones, C. E., GrÖcke, D. R., Hesselbo, S. P., Parkinson, D. N., 2002. Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society* 159(4), 351–378.
  - Jenkyns, H.C., 1988. The Early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. *Am. J. Sci.* 288, 101–151.
  - Jenkyns, H.C., Clayton, C.J., 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology*, 44: 687–706.
  - Jiang, S., Wise Jr, S. W., 2007. Taxonomic note: A new *Coccolithus* species that thrived during the Paleocene/Eocene Thermal Maximum. *Journal of Nannoplankton Research* 29, 88–91.
  - Jiang, S., Wise, S.W., 2006. Surface-water chemistry and fertility variations in the tropical Atlantic across the Paleocene/Eocene Thermal Maximum as evidenced by calcareous nannoplankton from ODP Leg 207, Hole 1259B. *Revue de Micropaléontologie* 49, 227–244.
  - Jones, T. D., Lunt, D. J., Schmidt, D. N., Ridgwell, A., Sluijs, A., Valdes, P. J., & Maslin, M., 2013. Climate model and proxy data constraints on ocean warming across the Paleocene–Eocene Thermal Maximum. *Earth-Science Reviews* 125 123–145.
  - Kafousia, N., Karakitsios, V., Mattioli, E., Kenjo, S., Jenkyns, H. C., 2014. The toarcian oceanic anoxic event in the ionian zone, Greece. *Palaeogeography, Palaeoclimatology, Palaeoecology* 393, 135–145.
  - Kahn, A., Aubry, M.P., 2004. Provincialism associated with the Paleocene/Eocene thermal maximum: Temporal constraint. *Marine Micropaleontology* 52, 117–131.
  - Kaiho, K., Takeda, K., Petrizzo, M.R., Zachos, J.C., 2006. Anomalous shifts in tropical Pacific planktonic and benthic foraminiferal test size during the Paleocene–Eocene thermal maximum. *Palaeogeography, Palaeoclimatology,*

Palaeoecology 237, 456–464.

- Karoui-Yaakoub, N., M'barek-Jemaï, M. B., Cherni, R., 2011. Le passage Paléocène/Eocène au nord de la Tunisie (Jebel Kharouba): foraminifères planctoniques, minéralogie et environnement de dépôt. *Revue de Paléobiologie* 30(1), 105–121.
- Katz, M. E., Wright, J. D., Miller, K. G., Cramer, B. S., Fennel, K., Falkowski, P. G., 2005. Biological overprint of the geological carbon cycle. *Marine Geology* 217(3-4), 323–338.
- Kelly, C. D., Bralower, T. J., Zachos, J. C., Silva, I. P., Thomas, E., 1996. Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum. *Geology* 24(5), 423–426.
- Kelly, D. C., 2002. Response of Antarctic (ODP Site 690) planktonic foraminifera to the Paleocene–Eocene thermal maximum: faunal evidence for ocean/climate change. *Paleoceanography* 17(4), 23–1.
- Kelly, D. C., Zachos, J. C., Bralower, T. J., Schellenberg, S. A., 2005. Enhanced terrestrial weathering/runoff and surface ocean carbonate production during the recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography* 20(4).
- Kelly, D.C., Bralower, T., J., Zachos, J.C., 1998. Evolutionary consequences of the latest Paleocene thermal maximum for tropical planktonic foraminifera. *Palaeogeography, Palaeoclimatology, Palaeoecology* 141, 139–161.
- Kelly, D.C., Nielsen, T.M.J., McCarren, H.K., Zachos, J.C., Röhl, U., 2010. Spatiotemporal patterns of carbonate sedimentation in the South Atlantic: Implications for carbon cycling during the Paleocene–Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 293, 30–40.
- Kelly, D.C., Zachos, J.C., Bralower, T.J., Schellenberg, S.A., 2005. Enhanced terrestrial weathering/runoff and surface ocean carbonate production during the recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography* 20.
- Kemp, D. B., Coe, A. L., Cohen, A. S., Weedon, G. P., 2011. Astronomical forcing and chronology of the early Toarcian (Early Jurassic) oceanic anoxic event in Yorkshire, UK. *Paleoceanography* 26(4).

- Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature* 437, 396–399.
- Kennedy, J., Gale, A.S., Bown, P.R., Caron, M., Davey, R., Gröcke, D., Wray, D.S. 2000. Integrated stratigraphy of the Aptian-Albian boundary interval in the Marnes Bleues, at the Col de Pré-Guittard, Arnayon (Drôme), and at Tartonne (Alpes-de-Haute-Provence), France, a candidate Global Boundary Stratotype Section and Boundary Point for the base of the Albian stage. *Cretaceous Research* 21, 591–720.
- Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* 353, 225–229.
- Kısakürek, B., Eisenhauer, A., Böhm, F., Hathorne, E. C., Erez, J., 2011. Controls on calcium isotope fractionation in cultured planktic foraminifera, *Globigerinoides ruber* and *Globigerinella siphonifera*. *Geochimica et Cosmochimica Acta* 75(2), 427–443.
- Koch, P. L., J. C. Zachos, and P. D. Gingerich (1992), Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary, *Nature* 358, 319– 322.
- Komar, N., Zeebe, R. E., 2011. Oceanic calcium changes from enhanced weathering during the Paleocene-Eocene thermal maximum: No effect on calcium-based proxies. *Paleoceanography*, 26(3).
- Komar, N., Zeebe, R. E., 2016. Calcium and calcium isotope changes during carbon cycle perturbations at the end-Permian. *Paleoceanography* 31(1), 115–130.
- Korte, C. and Hesselbo, S. P, 2011. Shallow-marine carbon- and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic, *Paleoceanography* 26, PA4219.
- Kozdon, R., Kelly, D. C., Kitajima, K., Strickland, A., Fournelle, J. H., & Valley, J. W., 2013. In situ  $\delta^{18}\text{O}$  and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene-Eocene thermal maximum. *Paleoceanography*, 28(3), 517–528.
- Krebs, C.J., 1998. *Ecological methodology* (2nd edition). Addison Wesley Longman (Eds., Pearson Education), pp. 620.

- Kroon, D., Norris, R.D., Klaus, A., 1998. Proceeding of the Ocean Drilling Program. Initial Reports 171B.
- Lemarchand, D., Wasserburg, G. J., Papanastassiou, D. A., 2004. Rate-controlled calcium isotope fractionation in synthetic calcite. *Geochimica et cosmochimica acta*, 68(22), 4665–4678.
- Léonide, P., Floquet, M., Durllet, C., Baudin, F., Pittet, B., Lécuyer, C., 2012. Drowning of a carbonate platform as a precursor stage of the Early Toarcian global anoxic event (Southern Provence sub-Basin, South-east France). *Sedimentology* 59, 156–184.
- Little, C.T.S., Benton, M.J., 1995. Early Jurassic mass extinction: a global long term event. *Geology* 23, 495–498.
- Littler, K., Hesselbo, S. P., Jenkyns, H. C., 2010. A carbon-isotope perturbation at the Pliensbachian–Toarcian boundary: evidence from the Lias Group, NE England. *Geological Magazine*, 147(2), 181-192.
- Lu G., Keller, G., Adattte T., Ortiz, N., Molina, E., 1996. Long-term ( $10^5$ ) or short-term ( $10^3$ )  $\delta^{13}\text{C}$  excursion nearthe Palaeocene-Eocene transition: evidence from the Tethys. *Terra Nova* 8, 347-355.
- Luo, Y., Boudreau, B. P., Dickens, G. R., Sluijs, A., & Middelburg, J. J. (2016). An alternative model for  $\text{CaCO}_3$  over-shooting during the PETM: biological carbonate compensation. *Earth and Planetary Science Letters*, 453, 223–233.
- Ma, Z., Gray, E., Thomas, E., Murphy, B., Zachos, J., & Paytan, A. (2014). Carbon sequestration during the Palaeocene–Eocene Thermal Maximum by an efficient biological pump. *Nature Geoscience* 7(5), 382–388.
- Mailliot, S., Mattioli, E., Guex, J., Pittet, B., 2006. The Early Toarcian anoxia, a synchronous event in the Western Tethys? An approach by quantitative biochronology (Unitary Associations), applied on calcareous nannofossils. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 240(3–4), 562–586.
- Mallarino, G., Goldstein, R.H., Di Stefano, P., 2002. New approach for quantifying water depth applied to the enigma of drowning of carbonate platforms. *Geology* 30, 783–786.
- Marcantonio, F., Thomas, D.J., Woodard, S., McGee, D., Winckler, G., 2009. Extraterrestrial  $^3\text{He}$  in Paleocene sediments from Shatsky Rise: Constraints on sedimentation rate variability. *Earth and Planetary Science Letters* 287, 24–30.



- Martin, J.E., Tacail, T., Adnet, S., Girard, C., Balter, V., 2015. Calcium isotopes reveal the trophic position of extant and fossil elasmobranchs. *Chemical Geology* 415, 118–125.
- Martindale, R.C., Aberhan, M., 2017. Response of macrobenthic communities to the Toarcian Oceanic Anoxic Event in northeastern Panthalassa (Ya Ha Tinda, Alberta, Canada). *Palaeogeography, Palaeoclimatology, Palaeoecology* 478, 103–120.
- Martinez, M., Krencker, F.-N., Mattioli, E., Bodin, S., 2017. Orbital chronology of the Pliensbachian – Toarcian transition from the Central High Atlas Basin (Morocco). *Newsletters on Stratigraphy* 50(1), 47–69.
- Martini, E., 1971. Standard Tertiary and Quaternary calcareous nannoplankton zonation. In: Farinacci, A., *Proceedings of the 2<sup>nd</sup> International Conference on Planktonic Microfossils* 2, 739–785
- Mattioli, E. 1996. New calcareous nanofossil species from the Early Jurassic of Tethys. *Rivista Italiana di Paleontologia e Stratigrafia* 102(3).
- Mattioli, E., Erba E., 1999. Synthesis of calcareous nanofossil events in tethyan lower and middle Jurassic successions. *Rivista Italiana di Paleontologia e Stratigrafia* 105, 343–376.
- Mattioli, E., Pittet, B., 2002. Contribution of calcareous nannoplankton to carbonate deposition: a new approach applied to the Lower Jurassic of central Italy. *Marine micropaleontology*, 45(2), 175–190.
- Mattioli, E., Pittet, B., Palliani, R., Rohl, H.-J., Schmid-Rohl, A., Morettini, E., 2004b. Phytoplankton evidence for the timing and correlation of palaeoceanographical changes during the early Toarcian oceanic anoxic event (Early Jurassic). *Journal of the Geological Society* 161(4), 685–693.
- Mattioli, E., Pittet, B., Petitpierre, L., Mailliot, S., 2009. Dramatic decrease of pelagic carbonate production by nannoplankton across the Early Toarcian anoxic event (T-OAE). *Global and Planetary Change* 65(3–4), 134–145.
- Mattioli, E., Pittet, B., Suan, G., Mailliot, S. 2008. Calcareous nannoplankton changes across the early Toarcian oceanic anoxic event in the western Tethys. *Paleoceanography* 23(3).
- Mattioli, E., Pittet, B., Young, J.R., Bown, P.R., 2004a. Biometric analysis of Pliensbachian-Toarcian (Lower Jurassic) coccoliths of the family Biscutaceae:

- intra- and interspecific variability versus palaeoenvironmental influence. *Marine Micropalaeontology* 52, 5–27.
- Mattioli, E., Pittet, B., Young, J.R., Bown, P.R., 2004b. Biometric analysis of Pliensbachian-Toarcian (Lower Jurassic) coccoliths of the family Biscutaceae: intra- and interspecific variability versus palaeoenvironmental influence. *Marine Micropalaeontology* 52, 5-27.
  - Mattioli, E., Plancq, J., Boussaha, M., Duarte, L.V., Pittet, B., 2013. Calcareous nannofossil biostratigraphy: new data from the Lower Jurassic of the Lusitanian Basin. *Comunicacoes Geologicas T. 100, 100 (Especial I)*, 69–76.
  - McArthur, J. M., D. T. Donovan, M. F. Thirwall, B. W. Fouke, and D. Matthey, 2000. Strontium isotope profile of early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belmnite palaeotemperature, *Earth and Planetary Sciences Letters* 179, 269–285.
  - McArthur, J.M., Donovan, D.T., Thirwall, M.F., Fouke, B.W., Matthey, D., 2000. Strontium isotope profile of early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belmnite palaeotemperature. *Earth Planet. Sci. Lett.* 179, 269–285.
  - McCarren, H., Thomas, E., Hasegawa, T., Röhl, U., Zachos, J.C., 2008. Depth dependency of the Paleocene-Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker records (Ocean Drilling Program Leg 208, Walvis Ridge). *Geochemistry, Geophysics, Geosystems* 9, 1–10.
  - McElwain, J.C., Wade-Murphy, J., Hesselbo, S.P., 2005. Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature* 435, 479–482.
  - Medd, A. W., 1982. Nannofossil zonation of the English Middle and Upper Jurassic. *Marine Micropalaeontology*. 7, 73–95.
  - Mehrbach, C., Culberson, C. H., Hawley, J. E., & Pytkowicz, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure 1. *Limnology and oceanography* 18(6), 897–907.
  - Menini, A., Mattioli, E., Spangenberg, J. E., Pittet, B., and Suan, G., 2019. New calcareous nannofossil and carbon isotope data for the Pliensbachian/Toarcian boundary (Early Jurassic) in the western Tethys and their paleoenvironmental implications. *Newsletters on Stratigraphy*, 173–196.

- Mensik, H., 1965. Stratigraphie und Palaeogeographie des marinen Jura in der nord-westlichen Iberischen Keten (Spanien). *Bein. Geol. Ib.*, 55-102.
- Milliman, J. D., 1993. Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state. *Global geochemical cycles* 7(4), 927–957.
- Monechi, S., Angori, E., von Salis, K., 2000. Calcareous nannofossil turnover around the Paleocene/Eocene transition at Alamedilla (southern Spain). *Bulletin de la Soceté Géologique de France* 171 (4), 477–489.
- Morard, A., Guex, J., Bartolini, A., Morettini, E., De Wever, P., 2003. A new scenario for the Domerian - Toarcian transition. *Bull. Soc. géol. Fr.* 4, 351–356.
- Morgan, J. L., Skulan, J. L., Gordon, G. W., Romaniello, S. J., Smith, S. M., & Anbar, A. D., 2012. Rapidly assessing changes in bone mineral balance using natural stable calcium isotopes. *Proceedings of the National Academy of Sciences* 109(25), 9989-9994.47.
- Murphy, B.H., Farley, K.A., Zachos, J.C., 2010. An extraterrestrial <sup>3</sup>He-based timescale for the Paleocene–Eocene thermal maximum (PETM) from Walvis Ridge, IODP Site 1266. *Geochimica et Cosmochimica Acta* 74, 5098–5108.
- Mutterlose, J., Linnert, C., Norris, R., 2007. Calcareous nannofossils from the Paleocene-Eocene Thermal Maximum of the equatorial Atlantic (ODP Site 1260B): Evidence for tropical warming. *Marine Micropaleontology* 65, 13–31.
- Nicolo, M. J., Dickens, G. R., Hollis, C. J., 2010. South Pacific intermediate water oxygen depletion at the onset of the Paleocene-Eocene thermal maximum as depicted in New Zealand margin sections. *Paleoceanography* 25(4).
- Nicolo, M.J., Dickens, G.R., 2006. Data Report: Terrigenous Grain-Size Distributions at Sites 1263 and 1267: Testing the Applicability of Leg 208 Sediments for Eolian Analysis, in: Kroon, D., Zachos, J.C., Richter, C. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results Volume 208*, College Station, TX 1–13.
- Nielsen, L. C., Druhan, J. L., Yang, W., Brown, S. T., DePaolo, D. J., 2012. Calcium isotopes as tracers of biogeochemical processes. In *Handbook of environmental isotope geochemistry*, 105–124. Springer, Berlin, Heidelberg.
- Noël, D., 1965. Sur les Coccolithes du Jurassique Européen et d'Afrique du Nord. *Éditions du Centre National de la Recherche Scientifique*, 110-111, Paris.

- Noël, D., 1972. Nannofossiles calcaires de sediments jurassiques finement laminés. *Bull. Mus. Hist. Natur.*, 3e sér., 75, pp. 95-116, 9 text-figs., 15 pls.
- Norris, R. D., 1996. Symbiosis as an evolutionary innovation in the radiation of Paleocene planktic foraminifera. *Paleobiology*, 461–480.
- O’Dea, S.A., Gibbs, S.J., Bown, P.R., Young, J.R., Poulton, A.J., Newsam, C., Wilson, P.A., 2014. Coccolithophore calcification response to past ocean acidification and climate change. *Nature Communcations* 5 (5363).
- Okada, H., and Honjo, S., 1973. The distribution of oceanic coccolithophorids in the Pacific, *Deep Sea Res. Oceanogr. Abstr.*, 20, 355– 374.
- Okada, H., Bukry, K., 1980. Supplementary modification and introduction of code numbers to the low-latitude coccolith biostratigraphic zonation. *Marine Micropaleontology* 5, 321–325.
- Paasche, E., 1968. Biology and physiology of coccolithophorids, *Annual Review of Microbiology* 22, 71–86.
- Pagani, M., Zachos, J. C., Freeman, K. H., Tipple, B., Bohaty, S., 2005. Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Science* 309(5734), 600–603.
- Page, K.N., 2003. The Lower Jurassic of Europe: its subdivision and correlation. *Geol. Surv. Den. Greenl. Bull.*1, 23–59.
- Pak, D. K., Miller, K. G., 1992. Paleocene to Eocene benthic foraminiferal isotopes and assemblages: Implications for deep water circulation, *Paleoceanography* 7, 405– 422.
- Pak, D., Miller, K., Browning, J., 1997. Global significance of an isotopic record from the New Jersey coastal plain: linkage between the shelf and deep sea in the late Paleocene to early Eocene. In *Proceedings of the Ocean Drilling Program. Scientific results* 156, 305–315.
- Pálffy, J., Smith, P.L., 2000. Synchrony between Early Jurassic extinction, oceanic anoxic event, and the Karoo-Ferrar flood basalt volcanism. *Geology* 28, 747-750.
- Palliani, R. B., Mattioli, E., Riding, J. B., 2002. The response of marine phytoplankton and sedimentary organic matter to the early Toarcian (Lower Jurassic) oceanic anoxic event in northern England. *Marine micropaleontology* 46(3–4), 223–245.

- Pancost, R. D., Crawford, N., Magness, S., Turner, A., Jenkyns, H. C., Maxwell, J. R., 2004. Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events, *Journal of the Geological Society of London*, 161, 1–12.
- Penman, D. E., Zachos, J. C., 2018. New constraints on massive carbon release and recovery processes during the Paleocene-Eocene Thermal Maximum. *Environmental Research Letters* 13(10), 105008.
- Penman, D.E., Hönisch, B., Zeebe, R.E., Thomas, E., Zachos, J.C., 2014. Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* 29, 2014 PA002621.
- Penman, D.E., Turner, S.K., Sexton, P.F., Norris, R.D., Dickson, A.J., Boulila, S., Ridgwell, A., Zeebe, R.E., Zachos, J.C., Cameron, A., Westerhold, T., Röhl, U., 2016. An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene Thermal Maximum. *Nature Geoscience* 9, 575–580.
- Perch-Nielsen, K., 1985. Cenozoic calcareous nannofossils. In: Bolli, H.M., Saunders, J.B., Perch-Nielsen, K. *Plankton Stratigraphy*. Cambridge University Press, Cambridge, 427–554.
- Percival, L. M. E., Witt, M. L. I., Mather, T. A., Hermoso, M., et al., 2015. Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo–Ferrar Large Igneous Province. *Earth and Planetary Science Letters* 428, 267–280.
- Percival, L.M.E., Cohen, A.S., Davies, M.K., Dickson, A.J., Hesselbo, S.P., Jenkyns, H.C., Leng, M.J., Mather, T.A., Storm, M.S., Xu, W., 2016. Osmium isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcanism and climate change. *Geology* 44, 759–762.
- Peti, L., Thibault, N., Clémence, M.-E., Korte, C., Dommergues, J.-L., Bougeault, C., Pellenard, P., Jelby, M.E., Ullmann, C.V., 2017. Sinemurian–Pliensbachian calcareous nannofossil biostratigraphy and organic carbon isotope stratigraphy in the Paris Basin: Calibration to the ammonite biozonation of NW Europe. *Palaeogeography, Palaeoclimatology, Palaeoecology* 468, 142–161.
- Petrizzo, M. R., 2007. The onset of the Paleocene–Eocene Thermal Maximum (PETM) at Sites 1209 and 1210 (Shatsky Rise, Pacific Ocean) as recorded by planktonic foraminifera. *Marine Micropaleontology* 63(3–4), 187–200.

- Petrizzo, M. R., Leoni, G., Speijer, R. P., De Bernardi, B., & Felletti, F., 2008. Dissolution susceptibility of some Paleogene planktonic foraminifera from ODP site 1209 (Shatsky Rise, Pacific Ocean). *The Journal of Foraminiferal Research*, 38(4), 357–371.
- Philippe, M., Pujalon, S., Suan, G., Mousset, S., Thévenard, F., Mattioli, E., 2017. The palaeolatitudinal distribution of fossil wood genera as a proxy for European Jurassic terrestrial climate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 466, 373 –381.
- Pittet, B., Suan, G., Lenoir, F., Vitor, L., Mattioli, E., 2014. Carbon isotope evidence for sedimentary discontinuities in the lower Toarcian of the Lusitanian Basin (Portugal): Sea level change at the onset of the Oceanic Anoxic Event. *Sedimentary Geology*, 303, 1–14.
- Poulton, A. J., Sanders, R., Holligan, P. M., Stinchcombe, M. C., Adey, T. R., Brown, L., Chamberlain, K., 2006 Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean. *Global Biogeochemical Cycles* 20(4).
- Price, G. D., 1999. The evidence and implications of polar ice during the Mesozoic, *Earth-Sciences Reviews* 48, 183–210.
- Quillévéré, F., Norris, R. D., Moussa, I., Berggren, W. A., 2001. Role of photosymbiosis and biogeography in the diversification of early Paleogene acarininids (planktonic foraminifera). *Paleobiology* 27(2), 311–326.
- Raffi, I., Backman, J., Pälike, H., 2005. Changes in calcareous nannofossil assemblages across the Paleocene/Eocene transition from the paleo-equatorial Pacific Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology* 226, 93–126.
- Raffi, I., Backman, J., Zachos, J.C., Sluijs, A., 2009. The response of calcareous nannofossil assemblages to the Paleocene Eocene Thermal Maximum at the Walvis Ridge in the South Atlantic. *Marine Micropaleontology* 70, 201–212.
- Raffi, I., De Bernardi, B., 2008. Response of calcareous nannofossils to the Paleocene– Eocene thermal maximum: observations on composition, preservation and calcification in sediments from ODP Site 1263 (Walvis Ridge - SW Atlantic). *Marine Micropaleontology* 69, 119–138.
- Ravizza G., Norris R. N., Blusztajn J., Aubry M.P., 2001. An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of

intensified chemical weathering. *Paleoceanography and Paleoclimatology* 16(2), 155–163

- Reggiani, L., Mattioli, E., Pittet, B., Duarte, L.V., Veiga de Oliveira, L.C., Comas-Rengifo, M.J., 2010. Pliensbachian (Early Jurassic) calcareous nanofossils from the Peniche section (Lusitanian Basin, Portugal): A clue for palaeoenvironmental reconstructions. *Marine Micropaleontology* 75 (1–4), 1–16.
- Reolid, M., Emanuela, M., Nieto, L.M., Rodriguez-Tovar, F.J., 2014. The Early Toarcian Oceanic Anoxic Event in the External Subbetic (Southiberian Palaeomargin, Westernmost Tethys): Geochemistry, nanofossils and ichnology. *Palaeogeography, Palaeoclimatology, Palaeoecology* 411, 79–94.
- Révész, K., Landwehr, J.M., 2002.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic composition of  $\text{CaCO}_3$  measured by continuous flow isotope ratio mass spectrometry: statistical evaluation and verification by application to Devils Hole core DH-11 calcite. *Rapid Communications in Mass Spectrometry* 16, 2102–2114.
- Ridgwell, A., 2007. Interpreting transient carbonate compensation depth changes by marine sediment core modeling. *Paleoceanography*, 22(4).
- Ridgwell, A., Zeebe, R. E., 2005. The role of the global carbonate cycle in the regulation and evolution of the Earth system. *Earth and Planetary Science Letters*, 234(3–4), 299–315.
- Riley, T. R., Millar, I. L., Watkeys, M.K., Curtis, M. L., Leat, P.T., Klausen, M. B., Fanning, C. M., 2004. U–Pb zircon (SHRIMP) ages for the Lebombo rhyolites, South Africa: refining the duration of Karoo volcanism. *Journal of the Geological Society* 161(4), 547–550.
- Roberts, J., Kaczmarek, K., Skinner, L.C., Bijma J., Bradbury, H., Turchyn A.V., Misra, S., Lithium Isotopes in Benthic Foraminifera, *GCA* 2020.
- Rocha, R. Mattioli, E., Duarte, L.V., Pittet, B., Elmi, S., Mouterde, R., Cabral, M.C., Comas-Rengifo, M.J., Gómez, J.J., Goy, A., Hesselbo, S.P., Jenkyns, H.C., Littler, K., Mailliot, S., Veiga de Oliveira, L.C., Osete, M.L., Perilli, N., Pinto, S., Ruget, C. and Suan, G., 2016. Base of the Toarcian Stage of the Lower Jurassic defined by the Global Boundary Stratotype Section and Point (GSSP) at the Peniche section (Portugal). *Episodes* 39, 460-481.
- Röhl, H. J., A. Schmid-Röhl, O. Wolfgang, A. Frimmel, S. Lorenz, 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: An oxygen-depleted



- ecosystem controlled by sea level and palaeoclimate, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 165, 27 – 52.
- Rohl, H. J., Schmid-Rohl, A., O. Frimmel, Wolfgang, A., Lorenz, S., 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: An oxygen-depleted ecosystem controlled by sea level and palaeoclimate, *Palaeogeography, Palaeoclimatology, Palaeoecology* 165, 27–52.
  - Röhl, U., L. J. Abrams, 2000, High-resolution, downhole and non-destructive core measurements from Sites 999 and 1001 in the Caribbean Sea: Application to the late Paleocene thermal maximum, *Proceedings of the Ocean Drilling Program Sci. Results* 165, 191–203.
  - Röhl, U., L. J. Abrams, 2000, High-resolution, downhole and non-destructive core measurements from Sites 999 and 1001 in the Caribbean Sea: Application to the late Paleocene thermal maximum, *Proceedings of the Ocean Drilling Program Sci. Results* 165, 191–203.
  - Röhl, U., Westerhold, T., Bralower, T.J., Zachos, J.C., 2007. On the duration of the Paleocene–Eocene thermal maximum (PETM). *Geochemistry, Geophysics, Geosystems* 8
  - Romein, A.J.T., 1979. Lineages in early Paleogene calcareous nannoplankton (Doctoral dissertation, Utrecht University), 76–78.
  - Rosales, I., Quesada, S., Robles, S., 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque - Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 203, 253–275.
  - Rosales, I., Quesada, S., Robles, S., 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque - Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 203, 253–275.
  - Rost, B., Riebesell, U., 2004. Coccolithophores and the biological pump: responses to environmental changes. In *Coccolithophores* (pp. 99-125). Springer, Berlin, Heidelberg.
  - Roth, P.H., 1984. Preservation of calcareous nanofossils and fine-grained carbonate particles in mid-Cretaceous sediments from the southern Angola

- Basin. In: Hay, W.W. (Ed.), Initial Reports of Deep Sea Drilling Project 75. U.S. Government Printing Office, Washington, 651–655.
- Ruhl, M., Hesselbo, S. P., Hinnov, L., Jenkyns, H. C., Xu, W., et al., 2016. Astronomical constraints on the duration of the Early Jurassic Pliensbachian Stage and global climatic fluctuations. *Earth and Planetary Science Letters* 455, 149–165.
  - Sabatino, N., Neri, R., Bellanca, A., Jenkyns, H. C., Baudin, F., Parisi, G., Masetti, D., 2009. Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria–Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. *Sedimentology* 56, 1307–1328.
  - Sandoval, J., Bill, M., Aguado, R., O’Dogherty, L., Rivas, P., Morard, A., Guex, J., 2012. The Toarcian in the Subbetic basin (southern Spain): Bio-events (ammonite and calcareous nannofossils) and carbon-isotope stratigraphy. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 342–343(May 2012), 40–63.
  - Shannon, C.E., Weaver, W., 1949. *The Mathematical Theory of Communication*, Univ. of Ill. Press, Urbana, Ill.
  - Schmid-Rohl, A., Rohl, H. J., O. Frimmel, W., A., Schwark L., 2002, Palaeoenvironmental reconstruction of lower Toarcian epiconinental black shales (Posidonia Shale, SW Germany): Global versus regional control, *Geobios (Jodhpur India)* 35, 13–20.
  - Schneidermann, N., 1977. Selective dissolution of recent coccoliths in the Atlantic Ocean. In: Ramsay, A.T.S. (Ed.), *Oceanic Micropaleontology*. Vol. 2, pp. 1009–1053.
  - Schouten, S., M. Woltering, W. I. C. Rijpstra, A. Sluijs, H. Brinkhuis, and J. S. Sinninghe Damste, 2007. The Paleocene-Eocene carbon isotope excursion in higher plant organic matter: Differential fractionation of angiosperms and conifers in the Arctic, *Earth and Planetary Sciences Letters* 258, 581–592.
  - Self-Trail, J. M., Powars, D. S., Watkins, D. K., Wandless, G., 2012. Calcareous nannofossil assemblage changes across the Paleocene-Eocene thermal maximum: Evidence from a shelf setting, *Marine Micropaleontology* 92–93, 61–80.

- Self-Trail, J. M., Powars, D. S., Watkins, D. K., Wandless, G., 2012. Calcareous nannofossil assemblage changes across the Paleocene-Eocene thermal maximum: Evidence from a shelf setting, *Marine Micropaleontology* 92–93, 61–80,
- Sellwood, B.W., Jenkyns, H.C., 1975. Basins and swells and the evolution of an epeiric sea (Pliensbachian–Bajocian of Great Britain). *Journal of the Geological Society of London* 131, 373–388.
- Shamrock, J. L., Watkins, D. K., 2012. Eocene calcareous nannofossil biostratigraphy and community structure from Exmouth Plateau, Eastern Indian Ocean (ODP Site 762). *Stratigraphy* 9 (1), 1–11.
- Sime, N. G., Christina, L., Galy, A., 2005. Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera. *Earth and Planetary Science Letters* 232(1–2), 51–66.
- Simms, M.J., Chidlaw, N., Morton, N., Page, K.N., 2004. British Lower Jurassic Stratigraphy. Geological Conservation Review Series 30. Joint Nature Conservation Committee, Peterborough.
- Sluijs, A., Bowen, G., Brinkhuis, H., Lourens, L., Thomas, E., 2007. The Palaeocene-Eocene Thermal Maximum super greenhouse: biotic and geochemical signatures, age models and mechanisms of global change. *Deep Time Perspectives on Climate Change: Marrying the Signal From Computer Models and Biological Proxies*, 323–347.
- Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S. M., John, C. M., Zachos, J. C. et al., 2007. Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature*, 450(7173), 1218–1221.
- Sluijs, A., Röhl, U., Schouten, S., Brumsack, H. J., Sangiorgi, F., Damsté, J. S. S., Brinkhuis, H., 2008. Arctic late Paleocene–early Eocene paleoenvironments with special emphasis on the Paleocene-Eocene thermal maximum (Lomonosov Ridge, Integrated Ocean Drilling Program Expedition 302). *Paleoceanography* 23(1).
- Sluijs, A., Schouten, S., Pagani, M. et al., 2006. Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature* 441, 610–613.

- Sluijs, A., Van Roij, L., Harrington et al., 2014. Warming, euxinia and sea level rise during the Paleocene–Eocene Thermal Maximum on the Gulf Coastal Plain: implications for ocean oxygenation and nutrient cycling. *Climate of the Past* 10, 1421–1439, 2014.
- Spangenberg, J.E., Herlec, U., 2006. Hydrocarbon biomarkers in the Topla-Mežica zinc-lead deposits, northern Karavanke/Drau Range, Slovenia: Paleoenvironment at the site of ore formation. *Economic Geology* 101(5), 997–1021.
- Stap, L., Sluijs, A., Thomas, E., Lourens, L., 2009. Patterns and magnitude of deep sea carbonate dissolution during Eocene Thermal Maximum 2 and H2, Walvis Ridge, southeastern Atlantic Ocean. *Paleoceanography* 24.
- Stoll, H. M., Bains, S., 2003. Coccolith Sr/Ca records of productivity during the Paleocene-Eocene thermal maximum from the Weddell Sea. *Paleoceanography* 18(2), 1–11.
- Stoll, H. M., Shimizu N., Archer D., Ziveri P., 2007. Coccolithophore productivity response to greenhouse event of the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* 258, 192–206.
- Stoll, H. M., Shimizu N., Arevalos A., Matell N., Banasiak A, Zeren S., 2007. Insights on coccolith chemistry from a new ion probe method for analysis of individually picked coccoliths. *Geochemistry, Geophysics, Geosystems* 8 (6), 1–8.
- Storm, M. S., Hesselbo, S. P., Jenkyns, H. C., Ruhl, M., Ullmann, C. V., Xu, W. et al., 2020. Orbital pacing and secular evolution of the Early Jurassic carbon cycle. *Proceedings of the National Academy of Sciences* 117(8), 3974–3982.
- Storme, J.Y., Devleeschouwer, X., Schnyder, J., Cambier, G., Baceta, J.I., Pujalte, V., Di Matteo, A., Iacumin, P., Yans, J., 2012. The Palaeocene/Eocene boundary section at Zumaia (Basque-Cantabric Basin) revisited: New insights from high-resolution magnetic susceptibility and carbon isotope chemostratigraphy on organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ). *Terra Nova* 24, 310–317.
- Stradner, H., Papp, A., 1961. Tertiäre Discoasteriden aus Österreich und deren stratigraphische Bedeutung mit Hinweisen auf Mexico, Rumanien und Italien. *Jahrbuch der Geologischen Bundesanstalt (Wien)* 7, 1–159.

- Suan, G., Mattioli, E., Pittet, B., Lécuyer, C., Suchéras-Marx, B., Duarte et al., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* 290 (3–4), 448–458.
- Suan, G., Mattioli, E., Pittet, B., Lécuyer, C., Suchéras-Marx, B., Duarte, L.V., Martineau, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* 290(3–4), 448–458.
- Suan, G., Mattioli, E., Pittet, B., Mailliot, S., Lécuyer, C., 2008a. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal, *Paleoceanography* 23, PA1202.
- Suan, G., Pittet, B., Bour, I., Mattioli, E., Duarte, L. V., Mailliot, S., 2008b. Duration of the Early Toarcian carbon isotope excursion deduced from spectral analysis: consequence for its possible causes. *Earth and Planetary Science Letters* 267(3–4), 666–679.
- Suchéras-Marx, B., Mattioli, E., Allemand, P., Giraud, F., Pittet, B., Plancq, J., & Escarguel, G. (2019). The colonization of the oceans by calcifying pelagic algae.
- Svensen, H., Planke, S., Chevallier, L., Malthe-Sorensen, A., Corfu, F., Jamtveit, B., 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global warming. *Earth and Planetary Sciences Letters* 256, 554–566.
- Tacail T, Albalat E, Télouk P, Balter V., 2014. A simplified protocol for measurement of Ca isotopes in biological samples. *J. Anal. At.Spectrom.* 29,5 29–535.
- Tacail, T., Télouk, P., Balter, V., 2016. Precise analysis of calcium stable isotope variations in biological apatites using laser ablation MC-ICPMS. *Journal of Analytical Atomic Spectrometry* 31(1), 152–162.
- Tacail, T., Thivichon-Prince, B., Martin, J. E., Charles, C., Viriot, L., Balter, V., 2017. Assessing human weaning practices with calcium isotopes in tooth enamel. *Proceedings of the National Academy of Sciences* 114(24), 6268–6273.
- Takeda, K., Kaiho, K., 2007. Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 251, 175–197.

- Them, T.R., Gill, B. C., Caruthers, A.H., Gröcke, D.R., Tulskey, E.T., Martindale, R.C., ... Smith, P.L., 2017. High-resolution carbon isotope records of the Toarcian Oceanic Anoxic Event (Early Jurassic) from North America and implications for the global drivers of the Toarcian carbon cycle. *Earth and Planetary Science Letters* 459, 118–126.
- Thierry, J. and Barrier, E., 2000. Middle Toarcian. In: J. Dercourt and M.e.a. Gaetani (Eds.), *Atlas Peri-Tethys, Palaeogeographical Maps CCGM/CGMW*, Paris.
- Thierstein, H.R., Roth, P.H., 1991. Stable isotopic and carbonate cyclicity in Lower Cretaceous deep-sea sediments: Dominance of diagenetic effects. *Marine Geology* 97, 1– 34.
- Thierstein, H. R., Corte`s, M. Y., Haidar, A. T., 2004. Plankton community behaviour on ecological and evolutionary timescales: When models confront evidence, in *Coccolithophores From Molecular Processes to Global Impact*, edited by H. R. Thierstein and J. R. Young, 455– 480.
- Thomas, E., Shackleton, N.J., 1996. The latest Paleocene benthic foraminiferal extinction and stable isotope anomalies. In: Knox, R.O., Corfield, R.M., Dunay, R.E. *Correlation of the Early Paleogene in Northwest Europe*. Geological Society of London Special Publication 101, 40–441.
- Thomas, E., Shackleton, N.J., 1996. The latest Paleocene benthic foraminiferal extinction and stable isotope anomalies. In: Knox, R.O., Corfield, R.M., Dunay, R.E. *Correlation of the Early Paleogene in Northwest Europe*. Geological Society of London Special Publication 101, 40–441.
- Tjalsma, R. C., Lohmann, G. P., 1983. Paleocene-Eocene bathyal and abyssal benthic foraminifera from the Atlantic Ocean. *Micropaleontology Special Publication* 4, 1–90.
- Tremolada, F., Bralower, T.J., 2004. Nannofossil assemblage fluctuations during the Paleocene-Eocene Thermal Maximum at Sites 213 (Indian Ocean) and 401 (North Atlantic Ocean): Palaeoceanographic implications. *Marine Micropaleontology* 52, 107–116.
- Tremolada, F., Van de Schootbrugge, B., Erba, E., 2005. Early Jurassic schizosphaerellid crisis in Cantabria, Spain: implications for calcification rates

and phytoplankton evolution across the Toarcian oceanic anoxic event. *Paleoceanography* 20(2).

- Tripathi, A., Elderfield, H., 2005. Deep-sea temperature and circulation changes at the Paleocene-Eocene thermal maximum. *Science*, 308(5730), 1894–1898.
- Tyson, R. V., 1995. Abundance of organic matter in sediments: TOC, hydrodynamic equivalence, dilution and flux effects. In *Sedimentary organic matter*. 81–118. Springer, Dordrecht.
- Uppstrom, L. R. (1974). The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep Sea Research* 21, 161–162.
- van de Schootbrugge, B., McArthur, J.M., Bailey, J.M., Rosenthal, Y., Wright, J.M., Miller, K.G., 2005, Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records, *Paleoceanography*, 20.
- van der Meulen, B., Gingerich, P. D., Lourens, L. J., Meijer, N., van Broekhuizen, S., van Ginneken, S., Abels, H. A., 2020. Carbon isotope and mammal recovery from extreme greenhouse warming at the Paleocene–Eocene boundary in astronomically-calibrated fluvial strata, Bighorn Basin, Wyoming, USA. *Earth and Planetary Science Letters* 534, 116044.
- Vink, A., Brune, A., Höll, C., Zonneveld, K. A., Willems, H., 2002. On the response of calcareous dinoflagellates to oligotrophy and stratification of the upper water column in the equatorial Atlantic Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology* 178(1–2), 53–66.
- von Salis, K., Monechi, S., Bybell, L.M., Young, J., 2000. Remarks on the calcareous nannofossil markers *Rhomboaster* and *Tribrachiatus* around the Paleocene/Eocene boundary. *Journal of the Geological Society of Sweden* 122, 138–140.
- Wei, W., Zhong, S., 1996. Taxonomy and magnetobiochronology of *Tribrachiatus* and *Rhomboaster*, two genera of calcareous nannofossils. *Journal of Paleontology* 70, 7– 22.
- Westerhold, T., Röhl, U., Donner, B., McCarren, H. K., Zachos, J. C., 2011. A complete high-resolution Paleocene benthic stable isotope record for the central Pacific (ODP Site 1209). *Paleoceanography* 26(2).
- Westerhold, T., Röhl, U., Donner, B., Zachos, J. C., 2018. Global extent of early Eocene hyperthermal events: A new Pacific benthic foraminiferal isotope record



- from Shatsky Rise (ODP Site 1209). *Paleoceanography and Paleoclimatology* 33(6), 626–642.
- Westerhold, T., Röhl, U., Laskar, J., Raffi, I., Bowles, J., Lourens, L.J., Zachos, J.C., 2007. On the duration of magnetochrons C24r and C25n and the timing of early Eocene global warming events: Implications from the Ocean Drilling Program Leg 208 Walvis Ridge depth transect. *Paleoceanography* 22, 1–19.
  - Westerhold, T., Röhl, U., Raffi, I., Fornaciari, E., Monechi, S., Reale, V., Bowles, J., Evans, H.F., 2008. Astronomical calibration of the Paleocene time. *Palaeogeography, Palaeoclimatology, Palaeoecology* 257 377–403.
  - Westerhold, T., Röhl, U., Wilkens, R.H., Gingerich, P.D., Clyde, W.C., Wing, S.L., Bowen, G.J., Kraus, M.J., 2018b. Synchronizing early Eocene deep-sea and continental records – cyclostratigraphic age models for the Bighorn Basin Coring Project drill cores. *Clim. Past* 14, 303–319.
  - Wiggan, N.J., Riding, J.B., Fensome, R.A., Mattioli, E., 2018. The Bajocian (Middle Jurassic): A key interval in the early Mesozoic phytoplankton radiation. *Earth-Science Reviews* 180, 126-146.
  - Wignall, P.B., Hallam, A., Newton, R.J., Sha, J.G., Reeves, E., Mattioli, E., Crowley, S., 2006. An eastern Tethyan (Tibetan) record of the Early Jurassic (Toarcian) mass extinction event. *Geobiology* 4, 179–190.
  - Winter, A., Siesser W.G., 2006. *Coccolithophores*. Cambridge University Press.
  - Wise, S.W., Wind, F.H., 1977. Mesozoic and Cenozoic calcareous nannofossils recovered by DSDP Leg 36 drilling on the Falkland Plateau, south-west Atlantic sector of the Southern Ocean. *Initial Reports of the Deep Sea Drilling Project* 36, 269–491.
  - Woodard, S.C., Thomas, D.J., Hovan, S., Röhl, U., Westerhold, T., 2011. Evidence for orbital forcing of dust accumulation during the early Paleogene greenhouse. *Geochemistry, Geophysics, Geosystems* 12.
  - Woodland, A. W., 1971. The Llanbedr (Mochras Farm) Borehole, Report 71/18, Institute of Geological Sciences.
  - Xu, W., Ruhl, M., Jenkyns, H. C., Hesselbo, S. P., Riding, J. B., et al., 2017. Carbon sequestration in an expanded lake system during the Toarcian oceanic anoxic event. *Nature Geoscience*, 10(2), 129-134.

- Xu, W., Ruhl, M., Jenkyns, H. C., Leng, M. J., Huggett, J. M., et al., 2018. Evolution of the Toarcian (Early Jurassic) carbon-cycle and global climatic controls on local sedimentary processes (Cardigan Bay Basin, UK). *Earth and Planetary Science Letters* 484, 396–411.
- Young, J. R., 1992. The description and analysis of coccolith structure. *Nannoplankton Research*. Hamrsmid B, Young JR (eds) ZPZ, Knihovnica, 35–71.
- Young, J. R., 1994. Functions of coccoliths, in *Coccolithophores*, edited by A. Winter and W. Siesser, 63–82.
- Young, J. R., Ziveri, P., 2000. Calculation of coccolith volume and its use in calibration of carbonate flux estimates. *Deep sea research Part II: Topical studies in oceanography*, 47(9-11), 1679–1700.
- Zachos, J. C., Dickens, G. R., Zeebe, R. E., 2008. An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics. *Nature*, 451(7176), 279–283.
- Zachos, J.C., Kroon, D., Blum, P., Bowles, J., Gaillot, P., Hasegawa, T., Hathorne, E.C., Hodell, D. A., Kelly, D. C., Jung, J. H., Keller, S. M., Lee, Y. S., Leuschner, D. C., Lohmann, K. C., Lourens, L., Monechi, S., Nicolo, M., Raffi, I., Riesselman, C., Röhl, U., Schellenber, S. A., Schmidt, D., Sluijs A., Thomas, D., Thomas, E., Vallius, H. , 2004. Early Cenozoic extreme climates: the Walvis Ridge transect. *Proceedings of the Ocean Drilling Program. Initial Reports* 208.
- Zachos, J.C., Lohmann, K.C., Walker, J.C.G., Wise, S.W. Jr., 1993. Abrupt climate change and transient climates during the Paleogene: A marine perspective, *J. Geol.* 101, 191 – 213.
- Zachos, J.C., Pagani, M., Sloan, L.C., Billups, K., Thomas, E., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* 292, 686–693.
- Zachos, J.C., Rohl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H., Kroon, D., 2005. Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science* 308, 1611–1615.
- Zeebe, R. E., 2012. History of seawater carbonate chemistry, atmospheric CO<sub>2</sub>, and ocean acidification. *Annual Review of Earth and Planetary Sciences*,

40(141), 2012.

- Zeebe, R. E., Zachos, J. C., Dickens, G. R., 2009. Carbon dioxide forcing alone insufficient to explain Palaeocene–Eocene Thermal Maximum warming. *Nature Geoscience*, 2(8), 576–580.
- Zeebe, R.E., Lourens, L.J., 2019. Solar System chaos and the Paleocene–Eocene boundary age constrained by geology and astronomy. *Science* 365, 926–929.



## **Annexe 1 : Liste taxinomique**

Dans cette liste sont reportés tous les taxa cités dans cette thèse. La taxinomie et les références bibliographiques suivent Bown, 1987, Bown, 1998, de Kaenel and Bergen, 1993, Mattioli et al., 2004a et Menini et al., 2019 pour l'intervalle Pliensbachien-Toarcien. La taxinomie et les références bibliographiques suivent Perch-Nielsen, 1985 et Bown 2005a pour le Paléocène-Eocène.

### **Liste taxinomique pour l'intervalle Pliensbachien-Toarcien**

*Axopodorhabdus atavus* (Grün et al., 1974) Bown, 1987

*Axopodorhabdus cylindratus* (Noël, 1965) Wind and Wise in Wise and Wind, 1977

*Biscutum dubium* (Noël, 1965) Grün in Grün et al., 1974

*Biscutum grande* Bown, 1987

*Biscutum intermedium* Bown, 1987

*Bussonius prinsii* (Noël, 1973) Goy, 1979

*Calyculus* spp. Noël, 1973

*Carinolithus poulabronei* Mattioli, 1996

*Carinolithus superbus* (Deflandre in Deflandre and Fert, 1954) Prins in Grün et al., 1974

*Crepidolithus cavus* Prins ex Rood et al., 1973

*Crepidolithus crassus* (Deflandre in Deflandre and Fert, 1954) Noël, 1965

*Crepidolithus crucifer* Prins 1969

*Crepidolithus granulatus* Bown, 1987

*Crepidolithus impontus* Grün et al., 1974

*Crucirhabdus minutus* Jafar, 1983

*Crucirhabdus primulus* Prins, 1969 ex Rood et al., 1973 emend.  
*Diductius constans* Goy in Goy et al., 1979  
*Ethmorhabdus crucifer* Noël, 1965  
*Ethmorhabdus gallicus* Noël, 1965  
*Lotharingius barozii* Noël, 1973  
*Lotharingius crucicentralis* (Medd, 1971) Grün and Zweili, 1980  
*Lotharingius frodoi* Mattioli, 1996  
*Lotharingius hauffii* Grün and Zweili in Grün et al., 1974  
*Lotharingius sigillatus* (Stradner, 1961) Prins in Grün et al., 1974  
*Lotharingius umbriensis* Mattioli, 1996  
*Lotharingius velatus* Bown and Cooper, 1989  
*Mazaganella protensa* Bown, 1987  
*Mitrolithus elegans* Deflandre in Deflandre and Fert, 1954  
*Mitrolithus jansae* (Wiegand, 1984) Bown and Young in Young et al., 1986  
*Mitrolithus lenticularis* Bown, 1987  
*Orthogonoides hamiltoniae* Wiegand, 1984  
*Parhabdolithus liasicus* Deflandre in Grassé, 1952  
*Parhabdolithus liasicus* subsp. *distinctus* Bown, 1987  
*Parhabdolithus liasicus* subsp. *liasicus* Deflandre in Grassé, 1952  
*Schizosphaerella* Deflandre & Dangeard, 1938  
*Silimiscutum cruciulus* subsp. *avitum* Mattioli et al., 2004b  
*Similiscutum cruciulus* subsp. *cruciulus* Mattioli et al., 2004b  
*Similiscutum finchii* (Crux, 1984 emend. Bown, 1987) de Kænel and Bergren, 1993  
*Similiscutum novum* (Goy, 1979) Mattioli et al., 2004  
*Similiscutum precarium* de Kænel and Bergen, 1993

*Sollasites arctus* (Noël, 1973) Bown, 1987  
*Sollasites* sp. Black, 1967  
*Stradnerlithus* Black, 1971  
*Tubirhabdus patulus* Prins ex Rood et al., 1973  
*Zygrhablithus bijugatus* Deflandre 1959  
*Zygrhablithus* Deflandre 1959

### **Liste taxinomique pour l'intervalle Paléocène-Eocène**

*Bomolithus aquilus* Bown 2010  
*Bomolithus megastypus* (Bramlette and Sullivan 1961) Bown 2010  
*Bomolithus* Roth 1973  
*Bomolithus supremus* Bown and Dunkley Jones 2006  
*Braarudosphaera* Deflandre 1957  
*Bussonius leufuensis* Bown and Kielbowicz, 1987 in Bown, 1987  
*Calciosolenia aperta* (Hay and Mohler 1967) Bown 2005a  
*Campylosphaera dela* (Bramlette and Sullivan 1961) Hay and Mohler 1967  
*Campylosphaera differta* Bown 2010  
*Campylosphaera eodela* Bukry 1971  
*Campylosphaera* Kamptner 1963  
*Chiasmolithus bidens* (Bramlette and Sullivan 1961) Hay and Mohler 1967  
*Chiasmolithus consuetus* (Bramlette and Sullivan 1961) Hay and Mohler 1967  
*Chiasmolithus* Hay et al. 1966  
*Coccolithus bownii* Jiang and Wise 2007  
*Coccolithus pelagicus* Schiller 1930



*Coccolithus* Schwarz 1894

*Cruciplacolithus* Hay and Mohler 1967

*Discoaster anartios* Bybell and Self-Trail 1995

*Discoaster araneus* Bukry 1971

*Discoaster delicatus* Bramlette and Sullivan 1961

*Discoaster diastypus* Bramlette and Sullivan 1961

*Discoaster lenticularis* Bramlette and Sullivan 1961

*Discoaster mohleri* Bukry and Percival 1971

*Discoaster multiradiatus* Bramlette and Riedel 1954

*Discoaster nobilis* Martini 1961

*Discoaster salisburgensis* Stradner 1961

*Discoaster* Tan 1927

*Discorhabdus ignotus* (Górka, 1957) Perch-Nielsen, 1968

*Discorhabdus striatus* Moshkovitz & Ehrlich, 1976

*Ericsonia aliquanta* Bown 2016

*Ericsonia* Black 1964

*Ericsonia orbis* Bown 2016

*Ericsonia robusta* (Bramlette and Sullivan 1961) Edwards and Perch-Nielsen 1975

*Ericsonia subpertusa* Hay and Mohler 1967

*Fasciculithus alanii* Perch-Nielsen 1971

*Fasciculithus* Bramlette and Sullivan 1961

*Fasciculithus hayi* Haq 1971

*Fasciculithus involutus* Bramlette and Sullivan 1961

*Fasciculithus mitreus* Gartner 1971

*Fasciculithus richardii* group *sensu* Agnini et al. 2014

*Fasciculithus richardii* Perch-Nielsen 1971

*Fasciculithus schaubii* Hay and Mohler 1967

*Fasciculithus thomasii* Perch-Nielsen 1971

*Fasciculithus tonii* Perch-Nielsen 1971

*Fasciculithus tympaniformis* Hay and Mohler 1967

*Fasciculithus tympaniformis* Hay and Mohler *in* Hay et al. 1967

*Gladiolithus* Jordan and Chamberlain 1992

*Gladiolithus flabellatus* (Halldal and Markali 1955) Jordan and Chamberlain 1993

*Hornibrookina* Edwards, 1973

*Holodiscolithus* Roth 1970

*Jakubowskia leoniae* Varol 1989

*Markalius apertus* Perch Nielsen 1979

*Prinsius* Hay and Mohler 1967

*Rhombiaster calcitrapa* group *sensu* Raffi et al. 2005

*Rhomboaster* (Bramlette and Sullivan 1961)

*Semihololithus* Perch-Nielsen 1971

*Semihololithus biskayae* Perch-Nielsen 1971

*Semihololithus dimidus* Bown 2005

*Semihololithus kanungoi* Bown 2005

*Semihololithus tentorium* Bown 2005

*Sphenolithus anarrhopus* Bukry and Bramlette 1969

*Sphenolithus* Deflandre *in* Grassé, 1952

*Sphenolithus moriformis* group *sensu* Agnini et al. 2014

*Thoracosphaera* Kamptner 1927

*Toweius callosus* Perch-Nielsen 1971

*Toweius eminens* (Bramlette and Sullivan, 1961) Perch-Nielsen, 1971

*Toweius* Hay and Mohler 1967

*Toweius serotinus* Bybell and Self Trail 1995

*Tibrachiatus bramlettei* (Bronnimann and Stradner 1960) Proto-Decima et al. 1975

*Tibrachiatus* Shamrai 1963



