

## Detrital signatures of Late Quaternary paleoenvironmental changes in the northern South China Sea

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Par

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Signatures d étritiques des changements pal éoenvironnementaux du Quaternaire r écent dans le bassin nord de la Mer de Chine du Sud

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# Detrital signatures of Late Quaternary paleoenvironmental changes in the northern South China Sea

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## 博士学位论文

# 南海北部晚第四纪古环境变化的 陆源碎屑指标

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# Signatures détritiques des changements paléoenvironnementaux du Quaternaire récent dans le bassin nord de la Mer de Chine du Sud

### Résumé

La mer de Chine du Sud est un laboratoire naturel pour beaucoup d'aspects. Elle est entourée par le continent asiatique, où se trouvent trois des plus grands fleuves du monde et et de nombreuses îles avec des rivières montagneuses qui fournissent une très grande quantité de sédiments terrigènes à la mer de Chine du Sud (Milliman et Farnsworth, 2011). En mer, les sédiments terrigènes sont transportés par divers courants qui sont liés aux vents de mousson sud-est asiatique, à l'intrusion du courant de Kuroshio et à l'échange d'eau profonde avec le Pacifique. Les sédiments terrigènes déposés en mer de Chine du Sud portent donc des signaux mixtes d'environnement continental et de transport océanique, faisant de cette mer un laboratoire naturel pour étudier les processus depuis la source jusqu'au dépôt (Liu et al., 2016).

Sur le continent, les conditions climatiques jouent un rôle de premier plan dans la formation des minéraux. Comme la mer de Chine du Sud se situe à basse latitude sur le côté ouest du Pacifique, la mousson sud-est asiatique est la caractéristique climatique dominante (Webster, 1987; Zahn, 2003). La mousson est caractérisée par des changements saisonniers dans la direction du vent et dans l'humidité. Lors de la mousson d'été asiatique, l'humidité est transportée de l'océan vers le continent, tandis que la mousson d'hiver asiatique s'accompagne d'une aridité à terre (Chu et Wang, 2003). L'intensité de la mousson est principalement contrôlée par les changements d'insolation liés au forçage orbital, et les conditions climatiques de cette région sont donc variables à l'échelle de temps orbitale. En outre, le changement climatique global à l'échelle glaciaire-interglaciaire joue également un rôle dans l'environnement régional non seulement en influençant le climat local, mais aussi en modifiant la répartition terre-mer. En effet, au cours des périodes glaciaires, lorsque les calottes glaciaires se développent et que le niveau de la mer descend, le plateau continental est émergé ainsi que la plupart des détroits. Etant donnée la très grande taille des marges continentales en Mer de Chine du Sud, cette situation modifie considérablement la répartition terre-mer, En conséquence, les transports fluviatiles et les circulations océaniques s'en trouvent modifiés, ce qui entraîne un schéma différent de dépôt de sédiments terrigènes au cours des périodes glaciaires (Huang et al., 1999, Liu et al., 2003, Wang et al., 1995).

Afin de mieux comprendre comment les changements paléoenvironnementaux sont enregistrés dans les sédiments marins et proposer des traceurs appropriés pour reconstruire leur évolution à différentes échelles de temps, nous avons étudié à haute résolution et en multi-paramètres une séquence de sédiments, la carotte MD12-3432, prélevée au nord de la mer de Chine du Sud lors de la campagne franco-chinoise CIRCEA à bord du R/V *Marion Dufresne*. L'étude a porté sur la minéralogie argileuse, les propriétés magnétiques, les éléments majeurs et la granulométrie sédimentaire.

La première phase de mes travaux a concerné les résultats obtenus sur la composition en éléments majeurs du sédiment total dans la séquence MD12-3432. Cette composition a été mesurée à l'aide d'un scanner XRF car c'est un instrument rapide et la masure est non destructive. Cependant, des questions controversées ont été soulevées au sujet de la fiabilité des données obtenues, car le XRF core-scanning mesure des intensités élémentaires semi-quantitatives qui peuvent être influencées par divers facteurs, tels que la teneur en eau, la granulométrie et l'effet de matrice (Hennekam Et de Lange, 2012, Löwemark et al., 2011; Lyle et al., 2012; Tjallingii et al., 2007; Weltje et al., 2015; Weltje et Tjallingii, 2008). Nous avons comparé les résultats obtenus par scan avec les résultats obtenus quantitativement par WD-XRF et nous avons calculé les coefficients de corrélation linéaire et les erreurs relatives. En termes de données brutes de XRF-scanning, la corrélation avec les mesures de WD-XRF est modérée à élevée pour la plupart des éléments sauf pour Al et Si qui ont des erreurs relatives plus élevées en partie haute de la séquence qu'en partie basse. Les calibrations existantes améliorent les corrélations mais la tendance à long terme d'erreur relative est encore observée. Il apparaît que la diminution de la teneur en eau interstitielle est le facteur principal qui dévie de manière préférentielle les données de XRF-scanning des éléments légers et que les méthodes existantes ne peuvent pas corriger totalement cet effet. Afin de mieux prendre en compte cet effet, nous avons proposé une correction polynomiale pour les données brutes de XRF-scanning et nous l'avons implémenté dans les deux méthodes existantes. Les résultats calibrés par ces deux méthodes améliorées montrent une meilleure corrélation avec les mesures WD-XRF et des erreurs relatives des moindres carrés très faibles. La tendance à long terme n'est plus observée dans les erreurs relatives. Ces méthodes de correction des

données XRF sont donc les plus appropriées pour les séquences de sédiments longs avec des variations de la teneur en eau interstitielle. Ces méthodes de calibration fournissent au moins des enregistrements robustes de la composition en éléments majeurs de la carotte MD12-3432 pour des études paléoenvironnementales (Chen et al., 2016).

Sur la base de la calibration des données XRF-scan, un enregistrement à haute résolution de la teneur en carbonate de calcium de la carotte MD12-3432 a permis de transférer celle-ci sur le cadre chronologique du site ODP 1146 (Clemens et al., 2008, Caballero-Gill et al. 2012). Ce modèle d'âge préliminaire a été ensuite affiné grâce aux variations de l'intensité du champ magnétique terrestre. En effet, dans la carotte MD12-3432, les variations du champ magnétique terrestre sont enregistrées de manière fiable avec une inclinaison moyenne de  $34.7 \pm 9.4$ °, cohérente avec celle attendue à cette latitude sur l'hypothèse d'un dipole axial centré (34,9°). La déclinaison magnétique est également stable et la direction du champ est définie à mieux que 10°. La paléointensité relative du champ magnétique terrestre enregistrée est donc utilisée pour préciser le modèle d'âge en corrélant l'enregistrement dans la carotte MD12-3432 avec la courbe de référence globale PISO-1500 (Channel et al., 2009). Des points de corrélation sont ainsi ajoutés aux minima de paléointensité, en particulier ceux associés à l'excursion de Laschamp à 40 ka et à l'excursion de Blake à 95 et 120 ka. Le modèle d'âge indique que la sequence sédimentaire MD12-3432 couvre les derniers 404 mille ans avec un taux de sédimentation moyen d'environ 12,6 cm/kyr.

Comme l'altération chimique modifie principalement la composition des éléments, l'enregistrement à haute résolution des éléments majeurs calibrés est utilisé pour évaluer l'évolution de l'altération à la fin du Quaternaire. Le résultat montre que les teneurs de tous les éléments terrigènes ont des variations semblables, opposes à celle du carbonate de calcium biogénique. Pour mieux illustrer le signal d'altération, le rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> est utilisé parce que le potassium est plus mobile que l'aluminium et que l'effet granulométrique est négligeable puisque les deux éléments sont principalement transportés par des minéraux argileux dans cette zone. Par conséquent, un faible rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> indique que le sédiment total a subi une forte altération chimique. Dans la carotte MD12-3432, le rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> présente une périodicité d'excentricité dominante avec des augmentations pendant les interglaciaires, ce qui indique que l'altération continue à s'affaiblir pendant les interglaciaires. Cela contraste

avec la compréhension antérieure que l'altération est renforcée par le climat chaud pendant les interglaciaires. Par conséquent, le degré d'altération du sédiment total, tel qu'indiqué par le rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, ne correspond pas à l'altération chimique contemporaine sur terre et des changements de sources peuvent être invoquées. Les études préalables des sédiments de rivières ont montré que la fraction détritique déposée en Mer de Chine du Sud provient principalement du bassin de la rivière des Perles, de Taïwan et de Luzon (Liu et al., 2008a). Taïwan est la région parmi les trois qui exporte la plus grande quantité de sédiments (Dadson et al., 2003, Milliman et Farnsworth, 2011) car l'intense précipitation d'été y augmente le taux de dénudation des rivières et, ainsi, la contribution relative de la fraction détritique érosive. En raison de l'érosion physique forte et de l'altération chimique faible, le rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> des sédiments à Taiwan est plus élevé que celui de Luzon et du bassin de la rivière des Perles (Selvaraj and Chen, 2006; Chen and Selvaraj, 2007). L'augmentation du rapport K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> dans les sédiments totaux de la carotte illustre cette forte dénudation fluviale à Taiwan dans bande spectrale de l'excentricité.

L'altération chimique influe également sur la formation de minéraux argileux à terre (Chamley, 1989). Dans le cas du nord de la Mer de Chine du Sud, les trois provenances terrigènes fournissent des minéraux argileux différents en raison de leurs contextes géologiques et tectoniques. Le bassin de la rivière des Perles a un régime tectonique stable, une topographie plate et un climat de mousson chaud et humide. Les roches et les sols du bassin de la rivière des Perles subissent de fortes altérations chimiques et une érosion physique relativement faible. Ces conditions favorisent la formation et l'accumulation de sols kaolinitiques qui peuvent prendre plus de 1 Ma à se développer (Liu et al., 2007; Thiry, 2000). Le sédiment provenant du bassin de la rivière des Perles est donc riche en kaolinite (Liu et al., 2007). À Taïwan, la dénudation des rivières est intense en raison de la topographie, de la tectonique active, et de fortes précipitations de mousson et/ou de passages de typhons (Dadson et al., 2003; Milliman and Farnsworth, 2011). Les formations sédimentaires et métamorphiques y sont rapidement érodées. Cette forte érosion physique inhibe l'altération chimique et favorise la formation et la distribution de minéraux primaires d'illite et de chlorite (Liu et al., 2008b). Étant donné la similitude des paramètres tectoniques et climatiques à Taïwan et à Luzon, les fortes précipitations de mousson peuvent également entraîner une dénudation intense des rivières à Luzon. Cependant, la géologie de Luzon est dominée par des roches volcaniques qui peuvent être dégradées rapidement pour former des smectites en abondance (Oliva et al., 2003; Sasaki et al., 2003; Schopka et al. 2011). L'assemblage minéral argileux de la carotte MD10-3432 se compose principalement de smectite (23%-59%) et d'illite (22%-43%) avec de la chlorite (13%-27%) et de la kaolinite (4%-13%). La cristallinité de l'illite (0,13-0,18 ° Δ2θ) varie dans la plage observée dans les sédiments modernes de Taiwan. Ces résultats indiquent que (1) l'illite et la chlorite proviennent principalement de Taiwan et sont formées par l'érosion physique, (2) la smectite provient de Luzon et est formée par l'altération chimique rapide des roches volcaniques abondants à Luzon et (3) les kaolinites sont formées par l'altération à long terme dans le bassin de la rivière des Perles. Par conséquent, la teneur en kaolinite, habituellement utilisée comme indicateur de l'altération chimique à l'échelle tectonique reflète ici la contribution relative de l'approvisionnement terrigène de la rivière des Perles pendant le Quaternaire, tandis que le rapport smectite/(illite+chlorite) constitue un indicateur de l'altération contemporaine à Luzon. Concernant les variations temporelles, l'analyse spectrale révèle une périodicité de 100 kyr liée à l'excentricité dans le rapport smectite/(illite+chlorite) de la carotte MD12-3432 avec des valeurs élevées pendant les interglaciaires. Il est logique que la température élevée pendant les interglaciaires favorise l'altération chimique et, par conséquent, augmente le rapport smectite/(illite+chlorite). Outre la cyclicité glaciaire et interglaciaire, la caractéristique la plus importante du rapport smectite/(illite+chlorite) de la carotte MD12-3432 est les fluctuations à court terme avec des valeurs élevées correspondant à chaque maxima d'insolation estivale dans l'hémisphère nord dans la bande de précession (23 kyr). Des variations similaires du rapport smectite/(illite+chlorite) ont également été observées aux sites ODP 1145 et 1146 situés à proximité (Liu et al., 2003; Boulay et al., 2005), Puisque l'insolation estivale de l'hémisphère Nord est la force motrice de la mousson d'été asiatique, qui est caractérisée par un climat chaud et humide favorisant l'altération chimique, ces variations en phase avec la précession indiquent que le rapport smectite/(illite+chlorite) est un traceur des changements de l'altération chimique contemporaine provoquée par l'évolution de la mousson d'été asiatique et, par conséquent, un traceur de la mousson d'été asiatique au Quaternaire. Tout ceci a fait l'objet d'un article sous presse à Scientific Reports.

La fraction magnétique des sédiments du nord de la mer de Chine du Sud fournit des informations complémentaires sur les changements environnementaux. Les propriétés magnétiques à savoir la concentration, la taille et la nature des particules magnétiques sont variables dans le temps comme illustré par les paramètres de base (susceptibilité en champ faible (k), aimantations rémanentes anhystérétique (ARM) et isotherme (IRM)).

Pour mieux comprendre ces variations, nous analysons en détail la nature des minéraux magnétiques à l'aide de la décomposition Gaussienne logarithmique cumulée des courbes d'acquisition à haite résolution de l'IRM (Kruivier et al., 2001) et de la désaimantation thermique de l'IRM sur trois axes. Un mélange de différentes familles coercitives est reconnu avec une dominance des familles de coercivité faible à moyenne tandis que la famille de haute coercivité contribue de 3% à 22% à l'IRM à saturation. Le comportement thermique de ces familles indique que la fraction de coercivité élevée est composée d'hématite et les familles de coercivité faible à moyenne sont constituées de magnétite et de sulfures de fer. Puisque qu'aucune aimantation gyrorémanente (GRM) est observée au cours de la désaimantation de ARM jusqu'à 80 mT, il est peu probable que les sulfures de fer soient de la greigite. Nous interprétons donc cette composante comme étant portée par la pyrrhotite qui a par ailleurs été largement identifiée dans la partie nord de la mer de Chine du Sud, à Taiwan (Horng et Huh, 2011; Horng et al., 2012).

Des variations aussi bien de la granulométrie sédimentaire que de la teneur en hématite sont observées à l'échelle de la précession. En effet, des apports importants d'hématite, en phase avec du sédiment plus fin coïncident avec les minima de précession. Étant donné que l'hématite n'est pas abondante dans les systèmes fluviatiles environnants, ces événements se produisant pendant les périodes arides peuvent illustrer des changements d'apports éoliens venant des déserts de Chine centrale. Bien que les poussières éoliennes soient principalement transportées vers l'est par les vents d'ouest de latitude moyenne (Seo et al., 2014), des études antérieures ont découvert des apports éoliens dans les séquences sédimentaires de la mer de Philippine (Maher, 2009, Xu et al. Et al., 2016), qui est à la même latitude que notre site. Deux mécanismes ont été proposés: (1) la mousson d'hiver asiatique intensifiée livre plus de poussières éoliennes vers le sud (Xu et al., 2014), et (2) les poussières éoliennes peuvent se disperser vers le sud comme les aérosols (Prospero et al., 1994) et retomber avec la pluie liée à la mousson d'été asiatique. Nos résultats montrent que de forts apports éoliens se produisent simultanément à la faible mousson d'été asiatique, lorsque la zone de convergence intertropicale migre vers le sud, permettant à plus d'aérosols d'arriver à basse latitude. En dépit du fait que la poussière éolienne

est une fraction mineure dans les sédiments du nord de la mer de Chine du Sud, nos résultats suggèrent que la teneur de hématite peut constituer un puissant traceur pour révéler ces signaux même très faibles et, ainsi, indiquer des changements de l'intensité de la mousson d'été asiatique.

Outre les changements climatiques de basse latitude, l'activité tectonique et le climat mondial influencent également la composition terrigène au site étudié à différentes échelles de temps. Nos résultats montrent des augmentations à long terme sur 400 000 ans de la teneur en pyrrhotite par rapport à la magnétite et à l'hématite et de teneurs en illite et chlorite par rapport aux autres argiles. Ces augmentations indiquent une contribution croissante des sédiments provenant de Taïwan. Cela est probablement lié à l'intensification de l'orogène taiwanaise sur les derniers 400 000 ans.

Enfin, à l'échelle glaciaire-interglaciaire, les augmentations de la vitesse de sédimentation, de la teneur en magnétite et pyrrhotite, de la teneur en kaolinite et de la taille des grains pendant les périodes glaciaires sont attribuées aux changements du niveau de la mer. Le bas niveau de la mer au cours des périodes glaciaires expose la vaste marge continentale, rapproche le débouché de la rivière des Perles de notre site permettant à celle-ci de délivrer plus de sédiments terrigènes plus grossiers à notre site.

**Mots clés :** Mer de Chine du Sud, mousson d'été asiatique, changements de niveau marin, orogène Taiwanais, minéralogie argileuse, minéralogie magnétique

# Detrital signatures of Late Quaternary paleoenvironmental changes in the northern South China Sea

### ABSTRACT

The aim of this study is to reconstruct late Quaternary environmental changes in the northern South China Sea by applying multi-disciplinary proxies of land-sea interaction, East Asian monsoon, and oceanic circulation. Investigations of clay and magnetic mineralogy, major element composition, and grain size were performed on marine sediment Core MD12-3432 retrieved from the continental slope of the northern South China Sea. The core covers the last 400 ka with a sedimentation rate varying between 4.5 and 24 cm/ka.

We examined the accuracy of existing calibration methods on major element composition obtained by XRF core-scanning, because downcore variations in interstitial water content should strongly affect scanned element contents We proposed a quadratic polynomial correction to account for this effect and implemented it in the calibration methods. Data from Core MD12-3432 show that the improved calibration process now correctly converts XRF core-scanning data into major element concentrations.

Our results on high-resolution major element composition, clay and magnetic mineralogy, and grain size data indicate that low-latitude climate changes influence various terrigenous fractions in different ways.

In bulk sediment, K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio mainly reflects the relative contribution of detrital supply from Taiwan, and its variation exhibits eccentricity cycles. The ratio increases during interglacials, showing that strong precipitation and denudation are induced by enhanced East Asian summer monsoon. In clay fractions, smectite/(illite+chlorite) ratio presents both eccentricity and precession periodicities, in phase with the northern hemisphere summer insolation changes and therefore with the East Asian summer monsoon evolution. Based on the knowledge of sediment provenances, these results suggest that high smectite/(illite+chlorite) ratios illustrate

contemporaneous chemical weathering intensity in Luzon. It supports the understanding that East Asian summer monsoon is enhanced during interglacial periods and when the boreal summer insolation is strong. Therefore, these two ratios are appropriate sedimentary tracers for East Asian summer monsoon evolution in the South China Sea.

The magnetic fraction yields complementary information about environmental changes in the South China Sea. The magnetic mineral assemblage of Core MD12-3432 is mainly composed of magnetite, sulphide, and hematite, and the relative contributions of all these magnetic mineral contents change with time. Variations on precessional band related to the low latitude East Asian monsoon are observed in magnetic properties and grain size values. High magnetic inputs with high hematite proportion, which is part of fine-grain sediment, are observed during the precession minima. These events occurring during arid periods may illustrate enhanced eolian inputs caused by changes in intensity and/or winds pathway of winds, probably related to enhanced winter monsoon.

Besides the low-latitude climate changes, global climate and tectonic activity also influence the terrigenous composition at the studied site at different timescales. A long-term increase in pyrrhotite content with respect to magnetite and hematite and in illite/chlorite contents indicates an increasing contribution of fine grained sediments from Taiwan. This is most likely related to the intensification of Taiwanese orogeny over the last 400 ka. On glacial-interglacial scale, coeval increases observed in sedimentation rate, magnetite/pyrrhotite content, kaolinite content, and grain size during glacial periods are attributed to sea-level changes. Low sea-level during glacial periods exposes the vast shelf and allows the Pearl River to deliver more and coarser terrigenous sediments to our site.

**Key Words:** South China Sea, East Asian summer monsoon, sea-level changes, Taiwan orogeny, clay mineralogy, magnetic mineralogy

# 南海北部晚第四纪古环境变化的 陆源碎屑指标

### 摘要

本项研究旨在运用海陆相互作用、东亚季风和海洋环流的替代性指标,重建 南海北部晚第四纪以来的沉积古环境演化历史。研究采用来自南海北部陆坡的 MD12-3432 柱状样作为研究材料,开展了一系列实验分析,包括粘土矿物学、磁 性矿物学、主量元素地球化学和陆源碎屑粒度分析。碳酸盐地层学和磁性地层学 指示该柱状样记录了过去 40 万年来的古环境演变记录。

研究首先指出 XRF 岩芯元素扫描数据现有校正方法存在的问题,提出更新的 校正方案。结果显示,现有校正方法难以有效消除该柱状样中孔隙水含量变化对 XRF 岩芯扫描数据的影响。于是,我们针对该效应提出了一套多项式矫正方法, 将其与现有校正方法结合,形成两套完整的校正方案。通过运用到 MD12-3432 柱 状样上的测试结果,显示这两套校正方案能有效地将 XRF 岩芯扫描数据换算成高 精度高分辨率主量元素成分记录。

高分辨率主量元素、粘土矿物、磁性矿物和粒度记录显示,南海北部海洋沉积物中各陆源碎屑组分通过不同机制响应低纬气候过程的变化。整体上,主量元素 K20/A1203 比值主要反映了台湾陆源碎屑的贡献量,其变化特征主要体现为冰期间冰期旋回。间冰期时较高的 K20/A1203 比值指示了东亚夏季风的增强以及随之而来的强降雨和河流剥蚀。粘土组分对季风气候的响应机制有所不同。该站位粘土矿物主要由蒙脱石(23%-59%)、伊利石(22%-43%)、绿泥石(13%-27%)和高岭石(4%-13%)组成。其中,蒙脱石/(伊利石+绿泥石)比值的变化呈现出偏心率和斜率周期,与北半球夏季辐射量变化一致,说明其变化很可能受到低纬地区东亚夏季风的影响。基于对粘土矿物来源的认识,该站位蒙脱石供给主要受控于季风控制的吕宋化学风化强度和河流剥蚀力度,而伊利石和绿泥石的供给主要与台湾河流剥蚀有关。蒙脱石/(伊利石+绿泥石)比值主要反映了吕宋岛上同时期快速化学风化的强度。因此,该研究区域沉积物中的 K20/A1203 比值与蒙脱石/(伊利石+绿泥石)比值可用于指示晚第四纪东亚夏季风的演化。磁性组分通过另一种机制记录了低纬气候过程的演化历史。MD12-3432 柱状样中磁性矿物主要

包括低矫顽力的磁铁矿、硫化铁和高矫顽力的赤铁矿,其含量变化具有与低纬气 候活动相关的岁差周期。当北半球夏季辐射量较弱时,磁性矿物输入较高,并伴 随着赤铁矿相对含量的上涨和颗粒平均粒径的减小。基于对南海周边河流样品以 及中国西北地区沙漠样品的磁性矿物调查,这些现象很可能代表了风尘输入的增 强,与风尘搬运的强度或路径变化有关。因此,赤铁矿含量的增长和粒度的减小 很可能反映了东亚冬季风的变化。

除了低纬过程,全球气候变化和构造活动也在不同时间尺度上影响着南海北 部陆源碎屑沉积物的变化。本次研究的结果显示,磁性组分中磁黄铁矿的含量以 及粘土组分中伊利石与绿泥石的含量均呈现了 40 万年以来的持续性增长。由于 这三种矿物均是台湾的特征矿物,这一上升趋势指示了台湾对南海北部细粒陆源 碎屑物贡献量的持续增长。这很可能与台湾活跃的造山运动有关。在冰期间冰期 尺度上,高岭石含量、磁铁矿与磁黄铁矿含量均在冰期呈现高值,并伴随着颗粒 粒径的增加和沉积速率的上涨。分析显示,这一系列沉积物组分变化主要与海平 面变化有关。当全球变冷、两极冰盖发育时,海平面下降是南海北部宽广的陆架 出露,古珠江通过侵蚀出露陆架将大量陆源碎屑物和再悬浮沉积物搬运至南海北 部,从而导致沉积速率与粒径的增加以及沉积物矿物组分的改变。

关键词: 南海、东亚夏季风、海平面变化、台湾造山运动、粘土矿物学、磁性矿物学

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# **General Introduction**

## Aims and Scopes

In this section, we introduce the state-of-art of environmental evolution studies using terrigenous sediment in the South China Sea, as well as main objectives of this study. The main objective is to investigate past changes in the composition of terrigenous sediments deposited in the northern South China Sea to 1) identify tracers of land-sea interaction, East Asian monsoon, and oceanic circulation, and 2) reconstruct the late Quaternary evolution of the external forcing at different timescales in this region. The structure of the thesis and contents of the constituent chapters are provided.

The South China Sea is the largest marginal sea separating Asia from Pacific, being bordered by South China and Taiwan to the north, Luzon and Palawan to the east, Indochina Peninsula to the west, and Malay Peninsula, Sumatra, and Borneo to the South. More than 700 million tons of detrital sediments are delivered from these lands to the South China Sea by the well-developed drainage systems, including three of the largest rivers in the world (Dadson et al., 2003; Liu and Stattegger, 2014; Milliman and Farnsworth, 2011; Milliman et al., 1999; Milliman and Syvitski, 1992; Zhang et al., 2012). These terrigenous sediments are produced within diverse climatic, tectonic, and lithological settings on land (Liu et al., 2016). As the mineral formation on land is primarily controlled by weathering, which is indeed interactions between lithosphere, atmosphere, hydrosphere, and biosphere, a large variety of mineral assemblages and element compositions are documented in the terrigenous sediments on land (Horng et al., 2012; Liu et al., 2007; 2008b; 2009; 2012b; Schopka et al., 2011; Selvaraj and Chen, 2006; Wang et al., 2011b). Once entering the South China Sea, terrigenous sediments are transported by diverse currents which are related to East Asian monsoon winds, intrusion of Kuroshio Current, and deep water exchange with Pacific (Fang et al., 1998; Qu et al., 2006; Webster, 1994; Yuan et al., 2006; Yuan et al., 2014; Zhao et al., 2014). The transport patterns largely influence the distribution of terrigenous sediments (Liu et al., 2013a; Liu et al., 2010b; Zhang et al., 2014; Zhao et al., 2014). The terrigenous sediments in the South China Sea therefore carry mixed signals of continental environment and oceanic transport, making the South China Sea a natural laboratory to study the land-sea interactions.

Moreover, the South China Sea is situated in low latitude area where the East Asian monsoon is the prevailing climate feature that inserts far-reaching influences on both environment and society (Webster, 1987; Zahn, 2003). The modern monsoon study indicates that the East Asian monsoon is characterized by seasonal changes in wind direction and moisture, giving rise to the summer monsoon and the winter monsoon (Webster, 1994). The East Asian summer monsoon brings moisture from the ocean to the continent while the East Asian winter monsoon is accompanied by aridity on land (Chu and Wang, 2003). In order to predict future climate changes and in particular the role plaid by low latitudes in global climate, it is necessary to understand how the East Asian monsoon changed in the past and what controls its variations. As the monsoon evolution can be described in terms of wind speed and monsoonal precipitation rates and duration, which take part in the physical, chemical, and biological processes both

on land and at sea, proxies based on sediment sequences in the South China Sea can contribute to extend the historical record of the East Asian monsoon evolution at different timescales (e.g. Boulay et al., 2005; 2007; Chen et al., 2003; Clift et al., 2002; 2014; Hu et al., 2012; Huang et al., 2011; Liu et al., 2003; 2004; 2010b; 2010c; Meng et al., 2011; Sun et al., 2008; Tian et al., 2011; Wan et al., 2006; 2007; Wang et al., 1999; Wei et al., 2004; 2006). Besides the regional low latitude climatic conditions, the terrigenous sediments deposit in the South China Sea are also sensitive to global climate changes, not only because of the continental weathering but also because of the presence of vast shelves. During the glacial periods, when the ice sheets develop and sea-level descends, the land-sea distribution would be quite different and most straits around the South China Sea would be closed by the exposed shelves (Wang et al., 1995; Yao et al., 2009). Consequently, both fluvial transports and oceanic circulations would be altered, resulting in a different pattern of terrigenous sediment deposition during glacial periods (Huang et al., 1999; Liu et al., 2003; Wang et al., 1999; Wang et al., 1995). Therefore, the well-preserved sediment sequences characterized by high sedimentation rate in the South China Sea are ideal material for paleoenvironmental reconstructions (Wang et al., 2014).

For these reasons, the South China Sea has drawn attention from the paleoenvironmental and sedimentological communities. Numerous investigations have been performed on terrestrial and marine sediments in the South China Sea area to study the land-sea interactions and links among detrital sediments, the East Asian monsoon, and global climate changes (Clift et al., 2014; Liu et al., 2016; Wang et al., 2014; and references therein). Many of these researches focus on the northern part of the South China Sea, reconstructing a general blueprint of the environmental changes in this area to support further studies.

Among all the methods, clay mineralogy is one of the most frequently used to reconstruct paleoenvironmental evolution at different timescales. On tectonic scales, clay mineral records were used to illustrate the weathering history and to further reconstruct the evolution of the East Asian monsoon (Clift et al., 2002; Wan et al., 2006; 2007). A glacial-interglacial cyclicity was observed in the clay mineral assemblages in the South China Sea with high illite and chlorite contents during glacial periods and high smectite content during interglacial periods (Liu et al., 2003; 2004; Wan et al., 2007). Such periodicity was interpreted as results of either monsoon-related oceanic current transport (Liu et al., 2003) or climate-related continental weathering/erosion

condition (Liu et al., 2004; Wan et al., 2007). However, high resolution clay mineral records do not significantly vary on glacial-interglacial scale (Boulay et al., 2005; 2008; Liu et al., 2010c). Instead, mutual variations were observed in clay mineral assemblage at ODP Site 1145 and northern hemisphere autumn insolation on precessional band (Boulay et al., 2005). The extremely high-resolution clay mineralogical investigation on Core MD05-2904 revealed the complexity of clay mineral input from the adjacent drainage systems, involving clay mineral production, monsoon rainfall denudation, oceanic current transport, and sea-level changes (Liu et al., 2010c). It is therefore necessary to understand the continental provenance and the oceanic transport pattern of clay minerals before using them to reconstruct the paleoenvironmental changes. Recently, clay mineralogical investigations have been conducted on river or delta sediments from the Pearl River drainage area (Hu et al., 2013; Liu et al., 2007), Hainan island (Hu et al., 2014), Taiwan (Liu et al., 2008b), and Luzon (Liu et al., 2009). It turns out that the Pearl River is the main source of kaolinite in the northern South China Sea, Taiwan provides abundant primary minerals of illite and chlorite, and Luzon produces pure smectite in terms of clay minerals (Liu et al., 2007; 2008b; 2009). The oceanic transport pattern derived from surface sediment investigations and mooring system observations suggest that smectite from Luzon is mainly transported to the northern South China Sea by the Kuroshio-related surface currents, while illite and chlorite from Taiwan are delivered mainly by the deepwater currents (Liu et al., 2013a; Liu et al., 2010b; Zhao et al., 2015). This background knowledge allows further clay mineralogical studies on sediment sequences to better reconstruct the paleoenvironmental changes.

Magnetism has been considered as a key discipline for paleoenvironmental studies in the South China Sea (Kissel et al., 2003; Zhang et al., 2015; Zheng et al., 2016). Complementary to bulk sediment and clay fraction, the magnetic fraction is usually extremely fine and its distribution also depends on many environmental factors, such as provenance, climate conditions, transport capability, etc. It is therefore widely used as a tracer for variations in deep-water current (de Menocal et al., 1988; Kissel et al., 2009; 2013; Zheng et al., 2016), climate-related eolian input (Maher, 2011; Yamazaki, 2009; Yamazaki and Ioka, 1997; Ziegler et al., 2008), and climatic conditions on land (Colin et al., 1998; Kissel et al., 2010; Zhou et al., 2012). Environmental magnetism studies have also been conducted in sediment sequences retrieved from the South China Sea, indicating coherences between magnetic properties variations and climate changes (Hou et al., 1996; Ouyang et al., 2016; Yang et al., 2002; Zhang et al., 2015). However, due to the lack of knowledge about magnetic mineral provenances, the link between the magnetic properties in South China Sea sediments and climate conditions are still discussible. Recently, investigations of magnetic mineralogy and rock magnetism have been performed on lands surrounding the South China Sea (Horng et al., 2012; Kissel et al., 2016; Qiang et al., 2011), allowing to better understand the response of magnetic parameters to climatic changes and land-sea interactions.

On the basis of previous studies, we investigated the clay and magnetic mineralogy, together with major element composition and granulometry of a sediment sequence of Core MD12-3432 retrieved from the northern slope of the South China Sea. The aim of this study is to reconstruct the late Quaternary environmental changes in the northern South China Sea by applying multi-disciplinary proxies of land-sea interactions, the East Asian monsoon, and oceanic circulations. The results of all investigations performed as part of this thesis are organized in six chapters.

Chapter 1 is a general introduction of the background of the study area, including the geological, climatic, oceanographic settings of the northern South China Sea and the adjacent lands.

Chapter 2 introduces the material and analytical methods used in this study to achieve the objectives.

In Chapter 3, we establish a correction procedure to improve the feasibility of XRF core-scanning data in paleoenvironmental studies. We compare in detail the semiquantitative XRF core-scanning major element data, calibrated XRF core-scanning major element composition, and the quantitative major element composition. As variations in interstitial water content is identified to introduce non-linear influences in both raw and calibrated XRF core-scanning data, we propose a correction strategy and implement it to the previously developed calibration methods. We also demonstrate the reliability of the calibration with the proposed methods.

In Chapter 4, we propose mechanisms by which the East Asian summer monsoon controls the variations in clay mineral assemblage and major element composition. High-resolution clay mineralogical and major elements results obtained from Core MD12-3432 are presented based on an age model established using carbonate stratigraphy. Through the analysis of their variation pattern, we establish the connection between the East Asian summer monsoon intensity and the K/A1 and smectite/(illite+chlorite) ratios, and propose them as proxies for the summer monsoon

intensity.

In Chapter 5, we investigate the magnetic properties and grain size of the sedimentary sequence. The variations in the geomagnetic field intensity is additionally used to support and to refine the age model previously established by carbonate stratigraphy. The understanding of magnetic mineral assemblage and its variations in Core MD12-3432 is obtained by deciphering the magnetic properties. Different driven factors, i.e. the active Taiwan orogeny, the sea-level changes, and the East Asian summer monsoon intensity, are identified to be responsible for variations in magnetic mineral assemblage and grain size at various timescales.

Chapter 6 presents a summary of this study and suggestions are proposed for future research.

## Chapter 1 Geological and Environmental settings

In this section, we introduce the state-of-art of environmental evolution studies using terrigenous sediment in the South China Sea, as well as main objectives of this study. The main objective is to investigate past changes in the composition of terrigenous sediments deposited in the northern South China Sea in order to 1) identify tracers of land-sea interaction, East Asian monsoon, and oceanic circulation, and 2) reconstruct the late Quaternary evolution of the external forcing at different timescales in this region. The structure of the thesis and contents of the constituent chapters are provided.

### 1.1 Physiography of the South China Sea

The South China Sea is the largest marginal sea in the western North Pacific, covering  $3.5 \times 10^6$  km<sup>2</sup> with a deepest water depth of 5559 m. It is semi-enclosed basin, surrounded by, from north to south, South China, Indochina Peninsula, and the islandarcs of Philippines and Indonesia. The water mass exchange between the South China Sea and the outside occurs only through several straits: the Taiwan Strait (70 m water depth) in the northeast, the Luzon Strait (2600 m water depth) in the east, the Mindoro Strait (420 m water depth) and the Balabac Strait (100 m water depth) in the southeast, and the Karimata Strait (30 m water depth) and the Malacca Strait (10-20 m water depth) in the south (Fig. 1.1). The bathymetry of the South China Sea is characterized by the rhomboid shape of the deep basin, the continental slopes, and the enormous continental shelves. The continental shelves are vast in the north and south with well-developed submarine deltas and canyons, and become narrower in the west and east.



Figure 1.1 Topography of the South China Sea.

### 1.2 Geological settings of sediment source areas

The lands around the northern South China Sea include South China, Taiwan, Luzon, and the northern Indochina Peninsula. In the north, South China has been tectonically stable since Mesozoic. Its stratigraphy is mainly characterized by Mesozoic-Cenozoic granitic rocks and Paleozoic sedimentary rocks (Fig. 1.2). In particular, Permian-Triassic limestone dominates the upstream drainage area of Xijiang River, the main stream of the Pearl River, while Mesozoic-Cenozoic granitic rocks and Paleozoic limestones and sandstones dominate the downstream drainage area of the Pearl River. Taiwan is a tectonically active accretionary prism. It was developed by the eastward subduction of the South China Sea oceanic crust beneath the Philippine Sea Plate (Huang et al., 1997). The stratigraphy is mainly composed of Tertiary sedimentary rocks with associated metamorphic rocks in the Central Range and of volcanic arc complex in the Coastal Range (Fig. 1.2).



Figure 1.2 Geological map of Southeast Asia surrounding the South China Sea (after Liu et al., 2016). Stratigraphy after Commission for the Geological Map of the World (1975), major oceanic fault systems after Hall (2002).

Chapter 1 Geological and Environmental settings

In the east, the Philippine island arc is formed by the ongoing convergence of the Eurasian Plate, the Philippine Sea Plate, and the Pacific Plate. As part of the island arc, Luzon is therefore characterized by active faults, active volcanism, and active seismicity. The strata of Luzon are profiled by abundant Cenozoic intermediate intrusive rocks, which are usually associated with undifferentiated Cretaceous-Paleogene volcanic rocks, and Cretaceous-Quaternary sedimentary and extrusive rocks (Fig. 1.2). In particular, Southern Luzon is characterized by Pliocene-Quaternary volcanic deposits that are mainly composed of andesites and basalts.

### 1.3 Climatic settings of sediment source areas

The East Asian monsoon prevails in the lands adjacent to the northern South China Sea, controlling the seasonal precipitation and runoff regimes by the alternation of summer and winter monsoon wind directions. From November to April, the continent cools and the high pressure cell over northern Asia develops, inducing the northeast winter monsoon across the South China Sea; on the contrary, the southwesterly summer monsoon prevails from May to October, accompanied by continental heating and low pressure over central China (Wang and Li, 2009). Driven by the seasonality of monsoon winds, the inter-tropical convergence zone (ITCZ) shifts meridionally and the precipitation rate changes seasonally (Wang et al., 2003).

In South China, the mean temperature varies between 10-30 °C, and the annual precipitation reaches 1700-2000 mm with ~80% of the rainfall occurring in summer (Fig. 1.3). Taiwan is situated at the same latitude as South China. The temperature is also moderate and the precipitation also arrives mainly in summer (June-September) (Fig. 1.3), with heavier annual rainfall than in South China (over 2500 mm) because Taiwan is located in the "typhoon corridor". There were 255 typhoons that hit Taiwan between 1949 and 2009 (Liu et al., 2013b). The frequent typhoon events and tropical storms largely increase the precipitation in summer. In Luzon located south of Taiwan, the temperature is high and stable (27 °C  $\pm$  5 °C), while the precipitation pattern is more complex (Fig. 1.3). In northern and central Luzon, the rainy season with 80% of the total rainfall occurs in Summer (June-October), while the dry season dominates the rest of the year. Such a shift in precipitation is not observed in southern Luzon where 45% of the total rainfall occurs in October to December, while 55% of the rest is distributed during the other seasons (Schopka et al., 2011).

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Figure 1.3 Mean monthly temperature and precipitation observed at stations of different cities surrounding the northern South China Sea.

Observed data of 1951-1960 (Peterson and Vose, 1997) were used for the mean values.

### 1.4 Oceanic circulation

### 1.4.1 Surface current

The upper-layer circulation in the South China Sea presents a clear seasonality in response to the seasonal changes of monsoon winds with additional influence from the Kuroshio that intrudes the South China Sea through the Luzon Strait (Fang et al., 1998; Qu, 2010; Shaw and Chao, 1994; Su, 2004). In winter, the northeasterly monsoon drives the cold water to enter the South China Sea through the Taiwan Strait and to exit through Sunda shelf, forming a basin-wide cyclonic gyre with two cores located in central basin and northwest to Luzon (Fang et al., 1998; Li et al., 2000; Qu, 2010; Wyrtki, 1961). On the contrary, the southwesterly summer monsoon drives the prevailing northeastward surface current, reducing the basin-wide gyre and merging with the reversed Guangdong coastal current.

Chapter 1 Geological and Environmental settings



Figure 1.4 Oceanic circulation system in the South China Sea (after Liu et al., 2016).

Major currents are noted by numbers: 1. Loop Current, 2. South China Sea branch of Kuroshio, 3.
NW Luzon Cyclonic Gyre, 4. NW Luzon Cyclonic Eddy, 5. NW Luzon Coastal Current, 6. South China Sea warm current, 7. Guangdong Coastal Current, 8. South China Sea Southern Cyclonic Gyre, 9. South China Sea Sothern Anticyclonic Gyre, 10. SE Vietnam Offshore Current, 11. Gulf of Tonkin surface current, 12. Luzon Deep Current, 13. South China Sea Contour Current, 14. Deep Cyclonic Current.

Meanwhile, the intrusion of Kuroshio Current is an important component of the surface circulation. It is a key process to exchange mass and energy between the South China Sea and the Pacific Ocean (Qu et al., 2004), and mesoscale eddies originated from it can transport mass, heat, salt, and sediment in the northern South China Sea

(Zhang et al., 2014). In winter, the Kuroshio Current flows from the northeast of Luzon to the southwest of Taiwan and then southwestward along the northern slope of the South China Sea. Because of the topography, the Kuroshio-Island interaction produces a series of mesoscale anticyclonic eddies between the southwest Taiwan and the Dongsha islands (Hu et al., 2000; Wang et al., 2003; Yuan et al., 2006). The dominant path of the South China Sea branch of Kuroshio Current shifts southward and becomes weak in summer (Yuan et al., 2006). Besides the seasonal changes driven by monsoon, the cyclonic eddy west to Luzon is active all year around at approximately the same location, and the Luzon coastal current always flows to the north.



Figure 1.5 Land-sea distribution configurations of the South China Sea with surface circulation patterns during interglacial and glacial periods (after Liu et al., 2016).

(A) Modern/interglacial situation; (B) Glacial situation with a 120-m descending of sea-level.

Looking back in time, the surface circulation may not be always the same as what we presently observe. On the glacial-interglacial scale, sea-level changes dramatically. The low sea-level during glacial periods exposes the vast shelves and reduces the basin surface by approximately half. Most of the straits were closed, water exchanges can only occur between the South China Sea and the Pacific Ocean through the Luzon Strait. Assuming that the direction of monsoon winds did not change in glacial periods, a basin-wide cyclonic (anticyclonic) gyre would form in winter (summer) (Wang et al., 1995), while the Guangdong coastal current would be driven by the winter (summer) monsoon to flow southwestward (northeastward) in winter (summer) (Fang et al., 1998). The time-series variations in the intrusion of Kuroshio Current may not response directly to this glacial-interglacial cyclicity. Modern observations and numerical modellings suggest that the intrusion is related to the state of the El Nino Southern Oscillation (ENSO) (Chiang et al., 2010; Qu et al., 2004; Yang et al., 2014). The Luzon strait transport can therefore deliver the signal of ENSO to the South China Sea (Qu et al., 2004).

#### 1.4.2 Deepwater current

Differently from the surface circulation that is predominantly driven by the wind field, the deepwater current is mainly driven by the temperature and salinity gradients between water masses. The deepwater in the South China Sea, which is usually defined as the water mass below 1500 m water depth, originates only from the Pacific Ocean through the Luzon Strait. Hydrological observations at the Luzon Strait and numerical modelling show that, at present, the deep Pacific water firstly enters the Luzon Strait, then flows southward along the Luzon Trough, and finally intrudes the South China Sea through two gaps in the Heng-Chun Ridge (Zhao et al., 2014) (Fig. 1.6). Although the path of the Pacific water in the deep South China Sea has not been directly observed, numerical modellings and hydrological investigations shed light on the deep South China Sea circulation. The density distribution in the sea basin suggests a cyclonic boundary current system (Qu et al., 2006). Numeric modelling confirms the existence of such a basin-scale cyclonic circulation, which is related to the salinity gradient and the deepwater overflow in Luzon Strait (Lan et al., 2013; Wang et al., 2011a). The insitu observation by mooring systems and clay mineral distribution in the surface samples suggest that this deepwater current and the associated mesoscale eddies can efficiently deliver the suspended particles westward along the northern slope (Liu et al., 2016; Zhang et al., 2014; Zhao et al., 2015) (Fig. 1.4).



Figure 1.6 Mean volume transport of deepwater at the bottom layer (1900 m to bottom) crossing the Luzon Strait (after Zhao et al., 2014).

The cross sections are illustrated by pink lines with corresponding volume transports noted beside.

### 1.5 Fluvial inputs and surface sediments distribution

The highest erosion rate occurs in western tropical Pacific and South China. The continents and islands in this region represent only 2% of total lands, but they annually deliver  $4.2 \times 10^3$  Mt of clastics to the ocean, representing 20-25% of the global fluvial sediment discharge (Milliman and Farnsworth, 2011; Milliman et al., 1999). Acting as the largest marginal sea, the South China Sea annually receives more than 700 Mt of terrigenous sediments, and most of them are supplied from the adjacent lands by three world-class large rivers (i.e., the Mekong River, the Red River, and the Pearl River) and numerous mountainous rivers on islands (Fig. 1.7) (Liu and Stattegger, 2014).

In general, the fluvial sediment discharge exponentially depends on the drainage area and the altitude difference. That is the reason that the large rivers present strong sediment discharges. For instance, the Mekong River, the Red River, and the Pearl River annually delivers 160 Mt, 130 Mt, and 84 Mt of sediments, respectively, into the South

China Sea (Milliman and Farnsworth, 2011; Milliman and Syvitski, 1992; Zhang et al., 2012). However, the sediments from the Mekong River and the Red River can barely reach the northern part of the South China Sea due to the well-developed deltas and the topography of the Gulf of Tonkin. The Pearl River is therefore the only major river that supplies the northern South China Sea.



Figure 1.7 Fluvial drainage systems and their annual sediment discharge to the northern South China Sea (after Liu et al., 2016).

Taiwan is an island of 36000 km<sup>2</sup> with the highest altitude of over 3000 m at the central ridge. It is the most important source of terrigenous clastics for the northern South China Sea, annually supplying 176 Mt of sediments (Dadson et al., 2003; Huh et al., 2009; Liu et al., 2006; Milliman and Farnsworth, 2011). Although the drainage areas of rivers in Taiwan are much less than that of the Pearl River, several factors, including the steep topography, the active tectonic, and the frequent catastrophic typhoon/storm events, largely increase the river denudation in Taiwan. For instance, the cyclone-driven floods have been observed to deliver huge amounts of clastic sediments to the abyssal basin of the South China Sea (Hilton et al., 2008; Liu et al., 2012a), and seismic-triggered landslides can sharply enhance the fluvial sediment evacuation (Hovius et al., 2011; Meunier et al., 2008).

Luzon is also located on the Pacific Rim of Fire with active volcanic activity. Its fluvial drainage system is well-developed. The biggest river, the Cagayan River, drains the northern part of Luzon and finally flows into the Luzon Strait. The second biggest river, the Pampanga River, flows through the southern part of Luzon to the Manila Bay. Numerous small rivers that supply the South China Sea are distributed in the western part of Luzon. Based on the available sediment load data, the total sediment discharge of Luzon to the South China Sea is estimated to be 42 Mt/yr at present (Liu and Stattegger, 2014).

These terrigenous sediments compose approximately 80% of the total deposits in the northern part of the South China Sea while the rest 20% is biogenic carbonates and silicates (Wang and Li, 2009). Their distribution in the surface sediments is closely related to water depth and topography. In general, the shallow shelf deposits mainly consist of terrigenous clays and silts with minor bioclasts, the deposits on slope are composed of both biogenic (carbonates and silicates) and terrigenous clastics, and the abyssal deposits are mainly terrigenous clays with biogenic silicates (Wang and Li, 2009).

## **Chapter 2**

### Material and Methods

In order to reach the goals of this study as described in the "General Introduction", the sediment core MD12-3432, retrieved from the northern South China Sea, is analyzed. Clay mineralogy, magnetic properties, major element compositions, and grain sizes are investigated. In the present chapter, the sediment core and the analytical methods adopted to achieve the objectives will be presented in details.

#### 2.1 Material

The 50.8 m long Calypso core MD12-3432 (19°16.88' N, 116°14.52' E, water depth 2125 m) was retrieved in 2012 on board the R.V. *Marion Dufresne* during the French-Chinese CIRCEA cruise organized within the co-laboratory frame "Laboratoire International Associé - MONsoon, Ocean and Climate" (LIA-MONOCL). It is located on the East slope of a giant canyon, which is supposed to be paleo-Pearl River canyon, in the northern South China Sea. Sediment of core MD12-3432 is homogenously dominated by gray clays with several intervals rich in foraminifera and organic matter (Kissel et al., 2012). No turbiditic layer is observed in the sediment sequence of core MD12-3432.



Figure 2.1 Map of the northern South China Sea.

The location of core MD12-3432 illustrated by the yellow star.

On board the *Marion Dufresne*, after the core has been brought back on the deck, a fiducial line was drawn along the plastic tube before cutting the core into 1.5 m segments. Although the core was not azimuthally oriented, the relative orientation of the different sections was preserved within about 5°. The core sections were then split longitudinally along the fiducial line. The split-cores were wrapped and packed in Dtubes and stored in 4°C cold container onboard. The working half of the core is stored
at State Key Laboratory of Marine Geology (China) and the archive half is stored at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, France).

## 2.2 Clay minerology

X-ray diffraction identification of clay minerals was conducted on clay fraction (<2  $\mu$ m) of 504 discrete samples collected on the working halves of the core. The raw sediments were firstly leached with 0.1 N hydrochloride acids (HCl) to remove carbonate fractions. The mixtures were then rinsed several times by deionized water to remove the acid residues. Once the potential of hydrogen (pH) of the solution was close to neutral (pH $\approx$ 7), it is prepared to make the oriented-mounts of non-calcareous clay fractions. The mixture was carefully shaked to make it homogeneously dispersed, and kept immobile for 95 min for decantation. The uppermost 2 cm of the mixture was then extracted using a needle syringe. According to the Stokes' Law, after a 95 minutes' settling, the uppermost 2 cm of the mixture is totally composed of particles <2  $\mu$ m, if we take 2.65 g/cm3 as the average density of the clay (typical value for clay minerals, Holtzapffel, 1985). The obtained mixtures were centrifuged at 5000 rpm (revolutions per minute) for 15 min to separate water from the clayey sediments. The muds were carefully smeared on customized glass slides to make the oriented mounts and were air-dried.

The air-dried samples were measured on an X-ray diffractometer to obtain the spectra. The oriented slides were then measured again after being placed into an atmosphere of ethylene glycol vapor for at least 24 hours. As smectite is a group of stratified minerals the structures of which are expansible, the ethylene glycol saturation action will make the smectite yields extra d-spacing so that it can be distinguished from chlorite on the X-ray diffractograms. One out of every five samples was measured after heating at 490°C during 2 hours to identify potential changes in the nature of clay minerals. The measurements were performed using PANalytical X'Pert Pro Diffractometer at State Key Laboratory of Marine Geology, Tongji University. The samples were X-rayed in the range  $3-30^{\circ}2\theta$  with a step of  $0.03^{\circ}2\theta$  and a measuring time of ~1 second/step.

Proportions of different clay groups were semi-quantitatively calculated by MacDiff program (Petschick, 2001) basing on peak areas of basal reflections for the main clay mineral groups on ethylene glycol saturated samples. Mixed-layers of smectite-illite (15–16 Å) were included in "smectite", whereas mixed-layers of chloriteillite (11–13 Å) with very minor abundance were not calculated. As the (002) reflection of chlorite (d $\approx$ 7.1 Å) overlaps the (001) reflection of kaolinite (d $\approx$ 7.1 Å), relative proportions of kaolinite and chlorite were determined by ratios of areas of the kaolinite (002) peak (3.57 Å) and chlorite (004) peak (3.54 Å). Relative content of smectite, illite, chlorite and kaolinite were given in percentages of total clay mineral assemblage. The weighting factors introduced by Biscaye (1965) or Holtzapffel (1985) were not employed when generating relative weight percentages of each clay mineral, because such regular weighting factors actually do not exist by systemic experiences (Gensac, 2008). In addition, some mineralogical characters of illite were determined on glycolated curve. Illite crystallinity was estimated using the half height width of the 10 Å peak (Petschick et al., 1996). The low value represents the high crystallinity, which can be an indication of weak hydrolysis in continental sources and arid and cold climate conditions (Chamley, 1989). All the clay mineralogical measurements were carried out at State Key Laboratory of Marine Geology, China.

## 2.3 Magnetic properties

The archive half of the core was sampled using  $2 \times 2 \times 150$  cm, open-sided, u-shaped, non-magnetic, stiff and transparent plastic tubes (u-channels) (Weeks et al., 1993) in order to continuously measure the magnetic properties of magnetic susceptibility and remanent magnetizations (e.g. King et al., 2000; Kissel et al., 2010; 2013; Sagnotti et al., 2003; Stoner and St-Onge, 2007; Weeks et al., 1993). The u-channels were pushed into the central surface of the split-core, cut free using fishing lines, removed from the core, wrapped with plastic film and capped with matching plastic lids. After the measurements of u-channels at 321 horizons to measure the hysteresis parameters. Standard discrete samples were also collected on the archive halves at 14 horizons for the investigation of thermal behavior of magnetic fractions. The  $2 \times 2 \times 2$  cm plastic cubic boxes with a small hole at bottom were pushed into the split-cores, cut free, removed from the sediment, wrapped with plastic film and closed with matching caps. An arrow towards core-top was drawn at the bottom of each box to orient the samples. All the magnetic properties were measured at LSCE, France.

## 2.3.1 Magnetic susceptibility and remanent magnetizations

The continuous measurements of low-field susceptibility and remanent magnetizations were performed on the u-channels of core MD12-3432 following the standard procedure followed at LSCE (Kissel et al., 1998; 2010; 2013).

The magnetic susceptibility was measured with a Bartington MS2C 45-mm diameter susceptibility bridge at 2 cm intervals with a resolution of about 4 cm. The susceptibility ( $\kappa$ ) was normalized to volume.

The Natural Remanent Magnetization (NRM) was measured every 2 cm using a 2G-755R cryogenic magnetometer equipped with high-resolution pick-up coils (~ 4 cm resolution) and placed in the  $\mu$ -metal shielded room at LSCE. It was stepwise demagnetized using alternating fields (AF) along the three perpendicular axes using AF coils installed in-line with the magnetometer. The successive peak fields used for demagnetization are 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60 and 80 mT. The u-channels were translated at a 4 cm/s speed through the coils. The stepwise demagnetizations allow to remove the contribution of low-stability secondary magnetization that formed after deposition and thus to define the stable component of NRM called Characteristic Remanent Magnetization (ChRM). The direction (declination and inclination) of the ChRM at each horizon has been determined using a principle component analysis and a least-square fit (Kirschvink, 1980; Mazaud, 2005). The accuracy of the directions was given by the maximum angular deviation (MAD). The obtained declinations were used to orient the core in geographic frame assuming that on the long-term, declinations should average around 0°.

The Anhysteretic Remanent Magnetization (ARM) was acquired in-line along the vertical axis in a 100 mT alternating field superimposed to a steady 50  $\mu$ T bias field parallel to the AF. The samples were translated through the coil at a speed of about 1 cm/s during the acquisition (Brachfeld et al., 2009). The ARM was then progressively demagnetized with 11 steps at 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 80 mT and measured after each demagnetization step using the same instrument and same setting as for NRM.

The Saturation Isothermal Remanent Magnetizaiton (SIRM) was acquired within 6 steps (0.05, 0.1, 0.2, 0.3, 0.5, 1 T) also along the vertical (z) axis using a 2G 1.6 m long pulsed solenoid. The IRM was also measured every 2 cm after each step in order to construct the acquisition curves giving the access to the magnetic hardness of the sediment at each measured horizon. The SIRM was then stepwise demagnetized using the same steps as for ARM. During the demagnetization and measurement, the samples

moved at a speed of about 4 cm/s through the coils. The median destructive field of IRM (MDF<sub>IRM</sub>) as well as the percentage of magnetization remaining after demagnetization at 80 mT with respect to SIRM (IRM<sub>AF@80mT/RM1T</sub>) =  $100\% \times$  IRM<sub>AF@80mT/IRM1T</sub>) could be calculated. A backfield of -0.3 T was applied to the SIRM1T to calculate the S-ratio (S<sub>0.3T</sub> = -IRM<sub>-0.3T</sub>/IRM<sub>1T</sub>) (King and Channell, 1991), HIRM (=  $0.5 \times$ (SIRM+IRM<sub>-0.3T</sub>)) (Robinson, 1986).

## 2.3.2 Hysteresis parameters

The hysteresis loops were obtained between +1 and -1 T using an alternating gradient magnetometer (AGM2900). Saturation magnetization (Ms), remanent saturation magnetization (Mrs), and coercive force (Hc) were determined after the correction for high field slope representing the para- and diamagnetic components. The remanent coercive force (Hcr) was measured separately after applying stepwise increasing back-fields to the Mrs. Replicate measurements were performed on randomly selected samples to check the precision and sample representativeness. High-resolution IRM acquisition curves (150-200 steps between 0 and 1 T) were then obtained from 32 samples. They were decomposed (Kruiver et al., 2001; Robertson and France, 1994) into different coercivity components defined by their half IRM acquisition field (B1/2) and their relative contribution to SIRM.

## 2.3.3 Thermal demagnetization

The thermal evolution of the different coercivity components has been evaluated by high-temperature demagnetization of three-axis IRM. Fields of 1, 0.3, and 0.1 T were successively applied to the three axes of dried cubic samples using the Applied Physics pulse magnetizer 2G660. The samples were then demagnetized by stepwise heating from room temperature to 700°C using a zero-field PYROX furnace, in which the temperature gradient over the samples are lower than 3-4 °C at high temperature. The IRM remaining on each axis after each step was measured using a 2G-755R cryogenic magnetometer equipped with high-homogeneity pick-up coils also placed in the  $\mu$ metal shielded room at LSCE together with the furnace.

## 2.4 Major element compositions

The major element compositions were measured by two means, the low-resolution quantitative X-ray fluorescence (XRF) analysis and the high-resolution semiquantitative XRF core-scanning. Both of them were conducted at State Key Laboratory of Marine Geology, China. The analytical procedures are introduced below. The semiquantitative XRF core-scanning data were further corrected and converted into quantitative major element compositions in order to better evaluate the environmental evolution. The method of the correction and conversion is introduced in Chapter 3.

## 2.4.1 Low-resolution quantitative analysis

To quantitatively determine the major element composition, wavelength dispersive X-ray fluorescence analyses (hereafter called "WD-XRF") were conducted on 102 discrete bulk sediment samples taken every 50 cm from the center of the working sections with a cubic container  $(2 \times 2 \times 2 \text{ cm})$ . These discrete samples were firstly freezedried and manually ground in order to eliminate the potential influences of grain size and water content. Then,  $0.70000\pm0.0008$  g of sediment was melted with  $7.0000\pm0.0008$  g of a fusion agent (mixture of lithium tetraborate and lithium metaborate) into a bead (3.7 cm diameter, 0.7 cm thick). The prepared sample beads were measured with a PANalytical AXIOSmAX wavelength dispersive XRF spectrometer. Replicated analyses were performed on the Chinese rock and sediment standards (i.e. GSR6 and GSD15) every day at the beginning of the measurement runs to control the analytical precision and accuracy. These analyses indicate a relative standard deviation lower than 1% and a relative accuracy lower than 6%.

The inductive coupled plasma atomic emission spectrometer (ICP-AES) analyses were performed on 22 additional samples to confirm the reliability of WD-XRF major element concentrations. Dried and ground bulk sediments were heated at 600°C for 4 hours to remove organic matter. Their weights were measured before and after heating to calculate the loss on ignition (LOI). The sediments were digested in HF+HNO3 mixed acid. Major elements were then measured on an IRIS Advantage ICP-AES. A series of Chinese rock and sediment standards (i.e. GSR5, GSR6 and GSD9) were measured together with the sediments. The mean relative accuracy estimated from these standard samples is better than 4%.

## 2.4.2 High-resolution semi-quantitative analysis

High-resolution XRF core-scanning was performed on the working half of the core using an Avaatech XRF Core Scanner to semi-quantitatively estimate the variations in major elements compositions. The measurements were conducted following the standard procedure (Xie et al., 2014). Each core section was firstly moved from refrigeration to the lab to be stored at room temperature for at least 2 hours. The sediment surface was then smoothed and covered with a 4  $\mu$ m-thick ultralene film. XRF-scanning data were collected every 1 cm over a 1×1.6 cm<sup>2</sup> area with a counting time of 30 seconds per sample. A generator setting with a voltage of 10 kV and a current of 0.2 mA was used for the major element (<sup>13</sup>Al to <sup>26</sup>Fe) measurements. No filter was used.

## 2.5 Granulometry (sortable silt)

The mean size of the detrital fraction in the sortable silt range ( $\overline{SS}$ ) was investigated on 140 discrete samples collected in the archive half of the core. The samples were dried at 50°C. Biogenic carbonates were dissolved by acetic acid (20%). The excessive acid was removed through centrifuging (2000 rpm, 7 min) and rinsing with deionized water for three times. Organic matter was removed using hydrogen peroxide (33%) at 85°C, and the mixture was centrifuged (2500 rpm, 10 min) three times to isolate the terrigenous component. The samples were sieved using a 63 µm mesh and mixed in a Calgon solution (sodium hexametaphosphate, 0.2%) in an ultrasonic bath for 2 min. The grain size distribution was measured using a Beckman Multisizer 3 Coulter Counter, counting 10,000 particles with a 100 µm aperture tube on samples suspended in Coulter Isoton II diluent. Two runs were performed with a total of 500,000 to 600,000 particles passing through the aperture. The number of particles counted in the 10-63 µm range exceeds 10,000 (McCave et al., 2005). A total of 33 replicate samples were prepared and measured and the results indicate a standard deviation  $\leq 4.1\%$  and an uncertainty of  $\pm 0.71 \mu m$ . The grain size analysis was conducted at LSCE, France.

## **Chapter 3**

## Marine sediment XRF scanning calibration

X-ray fluorescence (XRF) core-scanning provides a fast and nondestructive solution to obtain compositional variations of major and trace elements in sediment sequences. Over the past decades, it has been increasingly used in reconstructing paleoenvironment (Collins et al., 2013; Govin et al., 2014; Jaccard et al., 2005; Mulitza et al., 2010; Norris and Röhl, 1999; Peterson et al., 2000; Röhl and Abrams, 2000; Tjallingii et al., 2010). However, controversial issues have been raised regarding the its reliability, because the XRF core-scanning semi-quantitatively measures the element compositions as intensities, which may be notably influenced by various factors, such as water content, grain size, and matrix effect (Hennekam and de Lange, 2012; Löwemark et al., 2011; Lyle et al., 2012; Tjallingii et al., 2007; Weltje et al., 2015; Weltje and Tjallingii, 2008). It is therefore necessary to examine the accuracy of existing calibration methods on major element composition of Core MD12-3432 obtained by XRF core-scanning before using their results for paleoenvironmental interpretations. In this study, we compared the raw XRF core-scanning data and calibrated results with quantitatively measured major element composition of Core MD12-3432. We also identified the main factor that influences the accuracy of XRF core-scanning and calibrated data. A correction is then proposed and implemented in the calibration methods to account for this effect. We finally examined the performances of these improved calibration approaches by applying them on Core MD12-3432. The results indicate that they are so far the most appropriate calibration approaches for long sediment sequences with large downcore variations in interstitial water content. Although they were tested on only one sediment sequence, these calibration methods at least provide robust major element records of Core MD12-3432 for paleoenvironmental studies. It is highly recommended to apply these calibration approaches on more long sediment sequences.

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#### **Key Points:**

- Changes in interstitial water is the main factor to be corrected for XRF intensities in long cores
- A polynomial correction of interstitial water effect is proposed and applied to two existing XRF calibration methods
- The two improved calibrations proposed here are suited for correcting varying water contents in long sediment cores

#### Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3

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## Correction of interstitial water changes in calibration methods applied to XRF core-scanning major elements in long sediment cores: Case study from the South China Sea

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**Abstract** Fast and nondestructive X-ray fluorescence (XRF) core scanning provides high-resolution element data that are widely used in paleoclimate studies. However, various matrix and specimen effects prevent the use of semiquantitative raw XRF core-scanning intensities for robust paleoenvironmental interpretations. We present here a case study of a 50.8 m-long piston Core MD12-3432 retrieved from the northern South China Sea. The absorption effect of interstitial water is identified as the major source of deviations between XRF core-scanning intensities and measured element concentrations. The existing two calibration methods, i.e., normalized median-scaled calibration (NMS) and multivariate log-ratio calibration (MLC), are tested with this sequence after the application of water absorption correction. The results indicate that an improvement is still required to appropriately correct the influence of downcore changes in interstitial water content in the long sediment core. Consequently, we implement a new polynomial water content correction in NMS and MLC methods, referred as NPS and P\_MLC calibrations. Results calibrated by these two improved methods indicate that the influence of downcore water content changes is now appropriately corrected. We therefore recommend either of the two methods to be applied for robust paleoenvironmental interpretations of major elements measured by XRF-scanning in long sediment sequences with significant downcore interstitial water content changes.

#### 1. Introduction

Major element compositions of marine and lacustrine continuous sedimentary sequences have a great potential in a wide variety of research topics such as chronology, stratigraphy, sedimentology, paleoenvironment, and paleoceanography [*Norris and Röhl*, 1999; *Peterson et al.*, 2000; *Röhl and Abrams*, 2000; *Jaccard et al.*, 2005; *Mulitza et al.*, 2010; *Tjallingii et al.*, 2010; *Collins et al.*, 2013; *Govin et al.*, 2014]. Different approaches and methods have been used during the last years. The conventional geochemical analytical methods have high precision and accuracy. However, they are time consuming and, more importantly, they require a large number of destructive analyses to produce high-resolution downcore records of major element concentrations. X-ray fluorescence (XRF) core scanning techniques provide a nondestructive alternative to rapidly perform nearly continuous element measurements directly from the surface of untreated split sediment cores [*Jansen et al.*, 1998; *Kido et al.*, 2006; *Weltje and Tjallingii*, 2008]. The advantages of XRF core scanner over conventional destructive techniques led to its intensified use over the last decade.

The main drawback of XRF core-scanning (hereafter referred as "XRF-scanning") is that the element compositions are only semiquantitatively measured as element intensities and do not directly represent element concentrations in bulk sediments. Although XRF-scanning intensities are reported to be linearly correlated with element concentrations [e.g., *Jansen et al.*, 1998; *Böning et al.*, 2007], the linear relationship may be notably altered by various specimen and matrix effects [*Tjallingii et al.*, 2007; *Weltje and Tjallingii*, 2008; *Löwemark et al.*, 2011; *Hennekam and de Lange*, 2012; *Lyle et al.*, 2012; *Weltje et al.*, 2015]. Because these effects have different amplitudes depending on the element, even element ratios derived from XRFscanning intensities may be strongly affected, inducing large uncertainties for paleoenvironmental interpretations. These features prevent the use of raw XRF-scanning element intensities or ratios from most paleoclimatic studies. Correction of these effects is, therefore, necessary for robust paleoenvironmental interpretations [e.g., *Tjallingii et al.*, 2007; *Hennekam and de Lange*, 2012; *Dang et al.*, 2015]. Most existing correction methods only partially correct the matrix and specimen effects in sediment sequences [e.g., *Kido et al.*, 2006; *Tjallingii et al.*, 2007; *Löwemark et al.*, 2011; *Hennekam and de Lange*, 2012]. Besides "single-effect" corrections [e.g., *Löwemark et al.*, 2011; *Hennekam and de Lange*, 2012], integrated calibration methods have been developed to take into account multiple effects. *Weltje and Tjallingii* [2008] proposed the log-ratio calibration equation (LRCE), which has recently been updated to a multivariate log-ratio calibration (MLC) that better accounts for the matrix effect and is able to predict bulk element concentrations [*Weltje et al.*, 2015]. In parallel, *Lyle et al.* [2012] suggested a quick approach, the normalized median-scaled (NMS) method, to estimate sedimentary component concentrations in bulk sediments. The NMS method takes into account downcore density changes and differences in element efficiencies in producing characteristic X-ray.

XRF-scanning element intensities of long sedimentary sequences may exhibit an additional bias due to the downcore decrease in interstitial water induced by sediment compaction. So far, the NMS method is the only existing XRF calibration that has been applied on long sedimentary sequences, but a long-term bias was still observed in the NMS-calibrated CaCO<sub>3</sub> profile [*Lyle and Backman*, 2013].

In order to propose the most appropriate calibration methods to be applied in long sediment sequences, we use here a case study, performing element composition and XRF-scanning analyses on a 50.8 m-long core (MD12-3432) retrieved from the northern South China Sea. Through a quantitative comparison of XRF-scanning intensities and measured concentrations, we identify downcore changes in interstitial water content as the key factor influencing XRF-scanning intensities in this core. We then assess the performance of the existing correction and calibrations. Because they do not efficiently correct such water content changes, we implement them with a new correction, bringing us one step forward toward robust quantitative interpretations of major elements in long sedimentary sequences.

#### 2. Material and Analytical Methods

Core MD12-3432 (19°16.88' N, 116°14.52' E, 2125 m water depth) was retrieved in 2012 onboard the R.V. *Marion Dufresne* during the French-Chinese CIRCEA cruise organized within the LIA-MONOCL framework [*Kissel et al.*, 2012]. The core is 50.8 m long and it is located on the northern slope of the South China Sea, approximately 340 km offshore the Pearl River mouth. The sediment lithology is homogenously dominated by gray clays with several layers rich in organic matter, and the fractional porosity is higher in top sections than in lower sections [*Kissel et al.*, 2012].

XRF core-scanning of major elements was performed on the working half of the core using an Avaatech XRF Core Scanner with standard procedures [*Xie et al.*, 2014]. Each core section was removed from refrigeration at least 2 h before smoothing the surface and covering with a 4  $\mu$  thick ultralene film to avoid water condensation below the film. XRF-scanning data were collected every 1 cm over a 1.6 cm<sup>2</sup> area with a downcore slit size of 10 mm and a counting time of 30 s per sample. Major element (<sup>13</sup>Al to <sup>26</sup>Fe) measurements were performed with a generator setting of 10 kV and a current of 0.2 mA, no filter was used.

In order to calibrate XRF-scanning intensities, 102 discrete bulk sediment samples were taken every 50 cm from the center of the working sections with a cubic container ( $2 \times 2 \times 2$  cm). These discrete samples were first freeze-dried and weighted to calculate their dry bulk density. To quantitatively determine the major element composition of discrete sediment samples, wavelength dispersive XRF analyses (hereafter called "WD-XRF") were conducted. The dried bulk sediment was first manually ground in order to eliminate the potential influences of grain size. Then,  $0.70000 \pm 0.0008$  g of sediment was melted with 7.0000  $\pm$  0.0008 g of a fusion agent (mixture of lithium tetraborate and lithium metaborate) into a sample bead (3.7 cm diameter, 0.7 cm thick). The prepared sample beads were measured with a PANalytical AXIOS<sup>mAX</sup> wavelength dispersive XRF spectrometer. Replicated analyses of the Chinese rock and sediment GSR6 and GSD15 standards were conducted every day at the beginning of the measurement runs to control the analytical precision and accuracy, and indicated a relative standard deviation lower than 1% and a relative accuracy lower than 6%. The use of complementary inductive coupled plasma atomic emission spectrometer (ICP-AES) analyses performed on additional discrete samples confirms the reliability of WD-XRF major element concentrations (see details in supporting information text S1).

Water content was measured at LSCE, France, by weighing 53 bulk sediment samples taken from the same horizons as WD-XRF samples, before and after drying. All other geochemical analyses were completed at the State Key Laboratory of Marine Geology (Tongji University), China. All data sets are available in supporting information.

#### 3. Experimental Results

Noncalibrated XRF-scanning intensities (supporting information Data Set S1) and WD-XRF concentrations (supporting information Data Set S2) obtained in Core MD12-3432 are shown in Figure 1.

In this core, XRF-scanning Al, Si, and K intensities are relatively constant along the lower 25 m and progressively decrease upward along the upper 25 m of the core. Ca intensity continuously decreases upward, while Ti and Fe intensities remain relatively stable. WD-XRF concentrations do not exhibit such clear longterm trends, except for Si and Ca concentrations that slightly increase and decrease, respectively, upward along the core. WD-XRF concentrations of other elements are relatively stable throughout the core. Besides these long-term variations, rapid changes are observed both in XRF-scanning intensities and WD-XRF concentrations (despite their lower resolution) throughout the core. They are characterized by low intensities or concentrations of terrigenous elements (Al, Si, K, Ti, and Fe) and synchronous high Ca intensities or concentrations (Figure 1, yellow-shaded areas).

The linear relationship between XRF-scanning intensities and WD-XRF concentrations is not always sufficiently well-defined for direct linear calibration. The correlation coefficient (R<sup>2</sup>), which is calculated using the WD-XRF data and XRF-scanning intensities from the same horizon, is high for Ca, moderate for K, Ti, and Fe, and low for Al and Si (Table 1).

To evaluate the differences between the between XRF-scanning and WD-XRF data measured at the same horizon, intensities are first scaled to the median concentration value of a given element, and relative differences ( $\Delta$ ) are then calculated. For element *e* at depth *d*, the relative difference ( $\Delta_{e,d}$ ) is defined using equation (1):

$$\Delta_{e,d} = (I_{e,d}/I_{e,M} \times W_{e,M} - W_{e,d})/W_{e,d}$$
(1)

where  $W_{e,M}$  and  $I_{e,M}$  are the median values of all WD-XRF concentrations, and all XRF scanning intensities, respectively, of element *e*,  $W_{e,d}$  and  $I_{e,d}$  are WD-XRF concentration and the XRF scanning intensity, respectively, of element *e* at depth *d*.

These relative differences are also reported in Figure 1 for each element. They present diverse but notable long-term evolutions for the different elements. Indeed, while  $\Delta_{Ti}$  and  $\Delta_{Fe}$  are relatively constant through-out the core,  $\Delta_{Al}$ ,  $\Delta_{Si}$ , and  $\Delta_K$  are relatively high (~10%) in the lower 25 m of the core and decrease to negative values in the upper section. In contrast,  $\Delta_{Ca}$  decreases by about 40% from the bottom to the top of the core. Such trends in relative differences suggest that specimen or matrix effects have affected the XRF-scanning intensities of Core MD12-343.

#### 4. Assessing the Influence of Matrix and Specimen Effects in Core MD12-3432

The matrix effect corresponds to the scattering, absorption, and enhancement of XRF-scanning intensity caused by the presence of other elements. For instance, high Ca concentration absorbs the X-ray fluorescence of Ti and Fe, and causes excess excitation for K, resulting in artificially decreased Ti and Fe intensities and increased K intensities [*Kido et al.*, 2006; *Böning et al.*, 2007; *Kujau et al.*, 2010]. In Core MD12-3432, the absence of a clear pattern in  $\Delta$  records of K, Ti, and Fe in the intervals corresponding to Ca concentration peaks (Figure 1, yellow-shaded areas) indicates (1) that these short-term variations result from the relative dilution of biogenic material by terrigenous input and (2) that the Ca-content-related matrix effect has a very limited influence in Core MD12-3432.

Several sedimentary conditions are included in the so-called specimen effects. They were partly reduced in this case by smoothing the surface of split core before covering with the ultralene film and by the removal of low-quality data points induced by gaps and cracks within the sediment. Another possible specimen effect is the dry bulk density, which may increase the volume-normalized intensity of a given element. Indeed, higher dry bulk density increases the amount of all measured target elements and hence results in

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**Figure 1.** Downcore changes in XRF-scanning intensities and discrete WD-XRF element concentrations. (a) Dry bulk density (black dots); (b) XRF-scanning CI intensity; (c) water content (blue dots); (d–i) WD-XRF element concentrations of both calibration (open brown diamonds) and evaluation data sets (solid brown diamonds), XRF-scanning intensities (gray lines), and relative differences ( $\Delta$ , blue diamonds) of (d) AI, (e) Si, (f) K, (g) Ca, (h) Ti, and (i) Fe. Red and dark gray lines are the quadratic polynomial fits calculated from all discrete bulk sediment concentrations and XRF-scanning intensities, respectively. Yellow-shaded areas highlight short time intervals with high Ca concentrations (see sections 3 and 4).

higher intensities of all elements [*Lyle et al.*, 2012]. However, increased density may also reduce the transmission distance of X-ray, resulting in a decrease of analyzed sediment volume. In Core MD12-3432, the dry bulk density is significantly higher at the bottom than at the top of the core (Figure 1a), as commonly observed in long sediment cores because of the natural sediment compaction (e.g., in IODP sediment sequences [*Lyle et al*, 2012] and Calypso cores) and potential coring-induced stretching. Relatively constant XRF-scanning intensities and  $\Delta$  values of heavy elements (Ti and Fe) throughout the core (Figures 1h and 1i) suggest here a limited influence of downcore changes in dry bulk density on XRF-scanning intensities in Core MD12-3432. **Table 1.** Comparative Performance of Calibrations Based on the Independent Evaluation Data Set (Except for Regressions With Raw XRF-Scanning Intensities, see Footnote)<sup>a</sup>

					R²			
	MSRE	AI	Si	К	Ca	Ti	Fe	Average
Raw intensities <sup>b</sup>		0.29	0.21	0.62	0.95	0.77	0.73	0.59
W_NMS <sup>c</sup>	0.00169	0.93	0.94	0.92	0.98	0.84	0.66	0.88
W_MLC <sup>c</sup>	0.00183	0.81	0.96	0.91	0.99	0.68	0.49	0.81
NPS' <sup>d</sup>	0.00173	0.90	0.93	0.90	0.97	0.85	0.66	0.87
NPS <sup>e</sup>	0.00159	0.91	0.95	0.92	0.97	0.86	0.68	0.88
P_MLC <sup>e</sup>	0.00174	0.90	0.95	0.91	0.97	0.74	0.54	0.83

<sup>a</sup>The calibration results are evaluated using their mean squared relative errors (MSRE) and R<sup>2</sup> with respect to concentrations or relative element proportions of the WD-XRF evaluation data set.

<sup>b</sup>The R<sup>2</sup> values are calculated from linear regressions between raw XRF-scanning intensities and WD-XRF concentrations from the same horizon (102 horizons).

<sup>c</sup>The water attenuation correction defined by *Hennekam and de Lange* [2012] was applied to XRF-scanning intensities prior to running the NMS and MLC calibrations.

<sup>d</sup>NPS calibration with normalizing to unity rather than to WD-XRF sums (section 6.1).

<sup>e</sup>The polynomial correction proposed in this study was applied to account for downcore interstitial water changes in long sediment cores.

Water attenuation is the most discussed specimen effect for sedimentary sequences, because the presence of water absorbs X-ray energy, preferentially affecting light elements with weak fluorescence energies, in particular Al and Si [*Ge et al.*, 2005; *Kido et al.*, 2006; *Tjallingii et al.* 2007; *Hennekam and de Lange*, 2012]. The water attenuation effect can derive from the water film formed under the covering foil or from downcore changes in the water content, which both need to be scrutinized.

In marine sediment cores, XRF-scanning CI intensity can be used as a proxy for water content [Kido et al., 2006; Tjallingii et al. 2007; Hennekam and de Lange, 2012]. In Core MD12-3432, Cl intensity decreases downcore (Figure 1b), similarly to the low-resolution water content decrease (Figure 1c) and in opposition with the dry bulk density increase (Figure 1a). Long-term changes in Cl intensity hence mainly represent variations in interstitial water content in this core. As core stretching is limited with the new coring device onboard R/V Marion Dufresne (we checked with other analyses that it does not exceed the top 1.5 m in Core MD12-3432), these simultaneous variations suggest that water content is gradually reduced downward due to natural sediment compaction. Therefore, the long-term trends of element intensities and  $\Delta$  values of lighter elements (Al, Si, K, and Ca), compared to the stability of heavier elements (Ti and Fe), most likely result from the increasing water contents in upper sections (Figure 1). In addition, coeval short-term increases in Cl intensity and decreases in dry bulk density (Figure 1, yellow-shaded areas) indicate that these short-term Cl changes predominantly represent variations in interstitial water content in this study (and not changes in the thickness of the water film as reported by Hennekam and de Lange [2012]). Coeval with low XRF intensity values for all terrigenous elements, independently from their atomic mass, these short-term water content increases have, however, a very limited impact on XRF-scanning intensities. Therefore, the XRF-scanning intensities in this study remain mainly affected by the long-term downcore decrease in interstitial water.

#### 5. Calibration Methods and Results

In order to determine which calibration method is the most suitable for long sedimentary sequences with large downcore water content variations, we tested on Core MD12-3432 the two most recent integrated calibrations, the NMS [*Lyle et al.*, 2012; *Lyle and Backman*, 2013], and MLC [*Weltje et al.*, 2015]. To test the most up-to-date calibration methods accounting for the water attenuation effect, we applied the correction of water absorption effect defined by *Hennekam and de Lange* [2012], prior to running the NMS and MLC calibrations (see calculation details in supporting information text S2). Hereafter, we refer to these water-corrected calibration methods as W\_NMS and W\_MLC. The effect of this water correction on NMS- and MLC-calibrated results is evaluated in supporting information, text S2.4.

Thirty-four of the samples analyzed by WD-XRF (hereafter called "calibration dataset") are used to convert XRF-scanning intensities into calibrated concentrations and relative proportions of six major elements (AI, Si, K, Ca, Ti, and Fe). The remaining 68 WD-XRF samples (hereafter called "evaluation dataset") are used to evaluate the quality of tested calibrations. The evaluation of calibrations is therefore done independently

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from the calibration data set. Several tries with different numbers of calibration versus evaluation data points yielded very similar results (not shown).

The mean squared relative error (MSRE) of elements is used below to quantitatively compare the performance of different calibrations. MSRE is calculated following equation (2):

$$MSRE = \frac{1}{nD} \sum_{d=1}^{n} \sum_{e=1}^{D} \delta_{e,d}$$
(2)

where *n* and *D* are the number of measured horizons and calibrated elements, respectively;  $\delta_{e,d}$  is the relative error of element *e* at depth *d* defined as:

$$\delta_{e,d} = (C_{e,d} - W_{e,d}) / W_{e,d} \tag{3}$$

where  $C_{e,d}$  is the calibrated value of element *e* at depth *d*,  $W_{e,d}$  is the WD-XRF concentration of element *e* at depth *d*.

#### 5.1. Normalized Median-Scaled Calibration (NMS) Applied to This Case Study

The NMS calibration [*Lyle et al.*, 2012; *Lyle and Backman*, 2013] builds a reasonable model to quickly estimate the concentrations of sedimentary components in bulk sediments (i.e.,  $Al_2O_3$ ,  $SiO_2$ ,  $K_2O$ ,  $CaCO_3$ ,  $TiO_2$ , and  $Fe_2O_3$  in this study) from a limited number of discrete measurements (see supporting information text S2.2 for the detailed procedure). Note that it was performed here on the water-corrected XRF-scanning intensities of Core MD12-3432 (see above). The W\_NMS-calibrated component concentrations were then converted to element concentrations (e.g., %Ca for Ca) in bulk sediments to simplify the comparison to element percentages provided by the MLC method (section 5.2).

The W\_NMS calibration significantly improves R<sup>2</sup> values, in particular for Al%, Si%, and K% (Table 1), compared to the direct linear correlation of raw XRF-scanning intensities with WD-XRF concentrations. Although, in first approximation, the W\_NMS-calibrated Al%, Ti%, ln(Al/Ti), and ln(Al/K) follow the variations shown by the WD-XRF evaluation data, long-term deviations are still observed for these records (Figures 2a–2d). Indeed, W\_NMS-calibrated ln(Al/Ti), ln(Al/K), and Al% are lower than those in the evaluation data set in the upper sections of the core, while they are higher in the bottom part (Figures 2a–2c). Their relative differences hence exhibit an upward decreasing long-term trend. The Ti%, as well as the associated relative differences, exhibits an opposite relationship (Figure 2d). These deviations are similar to those observed in raw XRF-scanning intensities (Figure 1) and in carbonate content of IODP core U1338 [*Lyle and Backman*, 2013]. As water preferentially absorbs weak fluorescence energies of light elements, these deviations suggest that the impact of water attenuation effect is not appropriately corrected.

#### 5.2. Multivariate Log-Ratio Calibration (MLC) Applied to This Case Study

Derived from the LRCE [*Weltje and Tjallingii*, 2008], the MLC method [*Weltje et al.*, 2015] is a mathematically rigorous method designed to calibrate element concentrations in bulk sediments (see details in supporting information text S2.3). The use of centered log-ratios and partial least squares regression allows MLC to better account for the matrix effect [*Weltje et al.*, 2015].

The MLC was performed on water-corrected XRF-scanning intensities of Core MD12-3432 (referred to as W\_MLC) using the XELERATE software available online (www.ascar.nl), choosing Ca as common denominator of all log-ratios (i.e., ln(Al/Ca), ln(Si/Ca), ln(K/Ca), ln(Ti/Ca), ln(Fe/Ca), mean  $R^2 = 0.97$ ). To ensure the comparison with other calibration methods, the W\_MLC was forced to perform the calibration with the entire WD-XRF calibration data set. As bulk concentrations are not predicted at the moment by the software, the calibrated relative proportions provided by the XELERATE software were used here to evaluate its performance.

W\_MLC-calibrated relative proportions of elements also show strong linear correlations to the WD-XRF evaluation data set. The R<sup>2</sup> value of MLC-calibrated Al% and Si% reach 0.81 and 0.96, respectively (Table 1), but the MSRE is larger than that of the W\_NMS calibration (Table 1). Similarly to W\_NMS-calibrated results, the W\_MLC-calibrated Al%, ln(Al/Ti), and ln(Al/K) are lower than the evaluation data points in the top sections of the core (Figures 2e–2g). These differences between W\_MLC-calibrated and WD-XRF results, which are also illustrated by the long-term trends in relative differences (Figures 2e–2h), suggest that the water attenuation effect is not appropriately corrected here either.

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Figure 2. Results of the improved calibrations. (a–d): NPS-calibrated results (orange lines) and W\_NMS results (blue lines), together with their relative errors (orange and small blue dots, respectively), are shown in Figure 2a (left) ln(Al/Ti), (b) ln(Al/K), and concentrations of (c) Al, (d) Ti. (e–h): P\_MLC-calibrated results (orange lines) and W\_MLC results (blue lines), together with their relative errors (orange and small blue dots, respectively), are shown in Figure 1e (right) ln(Al/Ti), (f) ln(Al/K), and relative proportions of (g) Al, (g) Ti. WD-XRF evaluation data are plotted as yellow dots.

#### 5.3. Ability of Existing Methods to Account for Interstitial Water Changes in This Case

The observed deviations between WD-XRF on one hand, and W\_NMS-calibrated (section 5.1) or W\_MLC-calibrated (section 5.2) results on the other hand, indicate that none of these two methods sufficiently accounts for downcore interstitial water changes, even after applying the water absorption correction to

raw intensities as proposed by *Hennekam and de Lange* [2012] (also see supporting information text S2.4).

The correction proposed by *Hennekam and de Lange* [2012], which was developed from three short sediment sequences where the effect of water absorption mainly derives from changes in the water film thickness, is indeed not sufficiently robust when water content variations are predominantly driven by interstitial water changes due to downcore sediment compaction as in this case study (see section 4). A more appropriate correction is therefore required for long sediment cores with large interstitial water content changes.

#### 6. Improved Correction and Its Implementation in XRF Calibrations

The major effect of the downcore decrease of interstitial water content on XRF-scanning intensities, expressed in this case study as a downcore increasing trend in light elements, suggests that it can be removed by correcting the long-term trend of XRF-scanning intensities. A quadratic polynomial fit, which is the simplest polynomial that best describes such downcore water content changes, is selected here to sub-tract this long-term variation. A simple polynomial subtraction directly applied to XRF-scanning intensities is not appropriate because gradual changes in XRF-scanning intensities and log-ratios incorporate not only the influence of water content changes but also long-term environmental signals. Therefore, the fit of the quadratic polynomial evolution of XRF-scanning intensities and log-ratios to that of WD-XRF data in the calibration data set allows to correct the gradual water content changes and to preserve environmental signals.

The details of correction and calibration procedures are summarized in the following sections and fully described in supporting information text S3.

#### 6.1. Normalized Polynomial-Scaled Calibration (NPS) Applied to This Case Study

The normalized polynomial-scaled calibration (NPS) proposed here, which is derived from the NMS calibration (section 5.1), also includes three steps: (1) scaling the raw XRF-scanning intensities to the range of WD-XRF component concentrations using quadratic polynomial fits (instead of median values as in NMS), (2) normalizing the sum of scaled intensities to that of WD-XRF concentrations (instead of unity as in NMS), which remains below 90% in Core MD12-3432 due to the presence of organic matter and other components not considered here, and (3) calibrating the normalized polynomial-scaled data to WD-XRF concentrations using linear regression equations. The calibrated component concentrations were then transformed to element concentrations to simplify the comparison with other methods.

In this case study, we first tested the normalization to unity (NPS') for comparison with NPS. Element concentrations calibrated with both normalizations are highly correlated with WD-XRF concentrations (Table 1). Although concentrations of excluded components (e.g., organic matter, Mg, Na) vary between 11 and 18% only, i.e., have a small range of variations (smaller than 7%), the NPS-calibrated results show smaller MSRE and higher mean R<sup>2</sup> than NPS'-calibrated ones. These results indicate that normalizing to interpolated WD-XRF sums in the NPS method (instead of to unity in NMS) better accounts for variations in sedimentary components that are not included in the calibration. This feature strongly improves the applicability of the NPS method, in particular for sediments in which organic matter is abundant.

NPS presents the smallest calibration error (smallest MSRE value) among all the evaluated methods in this case study (Table 1). The downcore variations in NPS-calibrated ln(Al/Ti) and ln(Al/K) (Figures 2a and 2b), as well as in Al% and Ti% (Figures 2c and 2d), better correlate to WD-XRF data points than W\_NMS-calibrated results. The relative errors of NPS results randomly distributed around zero with no long-term variations visible anymore (Figures 2a–2d). These results show that the polynomial scaling in NPS empirically and reasonably removes the influence of downcore interstitial water content decrease. Therefore, the NPS method better accounts for the influence of downcore water content changes than W\_NMS and it calibrates XRF-scanning intensities to robust individual element concentrations in long sediment cores with large downcore water.

More discrete geochemical analyses are probably required in the NPS method compared to NMS in order to build robust reference polynomial regressions and to reduce uncertainties derived from interpolating

reference sums. Small errors in NPS-calibrated results (Table 1 and Figure 2) suggest that 34 discrete measurements are sufficient in this case study.

Although, in this study, small relative errors of NPS-calibrated In(Al/Ti) and In(Al/K) (Figure 2a and 2b) indicate a good preservation of relative element proportions, the latter may be altered during calibration due to the fact that the linear regressions of the NPS calibration are performed on single elements and not on element ratios [e.g., *Aitchison and Egozcue*, 2005]. Such data evaluation is therefore strongly recommended after performing the NPS calibration.

#### 6.2. Polynomial-Corrected Multivariate Log-Ratio Calibration (P\_MLC) Applied to This Case Study

In the P\_MLC calibration, a polynomial correction is first performed on the raw XRF-scanning intensities in the log-ratio space. The standard MLC [*Weltje et al.*, 2015] is then performed on the polynomial-corrected intensities using the XELERATE software (section 5.2). In this case study, Ca was again chosen as the common denominator.

P\_MLC-calibrated relative proportions correlate well with WD-XRF concentrations (mean R<sup>2</sup> of 0.83) (Table 1). Compared to the W\_MLC method, P\_MLC produces smaller MSRE and improves the correlation for Al, Ti, and Fe (Table 1). The downcore variations in P\_MLC-calibrated ln(Al/Ti) and ln(Al/K) (Figures 2e and 2f), as well as in Al% and Ti% (Figures 2g and 2h), better correlate to WD-XRF data points than for W\_MLC results. Relative errors of P\_MLC results randomly distribute around zero without the long-term trend previously observed in XRF-scanning intensities (Figures 1d and 1h) and in W\_MLC-calibrated results (Figures 2e–2h). Altogether, these results indicate that the P\_MLC method efficiently corrects the effect of water content changes on XRF-scanning intensities and provides more accurate relative element proportions than the W\_MLC method.

Therefore, the polynomial-correction in the log-ratio space reasonably corrects the influence of downcore interstitial water content changes on XRF-scanning intensities. Based on the mathematically rigorous LRCE [*Weltje and Tjallingii*, 2008] and MLC [*Weltje et al.*, 2015] calibrations, the P\_MLC method respects the mathematical constraints imposed by compositional data [*Aitchison and Egozcue*, 2005] and preserves in particular the relative proportions of elements.

#### 7. Conclusions

The comparison of XRF-scanning intensities and WD-XRF major element concentrations in a 50.8 m-long sediment Core MD12-3432 used as a case study shows that the downcore decrease in interstitial water content in long sediment cores is the main source of deviations in XRF-scanning intensities. Previously proposed calibration approaches (W\_NMS and W\_MLC) fail to appropriately account for this influence of large downcore interstitial water changes and need to be improved.

We propose a quadratic polynomial correction to empirically remove the effect of downcore interstitial water content changes on XRF-scanning intensities and implement it in the two existing integrated NMS and MLC calibrations. From this case study, we show that the two improved NPS and P\_MLC calibrations are so far the most appropriate methods to correct the effect of interstitial water content changes on XRF-scanning intensities and provide accurate high-resolution concentrations of major elements derived from XRF core scanning in long sediment cores.

We strongly recommend testing and applying either the NPS or the P\_MLC method for robust paleoenvironmental interpretations based on major element contents in long sediment cores (e.g., Calypso cores collected with the R/V *Marion Dufresne*, and long-drilled sequences taken as part of the International Ocean Discovery Program).

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## Chapter 4

## Proxies for the East Asian summer monsoon

Acting as the prevailing climatic feature in East Asia, the East Asian monsoon has far-reaching influences on both environment and society. In order to better understand its variations, numerous studies have developed proxies based on terrestrial geologic records, such as magnetic susceptibility and grain size of Chinese Loess, oxygen isotope of stalagmites, element composition of lake sediments, etc., to reconstruct the evolution of the East Asian monsoon at different timescales. As 80% of marine sediments in the South China Sea are of continental origin (Wang and Li, 2009), the East Asian monsoon evolution should also leave traces in the marine sediments. Previous studies have revealed that variations in mineral assemblage and element composition of marine sediments exhibit similar patterns with the evolution of the East Asian monsoon. However, the terrigenous inputs are influenced by several factors, such as mineral formation on land and oceanic transport, the link between marine sediment records and the East Asian monsoon evolution is still discussible. Recently, detailed mineralogical and geochemical investigations have been performed on sediments from main drainage systems surrounding the northern South China Sea, and the oceanic circulation has been derived based on surface sediments and deepwater mooring observations. These fundamental researches allow to better understand the mechanism underlying the mutual variations in the East Asian monsoon and marine sediments. We therefore investigated the clay mineral assemblage and major element composition of a sediment sequence (Core MD12-3432) retrieved from the northern South China Sea. The link between the East Asian summer monsoon intensity, clay mineral assemblage, and major element composition is discussed. We finally proposed two proxies that reflect the East Asian summer monsoon intensity with different mechanisms.

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# **OPEN** Clay mineralogical and geochemical proxies of the East Asian summer monsoon evolution in the South **China Sea during Late Quaternary**

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The East Asian summer monsoon controls the climatic regime of an extended region through temperature and precipitation changes. As the East Asian summer monsoon is primarily driven by the northern hemisphere summer insolation, such meteorological variables are expected to significantly change on the orbital timescale, influencing the composition of terrestrial sediments in terms of both mineralogy and geochemistry. Here we present clay mineralogy and major element composition of Core MD12-3432 retrieved from the northern South China Sea, and we investigate their relationship with the East Asian summer monsoon evolution over the last 400 ka. The variability of smectite/(illite + chlorite) ratio presents a predominant precession periodicity, synchronous with the northern hemisphere summer insolation changes and therefore with that of the East Asian summer monsoon. Variations in K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> are characterized by eccentricity cycles, increasing during interglacials when the East Asian summer monsoon is enhanced. Based on the knowledge of sediment provenances, we suggest that these two proxies in the South China Sea are linked to the East Asian summer monsoon evolution with different mechanisms, which are (1) contemporaneous chemical weathering intensity in Luzon for smectite/(illite + chlorite) ratio and (2) river denudation intensity for  $K_2O/Al_2O_3$  ratio of bulk sediment.

The East Asian monsoon is a major component of the modern climate system<sup>1</sup>. It controls the environmental conditions prevailing over extended regions through seasonal changes of wind and precipitation<sup>2,3</sup>. As the monsoon system is primarily driven by the solar insolation received at the Earth's surface, in turn related to the changing Earth orbital parameters, its intensity and impact are variable on orbital timescales. Because information of monsoonal meteorological variables (temperature, precipitation, and wind stress) is not directly preserved in geological archives, many investigations have been carried out to reconstruct the variability of the East Asian monsoon with proxies that reveal the influence of monsoonal climatic changes on the physical, chemical, and biological processes on land and in ocean<sup>4-7</sup>.

Among the continental sequences, Chinese loess sequence is a unique archive because it records the variability of both wind strength and aridity. Grain-size of Chinese loess, generally increasing during glacials<sup>8-11</sup>, is interpreted as an indicator of the East Asian winter monsoon (EAWM) intensity. Magnetic susceptibility records from Chinese loess indicate periodical intensifications of the East Asian summer monsoon (EASM) in concert with the northern hemisphere summer insolation (NHSI) on both eccentricity and precession bands<sup>12-15</sup>. Meanwhile, oxygen isotope records from stalagmites in East and South China are considered as a proxy of the monsoonal precipitation intensity, the variations of which strongly support the hypothesis that the EASM is driven by NHSI changes on precession band<sup>16-18</sup>.

The marine sediment sequences provide alternatives to study the past variability of the East Asian monsoon. Proxies based on biogenetic materials such as foraminifera, coccolithophore, and radiolarian were developed to reconstruct the history of primary productivity and sea surface temperature and to reveal the evolution of the EASM on the orbital and suborbital timescales<sup>19-22</sup>. Terrigenous clastic particles in marine sediments also document the climate changes related to the EASM evolution. Clay mineral is one of the most frequently used tools to reconstruct paleoclimatic changes on different timescales. For instance, clay mineralogical investigations in

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**Figure 1. Topography of the northern South China Sea.** The map is generated from the ETOPO1 global relief model<sup>64</sup> (http://www.ngdc.noaa.gov/mgg/global/global.html) using Global Mapper (version 13 by Blue Marble Geographics<sup>®</sup>, http://www.bluemarblegeo.com/products/global-mapper.php). The locations of Core MD12-3432 (star) and ODP Sites 1145 and 1146 (dots) are presented.

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the Indian Ocean revealed orbital signals in illite/smectite ratio and the palygorskite/illite ratio, which were used to reconstruct the monsoon strength<sup>23,24</sup>. Such investigations were also performed on sedimentary sequences retrieved from the South China Sea (SCS). Glacial-interglacial cycles were observed with high smectite/ (illite + chlorite) ratio during interglacial periods<sup>25–27</sup>. The underlying mechanism was proposed to be either the surface circulation related to monsoon winds<sup>26</sup> or the balance of chemical weathering versus physical erosion on land<sup>25</sup>. However, high-resolution clay mineral records do not always present such glacial-interglacial cyclicity<sup>28,29</sup>. Indeed, a predominant control by precession is observed in the variations of smectite/(illite + chlorite) ratio at ODP Site 1145, which is probably induced by changes in weathering and transport<sup>28</sup>. The clay mineralogical record since the last glacial maximum revealed the complexity of terrigenous input from surrounding drainage systems and transport processes<sup>29</sup>. The mechanism that links the EASM evolution and the sediment composition remains discussible.

In order to better understand the relationship between the terrigenous sediment composition and the EASM evolution, and what the driving mechanism is, we investigated the clay mineral assemblage and major element composition in Core MD12-3432 that was retrieved from the northern SCS (Fig. 1).

#### Results

The clay mineral assemblage of Core MD12-3432 mainly consists of smectite (23–59%) and illite (22–43%) with minor chlorite (13–27%) and kaolinite (4–13%) (Fig. 2). The smectite record presents frequent and significant short-term variations, coeval and opposite to those of illite and chlorite. Kaolinite content shows a glacial-interglacial variability with relatively higher values during glacial periods compared to interglacials. The illite crystallinity varies between 0.13° and 0.18°  $\Delta 2\theta$  (Fig. 2).

The knowledge of sediment provenances is the basis for deciphering the climatic information preserved in the clay mineral assemblage. Detrital material deposited in the northern SCS has been shown to mainly derive from the Pearl River drainage area, Taiwan, and Luzon<sup>30</sup>. Due to the different geological and tectonic settings prevailing in each region, clay mineral species are distinct (Fig. 3) and they remain constant during the Late Quaternary<sup>26,29,31,32</sup>. The Pearl River drainage area has stable tectonic regime, flat topography, and warm/humid monsoonal climate. Rocks and soils in the Pearl River catchment experience strong and sustained chemical weathering with relatively weak physical erosion. These conditions favour the formation and accumulation of kaolinitic soils that may take more than 1 Ma<sup>31,33</sup>. In Taiwan, the river denudation is intense because of active tectonic, steep topography, and heavy monsoon/typhoon rainfall<sup>34–37</sup>. Sedimentary and metamorphic bedrocks in Taiwan are rapidly eroded. This strong physical erosion inhibits chemical weathering and fosters the formation and delivery of primary minerals of illite and chlorite<sup>38,39</sup>. Given the similarity of tectonic and climatic settings in Taiwan and Luzon, the strong monsoonal rainfall may also result in intense river denudation in Luzon. However, Luzon is characterized by widely spread volcanic rocks, which can be rapidly weathered to form abundant smectite<sup>32,40–43</sup>. The strong denudation would therefore promote the erosion and delivery of smectite, preventing



**Figure 2.** Variations in clay mineral assemblage of Core MD12-3432. Grey bars highlight interglacial periods with marine isotope stages (MIS) noted on top.





further weathering and production of kaolinite to occur<sup>32,40,44</sup>. Although human behaviour might alter the clay mineral assemblage in river samples<sup>45</sup>, this anthropogenic influence is minor and the clay minerals characterizing these three sources remain constant over the late Quaternary because of the unique geological and tectonic settings in these sources. Modern clay mineral assemblages in these sources are, therefore, appropriate references for provenance analysis.

The clay mineral assemblage of Core MD12-3432 is reported in a ternary diagram where end-members are illite + chlorite, kaolinite, and smectite. The regions associated to each end-member are determined on the basis of the studies of continental sediments from the different potential source areas<sup>23,25,31</sup>. The clay mineral assemblage of Core MD12-3432 is linearly distributed between end-members of illite + chlorite and smectite with higher kaolinite contents during glacial periods (Fig. 3), indicating a mixture of clay minerals from multiple sources: all smectite derives from Luzon, all kaolinite sources from the Pearl River, and illite and chlorite may originate from Taiwan and the Pearl River. Illite and chlorite are both primary minerals and they have a similar distribution in the SCS<sup>26,29,40</sup>. Thus, illite provenance analysis is also relevant to chlorite provenance. Although the ternary diagram cannot discriminate Taiwan and Pearl River provenances, illite from the Pearl River is well weathered with low crystallinity (0.19°-0.24° $\Delta 2\theta$ ), while illite from Taiwan is formed directly from strong physical erosion

with high crystallinity  $(0.12^{\circ}-0.18^{\circ}\Delta 2\theta)^{31,38}$ . The well crystallized illite of Core MD12-3432  $(0.13^{\circ}-0.18^{\circ}\Delta 2\theta)$  indicates Taiwan as the main contributor of illite and chlorite.

Smectite, illite and chlorite are the major components of the clay mineral assemblage in Core MD12-3432. Because they originate from different sources, the smectite/(illite + chlorite) ratio reflects the relative contribution of clay minerals from Luzon versus Taiwan<sup>29</sup>. As we discussed above, the supply of illite and chlorite from Taiwan results from the rainfall-driven erosion, and the supply of smectite from Luzon depends on both rapid chemical weathering and physical erosion. Smectite/(illite + chlorite) therefore constitutes an indicator of contemporaneous chemical weathering intensity on land. Regarding of the time series variations, the most prominent feature of smectite/(illite + chlorite) ratio of Core MD12-3432 is the short-term fluctuations, which are coeval with the previously reported smectite/(illite + chlorite) variations at ODP Site 1145<sup>28</sup> (Fig. 4a,b). The comparison with the clay mineral record at ODP Site 1146 is difficult due to the low resolution<sup>26</sup>, but we still observe some simultaneous peaks in Core MD12-3432 and ODP Site 1146 (Fig. 4a,c). In addition to these short-term fluctuations, smectite/(illite + chlorite) ratio of Core MD12-3432 generally increases during interglacial periods (Fig. 4a). This subtle glacial-interglacial cyclicity has also been reported at ODP Site 1146<sup>26</sup> (Fig. 4c). Redfit spectrum analyses<sup>46</sup> were applied to the smectite/(illite + chlorite) profiles at all three sites. A dominant precession periodicity (23 kyr) is observed at Core MD12-3432 and ODP Site 1145, while eccentricity signals are observed at all three sites and dominate the smectite/(illite + chlorite) variations at ODP Site 1146 due to the low resolution (Fig. 5a-c). These results suggest that the orbital forcing exerts a major influence on this ratio in this study area. The synchronicity of maxima in the smectite/(illite + chlorite) ratio and the NHSI (Fig. 4a-c and g) suggests that changes in chemical weathering intensity of the clay fraction in Luzon is related to the NHSI. The NHSI is the driving force of the EASM<sup>17</sup>, which controls the climate regime in the SCS region<sup>47</sup>. The strong EASM is accompanied by warm and humid climate, favouring the rapid chemical weathering of volcanic rocks in Luzon<sup>41,48</sup>. Therefore, the simultaneous variations in the smectite/(illite + chlorite) ratio and the NHSI indicate that the NHSI-driven EASM intensity plays a dominant role in controlling chemical weathering intensity in Luzon as revealed by the smectite/(illite + chlorite) ratio of marine sediments. Smectite/(illite + chlorite) ratio can, hence, act as a proxy of the EASM intensity.

Kaolinite is a minor component in the clay mineral assemblage in Core MD12-3432 (Fig. 2). As a weathering product, kaolinite has usually been used as an indicator of chemical weathering intensity on the tectonic timescale<sup>5</sup>. In Core MD12-3432, variations in kaolinite content are observed at glacial/interglacial timescale, which is much shorter than tectonic timescale, with high contents during cold and dry glacial periods (Fig. 4d and f). This observation does not fit with the understanding that chemical weathering giving rise to kaolinite content is fostered by warm/humid climate<sup>41,48</sup>. Indeed, the supply of kaolinite from the Pearl River reflects the intensity of physical erosion rather than chemical weathering and accumulation<sup>31</sup>. Furthermore, the transport in ocean is also a key process controlling the clay mineral assemblage of marine sediments<sup>49</sup>. Sea level changes seem to be the mechanism underlying the kaolinite variation pattern of Core MD12-3432. Due to the presence of largely extended shelf between the Pearl River mouth and our site, the lowering of sea level during glacials would enhance erosion by inducing river incision on the exposed shelf and notably reduce the transport distance of kaolinite from the Pearl River. Meanwhile, sea level changes have much weaker impacts on the other two provenances because the shelves off Taiwan and Luzon are narrow. Consequently, the low sea level during glacial periods increases the relative contents of kaolinite from the Pearl River (Figs 3 and 4d).

Major element composition offers an alternative to investigate the physical and chemical conditions of terrigenous sediments. Due to the relative contribution of biogenic/terrigenous materials, all terrigenous elements show the same variation pattern opposite to that of CaO% (see Supplementary Fig. S1 and Text S1). In order to examine the changes within terrigenous fraction, we focus on K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio. Indeed, because Al is resistant to leaching while K is more mobile during chemical weathering, K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio can trace the chemical weathering degree of bulk sediments<sup>5,50,51</sup>. Although grain-size effect may challenge the reliability of element ratio proxies, it does not control the K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio in Core MD12-3432 because K is preferably found in illite while Al is a major component of all clay minerals<sup>52-54</sup>. Therefore, an increase in K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio would indicate a decrease in chemical weathering degree of bulk sediments. The variations in K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of Core MD12-3432 present a glacial-interglacial cyclicity (Fig. 4e). This is confirmed by the spectral analysis that shows a predominant eccentricity periodicity (Fig. 5d). However, the periodic increase of this ratio occurs during interglacials (Fig. 4e), in phase with the increase in the chemical weathering as illustrated by smectite/(illite + chlorite) ratio (Fig. 4a). This apparent contradiction indicates that the increase of K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio does not correspond to contemporaneous weak chemical weathering at the source areas. Changes in source areas may be responsible for the apparent out-of-phase increases<sup>53,55</sup>. Due to strong physical erosion and weak chemical weathering, K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of sediments in Taiwan is higher than that in Luzon and the Pearl River drainage area<sup>31,32,38,39,56</sup>. Given the fact that Taiwan exports the largest amount of suspended sediments among all three provenances<sup>34–37</sup>, the intensified EASM rainfall tends to preferentially enhance the river denudation rate in Taiwan and, thus, increases the relative contribution of erosive detrital material with high K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio from Taiwan. Therefore, rather than contemporaneous chemical weathering on land, the increase of K2O/Al2O3 ratio in bulk sediments of Core MD12-3432 reflects strong river denudation that is fostered by intensifications of the EASM precipitation on eccentricity band.

#### **Discussion and Summary**

The EASM largely controls the climate regime prevailing in the SCS region<sup>47</sup>, bringing warm/humid climate with heavy precipitation in summer. Such climate features foster both chemical weathering and river denudation on land. As the three sediment sources of terrigenous sediments in the northern SCS are characterized by distinct geological and tectonic settings, their sediment supplies respond in different ways to such chemical and physical processes driven by the EASM changes on orbital timescales. Our clay mineralogical and geochemical



**Figure 4.** Time-series variations in clay mineral and major element ratios, which are (**a**) smectite/(illite + chlorite) of Core MD12-3432 with the 100-ka filtered curve (grey dashed line), (**b**) smectite/(illite + chlorite) at ODP Site 1145<sup>28</sup>, (**c**) smectite/(illite + chlorite) at ODP Site 1146<sup>26</sup>, (**d**) kaolinite content of Core MD12-3432, (**e**) K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of Core MD12-3432, (**f**) benthic foraminifera  $\delta^{18}$ O at ODP Site 1146<sup>26,3</sup>, and (**g**) mean summer insolation at latitude of 65°N<sup>65</sup> with the 100-ka filtered curve (grey dashed line). Vertical lines mark the glacial/interglacial boundaries with marine isotopic stage number noted on top, and shaded areas highlight the intervals of maximum insolation. The age model of ODP Site 1145 was correlated to the same ODP Site 1146 chronological framework as used for Core MD12-3432.

investigations on Core MD12-3432 sediments support the hypotheses that the chemical weathering intensity of volcanic rocks in Luzon is sensitive to the EASM induced warm/humid climatic changes, the river denudation is reactive to the EASM precipitation in Taiwan, and the weathering in the Pearl River drainage area does not respond to the EASM variations on orbital timescale.





Based on the knowledge of the different characteristics of each sediment source area, our results reveal the mechanism underlying the relationship between variations in the EASM intensity and the smectite/(illite + chlorite) and  $K_2O/Al_2O_3$  ratios of sediments in the northern SCS. Smectite/(illite + chlorite) constitutes a tracer of contemporaneous chemical weathering intensity in Luzon, the variability of which is dominated by the EASM induced variations in temperature and moisture.  $K_2O/Al_2O_3$  ratio reveals the glacial-interglacial cyclicity of the river denudation intensity controlled by the EASM precipitation. In addition, it is obvious that kaolinite content is not an appropriate indicator of EASM on the orbital timescale because it is primarily controlled by sea level changes rather than contemporaneous chemical weathering intensity in the source area.

#### Methods

Investigations of clay mineral assemblage and major element composition were conducted on Core MD12-3432 (19°16.88'N, 116°14.52'E, 2125 m water depth), which was retrieved from the northern SCS in 2012 with R.V. *Marion Dufresne* during the French-Chinese CIRCEA cruise organized within the LIA-MONOCL framework<sup>57</sup>. The core is 50.8 m long and it is located on the lower continental slope of the northern SCS (Fig. 1). The sediment lithology is homogenously dominated by grey clays<sup>57</sup>. All measurements presented in this study were performed at the State Key Laboratory of Marine Geology, Tongji University.

**Clay mineralogical investigation.** A total of 502 samples with a depth-resolution of 10 cm were taken for clay mineralogical analysis. Following previously published studies, oriented mounts were prepared, and clay minerals were identified by X-ray diffraction (XRD) on these oriented mounts of non-calcareous clay-sized ( $<2\mu$ m) particles<sup>25,26,58</sup>. The analysis was performed under three conditions, *i.e.*, air-drying, ethylene-glycol solvation for 24 h, and heating at 490 °C for 2 h, using a PANalytical X'Pert Pro diffractometer with CuK $\alpha$  radiation and Ni filter, under a voltage of 45 kV and an intensity of 40 mA.

Identification of clay minerals and calculation of their relative proportions were made according to the position and area of the (001) series of basal reflections on the three XRD diagrams, *i.e.*, smectite (001) including illite/smectite mixed-layers at 17 Å, illite (001) at 10 Å, and kaolinite (001) and chlorite (002) at 7 Å<sup>25,26,58</sup>. Relative proportions of kaolinite and chlorite were determined based on the ratio from the 3.57/3.54 Å peak areas. Additionally, illite crystallinity was obtained from the half height width of the 10 Å peak<sup>40,59</sup>. Semi-quantitative calculations of all the included peak parameters were performed on the glycolated curves using MacDiff software<sup>60</sup>.

**Analysis of major element composition.** Major element data of Core MD12-3432 were previously investigated<sup>61</sup> with XRF core-scanner and wavelength-dispersive XRF. We corrected the influence of water content changes on XRF core-scanning element intensities and calibrated these semi-quantitative data to oxide concentrations using the normalized polynomial scaled calibration method<sup>61</sup>.

**Establishment of age model.** A composite age model of the nearby ODP Site 1146 was firstly constructed by combining two published age models. The age model between 0 and 350 ka was established using the planktonic oxygen isotope record refereed to those of Chinese speleothem<sup>62</sup>. The remaining part at the bottom of the core was established by astronomical tuning of benthic oxygen isotope record<sup>63</sup>. This composite chronological framework was transferred to Core MD12-3432 using the very similar carbonate content records with a total of 27 correlation points (see Supplementary Fig. S2). Core MD12-3432 covers the last 400 ka with a sedimentation rate varying between 4.5 and 23.8 cm/ky.

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#### **Author Contributions**

Q.C. analysed the samples and wrote the manuscript. Z.F.L. initiated the idea, designed the study, and contributed to the writing. C.K. acted as the chief scientist of the CIRCEA cruise that retrieved the core and contributed to the writing.

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## **Chapter 5**

## Land-sea interactions in the northern South China Sea

Acting as the largest marginal sea in the west Pacific, the South China Sea receives huge amount of terrigenous clastics every year. These terrigenous sediments contain abundant information about both global/regional climate and land-sea interactions. In order to decipher these mixed signals, previous studies have investigated the wellpreserved sediment sequences retrieved from the northern South China Sea with various tools, such as clay mineralogy, geochemistry, grain size (Clift et al., 2014; Liu et al., 2016). As a complementary to bulk sediment and clay fraction, magnetic fraction is sensitive to external forcing and may record the environmental changes with a different mechanism. The studies on magnetic properties of marine sediment sequences have successfully reconstructed the paleoenvironmental evolutions, such as climate-related weathering on land and deepwater current intensity. However, such investigations have been rarely performed in the South China Sea. We therefore analyzed the magnetic properties of sediments in Core MD12-3432 in order to study the late Quaternary history of the land-sea interactions. The magnetic mineral assemblage and its variation patterns at different timescales are obtained by deciphering multiple magnetic properties. We then identified the driven factors of these variations and establish the links between them.

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## 1 Late Quaternary climatic forcing on the terrigenous supply in the

## 2 northern South China Sea: input from magnetic studies

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9 Abstract: In a marginal sea such as the South China Sea, the detrital component of marine sediment 10 is a powerful recorder of paleoenvironmental changes. This is in particular valid for the magnetic 11 fraction, which is probably one of the key parameters for paleoenvironmental studies in the South 12 China Sea. We report here the analysis of the magnetic properties of a sedimentary sequence retrieved from the northern South China Sea. Magnetic minerals with different coercivities 13 14 (magnetite, pyrrhotite, and hematite) are mixed. The variations in relative content of these magnetic 15 minerals illustrate influences of various external forcing at different timescales. The pyrrhotite 16 content exhibits a long-term increase, which is also observed in illite+chlorite content, indicating a 17 continuous enhancement of Taiwan supply most likely related to active Taiwan orogeny. Glacial-18 interglacial fluctuations, which are characterized by more magnetite and pyrrhotite with coarser 19 sedimentary and magnetic grains during glacial periods than during interglacials, are attributed to 20 sea-level changes exposing the enormous shallow continental shelf in turn affecting the sediment 21 transport pathway. On a shorter timescale, larger hematite inputs in fine-grained sediments coincide 22 with precession minima. We suggest that this periodic hematite supply change is related to the eolian

23	dust deposited at the studied site in addition to the fluvial and oceanic transported materials. The
24	higher hematite proportion may be used as a tracer for strong East Asian winter monsoon intensity
25	at this latitude.
26	
27	Key Words: magnetic minerals, hematite, sea-level changes, East Asian monsoon, South China Sea
28	Highlights:
29	A mixture of magnetite, pyrrhotite, and hematite is identified in South China Sea sediments
30	Supply from Taiwan increased over the last 400 ka most likely due to active orogeny
31	Sea-level changes control the terrigenous flux on glacial-interglacial scales
32	Higher hematite content indicates strong East Asian winter monsoon on precession band

#### 33 1. Introduction

34 The South China Sea is a natural laboratory to study past environmental changes (Wang and 35 Li, 2009), because it receives huge amounts of terrigenous clastics that contain key information 36 about global/regional climate and transport dynamic of sediments (Milliman and Farnsworth, 2011). 37 Numerous investigations (clay mineralogy, grain size, geochemistry, etc.) have been conducted on 38 the well-preserved surface marine samples from the South China Sea to decipher the transport 39 pattern of terrigenous material and to reconstruct the evolution of East Asian monsoon (Liu et al., 40 2010; Wang et al., 2009) 41 Complementary to bulk sediment and clay minerals, magnetic minerals also depend on 42 environmental changes. They have been widely used in the marine realm, for example, as a tracer 43 for bottom current intensity changes (e.g., Kissel et al., 1997; Zheng et al., 2016) and precipitation 44 and weathering on land (e.g., Kissel et al., 2010; Zhou et al., 2012). Although magnetic properties of marine sediments have the potential of yielding important information about land-sea interactions 45 and oceanic circulation, such investigations were, so far, rarely performed in the northern South 46 47 China Sea.

To better understand the climatic and oceanographic changes at different timescales in the South China Sea, we performed detailed analyses of the magnetic fraction in a long sediment sequence retrieved from the northern part of the South China Sea.

50

#### 51 **2.** Material and methods

52 Core MD12-3432 (19°16.88' N, 116°14.52' E, 2125 m water depth) was retrieved in 2012 with 53 R.V. *Marion Dufresne* during the French-Chinese CIRCEA cruise. The core is 50.8 m long and it is 54 located on the northern slope of the South China Sea, approximately 340 km off the Pearl River 55 mouth. The sediment lithology is homogenously dominated by grey clays. The fractional porosity 56 of the sediments decreases with depth in the core (Kissel et al., 2012).

57 Continuous measurements of various magnetic properties, including volume-normalized 58 susceptibility ( $\kappa$ ), natural remanent magnetization (NRM), anhysteretic remanent magnetization 59 (ARM), and isothermal remanent magnetization (IRM), were performed on u-channel samples 60 collected from the centre of the archive half of the core. The susceptibility ( $\kappa$ ) was measured using 61 a Bartington MS2C 45-mm diameter susceptibility bridge, at 2 cm intervals with a resolution of  $\sim$ 4 cm. The carbonate-free susceptibility is calculated ( $\kappa_{carb}$  free =  $\kappa \times 100 / (100 - CaCO_3\%)$ ) using 62 63 the calibrated XRF core-scanning carbonate content (Chen et al., 2016). The NRM was measured 64 every 2 cm using a 2G-755R cryogenic magnetometer equipped with high resolution pick-up coils 65 (~4 cm resolution) and placed in the  $\mu$ -metal shielded room at LSCE. It was stepwise demagnetized 66 using alternating fields (AF) along the three perpendicular axes using AF coils installed in-line with 67 the magnetometer. The successive peak fields used for demagnetization are 5, 10, 15, 20, 25, 30, 35, 68 40, 45, 50, 60 and 80 mT. The u-channels were translated at a 4 cm/s speed through the coils. 69 Declination and inclination of the characteristic remanent magnetization (ChRM) individualized by 70 this stepwise demagnetization, were calculated using a principal component analysis (Kirschvink, 71 1980). The accuracy with which the direction is defined is given by the mean angular deviation 72 (MAD). Following the demagnetization of NRM, the ARM was acquired in-line along the vertical 73 axis in a 100 mT alternating field superimposed to a steady 50 µT bias field. The acquisition was 74 made with a 1 cm/s translation speed (Brachfeld et al., 2004). The ARM was then progressively 75 demagnetized with 11 steps at 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 80 mT and measured after each 76 demagnetization step using the same instrument and same setting as for NRM. After ARM 77 demagnetization, the saturated IRM (SIRM) was acquired with 6 successive increasing fields (0.05, 78 0.1, 0.2, 0.3, 0.5, 1 T) applied along the vertical (z) axis using a 2G 1.6 m long pulsed solenoid. The 79 IRM was also measured every 2 cm after each step to construct the acquisition curves giving access 80 to the magnetic "hardness" of the sediment at each measured horizon. The SIRM was then stepwise 81 demagnetized using the same steps as for ARM. The percentage of magnetization remaining after 82 demagnetization at 80 mT with respect to SIRM ( $IRM_{AF@80mT}\% = 100\% \times IRM_{AF@80mT}/IRM_{1 T}$ ) 83 was calculated. A backfield of -0.3 T was applied to the SIRM<sub>1T</sub> to calculate the S-ratio ( $S_{0.3T}$  = -84 IRM<sub>-0.3T</sub>/IRM<sub>1T</sub>) (King and Channell, 1991) and HIRM (HIRM = 0.5×(SIRM+IRM<sub>-0.3T</sub>) (Robinson, 1986). 85

86 Small chips (2 to 10 mg) of sediments were taken at specific horizons to measure the hysteresis 87 parameters. The hysteresis loops were obtained between +1 and -1 T using an alternating gradient 88 magnetometer (AGM2900). Saturation magnetization (M<sub>s</sub>), remanent saturation magnetization 89  $(M_{rs})$ , and coercive force  $(H_c)$  were determined after the correction for high field slope representing 90 the para- and diamagnetic components. The remanent coercive force (H<sub>cr</sub>) was measured separately 91 after applying stepwise increasing back-fields to M<sub>rs</sub>. Replicate measurements were performed on 92 randomly selected samples to check the precision and sample representativeness. High-resolution 93 IRM acquisition curves (150-200 steps between 0 and 1 T) were then obtained. In order to reduce 94 the noise, repetitive measurements were performed on the selected samples to obtain synthetic

acquisition curves. These curves were decomposed into different log Gaussian curves (CLG) and the different coercivity components were defined by their half IRM acquisition field ( $B_{1/2}$ ) and their relative contribution to SIRM (Robertson and France, 1994; Kruiver et al., 2001).

98 The thermal evolution of the different coercivity components has been evaluated by high-99 temperature demagnetization of three-axis IRM. Fields of 1, 0.3, and 0.1 T were successively 100 applied to the three axes of dried cubic samples using an Applied Physics pulse magnetizer 2G660. The samples were then demagnetized by stepwise heating (50°C steps on the average) from room 101 102 temperature to 700°C using a zero-field PYROX furnace. The IRM remaining on each axis after 103 each step was measured using a 2G-755R cryogenic magnetometer equipped with high-104 homogeneity pick-up coils also placed into the  $\mu$ -metal shielded room at LSCE together with the 105 furnace.

Standard  $(2 \times 2 \times 2 \text{ cm})$  plastic cubic boxes were sampled for the study of the anisotropy of low-field magnetic susceptibility. The cubes were slowly and carefully pushed into the sediment (every 50 cm on the average) in order to avoid any perturbation due to sampling and they were measured using an AGICO KLY-3.

The mean size of sortable silt  $(\overline{SS})$  was investigated on discrete samples every 50 cm. The samples were dried at 50°C and biogenic carbonates and organic matter were removed by excessive acetic acid (20%) and hydrogen peroxide (33%), respectively. The samples were sieved through a 63 µm mesh and mixed with a Calgon solution (sodium hexametaphosphate, 0.2%) in an ultrasonic bath for 2 min. The grain size distribution was then measured using a Beckman Multisizer 3 Coulter Counter. Replicate measurements on 33 samples indicate a relative standard deviation  $\leq 4.1\%$  and an uncertainty of  $\pm 0.71$  µm. All the measurements presented in this study were conducted at the Laboratoire des Sciencesdu Climat et de l'Environnement (LSCE), Gif-sur-Yvette, France.

#### 119 **3. Results**

#### 120 **3.1 Age model**

121 The age model of Core MD12-3432 was established by transferring it from the nearby ODP 122 Site 1146. The age model of ODP Site 1146 at 0-350 ka interval was reported by Caballero-Gill et 123 al. (2012), and obtained by correlating planktonic foraminifera  $\delta^{18}$ O data to the  $\delta^{18}$ O profile of 124 Chinese stalagmites from Sanbao, Linzhu, and Hulu caves (Fig. 2a). Between 350 and 410 ka, the 125 age model was built by tuning benthic foraminifera  $\delta^{18}$ O record of ODP Site 1146 to astronomical 126 parameters (Fig. 2b) (Clemens et al., 2008).

127 The transfer of this age model to Core MD12-3432 is based on the correlation of the CaCO<sub>3</sub> 128 records available from both cores, and then refined by the correlation of the earth magnetic field 129 intensity profile of Core MD12-3432 to the PISO-1500 reference curve (Channell et al., 2009). Indeed, in Core MD12-3432, the earth magnetic field changes are reliably recorded as shown by the 130 131 rather constant inclination record around a mean value of 34.7±9.4°, which is similar to the expectation (34.9°) on the basis of the geocentric axial dipole at this latitude (suppl. Fig. S1). The 132 133 declination record is also stable and the MAD value rarely exceeds 10° (suppl. Fig. S1). In the 134 directional record of Core MD12-3432, a large deviation of both inclination and declination is 135 recognized around 190 ka and it is clearly associated to the Iceland Basin excursion (Channell et al., 136 2009). The relative paleointensity (RPI) record obtained by normalizing NRM with ARM,  $\kappa$  or IRM 137 is similar.

138	The correlation of the CaCO <sub>3</sub> record to that of ODP Site 1146 is based on 24 tie points
139	distributed all along the core (Fig. 2c and 2d). These points make the two RPI curves matching well
140	(Fig. 2e and 2f). The RPI curves are then used to refine the correlation for time periods where no
141	precise tie points could be defined using the carbonate content. Correlation points were added at
142	RPI minima, in particular those associated to the Laschamp excursion at 40 ka and the Blake
143	excursion at 95 and 120 ka (Fig. 2e and 2f). Core MD12-3432 covers the last 404 ka with an average
144	sedimentation rate of 12.6 cm/kyr.

#### 145 **3.2 Magnetic properties**

146 The bulk magnetic parameters are variable in time. κ varies by a factor of 8, while ARM and SIRM change by factors of 31 and 16, respectively (Fig. 3a-3c). The saturation magnetization Ms 147 148 exhibits the same variation pattern as that of  $\kappa$  and SIRM (Fig. 3a, 3c, and 3d). An abrupt decrease 149 is observed in ARM at about 80 ka (~12.5 m.b.s.f) (Fig. 3b). Below this horizon, the variations in 150 ARM are constrained within a small range of low values (Fig. 3b), most likely illustrating some 151 degree of dissolution of fine-grained iron oxides (Dunlop and Özdemir, 1997). However, the fact 152 that such an abrupt change is not present in κ, SIRM, or Ms (Fig. 3a, 3c, and 3d), and that the earth 153 magnetic field record is also well-preserved all along the core as discussed above indicates that the 154 primary magnetic signal is still preserved below 12.5 m.b.s.f. 155 All magnetic parameters are variable through the core. This may result from changes in

- 156 magnetic concentration, magnetic mineralogy, and magnetic grain size that we shall investigate now.
- 157 The S-ratio varies between 0.79 and 0.98, in opposition to IRM<sub>AF@80mT</sub>% (Fig. 3f and 3g). All
- 158 these parameters indicate changes in the relative concentration of different coercivity fractions. The
- 159 contribution of each coercivity fraction to the total IRM is therefore evaluated by decomposing high-
160 resolution IRM acquisition curves using the CLG method. Four coercitive components are identified 161 in the 33 studied samples: the first, very low coercivity component (CLG<sub>#1</sub>) is characterized by  $B_{1/2}$ 162 of 4 mT and carries only 3 to 12% of the total IRM. This component is often badly defined (mean half-width of the distribution  $\sim 0.85$  mT) and has probably no significant meaning. About 20% 163 164 (between 10% and 37%) of the SIRM<sub>1T</sub> is carried by the second coercivity component ( $CLG_{#2}$ ) with 165  $B_{1/2}$  between 10 and 20 mT (13 mT as an average). About 64% of the SIRM<sub>1T</sub> is carried by component three (CLG<sub>#3</sub>) with  $B_{1/2}$  ranging from 42 to 55 mT. The remaining 3% - 22% of the 166 167 SIRM<sub>1T</sub> correspond to a high coercivity family (CLG<sub>#4</sub>) with  $B_{1/2}$  between 316 and 650 mT 168 (Supplementary Fig. S2). 169 The thermal evolution of these coercivity components has been examined for 14 samples using 170 stepwise thermal demagnetization of three-axes IRM. Results obtained from four representative 171 samples in which the relative contribution of high and low coercivity fractions is variable are reported in Fig. 4c. The magnetization of the axis along which the lowest field (0.1 T) has been 172 applied, is removed between 550°C to 600°C, which is typical for magnetite. A change in the slope 173 174 of this decay curve as well as on that of the 0.1T < Hc < 0.3T component is sometimes observed 175 around 300°C. The change in the low-medium coercivity thermal decay rate may illustrate the 176 presence of iron sulphides, which are, in the marine realm, typically greigite or pyrrhotite that have slightly higher coercivity than magnetite. Because gyroremanent magnetization (GRM) is not 177 178 observed at all during the ARM AF demagnetization up to 80 mT, the signal of iron sulphides is 179 very unlikely related to greigite (Roberts et al., 2011) and we therefore interpret this component as 180 being carried by pyrrhotite that has been largely identified in the northern part of the South China 181 Sea (Horng and Huh, 2011; Horng et al., 2012). The magnetization of the high-coercivity component

182	(0.3T-1T) continuously decreases until its complete removal between 650°C and 700°C, indicating
183	that it is carried by hematite (Fig. 4c). The high coercivity component identified using the CLG
184	decomposition (CLG#4) is therefore carried by hematite. CLG#4 does not contribute by more than
185	20% to the SIRM <sub>1T</sub> , but given the weak saturation magnetization of hematite ( $0.4 \text{ Am}^2/\text{kg}$ ) compared
186	to magnetite (90 Am <sup>2</sup> /kg), this contribution represents a large proportion of particles in the sediment
187	(Frank and Nowaczyk, 2008). In summary, the magnetic assemblage in the core is most likely
188	composed of magnetite-titanomagnetite, hematite, and iron sulphide such as pyrrhotite. As shown
189	by the well correlated variations in $CLG_{#4}$ %, S-ratio and $IRM_{AF@80 mT}$ % (Fig. 3f-3g and 4a-4b), the
190	contribution of these different minerals to the total magnetization is variable along the core.
191	The hysteresis parameters plotted on a Day diagram (Day et al., 1977) indicate that the
192	magnetic particles can be classified into two grain-size fractions (Fig. 5). Younger than 80 ka, when
193	the coercivity is low (S-ratio $> 0.9$ ), the magnetic grains are the finest in the core and correspond to
194	pseudo-single domain magnetite. Older than 80 ka, the magnetic grains are coarser, also within the
195	pseudo-single domain but with some extensions into the multi-domain range (Fig. 5).
196	Therefore, the magnetic fraction at our site is mainly composed of pseudo-single domain to
197	multi-domain magnetite and iron-sulphide with some hematite contribution.

### 198 **4. Discussion**

199 Variations are observed at different timescales in all measured magnetic parameters. They result 200 from changes in both magnetic mineral assemblage and grain size. We shall examine them as well 201 as the different types of forcing that control them.

### 202 **4.1 Tectonic control of terrigenous supply**

203 The bulk magnetic parameters (susceptibility, ARM, IRM, and Ms) continuously increase since 204 400 ka (Fig. 3a-3d). The long-term increase of the S-ratio and decrease of IRMAF@80mT% and CLG#4% 205 indicate a gradual decrease in the relative proportion of high-coercivity minerals (e.g. hematite) with respect to low-medium coercivity minerals (Fig. 3f-3g). Such long-term trends may result either 206 from an increase in the amount of magnetite and sulfide, from a decrease in hematite content, or 207 both. The HIRM record, which illustrates the amount of hematite particles, does not present any 208 209 significant long-term trend (Fig. 3h). All these results indicate that the hematite content is relatively 210 constant and that the long-term pattern of the bulk parameters is mainly due to an increase in the 211 amount of low-medium coercivity magnetic particles (Fig. 3b). This low-medium coercivity fraction 212 also contributes to the IRM and, therefore, may account for the long-term increase of IRM. A long-213 term increase in H<sub>c</sub>, remaining in the range of low values (between 8 and 16 mT), is also observed 214 (Fig. 3e). This trend indicates an increase of the magnetic "hardness" within the low-medium coercivity fraction. This is also shown by the CLG analysis of the IRM acquisition curves, which 215 216 shows that the relative contribution of the medium coercivity fraction  $(CLG_{\#3})$  increases while the 217 low coercivity (CLG<sub>#2</sub>) remains rather constant (Fig. 3h-3i). As the low coercivity is most likely carried by magnetite while pyrrhotite is contributing to the medium coercivity fraction, we interpret 218 219 the long-term evolution in the magnetic parameters as an increase in pyrrhotite with respect to

220 magnetite and hematite content.

221	Magnetite is weakly discriminant because it may come from all three possible fluvial sources
222	(Pearl River catchment, Taiwan, and Luzon). Luzon delivers almost pure magnetite while, in the
223	Pearl River catchment, magnetite is dominant and associated with some hematite (Kissel et al.,
224	2016). In Taiwan, on the contrary, the magnetic mineral assemblage is dominated by pyrrhotite,
225	which originates from meta-sediments in the central range of Taiwan (Horng et al., 2012). Therefore,
226	the long-term increase in pyrrhotite with respect to magnetite most likely illustrates an increasing
227	contribution from the Taiwanese source to the sediments deposited at the site of core MD12-3432.
228	Clay mineral assemblages (Chen et al., submitted) at this site yield information that is
229	complementary to that obtained from magnetic parameters. The relative content of illite and chlorite
230	shows a long-term increasing trend through the last 400 ka (Fig. 3k) while that of smectite decreases.
231	Illite and Chlorite characterize the present-day river sediments from Taiwan while smectite
232	preferentially sources in Luzon.
233	All these observations of long-term evolution of magnetic mineralogy and clay mineral
234	assemblages, therefore, converge towards a contribution from Taiwan that is increasing with time
235	consistently with the observations made at the nearby ODP Sites1144 and 1146 (Kissel et al., 2003;
236	Wan et al., 2010).
237	This increase in terrigenous supply from Taiwan may result from changes in climatic
238	conditions and/or tectonics. Modern observations and investigations suggest that the sediment
239	discharge from Taiwan rivers is closely related to the runoff that increases with strong precipitations

and also the uplift of the central chain related to the active collision tectonic regime. More than 70%

241 of precipitation in Taiwan is induced by catastrophic typhoon events (Yang et al., 2011), while the

rest part of precipitation is probably related to the moisture brought by the East Asian monsoon. No 242 243 evidence for an increase in the frequency of the typhoon events has been suggested over such a long 244 period, and the  $\delta^{18}$ O records of Chinese stalagmite do not support a continuous intensification of 245 the monsoonal precipitation during the last 400 ka (Fig. 2a). Climatic forcing is therefore very 246 unlikely at the origin of the increasing terrigenous supply from Taiwan. Lee et al. (2006) showed 247 that the exhumation rate in Taiwan has increased about 1 Ma ago, from 4.76 mm/yr to 10 mm/yr. This is of course a very significant change. No specific evidence is given for a continuous increase 248 249 since 1 Ma because these studies only deliver an integrated value on such short time intervals with 250 respect to geological time scales. However, Tuo (2008), on the basis of the analysis of clay 251 mineralogical records and sedimentation rate at ODP Site 1144, concluded that the tectonic activity 252 increased in Taiwan since 980 ka. Wan et al. (2010) also reached the same conclusion after studying 253 ODP Site 1144 and 1146. Our results are consistent with this conclusion that the identification of 254 the various terrigenous fractions and of their provenance might be the right proxy to access the 255 tectonic forcing at that timescale.

### **4.2 Signatures of oceanic circulation and sea-level changes**

Variations of magnetic properties at a glacial-interglacial timescale are superimposed to the long-term trends. Susceptibility and SIRM records present similar fluctuations (Fig 3a and 3c), coeval with variations in S-ratio (Fig. 3f). As shown by the 100 yr filtering of the S-ratio curve, more magnetite-pyrrhotite with respect to hematite are observed during glacial periods (Fig. 6a). These changes are coeval with variations in the mean size of sortable silt ( $\overline{SS}$ ) and the ARM/IRM ratio (Fig. 6b and 6c). This indicates increases in grain size of bulk sediment and magnetitepyrrhotite particles, respectively, during glacial stages. The same variation pattern of the two grainsize proxies suggests that the magnetic particles are not present as inclusions in other minerals nor are integrated into aggregates but are "free" in the sediments of core MD12-3432. Both proxies therefore illustrate the same mechanism.

267 The grain-size fraction in the sortable silt range (10 to 63  $\mu$ m) is generally considered as a 268 proxy for bottom current strength because stronger bottom currents favor sediment re-suspension 269 and transport of fine particles (McCave et al., 1995). Increasing sedimentary and magnetic grain sizes during glacial periods would, therefore, indicate strengthening of bottom currents. Given the 270 271 fact that bottom currents are the main transporter of fine-grained detrital material from Taiwan (Liu 272 et al., 2010), the strengthening of the bottom currents could also explain the relative increase in magnetite-pyrrhotite contents. However, it can hardly result in the three-fold increase of 273 274 sedimentation rate during glacial periods (Fig. 6d) according to the information obtained by 275 studying the changes in orientation and shape of the magnetic fabric (Kissel et al., 1997, 2010). In core MD12-3432, the dominant magnetic carrier of the low-field magnetic susceptibility is 276 277 magnetite with a shape anisotropy. The preferential alignments of the long axes of the grains in the 278 sediment are, therefore, illustrated by grouped maximum susceptibility axes. More than 100 samples 279 have been analyzed and all of them are characterized by an oblate anisotropy ellipsoid with 280 minimum axes K<sub>min</sub> perpendicular to the bedding plane (Figure 7a). This is typical for a sedimentary 281 magnetic fabric acquired during deposition and possible subsequent compaction. Within the bedding 282 plane, the maximum axes of the AMS ellipsoid (Kmax) are rather well-grouped, marking a magnetic lineation. After reorientation of the core by aligning the mean declination of the ChRM at 0°, the 283 anisotropy lineation appears to be oriented WNW-ESE with no differences between glacial and 284 285 interglacial periods (Fig. 7b). Unfortunately, because this orientation is consistent with the

286 bathymetric lines at the site and with the axis of the Pearl River "canyon", it does not allow to 287 discriminate between contour current and fluvial supply nor to determine possible changes from one 288 to the other. Besides the direction of the principal axes of the anisotropy ellipsoid, changes in the 289 degree of anisotropy (P) on a glacial-interglacial scale are mainly related to changes in foliation, i.e. 290 compaction, but not to changes in lineation. No significant changes in the strength of the bottom 291 current velocity is therefore determined (Fig. 7c-7d). These results indicate that hydrodynamic 292 forces were continuously present at the site to align the magnetic grains with no significant intensity 293 changes.

294 Another possible cause for the increasing grain size and sedimentation rate during glacial 295 intervals is the sea-level changes. During the low sea-level stand, the enormous continental shelf in 296 the northern South China Sea is emerged and the sediment transport distance from the Pearl River 297 mouth to our site is largely reduced giving rise to larger amount of terrigenous sediment with coarser 298 grain sizes (Fig. 6b-6d). Clay minerals support this interpretation (Chen et al., submitted). Indeed, 299 kaolinite characterizing the Pearl River sediments (Liu et al., 2007) has a deposition center usually 300 near the river mouth due to flocculation effects (Chamley, 1989). Glacial increase in kaolinite% 301 illustrating an increased terrigenous supply to our site, from the Pearl River is therefore related to 302 the low sea-level (Fig. 6e). In addition, during the low sea-level stand, the Pearl River incised the 303 exposed continental shelf, which contains a large proportion of fine-grained detrital sediments 304 derived from Taiwan (Liu et al., 2008, 2010). This explains the relative increase of magnetite-305 pyrrhotite content during glacial periods. Although we cannot exclude the possibility that the bottom 306 current strengthened during glacial periods, it appears that the glacial-interglacial cycles observed 307 in the composition of the magnetic fraction and in the grain sizes mainly reflect the influence of sea308 level changes.

# 309 **4.3 Impact of the East Asian monsoon**

310	All magnetic signals present short-term precessional fluctuations superimposed to the long-
311	term trend and to the glacial-interglacial cyclicity (Fig. 8). At this timescale, as a general pattern, a
312	low S-ratio coincides with high susceptibility and high SIRM (Fig. 8a, 8c, and 8e). A low S-ratio
313	illustrates high proportions of high-coercivity minerals (Fig. 4a and 4b), clearly identified as
314	hematite by the 3-axes thermal demagnetization (Fig. 4c). Given the fact that hematite has low
315	susceptibility and IRM <sub>1T</sub> characteristic values, it is unlikely to be fully responsible for the observed
316	increases in susceptibility and SIRM values. It rather contributes to the general increase in total
317	magnetic supply during these events (highlighted by grey rectangles in Fig. 8). The hematite events
318	also generally correlate with minima of $\overline{SS}$ (Fig. 8f).
319	Although near the study area, the Pearl River catchment is the only fluvial source where
320	hematite is observed at present (Kissel et al., 2016), this source is very unlikely to be at the origin
321	of the increases observed in hematite. Indeed, hematite is a minor component of the magnetic
322	fraction in the Pearl River as it is detected only in the northern branch while magnetite dominates
323	the main stream. Accordingly, hematite is not found in the delta (Ouyang et al., 2013). In addition,
324	the kaolinite content, which dominates the clay mineral assemblage from this river, does not present

325 such fluctuations (Fig. 6e) (Chen et al., submitted). Moreover, an increased contribution from the

326 Pearl River cannot explain the coeval decrease in grain size.

Another possible candidate for the observed short-term variations in hematite content, is the hematite-rich eolian dust from the western and central Chinese deserts (Maher et al., 2009), which can be transported over long distances (Yamazaki and Ioka, 1997; Ziegler et al., 2008). Although the eolian dust is mainly transported by the westerlies in the mid-latitude, it has been reported to be a major component of sediments in the Philippine Sea that is east to the South China Sea but at the same latitude (Seo et al., 2014; Jiang et al., 2016).

333 Interestingly, the intervals rich in hematite and in fine-grained magnetic minerals in core 334 MD12-3432 show a clear 23 kyr periodicity with high values during low precipitation rate periods 335 (precession minima) (Fig. 8e-8f). It is opposite to the variations in the smectite/(illite+chlorite) ratio 336 considered to be a tracer for strong East Asian summer-monsoon intensity (Chen et al., submitted). 337 During low-precession periods, precipitation is weak and aridity increases, and our results suggest 338 that the eolian supply to our studied site increases accordingly (Fig. 8h). This may result from an 339 increased intensity in winter monsoon wind, thus delivering more dust from the west and central 340 Chinese deserts. This would facilitate the southward dispersion of eolian dust transported by the 341 Westerlies.

Glacial periods are also characterized by stronger winter monsoon with enhanced wind blowing from the desert areas (Ding et al., 1995). If hematite input is of eolian origin on the precession timescale, with increases induced by enhanced winter monsoon, changes at the glacialinterglacial scale with higher hematite content during glacial periods should also be observed, which is not the case. This is probably because the weak magnetic signal of eolian hematite is damped during glacial stages by the very large increase in magnetite-pyrrhotite fluvial supply.

The possibility of eolian supply to the northern South China Sea has not been described in previous studies. However, the eolian supply was estimated as not exceeding 10% of the total terrigenous supply in ODP Site 1144 (Boulay et al., 2007). This low amount is probably related to the peculiar position of ODP Site 1144, being in the core of the contour current, as illustrated by the 352 very high sedimentation rate (~60 cm/ka for the last 400 kyr; Bühring et al., 2004). The eolian 353 particles are, therefore, strongly diluted and difficult to trace, and so is the total magnetic fraction 354 (Solheid et al., 2002). Short-term fluctuations in susceptibility and IRM<sub>1T</sub>, similar to those observed in Core MD12-3432, have been reported for the nearby ODP Site 1146 (Fig. 8b and 8d) but have 355 356 not been studied in detail at that timescale (Kissel et al., 2003). Although further investigations on other cores from this area are needed to confirm our interpretation, we suggest that the relative 357 358 increase of hematite at the precession scale with associated finer grains may be a tracer for strong 359 East Asian winter monsoon.

360 **5.** Conclusions

The magnetic mineral assemblage of Core MD12-3432 is composed mainly by magnetite, pyrrhotite, and hematite in variable proportions. These minerals derive from different sources, making the site a key position to examine the paleoenvironmental evolution at different time scales. The long-term trends observed in both the magnetic properties and the clay content over the last 400 ka indicate a continuous increase in the terrigenous supply from Taiwan. This most likely relates to the Taiwanese active orogeny.

On the glacial-interglacial timescale, sea-level variability plays a dominant role in changing the mineral assemblages and grain size of both bulk sediment and magnetic particles. When sealevel is low during glacial periods, the Pearl River incises the wide emerged shelf with a mouth located closer to our site. It therefore delivers more terrigenous sediment originating both from its own catchment and from Taiwanese sediment previously deposited on the shelf.

Finally, on shorter timescales, changes are observed that are related to precessional cycles, thuslow latitude monsoonal climate. Our results indicate increased magnetic content, in particular

374	hematite, and decreased grain size during precession minima. These variations are thought to be
375	related to increased eolian input caused by intensified aridity and enhanced winter monsoon. In this
376	study area, hematite content associated with finer grains may be an adequate proxy for East Asian
377	winter monsoon.

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548 Figure 1 Map of the northern South China Sea showing the location of the sites discussed in the

549 text. The oceanic circulation pattern is also presented (after Liu et al., 2010).



Figure 2 Age model of Core MD12-3432. **a)** Referred correlations between planktonic oxygen isotopic record from ODP Site 1146 (in red) and oxygen record of Chinese speleothem from Sanbao, Linzhu, and Hulu cave (in blue) (Caballero-Gill et al., 2012; Cheng et al., 2009; Wang et al., 2001; Wang et al., 2008). The black dots indicate the high-confidence correlation points. **b)** Benthic isotopic signal from ODP Site 1146 reported for the 0-350 ka interval (in red) on the time scale established as in a) and extended (in blue) between 350 and 420 ka by astronomic tuning according to (Clemens et al., 2008). **c-d)** Correlations between CaCO<sub>3</sub>% profiles of ODP Site 1146 and Core

558	MD12-3432. The blue dashed lines are for the correlation points. e) Relative geomagnetic
559	paleointensity (RPI) records of Core MD12-3432 reported on two age models, one is the age model
560	of ODP Site 1146 transferred using carbonate records as in c) (in cyan), and the other is refined by
561	referring the paleointensity profile to the PISO1500 (Channell et al., 2009) in f) (in blue). New
562	correlation lines to refine the age model using the earth magnetic field intensity records are indicated
563	in black dashed lines.



Figure 3 Magnetic parameters of Core MD12-3432. a) carbonate-free susceptibility, b) ARM (in
black) and three-time amplified ARM (in grey), c) SIRM, d) saturation magnetization, e) coercive

- 567 force (H<sub>c</sub>), **f**) S-ratio with inversed scale, **g**)  $IRM_{AF@80mT}\%$  and  $CLG_{#4}\%$  (dots), and **h**)  $CLG_{#2}\%$  and
- 568 CLG<sub>#3</sub>%. They are compared with i) illite+chlorite% record (Chen et al., submitted). Long-term
- trends in these properties are highlighted by grey dash lines, the slopes of which are determined by
- 570 linear regression.



572 Figure 4 (a) S-ratio curve with stars showing the horizons where the examples of CLG 573 decomposition (b) and three-axes IRM thermal demagnetizations (c) are located (depths on top).





576 Figure 5 Day diagram of Core MD12-3432 (Day et al., 1977). The red circles and the blue dots

577 represent samples above and below the dissolution front, respectively.



Figure 6 Magnetic properties of **a**) S-ratio with inversed scale (high coercivities upward), **b**) mean size of sortable silt ( $\overline{SS}$ ), and **c**) ARM/SIRM with inversed scale (coarse magnetic grains upward), in comparison with **d**) linear sedimentation rate, **e**) kaolinite%, and **f**) benthic foraminifera  $\delta^{18}$ O at ODP Site 1146. Dash curves illustrates the 100-kyr filtering of S-ratio,  $\overline{SS}$ , and benthic  $\delta^{18}$ O. Vertical shades marks the interglacial periods with marine isotope stages (MIS) noted on top.



Figure 7 Anisotropy of magnetic susceptibility is illustrated in terms of a) inclinations of K<sub>max</sub> (blue
dots) and K<sub>min</sub> (orange squares), b) declination of K<sub>max</sub> during glacial periods (left) and interglacial
periods (right), c) degree of anisotropy (P) versus lineation (L), and d) degree of anisotropy (P)
versus foliation (F).



Figure 8 Short-term fluctuations in magnetic properties of **a**) carbonate-free susceptibility, **b**) susceptibility at ODP Site 1146 (Kissel et al., 2003), **c**) SIRM, **d**) SIRM at ODP Site 1146 (Kissel et al., 2003), and **e**) S-ratio with inversed scale (high coercivities upward), in comparison with **f**)  $\overline{SS}$ , **g**) smectite/(illite+chlorite) ratio (Chen et al., submitted), and **h**) mean summer insolation at 30°N (Laskar et al., 2004). Dash curves represent the 23-kyr filtering of S-ratio and smectite(illite+chlorite) ratio. Vertical shades highlight the intervals with low S-ratio.

# Chapter 6 Conclusions and Perspectives

The marine sedimentary sequence from Core MD12-3432, retrieved from the northern South China Sea, has been studied to reconstruct past changes in the terrigenous input in the northern South China Sea during the late Quaternary and the relationship with the East Asian monsoon evolution and the land-sea interactions. This has been accomplished by investigating clay mineralogy, magnetic properties, granulometry, and major element compositions. On the basis of the results, we emphasize the following conclusions:

# 1. Correction and calibration of XRF core scanning major element data

Downcore variations in interstitial water content is identified as the main source of deviations in XRF core-scanning data. The previously developed calibration approaches do not appropriately account for this influence which is common in long sediment sequences. Therefore, we propose a quadratic polynomial correction to empirically remove this effect, and we implemente it in the two existing integrated calibration approaches. The data obtained from Core MD12-3432 show that the improved calibrations, NPS and P\_MLC, are so far the most appropriate methods to account for the interstitial water changes and to provide accurate high-resolution major element concentrations.

### 2. Carbonate and magnetic chronology

We have transferred the well-established age model of the nearby ODP Site 1146 to Core MD12-3432 based on the similarity of carbonate records at these two sites. Comparison of the geomagnetic field intensity record with that of the global PISO1500 curve was then used to confirm and to refine the carbonate-based correlations chronology. A robust age model of Core MD12-3432 was therefore constructed, indicating that it covers the last 400 ka with sedimentation rate varying between 4.5 and 24 cm/ka (12.6 cm/ka on average).

### 3. Clay and magnetic mineral assemblage and major element compositions

The clay mineral assemblage of Core MD12-3432 consists of smectite (23%-59%) and illite (22%-43%) with minor chlorite (13%-27%) and kaolinite (4%-13%). The illite crystallinity (0.13-0.18°  $\Delta 2\theta$ ) varies within the range observed in modern sediments

from Taiwan. Based on the knowledge of the geological settings and clay mineral distributions in the main potential detrital sources, we suggest that (1) illite and chlorite are mainly originating from Taiwan and formed by physical erosion, (2) smectite originates from Luzon and is formed by rapid chemical weathering of the wide-spread volcanic rocks in Luzon, and (3) kaolinites are formed by the long-term weathering in the Pearl River catchment.

The magnetic mineral assemblage of core MD12-3432 is mainly composed by low-middle coercivity magnetite and iron-sulphide and high coercivity hematite. Magnetite could originate from all major drainage systems around the study area. Ironsulphide is most likely pyrrhotite from Taiwan. Hematite is only supplied by the Pearl River, although not dominant in this river, with probably some additional supply of eolian dusts.

The major element composition of bulk sediment in Core MD12-3432 is dominated by SiO<sub>2</sub> (29%-59%), followed by CaO (4%-25%) and Al<sub>2</sub>O<sub>3</sub> (10%-17%), and of minor content of Fe<sub>2</sub>O<sub>3</sub> (4%-7%), K<sub>2</sub>O (2%-4%), and TiO<sub>2</sub> (0.4%-0.7%). The most prominent feature is that contents of all terrigenous oxides exhibit similar variation patterns opposite to that of CaO%.

# 4. East Asian summer monsoon

East Asian summer monsoon is one of the most important climatic feature in the study area. It is accompanied by high temperature, strong southwesterly winds, and heavy precipitation in summer. Such meteorological conditions may largely influence the different fractions of terrigenous fractions with various mechanisms.

Intensification of East Asian summer monsoon is usually profiled by enhanced precipitation, which would directly increase the river runoff and sediment discharge. This is particularly important in Taiwan because of the steep topography. Strong East Asian summer monsoon rainfall is therefore expected to largely increase the detrital supply of Taiwan and thus increase the relative proportion of terrigenous sediment delivered at sea from Taiwan. Our results suggest that K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of bulk sediment mainly reflect the relative contribution of terrigenous input from Taiwan. The main variability of K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> in Core MD12-3432 is the glacial-interglacial cyclicity with significant increase of this ratio during interglacials. This supports the idea that East Asian summer monsoon intensifies during interglacial periods.

The influence of East Asian summer monsoon on fine-grain detrital supply is more complicated. The warm and humid climate associated with East Asian summer

monsoon would foster the rapid chemical weathering of volcanic rocks in Luzon to produce large amounts of smectite. Therefore, smectite/(illite+chlorite) ratio mainly reflects the intensity of contemporaneous chemical weathering intensity in Luzon, the variability of which depends on the monsoon-induced variations in temperature and moisture. The glacial-interglacial and precessional periodicities of smectite/(illite+chlorite) ratio are in-phase with the boreal summer insolation, supporting the understanding that East Asian summer monsoon is enhanced during interglacial periods and when the boreal summer insolation is strong and during precession highs.

Variations on precessional band related to the low latitude East Asian monsoon are also observed in magnetic properties and both sedimentary and magnetic grain sizes. High magnetic inputs with high hematite proportion, which is part of fine-grain particles, are observed during precession minima. As the fluvial sources cannot account for these variations, we suggest that they are related to enhanced eolian input caused by intensified aridity and probably enhanced winter monsoon. High hematite content associated with fine grain size may therefore serve as a tracer in this region for weak East Asian summer monsoon.

# 5. The land-sea interactions

Besides the East Asian summer monsoon evolution, terrigenous inputs also respond to other land-sea interactions, such as orogeny and sea-level changes. Their influences result in variations in mineralogy and grain sizes at different timescales. Long-term trends are observed in illite, chlorite, and pyrrhotite content. All these minerals characterize river sediments in Taiwan, indicating a continuously increase in the supply of fine-grain sediments from Taiwan. This long-term increase is most likely related to the active Taiwanese orogeny.

On glacial-interglacial scale, coeval variations are observed in magnetite, pyrrhotite and kaolinite contents, sedimentary and magnetic grain size, and sedimentation rates. These variabilities are attributed to sea-level changes. Indeed, when sea-level is low during glacial periods, the Pearl River incises the emerged shelf and delivers to our site more and coarser terrigenous sediments from the continent and from the shelf. Thus, sedimentation rate, magnetite and pyrrhotite content, kaolinite content, and both sedimentary and magnetic grain size increase during glacial periods. In a summary, this study based on the clay mineralogy, magnetic properties, major element composition, and grain sizes of detrital sediments from the northern South China Sea during the late Quaternary allows us to decipher the responses of terrigenous inputs to the East Asian summer monsoon, Taiwanese orogeny, and sea-level changes. Due to the limitation of material and methods, further researches are required to refine this study.

First, the two proposed improved calibration approaches for XRF core-scan data have been tested on only one sedimentary sequence. Both approaches are strongly recommended to be applied on other long sediment sequences to test their performances and to support the paleoenvironmental interpretations based on major element composition.

Second, Core MD12-3432 covers only four eccentricity periods. Although spectral and continuous wavelet analyses reveal the presence of eccentricity periodicity in the clay mineralogical and elemental proxies, this variability is recorded with weak amplitude changes in the detrital fraction in comparison with that on precessional band. It would help to check the meaning of these proxies at glacial-interglacial scale on other longer sediment sequences.

Third, the presence of pyrrhotite is mainly deduced from the facts that iron-sulfide is identified by remanent magnetization and the pyrrhotite is the only iron-sulfide observed in the surrounding river systems. As the presence of pyrrhotite is fundamental for discussion about terrigenous supply from Taiwan, it is worthy to study the lowtemperature magnetic behavior to verify the magnetic mineral composition.

Four, further analyses of the sedimentary grain size, covering the entire grain size spectrum including the coarse fraction might be useful to provide direct information about sediment transport dynamic, such as wind, oceanic current, and sea-level change.

Five, the use of the sedimentary composition to trace changes in the winter monsoon intensity is based on coeval changes in hematite content and grain size on the precessional band. Hematite content is shown by the coercivity and thermal spectra of different samples. This is a very powerful tracer at this site, because its obvious presence, in despite of its weak magnetization, indicates that it is very abundant in volume. This is true for the magnetic fraction within the sediment but other fractions may not be as sensitive as that one. Changes in grain sizes also appear quite clearly, although the resolution of the sortable silt data is at the lower limit to decipher changes at that time scale. Complementary analyses of the sediment composition (Quartz content, color, granulometry) might be useful to confirm the interpretation in terms of eolian inputs.

Six, all the interpretations about paleoenvironmental evolution are based on the assumption that mineralogical and elemental compositions of river sediments are not significantly altered by past environmental changes. There is yet no direct evidences to support this assumption. Future investigations on sediment sequences near the river mouths would be helpful to understand how environmental changes impact the composition of terrestrial sediments.

Finally, this study focuses on the northern South China Sea sedimentary records of East Asian monsoon, sea-level changes, and tectonic activities. These paleoenvironmental variables influence not only the northern part of South China Sea but an enormous area. It is therefore worthy to integrate the regional data with paleoenvironmental records from other related areas, e.g. the southern South China Sea, the East China Sea, and the Philippine Sea, to enrich the understanding of variation patterns and environmental significances of these variables.

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1:00 a.m., my bedroom, Shanghai. Lamps are off, the only lights originate from outside of the window and the screen in front of me. The city is still awake, I am still awake, typing the last chapter of my dissertation. I do not remember how many nights I have passed like this, but I know there is something different this time. No more anxiety, no more confusion. I am close to the objective I have been working for in the last 5 years! At this moment, I am excited and grateful. I want to express my gratitude to so many wonderful people who have guided me, supported me, accompanied me, and helped me through the five-year journey.

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## Appendix A

# **@AGU**PUBLICATIONS

Geochemistry, Geophysics, Geosystems

Supporting Information for

## Correction of interstitial water changes in calibration methods applied to XRF core-scanning major elements in long sediment cores: case study from the South China Sea

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#### Introduction

The reliability of WD-XRF concentrations used as reference datasets for XRF scanning calibration is evaluated in text S1. The detailed descriptions of existing and improved calibrations are introduced in text S2 and S3, respectively. The data used in the XRF scanning calibrations and in the evaluation of calibration methods are included in the supplemental data set S1 and S2. Data set S3 presents the ICP-AES analyses that are used to verify the accuracy of WD-XRF measurements.

# Text S1. Accuracy evaluation of WD-XRF element concentrations

The WD-XRF analysis of major elements has been reported to be of high accuracy by various studies [*e.g.* Tsuchiya et al., 1989; Rousseau et al., 1996; Rahmani et al., 2004; Gazulla et al., 2013; Hunt et al., 2014]. Therefore, quantitative element concentrations obtained by energy-dispersive or wavelength-dispersive XRF have been used as reference datasets for correcting or calibrating XRF-scan intensities in several previous studies [*e.g.* Tjallingii et al., 2007; Weltje and Tjallingii, 2008; Hennekam and De Lange, 2012]. To further confirm the reliability of WD-XRF concentrations used as reference datasets in this study, inductive coupled plasma atomic emission spectrometer (ICP-AES) analyses were performed on 22 discrete samples. Dried and ground bulk sediments were heated at 600°C for 4 hours to remove organic matter. Their weights were measured before and after heating to calculate the loss on ignition (LOI). The sediments, together with a series of Chinese rock and sediment standards (*i.e.* GSR5, GSR6 and GSD9), were digested in HF+HNO<sub>3</sub> mixed acid. Major elements were then measured on an IRIS Advantage ICP-AES. The mean relative accuracy estimated from the Chinese rock and sediment standard samples is better than 4%.

WD-XRF concentrations of six major-element oxides are plotted together with ICP-AES data in Fig S1. The associated uncertainties account for the instrument analysis. Because concentrations in bulk sediments are considered, the 1% analytical uncertainty of LOI [Heiri et al. 2001] is also taken into account in ICP-AES uncertainties.

WD-XRF and ICP-AES concentrations are very consistent within the analytical uncertainties and they follow the same variation patterns [Fig. S1a-S1e]. We observe

that the ICP-AES concentrations are slightly shifted with respect to the WD-XRF concentrations for all five elements. This may be due to the fact that Si is not measured by the ICP method but deduced from the measurement of all other elements and LOI. The observed shifts may therefore result from erroneous Si evaluation. In addition, the log-ratio values and variations are identical in the two datasets [Fig. S1i-S1v], indicating that the relative proportions of elements are exactly the same, no matter the method (ICP-AES or WD-XRF) used to measure the element concentrations. Because the WD-XRF analytical method allows direct measurements of Si concentrations (which account for about 50% of the geochemical composition of bulk sediments in this study), we prefer to use here WD-XRF measurements as reference datasets for the calibration of geochemical concentrations in core MD12-3432.



**Figure S1.** Comparison of ICP-AES and WD-XRF results in terms of oxide concentrations of a) CaO, b)  $Al_2O_3$ , c)  $Fe_2O_3$ , d)  $K_2O$ , and e)  $TiO_2$ , and of log-ratios i) ln(Al/Ti), ii) ln(Al/Ca), iii) ln(Fe/Ti), iv) ln(K/Ca), and v) ln(Ti/Ca). ICP-AES results (black lines) are plotted with their analytical uncertainties (blue lines), and WD-XRF results (black dots) are plotted with analytical uncertainties (blue error bar).

## Text S2. Description of existing XRF calibration methods

#### S2.1 Correction for water absorption effect

Based on high-resolution analysis of three short sediment sequences, Hennekam and De Lange [2012] proposed a routine approach to correct the influence of water absorption on log-ratios of XRF-scan intensities due to variations in water film thickness. According to the Lambert-Beer law [Hubbell, 1982] that describes the relationship between original intensity and residual intensity of a specific X-ray before and after passing through a homogeneous medium, the original intensity  $I_{e,d}$  of element e at depth d can be obtained following equation S1 by assuming that Cl intensity changes only represent variations in water film thickness:

 $I_{e,d} = I_{e,d} \exp\left(\mu_{e,C1} I_{Cl,d}\right) \qquad (\text{eq S1})$ 

where  $I_{e,d}$  is the intensity obtained for element *e* at depth *d* by XRF scanning,  $\mu_{e,Cl}$  is the specific attenuation coefficient for element *e*, and  $I_{Cl,d}$  is the XRF scanning Cl intensity at depth *d*.  $\mu_{e,Cl}$  is empirically obtained by changing its value to reach an optimal linear correlation between corrected XRF-scan intensities and WD-XRF concentrations of the target element.

In the case of core MD12-3432, the entire WD-XRF dataset (102 samples) was used to determine the  $\mu_{e,Cl}$  value for each element. The NMS and MLC methods (named as W NMS and W MLC) were then performed on the water-corrected intensities.

#### S2.2 Normalized median-scaled calibration (NMS)

In the NMS method [Lyle et al., 2012; Lyle and Backman 2013], XRF-scan intensities are first scaled to the range of sedimentary component concentration values, independently for each element. Indeed, various elements do not have the same efficiency of producing characteristic X-ray, and normalizing on XRF-scan intensities would, therefore, produce awry relative proportions with respect to the element compositions. The median-scaled value of an element component *e* at depth d (*S<sub>e,d</sub>*) is:

$$S_{e,d} = W_{e,M} \times I_{e,d} / I_{e,M}$$
 (eq S2)

where  $W_{e,M}$  is the median concentration of the corresponding sedimentary component *e* from the WD-XRF calibration dataset,  $I_{e,d}$  is the XRF-scan intensity of element component *e* at depth *d*, and  $I_{e,M}$  is the median intensity value of element component e over the entire XRF-scan dataset.

In a second step, the median-scaled values are summed and normalized to 100% to eliminate the variability caused by differences in density and cracks. The normalized median-scaled value of element component e at depth d ( $NMS_{e,d}$ ) is calculated as:

$$NMS_{e,d} = S_{e,d} \times 100\% / \Sigma S_d \tag{eq S3}$$

where  $S_{e,d}$  represents the median-scaled value of element component *e* at depth *d*, and  $\sum S_d$  is the sum of median-scaled values of the six sedimentary components at depth *d*.

Finally, normalized median-scaled values are calibrated against WD-XRF concentrations of sedimentary components through linear regression equations, providing high-resolution calibrated concentrations of each sedimentary component in bulk sediments.

#### S2.3 Multivariate log-ratio calibration (MLC)

MLC [Weltje et al., 2015] is developed from the previously proposed log-ratio calibration equation (LRCE) approach [Weltje and Tjallingii, 2008]. The use of centered log-ratios (clr) and partial least squares regression allows the MLC method to take account of multiple covariances at the same time [Weltje et al., 2015]. Therefore the MLC method can directly fit the absorption and enhancement of intensities caused by the presence of unmeasured elements. Benefiting from the multivariate calibration, MLC can also predict bulk element concentrations by including the union of unmeasured elements as one "element" [Weltje et al., 2015]. Moreover, the improved workflow, which includes uncertainty estimation and automatic selection of calibration samples, enhances the predictive power of the MLC method [Weltje et al., 2015].

To perform the MLC, XRF-scan element intensities and WD-XRF element concentrations are first transformed to centered log-ratios, and then scaled with the inverse of their uncertainties determined from replicate measurements. The calibration dataset can be automatically determined using a hierarchical cluster analysis of the scaled clr-transformed intensities. A reasonable model of calibration is then carried out using the calibration dataset by means of partial least squares regression, and is applied to the entire XRF-scan dataset for calibration. The calibration approach has been implemented in the XELERATE software available on line [www.ascar.nl].

# S2.4 Comparison between NMS and W-NMS results and between MLC and W-MLC results

The water absorption correction (described in text S2.1) improves the accuracy of NMS- and MLC-calibrated results by reducing their MSRE [Table S1]. Moreover, as indicated by the increased average  $R^2$  [Table S1], applying the water absorption correction improves their correlation to WD-XRF concentrations. Therefore, W\_NMS and W\_MLC are discussed in the main text (section 5).

However, calibrated W\_NMS and W\_MLC results remain quite similar to the original NMS and MLC calibrated results, respectively, and deviations from WD-XRF concentrations data are still observed for all methods in the top sections of core MD12-3234 [Fig. S2]. This comparison confirms our conclusions (section 5.3 of the main text) that the water absorption correction is insufficient to correct downcore water changes in our case study.



**Figure S2.** Calibration results. NMS (red lines) and W\_NMS (blue lines) results are shown in the left panel (a), MLC (red lines) and W\_MLC (blue lines) results are presented in the right panel (b). WD-XRF evaluation data are shown as yellow dots. Note that A1% and Ti% calibrated by MLC and W MLC refer to relative proportions of A1 and Ti.

## Text S3. Description of proposed improved calibration methods

#### S3.1 Normalized polynomial-scaled calibration (NPS)

In the NPS approach, the polynomial-scaled value of element component e at depth d is first calculated by the equation S4:

 $PS_{e,d} = (\mathbf{a}' \times d^2 + \mathbf{b}' \times d + \mathbf{c}') \times I_{e,d} / (\mathbf{a} \times d^2 + \mathbf{b} \times d + \mathbf{c})$ (eq S4)

where  $I_{e,d}$  is the XRF-scan intensity of element component *e* at depth *d*; a, b, c and a', b', c' are the coefficients of quadratic polynomials fitted through the XRF-scan intensities and WD-XRF concentrations of element component *e*, respectively [Table S2].

In the second step, this polynomial-scaled value is normalized to the sum of WD-XRF concentrations for all element components, instead of to unity as in the NMS, because the sum of all component concentrations is diluted by components that are not included in the calibration (*e.g.* organic matter, Na and Mg) and varies below 90% along the core. As the calibration dataset is smaller than polynomial-scaled dataset, WD-XRF concentration sums are interpolated to fit the polynomial-scaled dataset. The normalized polynomial-scaled value of element component *e* at depth *d* is then determined using the following equation:

$$NPS_{e,d} = \Sigma W_d \times PS_{e,d} / \Sigma S_d$$
 (eq S5)

where  $\Sigma W_d$  is the interpolated sum of WD-XRF concentrations for all element components at depth *d*,  $PS_{e,d}$  is obtained by equation S4, and  $\Sigma S_d$  is the sum of polynomial-scaled values of all element components at depth *d*.

Finally, normalized polynomial-scaled data are calibrated against WD-XRF concentrations for the six chosen major element components using linear regression equations.

#### S3.2 Polynomial corrected multivariate log-ratio calibration (P MLC)

In the polynomial-corrected MLC (P\_MLC) approach, XRF-scan element intensities are first summed to unity. A polynomial correction is then performed in log-ratio space on all possible ratio combinations. The polynomial-corrected log-ratio of element e and D at depth d ( $P_{eD,d}$ ) is calculated using equation S6:

$$P_{eD,d} = (a' \times d^2 + b' \times d + c') + \ln(I_{e,d} / I_{D,d}) - (a \times d^2 + b \times d + c)$$
(eq S6)

where  $I_{e,d}$  and  $I_{D,d}$  are normalized XRF-scan intensities of element *e* and *D* at depth *d*; a, b, c and a', b', c' are the coefficients of quadratic polynomial fitted through the XRF-scan intensities and WD-XRF element concentrations, respectively [Table S2].

All polynomial-corrected log-ratios are then tested to select the element used as common denominator in log-ratios in order to obtain the most robust correction. In this case of core MD12-3432, Ca is chosen as the common denominator. An inverse additive log-ratio transformation is then performed on the polynomial-corrected log-ratios with Ca as common denominator, transforming them to relative proportions of intensities. The transformed dataset is further calibrated using the MLC approach.

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	MSRE				$R^2$			
		AI	Si	К	Са	Ti	Fe	Average
NMS	0.00250	0.92	0.96	0.78	0.98	0.68	0.45	0.80
MLC	0.00289	0.85	0.96	0.78	0.98	0.46	0.20	0.71
W_NMS	0.00169	0.93	0.94	0. 92	0.98	0.84	0.66	0.88
W_MLC	0.00183	0.81	0.96	0.91	0.99	0.68	0.49	0.81

Table S1. Comparative performance of the NMS, W\_NMS, MLC and W\_MLC calibrations based on the independent WD-XRF evaluation dataset.

Table S2. Parameters of quadratic polynomial equations applied to XRF-scan element intensities and WD-XRF component concentrations in NPS calibration (equations S4), as well as XRF-scan and WD-XRF element log-ratios in P\_MLC calibration (equation S6).

	Σ	KRF core-scanning	g	WD-XRF			
	а	b	С	a'	b'	c'	
NPS							
$Al_2O_3$	-1.80469×10 <sup>-4</sup>	$1.68432 \times 10^{0}$	8.97978×10 <sup>3</sup>	2.78273×10 <sup>-9</sup>	-8.40326×10 <sup>-5</sup>	1.37066×101	
SiO <sub>2</sub>	-2.45332×10 <sup>-3</sup>	1.79966×10 <sup>1</sup>	1.00061×10 <sup>5</sup>	-1.81234×10 <sup>-7</sup>	2.41132×10 <sup>-4</sup>	4.51526×101	
K <sub>2</sub> O	-1.41146×10 <sup>-3</sup>	1.02346×101	$7.65880 \times 10^{4}$	-1.51777×10 <sup>-8</sup>	7.41048×10 <sup>-5</sup>	$2.50604 \times 10^{0}$	
CaCO <sub>3</sub>	7.41644×10 <sup>-3</sup>	1.63646×10 <sup>1</sup>	3.49452×10 <sup>5</sup>	7.16093×10 <sup>-8</sup>	1.12871×10 <sup>-3</sup>	1.62933×101	
TiO <sub>2</sub>	-3.86774×10 <sup>-4</sup>	$2.12999 \times 10^{0}$	2.59334×10 <sup>4</sup>	-1.23080×10 <sup>-9</sup>	1.69629×10 <sup>-6</sup>	3.50704×10 <sup>-1</sup>	
Fe <sub>2</sub> O <sub>3</sub>	-2.86182×10 <sup>-3</sup>	1.37946×10 <sup>1</sup>	2.67617×10 <sup>5</sup>	9.82231×10 <sup>-9</sup>	-4.98498×10 <sup>-5</sup>	$5.19958 \times 10^{0}$	
P_MLC							
Ln(Al/Ca)	-3.02644×10 <sup>-8</sup>	1.05644×10 <sup>-4</sup>	-3.62151×10 <sup>0</sup>	-1.09977×10 <sup>-9</sup>	-7.01019×10 <sup>-5</sup>	1.22727×10 <sup>-1</sup>	
Ln(Si/Ca)	-3.34144×10 <sup>-8</sup>	9.94519×10 <sup>-5</sup>	$-1.20827 \times 10^{0}$	-5.30853×10 <sup>-9</sup>	-5.91265×10 <sup>-5</sup>	$1.18852 \times 10^{0}$	
Ln(K/Ca)	-2.84439×10 <sup>-8</sup>	6.29718×10 <sup>-5</sup>	$-1.47834 \times 10^{0}$	-7.18546×10 <sup>-9</sup>	-3.55063×10 <sup>-5</sup>	$-1.12705 \times 10^{0}$	
Ln(Ti/Ca)	-2.62373×10 <sup>-8</sup>	2.14666×10 <sup>-5</sup>	$-2.56272 \times 10^{0}$	-3.60930×10 <sup>-9</sup>	-6.01153×10 <sup>-5</sup>	$-2.90324 \times 10^{0}$	
Ln(Fe/Ca)	-2.23219×10 <sup>-8</sup>	-7.08975×10 <sup>-6</sup>	-2.29677×10 <sup>-1</sup>	-4.20260×10 <sup>-10</sup>	-7.35452×10 <sup>-5</sup>	-5.66757×10 <sup>-1</sup>	

Data Set S1. Discrete measurements of core MD12-3432. WD-XRF data (both calibration and evaluation dataset), dry bulk density and water content are included.
Data Set S2. XRF core scanning data of core MD12-3432 used in the calibration.
Data Set S3. ICP-AES data of core MD12-3432 used to verify the accuracy of WD-

XRF analyses.

## **Appendix B**

## Supporting information for Chapter 4

Clay mineralogical and geochemical proxies of the East Asian summer monsoon evolution in the South China Sea during Late Quaternary

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## Contents of this file

Text S1 Figures S1 to S2

## Text S1 Major Element Composition

In Core MD12-3432, major elements of bulk sediment are dominated by SiO<sub>2</sub> (29%-59%), followed by CaO (4%-25%) and Al<sub>2</sub>O<sub>3</sub> (10%-17%), and minor content of Fe<sub>2</sub>O<sub>3</sub> (4%-7%), K<sub>2</sub>O (2%-4%), and TiO<sub>2</sub> (0.4%-0.7%). All terrigenous element oxides exhibit the same variation pattern, increasing during glacial periods (Fig. S2). On the contrary, CaO% decreases notably during glacials (Fig. S2). Short-term variations are also observed with the same opposed pattern between terrigenous element oxides and CaO (Fig. S2).





**Figure S1** Composition of major element oxides calibrated from XRF-scanning data<sup>1</sup>. Shaded areas highlight interglacial periods.



**Figure S2** Age model of Core MD12-3432. Carbonate content calibrated from XRF core-scanning data is displayed versus depth, together with the age-based CaCO<sub>3</sub>% profile and benthic foraminifera  $\delta^{18}$ O record form ODP Site 1146<sup>2,3</sup>. As a composite age model of ODP Site 1146 was used, the blue and red curves represent age models reported by Caballero-Gill et al.<sup>2</sup> and Clemens et al.<sup>3</sup>, respectively. Grey dashed lines illustrate the position of pair points.

#### Reference

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## Appendix C

## Supporting information for Chapter 5

## Late Quaternary climatic forcing on the terrigenous supply in the northern South China Sea: input from magnetic studies

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Appendix C Supporting information for Chapter 5



**Figure S1** Earth magnetic field records of Core MD12-3432. The red line represents the expected geocentered dipole inclination at the site latitude. Three excursion events are highlighted by blue shades.



**Figure S2** Examples of raw curves shown as examples in Figure 4. Normalized SIRM acquisition curves and backfield curves obtained at 30 and 31 m are illustrated on the left panel. The CLG decomposition of the curve obtained at 31 m is presented on the right panel as linear acquisition plot (LAP), gradient acquisition plot (GAP), and standardized acquisition plot (SAP).

## Appendix D

## Curriculum Vitae

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Date of Birth: December, 1988	Shanghai, 200092, China	tono la
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#### Education

2011.09–2016.12 Ph.D. program, Tongji University

2014.01-2016.01 Jointly-supervision Ph.D. program, Université Paris-Saclay Topic: Detrital signatures of Late Quaternary paleoenvironmental changes in the northern South China Sea

2007.09-2011.06 B.Sc. in Geology, Tongji University

2009.09-2010.06 Exchange program, B.Sc. in Earth Science, Université Lille 1

#### Publication

**Chen, Q.**, Kissel, C., Govin, A., Liu, Z., Xie, X., 2016. Correction of interstitial water changes in calibration methods applied to XRF core-scanning major elements in long sediment cores: Case study from the South China Sea. Geochemistry, Geophysics, Geosystems 17, 1925-1934. Doi: 10.1002/2016GC006320

**Chen, Q.**, Liu, Z., Kissel, C., 2017. Clay mineralogical and geochemical proxies of the East Asian summer monsoon evolution in the South China Sea during Late Quaternary. Scientific Reports 7, 42083. Doi: 10.1038/srep42083

#### Manuscripts in review

**Chen, Q.**, Kissel, C., Liu, Z., submitted. Late Quaternary climatic forcing on the terrigenous supply in the northern South China Sea: input from magnetic studies. Earth and Planetary Science Letters.

#### **Scientific Meetings**

**Chen, Q.**, Kissel, C., Liu, Z., 2015. Clay mineralogical records in the northern South China Sea during the last 410 kyr: implications of East Asian monsoon and sediments transportation evolution. Journée de Paléocéangraphie, Brest, France. Poster.

**Chen, Q.**, Liu, Z., Kissel, C., 2015. Sediment transport processes and East Asian monsoon evolution during the last 410 kyr in the northern South China Sea: a multi-proxy approach. EGU General Assembly, Vienne, Austria. Verbal.

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**Chen, Q.**, Liu, Z., Stattegger, K., Unverricht, D., 2013. Clay mineralogical records in the northwestern South China Sea since the last deglaciation: sea-level rise controlled red river contribution. 6<sup>th</sup> International Workshop on the Fluvial Sediment Supply to the South China Sea. Selangor, Malaysia. Verbal.

**Chen, Q.**, Liu, Z., Stattegger, K., 2012. Clay mineralogical record on the upper continental slope of the northwestern South China Sea since the Last Glacial Maximum. AGU Fall Meeting, San Francisco, USA. Poster.

#### **Fieldworks/Shipboard Experiences**

Apr., 2013. NSFC Open Cruise in the northern South China Sea

Sep., 2012. Scientific Cruise to retrieve and deploy mooring systems in the South China Sea

May, 2012. CIRCEA Cruise (MD190) in the northern South China Sea

Jun., 2011. Fieldwork in South China to sampling river sediments from numerous coastal rivers.

## UNIVERSITE

#### ÉCOLE DOCTORALE Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

**Titre :** Signatures d étritiques des changements pal écenvironnementaux du Quaternaire r écent dans le bassin nord de la Mer de Chine du Sud

Mots cl és : Mer de Chine du Sud, mousson d'été asiatique, changements de niveau marin, orog ène Taiwanais, min éralogie argileuse, min éralogie magn étique

**R ésum é:** La mer de Chine du Sud (SCS) est la plus grande mer marginale situ é àl'ouest du Pacifique. En raison de son emplacement unique et de son environnement particulier, c'est un laboratoire naturel pour étudier l'histoire du climat et des interactions terremer àbasses latitudes. Nous avons étudi é la min éralogie, la géochimie et la granulom étrie d'une s équence s édimentaire pr dev ée au nord de la SCS pour reconstruire

les changements environnementaux pass és dans cette région et pour identifier des traceurs fiables. Nous proposons dans cette étude trois traceurs d'intensit éde la mousson d'ét é asiatique, chacun contrôl é par des mécanismes différents. En outre, nos r ésultats indiquent également que l'orog ène continental et les changements du niveau marin influencent largement les apports d étritiques àdifférentes échelles de temps.

**Title :** Detrital signatures of Late Quaternary paleoenvironmental changes in the northern South China Sea

**Keywords :** South China Sea, East Asian summer monsoon, sea-level changes, Taiwan orogeny, clay mineralogy, magnetic mineralogy

**Abstract :** The South China Sea is the largest marginal sea located in the west Pacific. Because of its unique location and environment, it is a natural laboratory to study the history of climate and land-sea interactions at low latitudes. We investigated the mineralogy, geochemistry, and granulometry of a sedimentary sequence retrieved from the northern part of the South China Sea in order to reconstruct the past environmental changes in this area and to identify reliable tracers. We proposed three tracers of the East Asian summer monsoon intensity, each controlled by different mechanisms. In addition, our results also indicate that orogeny on land and sea-level changes largely influence the detrital supply at the studied site at different timescales.