

Fluid-rock interactions on icy moons

Amber Elizabeth Zandanel

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Amber Elizabeth Zandanel. Fluid-rock interactions on icy moons. Galactic Astrophysics [astro-ph.GA]. Université Grenoble Alpes [2020-..], 2021. English. NNT: 2021GRALU007. tel-03212098

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THÈSE

Pour obtenir le grade de

DOCTEUR DE L'UNIVERSITÉ GRENOBLE ALPES

Spécialité : Sciences de la Terre et de l'Univers et de l'Environnement

Arrêté ministériel : 25 mai 2016

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préparée au sein du Laboratoire Institut des Sciences de la Terre dans l'École Doctorale Sciences de la Terre de l'Environnement et des Planètes

Interaction fluide roche sur les satellites de glace

Fluid-rock interactions on icy moons

Thèse soutenue publiquement le **23 février 2021**, devant le jury composé de :

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Acknowledgments

It takes a village to finish a PhD, and in this case, I have had so much incredible help and support that it feels more like a village for every chapter. I am exceptionally grateful to my supervisors, Laurent Truche and Roland Hellmann, both for their expert guidance in the research process, and for their kind support in making the move to Grenoble. I want to thank especially Thomas McCollom and Damien Daval for taking the time to provide such thoughtful and thorough reviews of this manuscript, as well as to the Isabelle Daniel and Vassilissa Vinogradoff for their insight as members of the thesis jury. Much appreciation, also, to Fabrice Brunet and Lydie Bonal for providing direct, constructive feedback on my research progress during the PhD.

This PhD was funded by the Organic and Aqueous Systems on Icy Satellites (OASIS) ANR project led by Gabriel Tobie, so it is not a hyperbole to say this entire project would not exist in its current form without his expertise. Both he and Gaël Choblet at LPG in Nantes were instrumental in developing the project design, scope, and text of Chapter 2 and the focus of Chapter 3. The original structure of the reactive transport model used in Chapter 2 was designed by Andrey Myagkiy, who was also immensely supportive in adapting it to its current form. Yasuhito Sekine and one anonymous reviewer provided helpful feedback on Chapter 2. Eric Quirico at IPAG and Armelle Phillip at IGE graciously facilitated ice-olivine microscopy work, and Michel Mermoux at LEPMI designed and performed the Raman analyses, both presented in Chapter 3. I am grateful to Vladimir Roddatis at GFZ, Potsdam for his attention to detail in sample preparation and high-resolution TEM analyses presented in Chapters 3 and 4. Anne-Line Auzende, along with colleagues at the University of Marseille, and Anne-Claire Gaillot in Nantes contributed significantly to this manuscript by collecting and interpreting TEM data as presented in Chapter 4. Nathaniel Findling invented and constructed the chiller apparatus for the 0 °C flow-through experiments of Chapter 4. Yves Marocchi at CRPG in Nancy kindly provided all of the olivine used in the experimental studies in this manuscript. In addition, both he and David Bekeart introduced me to the Nebulotron synthesis of the organic material used in the experiments of Chapter 5 and offered timely responses to my many questions about chondrites and organic alteration. Laure Fort designed and executed the HPLC analyses, and Martine Lanson developed the capillary electrophoresis analyses methods, both discussed in Chapter 5. François-Régis Orthous-Daunay, Véronique Vuitton, Junko Isa, and Laurène Flandinet at IPAG and David Bekaert at CRPG helped design and direct the organic alteration experiment project presented in Chapter 5. Junko additionally took on the significant task of collecting and interpreting the Orbitrap data, also presented in Chapter 5.

I am indebted to the nearly everyone on the geochemistry and mineralogy research teams at ISTerre, including (though not limited to!) Delphine Tisserand, Martine Lanson, Sarah Bureau, Sylvain Campillo, Nathaniel Findling, Valérie Magnin, Benjamin Malvoisin, Axel Denys, Andrew Lauer, Mélusine Velde, and Boris Chauviré for analytical support and scientific insight. I also greatly enjoyed and benefited from scientific conversations with Colin Fauguerolles, Mathilde Kervazo, Mikail Zolotov, Christophe Sotin, and other OASIS researchers during the rare project meetings.

Finally, a lot of people deserve infinite thanks for just being good company during my PhD, including (though again, not limited to!) all of the perennially-injured anglophone climbers of Grenoble, the warmly welcoming community of students and researchers at ISTerre, and especially Jacques and Tobias for sharing in the daily drama of doing a PhD and making our little office a home. I actually could not have done this without such a supportive community of family, friends, and colleagues whose commiseration and encouragement kept me grounded, both in Grenoble and from afar. Finally, so much thanks to my partner Nate, for really everything.

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CHAPTER 1

Introduction

SUMMARY

Experimental and modelling approaches to studying the habitability of Enceladus and other icy worlds

Chapter 1

Chapter 1. Introduction

1.1 Hydrothermal systems on icy worlds: why so interesting?

Liquid water, and to some degree water-rock interaction, are considered to be necessary prerequisites to the emergence and sustenance of life. Traditionally, astrobiological exploration has then focused on the circumstellar habitable zone in any planetary system. This is generally considered to be the narrow distance from a star where incoming solar radiation to a sufficiently large satellite can maintain a surface temperature between the boiling point and freezing point of water. Too close to the star, and all water vaporizes; too far, and the satellite freezes solid (Fig. 1.1). This gives the name to the outer boundary of this zone: the 'frost line'. One of the most exciting recent developments in space exploration has challenged this model: the discovery that several small satellites beyond the frost line in our solar system are not frozen solid, and are likely supporting liquid water oceans beneath their icy crusts.



Fig. 1.1: The habitable or "Goldilocks" zone (modified from exoplanets.nasa.gov, 2020).

The existence of liquid water formed by endogenic activity on the icy moons orbiting Jupiter and Saturn has long been a theoretical possibility. As early as the 1970s, following observations from the Voyager missions, it was shown that tidal forces generated by orbital dynamics of Jupiter's moon Europa could generate a liquid water ocean (Cassen et al., 1979). Saturn's largest moon, Titan, had also been shown to have evidence of tidal dissipation indicating a liquid layer that decouples an outer icy crust from an inner rocky core (Sagan & Dermott, 1982). The proposed composition of this liquid layer has ranged from ammonia-water mixtures (Cynn et al., 1989; Fortes, 2000) to seas of liquid methane and hydrocarbons (Lunine et al., 1983). The smooth, uncratered surface of Enceladus had also been postulated to indicate resurfacing by cryovolcanism sustained by tidal heating due its orbital eccentricity (Squyres et al., 1983). Despite these discoveries, the thick icy crusts of these satellites meant that even direct observation of their hypothesized oceans was impractical, let alone extensive sampling or exploration that would better characterize their compositions and geochemical histories.

Saturn's tiny (500 km diameter) icy moon Enceladus provided an unprecedented exception to this challenge. Geyser-like plumes of water vapor emitting from Enceladus were discovered during the Cassini-Huygens mission's flybys of Saturn's moons (Hansen et al., 2006) and identified as the main source of the particles that compose Saturn's E-ring (Spahn et al., 2006). These vapor plumes are collocated with long fractures along the south pole, where there is also a significant high-temperature anomaly (Porco et al., 2006). Sampling of the E-ring by Cassini's ion and neutral mass spectrometer (INMS) showed that the water vapor also hosts salts, suggesting that the vapor plumes are sourced from an underlying liquid reservoir rather than from ablation of the icy crust (Postberg et al., 2009, 2011). Analyses with a second instrument, Cassini's cosmic dust analyzer (CDA), found silica nanoparticles (Postberg et al., 2013) and organic constituents (Postberg et al., 2015) in the E ring, further suggesting that this liquid reservoir is currently hosting water-rock-organic interaction in hydrothermal vents (Hsu et al., 2015; Postberg et al., 2018). Additional analyses positively identified H_2 emitting from the plumes, as well (Waite et al., 2017). The (high) H_2 :CH₄ ratio of these measurements identifies the H_2 as potentially sourced by in-situ inorganic reactions, specifically oxidation of iron in primary mafic minerals, and indicates that the H₂ has not been stored in the rocky core over long time periods (Waite et al., 2017). To date, this provides the most striking evidence of ongoing hydrothermal water-rock activity occurring in any icy ocean world.

The evidence of potential hydrothermal activity is exciting for its astrobiological implications, as early Earth hydrothermal systems have been proposed as a potential environment for the emergence of life on Earth (Hazen & Sverjensky, 2010; Holm, 1992; S. L. Miller & Bada, 1988). Origin-of-life theories are generally based on environments with both water and reduced organic species present (Martin et al., 2008). One longstanding theory for the origin of life, the "prebiotic soup" theory, supposes life arose from a concentrated solution of proteins that acted to transfer genetic information and multiply via adsorption of additional organic molecules (Oparin, 1938). However, this theory requires the spontaneous synthesis and amassing of complex organic molecules at high concentrations (S. L. Miller, 1953; S. L. Miller & Urey, 1959), something that is not often observed in natural systems (Martin et al., 2008). On Earth, seafloor hydrothermal vents – as a source of reducing fluids, organic carbon, thermal and chemical energy, and mineralogical mechanisms of concentrating organic molecules – are considered among the likely environments that might meet these criteria.

Seafloor hydrothermal vents associated with mid-ocean ridges were discovered in 1977, when an oceanographic expedition discovered the Galapagos Rift Thermal Springs (Corliss et al., 1979). These types of hydrothermal vents occur where seawater, heated by magma beneath the active spreading ridge, is vented back into the ocean at 360 °C or above. The venting fluid is acidic (pH 2-3), rich in reactive gases, sulfide, and dissolved elements, in particular metals including reduced iron and manganese. Interaction between reduced, reactive constituents with seawater creates thermal and redox potential gradients over small (cm to m) scales that can promote prebiotic reactions (Barge et al., 2015; Barge & White, 2017). However, the high temperatures at these vents are well beyond the currently assumed upper limits tolerated by life (122 °C: McKay, 2014; Takai et al., 2008). Such high temperatures generally drive decomposition of complex organic molecules, and are not thought to be conducive to sustaining the high concentrations of organic compounds needed for polymerization of prebiotic molecules, specifically proteins (Bada, 2004).

In light of these constraints, the discovery of the lower-temperature (75-116 $^{\circ}$ C) Lost City Hydrothermal Field (LCHF) in 2000 (Kelley et al., 2001) was all the more interesting as a potential environment for the emergence of life. The hydrothermal activity in the LCHF, rather than being driven by volcanic activity, is thought to be largely driven by the exothermic alteration of ultramafic peridotite massifs (discussed in section 1.3). As a by-product of this alteration, the fluids that are vented in LCHF are alkaline (pH 9-11) and rich in dissolved elements, H_2 , CH_4 , and abiotically generated hydrocarbons (Proskurowski et al., 2008). As a model for hydrothermal vents on Enceladus and other icy satellites, vents such as LCHF are cited as the most likely analogue (Fig. 1.2): low-temperature, alkaline vents driven by exothermic alteration of the same primary mafic minerals that are common in the chondrites and meteorites that compose these small satellites.



Fig. 1.2: conceptual model of hydrothermal activity at the south pole of Enceladus (nasa.jpl.gov). Surface jets are based on images of the plume source; the illustrated water-rock reactions and hydrothermal vents at the seafloor are conceptual models based on geochemical data (see section 1.2).

1.2 Models of hydrothermal activity on icy satellites

One question in evaluating the potential habitability of other worlds is the length of time that they can support habitable environments, such as hydrothermal vents, given the constraints detailed above. The emergence of life is sometimes framed as a probability based on a number of favorable conditions (Forgan, 2009), many of which are inherently undeterminable as long as the true origins of life are still under debate. However, as specific environmental conditions on geologically active worlds are by definition transient, the temporal factor at least can be considered (Ćirković, 2004). If favorable conditions for the emergence of life are only available for a vanishingly short time, then the likelihood of life emerging there is similarly vanishingly small. Defining the timescales of these environmental conditions on icy satellites of course presents its own challenges. Even the existence of hydrothermal vents in Enceladus is indirectly inferred from few, though exciting, data. Evaluating the geologic histories of these satellites, including the presence or duration of liquid oceans or hydrothermal activity, has then long relied on modelling constrained by remote observations.

In the Saturnian system, orbital and geophysical models have progressed rapidly in the past 20 years with the observational data provided by the Cassini mission. In particular, new geophysical constraints on the densities and differentiation within each moon have spurred an active debate on the ages and orbital histories of Saturn's moons and rings. The geophysical evidence for a liquid ocean on Enceladus that completely separates its icy crust from a rocky inner core has superseded previous assertions that the moon is too small to sustain a tidally heated liquid ocean. This, in turn, inspired new models of tidal heating (Choblet et al., 2017; Liao et al., 2020), which again must be reconciled with the evolution of the other moons. Thermal evolution models of Saturn's innermost moons show that tidal heating could sustain a liquid ocean on Enceladus for up to 1 Gyr, supposing a 4.5 Gyr orbital history (Neveu & Rhoden, 2019; Fig. 1.3). Other lines of reasoning have proposed radically different histories that attain the same current state of Enceladus, such as the analysis of Ćuk et al. (2016) that proposed a recent (< 100 Mya) disruption and re-accretion of Saturn's inner moons in order to explain their current orbital configurations. In short, while observations from the Cassini mission have provided a new wealth of geophysical constraints, these constraints have not yet led to a consensus on the ages, orbital histories, or structural evolutions of Saturn's moons.



Fig. 1.3: Thermal evolution of Enceladus (modified from Neveu and Rhoden, 2019). The legend indicates color for temperatures -273 to 327 $^{\circ}$ C (0-600 K), with a demarcation at the liquidus (total melting point, at 0 $^{\circ}$ C) of the NH₃-H₂O system. Y axis depths range from core (0) to surface. Yellow arrow at "Ocean" indicates the duration of Enceladus' history where the temperature inside the moon is > 0 $^{\circ}$ C and a liquid water ocean differentiates from the rocky core.

The recent and current scientific discussions exploring the history and current state of water-rock interaction within Enceladus is similarly active. Based on the $H_2:H_2O$ ratio in Enceladus' plumes, Waite et al. (2017) calculated the H_2 release rate from Enceladus as 10^9 moles yr⁻¹, the major proportion of which is interpreted to be attributable to inorganic mineral alteration. Based on the total amount of H_2 producible from a rock core the size of Enceladus', water-rock alteration could sustain this release rate for hundreds of millions of years. This can be compared to other models of water-rock interaction in Enceladus' core. The 1D reaction models of (Malamud & Prialnik, 2013, 2016) evaluate heat generation by water transport through the core, including a fixed alteration rate for primary minerals. As they do not assume a mechanism for the re-introduction of water into the porous core, their results show that water forced out of the core by compaction pressures quickly freezes, forming an ice crust in contact with the rock core before the primary mineralogy can be completely altered to secondary hydrous minerals. However, their results also show that even during this relatively brief geologic period (~20 Myr), the majority of primary minerals within the core are converted to hydrous secondary phases. Similarly, fracture-based models of primary mineral alteration by water do not yield results that extend the alteration timespan (Vance & Melwani Daswani, 2020).



Fig. 1.4: a. conceptual model the interior of Enceladus and b. an associated model of water flow and water-rock interaction regimes at Enceladus' shallow vs. deep core, as presented by Glein et al. (2018). The water-rock interaction regimes describe a differentiated core where carbonate geochemistry dominates the shallow core and serpentinized rock in a reduced environment is the major component of the deep core.

The existence and relative abundances of salts, N2, NH3, CO2, CH4, H2, and silica nanoparticles associated with the water vapor emitted from Enceladus have additionally been used to constrain various properties of Enceladus' liquid ocean and possible water-rock reactions therein. The CO₂:CH₄ ratios of the plume have been calculated to indicate largely reducing redox conditions (Glein et al., 2008). The presence of NH_3 and the calculated carbonate stability indicate an alkaline pH (Glein et al., 2015; Hsu et al., 2015) that is constrained to pH 8.5-10.5 (for a fluid at 25 °C), based on experimental and modelled silica nanoparticle formation and stability (Hsu et al., 2015; Sekine et al., 2015). Recent models of seafloor hydrothermal vents in Enceladus explore more localized geochemical scenarios, postulating a general divide between shallow, carbonate-driven seafloor water-rock interactions and deep-core alteration dominated by serpentinization reactions (Glein et al., 2018; Glein & Waite, 2020; Ray et al., 2020). Based on equilibrium models of the geochemical co-evolution of a rocky core having an idealized chondritic mineralogy and circulating water, Zolotov (2007) proposed a range of geochemical compositions for a liquid reservoir as might exist in Enceladus. The range proposed by Zolotov's model encompasses the range of ocean compositions subsequently calculated from the salts found in Enceladus' emissions (Waite et al., 2009, 2017), although some constituents of the model (namely magnesium and sulfur species) have not been identified in the plumes or E-ring and as such cannot be evaluated by comparison. All these models, consistent with the geochemical data collected by Cassini, indicate a history of hydrothermal water-rock interaction in Enceladus that has resulted in an ocean approaching equilibrium with a chondritic rocky core.

1.3 Experimental insights into olivine alteration on icy satellites

In any discussion of serpentinization-driven hydrothermal activity, the mechanism of serpentinization itself is a critical focus of inquiry. While the mechanisms between elementary reactions and overall reactions (usage as defined by Lasaga, 1984) are intimately interrelated, experimental studies by design often focus on fundamental processes by isolating reactions to better understand natural processes. For the purposes of this discussion, studies of olivine alteration in aqueous fluids can be loosely grouped by their focus on either olivine dissolution, or serpentinization. Dissolution studies as discussed here are generally structured to attain a steady-state, stoichiometric olivine dissolution rate. Most studies also provide information on the kinetic factors that influence measured dissolution rates. The serpentinization studies considered here, in a general sense, focus on the hydration of olivine or ultramafic rocks, and in particular the rates and mechanisms of the entire conversion process from primary to secondary phases.

1.3.1 Olivine dissolution

San Carlos olivine ($Mg_{1.83}Fe_{0.17}SiO_2$, which is close in composition to the pure Mg-end-member mineral forsterite) provides a convenient model mineral for evaluating alteration processes that may occur throughout the solar system, as magnesium-rich olivine is a common constituent of chondrites and meteorites. San Carlos olivine dissolution can be described by the following reaction:

 $Mg_{1.82}Fe_{0.17}SiO_4 + 4 H^+ \rightarrow 1.82 Mg^{2+} + 0.17 Fe^{2+} + SiO_2 + 2 H_2O$ Equation 1.1

The study of forsterite-water interactions benefits from decades of experimental research that report the rates and mechanisms of olivine dissolution (as well as overall serpentinization reactions, discussed below). Olivine dissolution as in Eq. 1.1 can be thought of as an elementary reaction of complex serpentinization reactions (although in reality, the process of dissolution itself can be framed as a complex reaction where breaking and rearranging each of the Mg-O and SiO-Mg bonds are elementary reaction steps. See for example Rimstidt et al. (2012) for a review).

Empirical studies of San Carlos olivine show that the strongest determining factors of the dissolution rate are temperature and pH. At low temperatures and pressures relevant to Enceladus (0-150 °C, up to 400 bar), the dissolution rate of olivine is one of the fastest of all silicate minerals, in accord with the Goldich mineral stability series formulated in the 1930s (Goldich, 1938). Some studies have shown that olivine dissolution is as much, or even more, sensitive to changes in pH as compared to temperature in the 0-150 °C range (Hänchen et al., 2006). Like other Mg-silicates (Oelkers, 2001), the solubility of olivine is generally modelled as decreasing with pH increase, even in very high pH fluids (pH 11-14). Based on aggregated empirical findings, the general mechanism of olivine alteration is interpreted to change from acid to alkaline conditions (e.g. Crundwell, 2014; Palandri & Kharaka, 2004; Pokrovsky & Schott, 2000a, 2000b). This generally assumes two parallel reactions: one at silica-rich surface sites that is active in acidic conditions and another at hydrated Mg surface sites that dominates in alkaline conditions (Fig. 1.5a). This conceptual model for forsterite dissolution is expressed as follows (as from Pokrovsky & Schott, 2000b):

$$R = k_{Si} \{>Si2O-H^+\} + k_{Mg} \{>MgOH2^+\}$$
 Equation 1.2

In the above equation, *R* indicates the overall dissolution rate in mol cm⁻² s⁻¹, k_i indicates a rate constant for Si and Mg and {>*j*} designates the concentration of surface species *j* in mol m⁻². The output of this empirically derived model describes a generally weaker dependence of dissolution rate on pH at alkaline vs. acid conditions. This is borne out by several recent meta-analyses of olivine dissolution rate studies (Brantley, 2003; Oelkers et al., 2018; Rimstidt et al., 2012).



Fig. 1.5 Forsterite dissolution mechanisms and rates. a. Forsterite dissolution mechanism in acid vs. alkaline solutions, adapted from Pokrovsky and Schott (2000b). b. Aggregated dissolution rate equations of olivine dissolution over pH, as presented by Oelkers et al. (2018). Lines plot the rate equation given by each of the noted publications (Crundwell, 2014; Palandri & Kharaka, 2004; Pokrovsky & Schott, 2000b; Rimstidt et al., 2012; Wogelius & Walther, 1991) and the grey shaded area indicates the approximate limits of the experimental data used in generating the plotted rate equations.

Olivine dissolution studies are notably better represented in the low- to neutral-pH range, and as pH increases the variance between calculated rates also increases (grey shaded area in Fig. 1.5b). Throughout the entire pH range, olivine dissolution often starts out non-stoichiometric before converging to a stoichiometric steady-state dissolution rate: at acid-to-neutral pH solutions, the initial behavior is Mg > Si, with stoichiometric steady-state dissolution occurring after several hours; in alkaline pH solutions, initially Si > Mg, with stoichiometric dissolution being achieved only after days or weeks (Pokrovsky & Schott, 2000b). Rates calculated from data obtained during the initial period do not therefore reflect the stoichiometric steady-state dissolution rate. The inclusion of rates calculated during experiments at non-stoichiometric dissolution may in part be the reason for the increased variance between rate data in alkaline conditions. In addition, the ambiguity of whether rates reported by all studies represent stoichiometric dissolution is far from the only potential difficulty in comparing rate data between different experimental data sets. Select studies of olivine alteration have shown the formation of an amorphous silica layer on the olivine surface that may slow olivine dissolution (Béarat et al., 2006; Sissmann et al., 2013), and that may even start forming within a matter of days (Daval et al., 2011). These same types of surface altered layers (SAL) have been found in olivine reacted in flowthrough experiments, implying that surface interfacial processes control the formation of SALs even when they are not predicted to form by bulk fluid chemistry (Hellmann et al., 2012). This calls into question the "steady-state" assumption of "stoichiometric steady-state" dissolution, as it implies that this apparent steady-state dissolution rate may actually decrease over time. To date, detailed studies at the nm-scale of fluid-solid interfaces have been restricted to olivine reacted in acid solutions; at basic pH conditions, there is a distinct lack of data on surface alteration reactions.

1.3.2 Serpentinization

Serpentinization is a process closely related to olivine dissolution that was originally formulated to describe the exothermic conversion of ultramafic primary minerals (namely, olivine and pyroxene) to

serpentine minerals (chrysotile, lizardite, and/or antigorite), magnetite, and H₂. The serpentinization of olivine specifically can be described by the following reactions:

$2 \text{ Mg}_2 \text{SiO}_4 \text{ (forsterite)} + 3 \text{ H}_2 \text{O} \rightarrow \text{Mg}_3 \text{Si}_2 \text{O}_5 \text{(OH)}_4 \text{ (serpentine)} + \text{Mg}(\text{OH})_2 \text{ (brucite)}$	Equation 1.3
3 Fe ₂ SiO ₄ (fayalite) + 2 H ₂ O \rightarrow 2 Fe ₃ O ₄ (magnetite) + 3 SiO ₂ + 2 H ₂	Equation 1.4

As with olivine dissolution, rates of serpentinization are similarly sensitive to temperature and pH. An abundance of studies constrain serpentinization at 200-350 °C, temperatures relevant to mid ocean ridge hydrothermal systems (Elderfield & Schultz, 1996). Generally, the rate of serpentinization increases with temperature, with maximum serpentinization rates occurring over a range of temperatures (250-310 °C) (Lamadrid et al., 2020; Malvoisin et al., 2012; Wegner & Ernst, 1983). The rate of conversion from primary to secondary minerals should not be considered to be a simple process (Seyfried et al., 2007), an assertion that is perhaps evident from the fact that "serpentinization" can start with a single mineral, or a complex ultramafic mineral assemblage. In addition, fluid chemistry properties such as pH, ionic strength, and redox potential often dynamically change during experiments. These complexities, of course, can then affect the rate of formation and stability of any secondary phases (Janecky & Seyfried, 1986). For example, (McCollom et al., 2020) recently showed that the type and abundance of secondary phases is sensitive to both the initial mineral assemblage (olivine vs. olivine-orthopyroxene) and to pH, while (Tutolo et al., 2018) found that the silicification of secondary brucite into tertiary serpentine can act as a rate-limiting step in serpentinization at 150 °C. Given these complexities, it is not surprising that reported rates of serpentinization vary by up to 5 orders of magnitude (Andreani et al., 2013; Lafay et al., 2012; Malvoisin et al., 2012; Ogasawara et al., 2013; Wegner & Ernst, 1983). All of these aspects of serpentinization rates and mechanisms have been recently reviewed by McCollom et al. (2016).

The heat from exothermic serpentinization reactions and the H₂ generated by Fe(II) oxidation to Fe(III) in magnetite (Eq. 1.4) are of particular interest to habitability constraints, as they may provide thermal and chemical energy where solar energy is nonexistent (Truche et al., 2020). While there remains no consensus on the lower temperature limits of serpentinization and little data to constrain rates of serpentinization at low temperatures, a number of recent studies have led to progress in this field (Table 1). Field studies have identified serpentine minerals and H_2 that are thought to have been produced at in-situ temperatures as low as 30 °C (H. M. Miller et al., 2016; Okland et al., 2012). Magnetite formation (Eq. 1.4) has been identified during low-temperature alteration experiments (H. M. Miller et al., 2017), but even where its formation is inhibited, iron oxidation can occur due to Fe(III) incorporation into serpentine, talc, and Fe(III)(oxy)-hydroxides (Mayhew et al., 2013; Neubeck et al., 2014; Seyfried et al., 2007). Low-T alteration experiments have been shown to produce H₂ from mafic mixed-mineral assemblages as low as 50 °C (Neubeck et al., 2016), and monomineralic lowtemperature studies of San Carlos olivine alteration have shown H_2 production at a range of temperatures as low as 25 °C in pure water (Okland et al., 2014) and 50 °C in carbonated water (Neubeck et al., 2016). Motivated by identifying alteration products on Martian surfaces, experiments focusing on secondary products have pushed the temperature limits even further. Olivine and basalt dissolution in highly acidic, unfrozen brines has been shown to continue to -19 °C (Hausrath & Brantley, 2010), and sulfates were identified after olivine alteration in partially frozen sulfuric acid solutions at -40 and -60 ^oC (Niles et al., 2017).

Study	T (⁰ C)	Minerals	H ₂ ?	CH ₄ ?	Paragenesis	Other remarks
Stevens & McKinley (2000)	30, 60	Basalt	Yes	No	Not reported	
Hausrath & Brantley (2010)	-19, 6, 22	Basalt, olivine	No	No	None identified	Reports olivine dissolution rates at 6 and 22 ºC.
Neubeck et al. (2011)	30, 50, 70	Olivine	Yes (all T)	Yes (T>30)	None identified	
Mayhew et al. (2013)	55, 100	Various (inc. olivine)	Yes	No	Fe(III)- (hydr)oxides	
Okland et al. (2014)	25	Unaltered, medium- altered, and highly-altered dunite	Yes (all)	Yes (from altered)	None identified	CH₄ possibly sourced from secondary minerals. NH₄⁺ is also produced.
Neubeck et al. (2014)						
Neubeck et al. (2016)	50	Dunite	Yes	No	Serpentine, carbonates	
Miller et al. (2017)	100	Partially serpentinized dunite	Yes	No	Serpentine, magnetite	Notes lack of carbonates in paragenesis
Niles et al. (2017)	-60, -40	Olivine	No	No	Sulfate minerals	Reports dissolution rates at both -60 and -40 ^o C.

Table 1: recent experimental studies of olivine alteration at ≤ 100 $^{\circ}C$

1.3.3 NH3 effect on olivine alteration

The evolution of hydrothermal vents on ocean worlds may still be quite distinct from terrestrial environments. Icy satellites beyond the frost line in the solar system in some cases never experience high temperatures, and so can preserve volatile species such as NH₃ and methanol that are miscible in water (Kargel, 1992; Waite et al., 2009). These volatile species may affect the evolution of hydrothermal vents by affecting the dissolution of primary minerals, or by affecting the serpentinization processes by stabilizing or otherwise controlling secondary phases. Considering the potential effect of NH₃ on olivine dissolution, a review of rate limiting factors on olivine dissolution suggest that changes to water activity, density, or nitrogen content are not known to significantly affect olivine dissolution rates (Rimstidt et al., 2012). However, NH₄⁺ conspicuously resembles H₂O in several respects (molar masses, bond angles, interatomic distances, partial molar volumes, and hydrogen bond strengths) and may therefore stabilize dissolved species owing to its tetrahedral shape and its ability to form hydrogen bonds (Brugé et al., 1999; Perrin & Gipe, 1987), or via redox processes (Chivers & Elder, 2013). The effects of these parameters on the rate constants of olivine dissolution, by potentially interacting with reactant species at the mineral surface or in the fluid, have not explicitly been explored. Some studies have already shown that NH₃ can stabilize minerals that are also secondary products of olivine alteration: industrial processes have proposed NH₃ as a process step in managing grain size distributions in silica nanoparticle production (Lazaro et al., 2013; Raza et al., 2018; Wang et al., 2011) and, in conjunction with carbonate species, in stabilizing metastable magnesium carbonate minerals such as nesquehonite and roguinite (Zhu et al., 2017). This in turn suggests the possibility that NH₃ may affect primary mineral dissolution rates by controlling the production and stability of secondary minerals formed at the primary mineral surface, inhibiting primary mineral interaction with the bulk water phase.

1.4 Synthesis and alteration of organics in exotic hydrothermal environments

Abiotic organic synthesis and concentration is a key point in discussions of the emergence of life, deep subsurface microbial activity, and global geochemical carbon cycling (Ménez, 2020; Truche et al., 2020). Currently, there are two major sources of abiotic organic compounds envisioned on Earth. First, abiotic organics may be formed within the shallow crust through reduction of inorganic carbon compounds (such as carbonates or CO). Second, they could be sourced from the mantle and supplied to the crust through the migration of magmatic fluids (Sephton & Hazen, 2013). This second theory presupposes the widespread existence of carbon and organics in the mantle that were inherited from cosmic sources, such as the abiotic organic matter found in meteorites and chondrites (Gold, 1985; Sephton & Hazen, 2013). Both the first and second processes are then of interest in investigating the habitability of Enceladus, where the presumed lack of biomass means that the sole sources of organics would be either in-situ abiotic organic synthesis, or inheritance of organic material from its parent bodies.

1.4.1 Abiotic synthesis

Generally, the process of abiotic organic synthesis is thought to be triggered by water-rock reactions involving molecular hydrogen (H₂) and a surface catalyst (McCollom, 2013; Seewald, 2001). The molecular hydrogen for these reactions may be produced abiotically by the reduction of water in the presence of Fe(II)-bearing minerals (Eq. 1.4), by reaction of FeS (pyrrhotite) with water to generate FeS₂ (pyrite) plus H₂, or even by the reaction of water with surface radicals during mechanical fracturing of silicate-bearing rocks (Klein et al., 2020). Water radiolysis due to radioactive decay, either by α-emitters such as U and Th or γ -ray emitter such as K⁴⁰, is also considered an important source H₂ in the Earth's crust (Lin et al., 2005; Sherwood Lollar et al., 2014).

Mechanisms of abiotic organic synthesis have been and continue to be well-studied in both science and industry. Even without catalysts or mineral surfaces, equilibrium reactions between single-carbon species in water are known to form simple organic compounds of biological interest such as formic acid (HCOOH, the water-gas shift reaction in Fig. 1.7a) and formaldehyde (CH₂O) (Andreani & Ménez, 2019). The presence of H₂ also favors these reactions yielding reduced organic compounds (to the left in the diagram of Fig. 1.7a), although even in ideal conditions these reactions are extremely slow (Newsome, 1980; Reeves & Fiebig, 2020). The role of metal or mineral catalysts in natural systems is then the focus of most discussions on abiotic organic synthesis. For example, Fischer-Tropsch or Fischer-Tropsch type (FTT) syntheses of CH_4 and straight-chain hydrocarbons (Fig. 1.7b) may occur through the following reactions:

$(2n+1)H_2 + nCO \rightarrow CnH(2n+2) + nH_2O$	Equation 1.5
CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2	Equation 1.6

FTT reactions (specifically those based on the Fischer-Tropsch reaction of Eq. 1.5) are used extensively in the industrial synthesis of H_2 from CO using native metal and metal alloy catalysts (Anderson et al., 1984; Schulz, 1999). This and other types of FTT reactions (including the Sabatier reaction shown in Eq. 1.6) have also traditionally been mobilized as industrial CO₂ scrubbers using Fe- and Ni-catalysts (Vogt et al., 2019). Experimental and field studies have long proposed that silicate minerals may also act as a catalyst for these reactions (Hazen & Sverjensky, 2010; McCollom & Seewald, 2006; Potter et al., 2004). Field studies of both fluids at mid-oceanic ridges and off-axis hydrothermal vents (Charlou et al., 2010; Proskurowski et al., 2008) have concluded that the fluids at these vents carry abiotic CH₄ and straightchain hydrocarbons. Aside from CH₄ and hydrocarbons, identifying the origin of organic species in terrestrial hydrothermal vents is complicated because of the overwhelming abundance of biotically derived organic compounds (Simoneit, 2004). Numerous studies (e.g. Aubrey et al., 2009; Marshall, 1994; Proskurowski et al., 2008) have shown the potential for amino acid synthesis at seafloor hydrothermal conditions through Strecker or Strecker-type reactions, that describe synthesis of amino acids from reaction of HCN and NH₃ with a catalyst. However, unambiguous identification of any abiotically produced amino acids in seafloor hydrothermal systems remains elusive.



Fig. 1.7: abiotic organic synthesis. a. oxidation states for reversible redox speciation reactions of single-carbon species in water (from Andreani & Ménez, 2019). PAH indicates polycyclic aromatic hydrocarbons. b. illustrates Fischer-Tropsch synthesis of saturated hydrocarbons from H₂ and CO with an idealized catalytic surface (after McCollom et al., 2013).

1.4.2 Inherited organics

The moons of Saturn and Jupiter are thought to be composed in part of carbonaceous chondrites, which comprise up to 2-3 % (dominantly organic) carbon constituents (Botta & Bada, 2002) and up to 1.5 % macromolecular organic matter (Chang et al., 1978; Sephton, 2002). This would provide a rich source of organic carbon to the interior of icy moons. Alteration of this organic matter in the vents of icy moons may then favor concentration and synthesis of complex compounds due to their presumably low temperatures and reducing environments, similar to the LCHF. Unlike the LCHF, the high concentration of NH₃ thought to be present in Enceladus may further serve to stabilize N-bearing species, including amino acids, through inhibiting deamination reactions. For example, alanine (an amino acid) can decompose through the following deamination pathway:

Alanine $(C_3H_7NO_2) + H_2O \rightarrow$ Propionic acid $(C_3H_6O_2) + NH_3$ Equation 1.7

From basic thermodynamic principles, increasing the NH_3 on the products side of the equation will lead to a stabilization of amino acids and other amines that are present on the reactants side of the

equation (Klingler et al., 2007). The low temperatures of icy satellites again favor prebiotic reactions, as decomposition reactions such as Eq. 1.7 proceed faster at higher temperatures (Abdelmoez et al., 2010; Bada et al., 1995; Sato et al., 2004). Recent models that evaluate the reaction kinetics of various amino acids in terms of the expected internal conditions in Enceladus similarly show that at low temperatures (< 25 °C), the decomposition timescales for certain amino acids (proline, glutamic acid) are on the order of millions or even billions of years (Truong et al., 2019).

1.4.3 Known organics in Enceladus

Small organic molecules, such as CH₄, identified in Enceladus' plume (Waite et al., 2006, 2009) have been attributed to abiotic hydrothermal activity and byproducts of water-rock interaction (Waite et al., 2017). In-situ analyses of Saturn's E-ring by the Cassini CDA initially showed evidence of ionized breakup particles, potentially created from larger hydrocarbons that were mechanically destroyed on impact with the mass spectrometer (Postberg et al., 2008). More recent analyses of the data from both the CDA and INMS positively identified macromolecular organic compounds of up to 200 atomic mass units (Postberg et al., 2018), as well as aromatic nitrogen- and oxygen-bearing compounds of lower atomic mass (Khawaja et al., 2019). Because these organic compounds were found embedded in the same populations of E-ring ice grains that also host salts, this was interpreted as promising evidence of complex organic compounds being hosted in Enceladus' ocean. However, the source of these organics – whether produced in-situ, or inherited from the parent bodies of Enceladus – is unknown. Short-lived species, such as the amino acids arginine or aspartic acid (Truong et al., 2019) that have decomposition timescales of < 1 Myr, represent an exciting focus for future missions that may seek to unambiguously identify prebiotic organic compounds created by in-situ synthesis in icy worlds.

1.5 Problematic

In the interest of expanding our understanding of geochemical processes on icy worlds, this thesis includes three main projects or subject areas: 1-D geochemical reactive transport modelling of olivine weathering; experimental investigation of olivine alteration rates and reaction products in NH_3 -water fluids; and experimental alteration of organic matter in the presence of NH_3 and olivine. The motivation for these projects can be conceptualized as characterizing the possible habitability of hydrothermal environments on icy worlds, and specifically Enceladus, as follows:

1. If we consider an actively serpentinizing hydrothermal environment to be the potentially habitable region on icy worlds, how long can serpentinization processes be sustained in a small icy world?

2. In icy bodies without a liquid ocean, what are olivine dissolution rates in contact with alkaline, partially frozen NH₃-rich solutions?

3. Can we exclude the possibility that other effects of NH_3 may impact hydrothermal alteration of primary minerals (namely, olivine) at temperatures relevant to Enceladus?

4. In these potentially short-lived hydrothermal environments in the rocky cores of icy worlds, does NH₃ or olivine facilitate prebiotic interactions by effectively stabilizing or catalyzing complex organic molecules?

In Chapter 2, we introduce the structure and results of the 1-D model addressing the first research question, as well how these results fit into the larger interpretation of the age of the ocean in Enceladus. Chapter 3 focusses on the design and results of olivine alteration in batch experiments at low temperatures (-20 to $25 \, {}^{\circ}$ C). Chapter 4 is dedicated to the design and results of high-temperature olivine alteration batch experiments (90-150 $\,{}^{\circ}$ C), as well as complementary data from continuous-flow olivine dissolution experiments (0-150 $\,{}^{\circ}$ C). Chapter 5 introduces the design and initial results of experiments characterizing alteration of a complex organic solid in hydrothermal conditions, including with NH₃ and olivine. Chapter 6 is a review of the findings from these chapters, how well they addressed the central questions that motivated these studies, and the future work that can build on the conclusions in a meaningful way.



Fig. 1.8: Constraints on Enceladus' chemistry and main research questions for this manuscript. Enceladus image credit: NASA/JPL-Caltech.

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Chapter 1



CHAPTER 2

1-D reactive transport modelling

RESEARCH QUESTION

How long can olivine alteration and serpentinization continue in an icy ocean world?

<u>Chapter 2. 1-D reactive transport modelling (PHREEQC): insights into olivine alteration processes</u> <u>in Enceladus</u>

Abstract. The discovery of a liquid ocean on Saturn's small moon Enceladus and evidence of modern hydrothermal activity provide an unexpected new environment in which to expand the search for life. However, as with the age of the moons themselves, the age of the liquid ocean and any hydrothermal activity therein remains an area of debate. Based on physical and chemical observations from the Cassini mission we can apply known mineral dissolution rates, estimated water-rock ratios from Enceladus' observed density, and variable water flow rates within the rocky core to constrain duration of active serpentinization, and therefore, the maximum age of the liquid water circulation in the core. On this basis we developed a 1-D reactive transport model to compare the effect of initial olivine percentage, grain size, temperature, and flow rate on timespans of primary olivine alteration in a rocky core the size and density of Enceladus'. In most cases, olivine alteration and precipitation of hydrous secondary minerals results in a water-limited alteration regime. An alteration front that propagates in the direction of water flow then controls the overall rate of olivine alteration. Of the parameters explored, high initial olivine percentages and slow fluid flow rates were the strongest predictors of long serpentinization times, while temperature and grain size had a smaller effect. The annual global H₂ production rate in all model cases (> 1×10^{12} moles yr⁻¹) is several orders of magnitude greater than the minimum H_2 release rate calculated from the observed H_2 in Enceladus' plume (1 ×10⁹ moles yr⁻¹), suggesting that any ongoing active serpentinization processes in the core are likely nearing completion. The longest timescales indicate the potential for olivine alteration and H₂ production for up to \sim 75 Myr, consistent with weathering rates of terrestrial peridotite massifs. If the H₂ produced from Enceladus is sourced from primary mineral alteration, these results suggest that hydrothermal activity in the core of Enceladus developed only very recently - even as recent as within the past 100 Myr.

Manuscript under review at *Icarus* as "Short lifespans of serpentinization in the rocky core of **Enceladus: implications for hydrogen production**", by A. Zandanel, L. Truche, R. Hellmann, A. Myagkiy, G. Choblet, and G. Tobie.

2.1 Introduction

Estimating the origin and evolution of the oceans of Saturn's icy moons is an area of research that has rapidly evolved since the acquisition of new data by the Cassini-Huygens mission (1997-2017). Geophysical observations acquired by the Cassini spacecraft indicate the presence of a liquid ocean on Enceladus beneath its icy outer shell (Beuthe et al., 2016; Čadek et al., 2016, 2019; Collins & Goodman, 2007; Iess et al., 2014; Thomas et al., 2016). Gravity data also indicate that the rocky core of Enceladus has a relatively low density (Beuthe et al., 2016; Čadek et al., 2016; Iess et al., 2014), implying porosity of the order of 20-30% (Choblet et al., 2017). An internal heat source from endogenic activity, likely tidal dissipation in the porous core (Choblet et al., 2017; Liao et al., 2020), is thought to be responsible for anomalously high temperatures and ice shell fracturing at the south pole (Porco et al., 2006; Spencer et al., 2006) collocated with vapor plumes emitting to space (Hansen et al., 2006; Waite et al., 2006). In-situ analyses using Cassini's ion and neutral mass spectrometer (INMS) during close flybys have shown that the vapor plume largely comprises water carrying a number of trace constituents, including organic species and ammonia (Waite et al., 2009, 2017). Salt residues found with water ice in the E-ring of Saturn are thought to be sourced by Enceladus' plumes, further indicating that a liquid

ocean currently or recently existed and interacted with a rocky core (Postberg et al., 2009, 2011). Moreover, the Cassini Cosmic Dust Analyzer (CDA) revealed the presence of nanometer-sized silica particles originating from the E-ring, indicative of active silicate-water interactions inside Enceladus (Hsu et al., 2015; Sekine et al., 2015). Finally, H₂ with relatively high H₂:CH₄ ratios was also measured within the vapor plume, both of which are compatible with inorganic H₂ production during hydration and alteration of ultramafic rocks (Waite et al., 2017).

These geophysical and geochemical constraints, combined with chemical constraints inferred from Cassini's CDA and INMS data, suggest a novel method of evaluating Enceladus' endogenic activity by estimating the timespan of H_2 generation that can result from hydrothermal water-rock reactions within the core. Hydrothermal alteration of ultramafic rocks containing Fe²⁺-bearing minerals that leads to significant H_2 production is a geologically rapid reaction process. The suite of reactions producing H_2 as a by-product of hydration of mafic and ultramafic minerals are often termed serpentinization, originally referring to reaction of Mg- and Fe-bearing olivine (i.e. forsterite and fayalite) to produce serpentine, brucite and magnetite:

$2 Mg_2SiO_4 + 3 H_2O \rightarrow Mg_3Si_2O_5(OH)_4$ (serpentine) + Mg(OH) ₂ (brucite)	Equation 2.1
$3 \operatorname{Fe_2SiO_4} + 2 \operatorname{H_2O} \rightarrow 2 \operatorname{Fe_3O_4}(\text{magnetite}) + 3 \operatorname{SiO_2} + 2 \operatorname{H_2}$	Equation 2.2

Previous estimates of total H_2 production potential in the core of Enceladus show that with a pristine rocky core of ultramafic mineralogy, oxidation of all Fe-bearing minerals would result in up to 2 ×10²⁰ moles H_2 produced (Waite et al., 2017). The annual minimum release rate of H_2 calculated from its concentration in the vapor plumes is estimated at 1-5 ×10⁹ moles yr⁻¹ (Waite et al., 2017). At this rate, water-rock reactions with only 1% of the mass of the rocky core could produce the observed amount of H_2 for hundreds of millions of years (Waite et al., 2017). However, efficient water-rock interaction processes may result in much faster rates of serpentinization (Malamud & Prialnik, 2013), and thus a shorter lifetime of active H_2 production (Vance & Melwani Daswani, 2020).

Analogous Earth environments where submarine peridotite (ultramafic rock composed of olivine and pyroxene minerals) weathering takes place offer a range of time intervals for active serpentinization and complete alteration of primary minerals. In the alkaline and low-temperature Lost City hydrothermal field (LCHF, located along the Mid-Atlantic Ridge), the rate of serpentinization is estimated to be between a maximum rate of $5.1 \times 10^{-3} \text{ km}^3 \text{ year}^{-1}$ and a conservative rate of $1.2 \times 10^{-4} \text{ km}^3$ year⁻¹ (Früh-Green et al., 2003). Based on these rates, total serpentinization of a peridotite core the size of that of Enceladus (Table 2.1) would take between 56 and 240 Myr. In contrast, experimental dissolution studies of olivine powders (Oelkers, 2001; Pokrovsky & Schott, 2000b)f as well as peridotite rock cores (Malvoisin & Brunet, 2014) have yielded chemical alteration rates that are orders of magnitude faster than the maximum alteration rates estimated for the serpentinization of peridotite massifs in submarine environments. This discrepancy between field and lab serpentinization rates is often reconciled by invoking greater water-rock ratios in lab experiments compared to submarine peridotite massifs (White & Brantley, 2003), which emphasizes the importance of rock porosity and water-rock ratios on weathering rates.

While terrestrial peridotite weathering rates present a convenient point of comparison, the physical properties of Enceladus' core differ in important ways from Earth's lithosphere. Specifically, the significantly greater geothermal and geobaric gradients on Earth preclude the widespread existence of

cool, low-pressure, high-porosity mafic rock on multi-kilometer scales. In contrast to the average geothermal gradient of 25–30 °C km⁻¹ in Earth (Arndt, 2011), Enceladus' core is estimated to have a temperature gradient of less than 1 °C km⁻¹ (Choblet et al., 2017). From the measured density of Enceladus, the entire 360-400 km diameter core is thought to be unconsolidated, comparable in porosity and water content to a water-saturated sand or sandstone (20-30% water-filled porosity, Choblet et al. 2017). Continuous fluid circulation, which is imposed by tidal forcing, coupled with the high porosity of the core suggests that chemical alteration rates may be closer to those determined in laboratory experiments, and thus far faster than those estimated for terrestrial submarine weathering of peridotite. Literature-based alteration rates for a primary H₂ producing minerals, variable water flow rates as imposed by heterogenous tidal heating patterns, and water-rock ratios expected from core density models may then be used to estimate timescales of active hydrogen production from primary mineral alteration occurring throughout the rocky core of Enceladus.

Property	Value
Core porosity	20 % ^a
Core volume (m ³)	$2.87 \times 10^{16 \text{ b}}$
Rock mass in core (kg)	6.26 ×10 ^{19 b}
Initial olivine in rock	Sum H ₂
mass	producible
100 %:	2.5×10^{20}
60 %:	1.5×10^{20}
20 %:	0.5×10^{20}

Table 2.1 Estimated physical properties of Enceladus' core

^afrom Choblet et al. (2017)

^bfrom Waite et al. (2017)

In order to provide constraints on the timescale of aqueous alteration processes inside Enceladus' core and hence new age estimates on its activity, we present here a 1-D reactive transport model of olivine alteration within an unconsolidated rocky core consistent with that of Enceladus and other mid-sized icy satellites that may have supported liquid water oceans during their evolution. First, we present the 1-D model structure and the parameter space of both representative and end-member alteration conditions, assuming tidally driven porous convection of interstitial water (Choblet et al., 2017). Second, we present the results showing alteration times are controlled by the flow rates of water induced by tidal forcing. Third, we define a range of timespans of active olivine dissolution and H_2 production from our model, and finally compare these results to conditions within the core of Enceladus and other icy moons.
2.2 The 1-D modelling method

2.2.1 Hydrodynamics and computational parameters

Olivine dissolution is simulated using a reactive multicomponent 1-D transport model in PHREEQC (V. 3.5.0) (Parkhurst & Appelo, 2013). The model simulates directional alteration of a vertical column of primary minerals (olivine) by a steady influx of water (input solution) from an overlying liquid ocean. Solute concentrations in every cell are solved by an Advection-Reaction-Dispersion equation in PHREEQC that is described in detail by Myagkiy et al. (2017). With this method, concentrations change by advection along concentration gradients or by reaction with solid material. Dispersion in our model is set to zero. Excluding dispersion will result in a sharper reaction front and higher solute concentration peaks; this model then underestimates spreading of the concentration front and slightly overestimates local solute concentrations.

The entire column initially contains a rock phase made up of a primary mineral in contact with an input solution. The chemistry of the input solution is a dilute Na-Cl-HCO₃ seawater solution with 0.8 weight % NH₃ (concentrations of input solution constituents (mmol L⁻¹): [Na] = 122, [Cl] = 78.6, $[HCO_3]$ = 39, $[NH_3] = 469$, [K] = 0.6, [Si] = 0.011, [Mg] = 0.007, $[Al] = 6 \times 10^{-8}$, and $[Fe] = 6 \times 10^{-8}$). This is consistent with a range of ocean compositions predicted by previous models equilibrating a carbonaceous chondrite with water (Zolotov, 2007) as well as with a predicted ocean composition based on analyses of the ice grains from Enceladus' vapor plume (Glein et al., 2015; Hsu et al., 2015). The rock phase adopted in our models is composed solely of pristine Mg-rich olivine (Mg_{1.82}Fe_{0.17}Al_{0.007}SiO₄). This composition is consistent with measurements of San Carlos olivine and of olivine compositions in chondrites (Buseck & Goldstein, 1969; Komatsu et al., 2001; Oelkers et al., 2018). Aluminum is a known trace constituent of olivine and is therefore included in the olivine composition. Olivine is the sole initial mineral in our calculation of H₂ production times and benefits from extensive dissolution kinetics data. While olivine is one of the primary constituents of chondrites, it is far from the sole mineral thought to make up Enceladus' core. Pyroxenes, native iron, and iron-nickel alloys are all found in chondrites and all contribute to H₂ generation during water-rock interaction (Holm et al., 2015). Olivine dissolution rates are here considered as a proxy for other Mg-Fe silicates, as pyroxene minerals have similar dissolution rates compared to olivine in the high pH range (Bandstra et al., 2008). Native iron and iron-nickel alloys are not included in our initial mineral assemblage because oxidation of native metals and alloys, and therefore H₂ kinetic production rates, is instantaneous compared to dissolution rates of silicates. Inclusion of native metals and alloys in the initial model would then increase the initial amount of H₂ produced but would not be expected to increase the overall duration of H₂ production. In addition, the inclusion of additional primary silicate phases (e.g. quartz, amorphous silica) in the initial rock assemblages may contribute to the silica budget and control secondary mineral formation during alteration (Frost & Beard, 2007). Sensitivity tests that included amorphous silica and quartz in the initial rock assemblage of our models showed that including these minerals had little effect on the secondary mineral paragenesis in the conditions of our model, and no effect on the duration of active H₂ production.

All of our models simulate the geochemical evolution of a 140 km long 1-D column, composed of 3500 cells of 40 m length (Fig. 2.1). 140 km represents ~80% of the core radius as estimated by geophysical observations of Enceladus (Čadek et al., 2016, 2019; Iess et al., 2014; McKinnon, 2015); an analysis of the impact of the column length on the results is included in the discussion section. Porosity for the 1-

D column is set at 20%, consistent with the expected porosity given the density of Enceladus (Choblet et al., 2017) and the compaction regime of a small satellite (Vance et al., 2007). Due to code limitations, porosity remains constant in the column for the model duration. It should be noted that while the available porosity remains constant, the amount of water-filled porosity within the pores is allowed to vary (decrease) due to hydration reactions during transport and therefore the water-rock ratio necessarily varies as well. In real weathering profiles, changes in the volume and density of the rock phase during precipitation of secondary minerals can result in complex processes such as compaction or fracturing (Farough et al., 2016; Lafay et al., 2018; Zhang et al., 2019) that are not modelled here.



Fig. 2.1 a. Conceptual model of flow-driven chemical alteration reactions in Enceladus' core (illustration adapted from Choblet et al. 2017): b1) "downwelling" alteration and b2) "upwelling" alteration. c. The PHREEQC geochemical model.

A flux boundary condition is imposed on the first cell of the column as fluid input, and on the last cell as fluid output. The flow rate is imposed by selecting the residence time that each batch of fluid interacts with the rock phase (primary olivine + secondary paragenesis) in a single 40 m cell before the fluid is shifted to the next cell in the column (Fig. 2.1). Each specific flow rate, equal to the residence time divided by the length of the cell (40 m), remains constant during each run (Table 2.2). The total computing time for 1-D transport calculations is the number of times the solution is shifted vertically through the column. The geologic time represented by each run is determined by multiplying the residence time of the solution in a single cell by the number of times the solution is shifted. Each model runs for an equivalent geologic time of at least 1 Myr, or until all the primary mineral (olivine) in the core is exhausted and the secondary paragenesis is at equilibrium with the incoming fluid.

Models use one of three different initial olivine:water (O:W) volume ratios: high (4:1), medium (2.5:1) and low (0.8:1). While we do not include additional primary minerals, the O:W ratios can be equated to a percent of the rock mass of the core. Given an assumed and constant 20 % water-filled porosity, a core of 80 volume % olivine (equal to 100 volume % of the rock phase) has a 4:1 volume ratio of O:W. In this manner, the high, medium, and low initial olivine ratios can be correlated to 80, 50, and 17 % of the core volume, respectively (or 100, 60, and 20 % of the rock phase by volume). The O:W ratios were

chosen as representative of the range of olivine percentages found in chondrites (Pollack & Chi, 1972). Medium and low O:W ratios are representative of chondrites where a portion of the initial olivine has already undergone aqueous alteration to secondary clay and serpentine minerals (Rubin et al., 2007; Velbel et al., 2012). While the current estimates for a low density core are not consistent with a core composed of 80 % unaltered olivine (Choblet et al., 2017; Waite et al., 2017), the high O:W model is nevertheless included here to represent an end-member scenario of maximum initial olivine. As the amount of H_2 produced is directly proportional to the amount of initial olivine (Eqs. 1 and 2), decreasing the initial olivine percent results in to a decrease in the total amount of H_2 that can be produced (Table 2.1). The majority of runs use an olivine grain size with 0.1 mm radius, consistent with the average size of olivine chondrules in a collection of carbonaceous chondrites (Rubin, 1989). We also ran cases with olivine grain sizes of 1 mm and 5 mm that simulate larger or more resistant olivine grains (Browning et al., 1996). Specific details of solution pH, O:W ratio, and other model parameters are shown in Table 2.2.

Case	Т (°С)	V (cm yr	pH (at T)	grain sz (mm)	0:W	ta	R _{front} km Myr ⁻¹	Flow
1	1	1	11	0.1	4.0:1	35 Myr	3.95	down
2	1	1	11	0.1	2.5:1	22 Myr	6.34	down
3	1	1	11	0.1	1.0:1	300,000 yr	N/A	down
4	1	1	11	1	4.0:1	37 Myr	3.89	down
5	1	1	11	5	4.0:1	58 Myr	3.80*	down
6	25	1	10.7	0.1	4.0:1	35 Myr	4.02	down
7	90	1	10.3	0.1	4.0:1	35 Myr	4.03	up
8	150	1	9.9	0.1	4.0:1	35 Myr	4.03	up
9	150	10	9.9	0.1	4.0:1	4 Myr	40	up
10	150	100	9.9	0.1	4.0:1	380,000 yr	432	up

Table 2.2 Model cases

Temperature (T) and flow rate (V) are constant for each case. pH is of the input solution, "grain sz" indicates the radius of the initial olivine grains. O:W is an olivine:water volume ratio. "Flow" describes whether the V and T are consistent with upwelling fluid or downwelling. t_d = time until all olivine in the column has been completely dissolved, and R_{front} = propagation rate of the alteration front (if formed) in km Myr⁻¹.

*R_{front} for case 5 is calculated for the propagation rate after the formation of an alteration front at ~28 Myr.

We ran a series of model cases at different temperatures and flow rates (Table 2.2) consistent with temperatures and flow rates constrained for Enceladus' core by Choblet et al. (2017). In the present study we focus on alteration below 150 °C, where olivine alteration is slower, to illustrate the maximum timescales of olivine dissolution and H_2 production. Computational limitations of the code required that flow rate (water velocity) be held constant over the length of each column for the entire run. Columns were reacted at one of three flow rates: 1, 10, or 100 cm yr⁻¹, corresponding to the range of flow rates obtained by Choblet et al. (2017) for rock permeabilities between 10⁻¹² to 10⁻¹⁵. Temperature

was also held constant over time and depth at one of 4 representative values (1, 25, 90, or 150 °C). We assume that water flow completes a circuit from seafloor to core center (downwelling) and from core center to seafloor (upwelling), where the paired temperature and flow rate of each case are relevant either to downwelling (comparatively cold, slow-flow) or upwelling (comparatively hot, fast-flow). As the temperatures of the interior of Enceladus are expected to change over time, some ranges of temperatures and flow rates that may occur in downwelling conditions for periods of the core evolution are consistent with upwelling conditions at other times. Thus, each 1-D case can represent either a downwelling case or an upwelling case as indicated in Table 2.2 and illustrated in Fig. 2.1.

2.2.2 Geochemical parameters: rate-controlled olivine dissolution

Geochemical calculations with PHREEQC used the associated llnl.dat thermodynamic database (Johnson et al., 2000), modified for this study to prevent redox equilibrium between two separate redox couples: $NH_3 - N_2$ and $CO_2 - CH_4$. Redox equilibrium between dissolved NH_3 and N_2 is kinetically hindered at temperatures at or below 300°C (Sekine et al., 2015), and the low N_2 measured in Enceladus' plume (Hansen et al., 2011) suggests NH_3 oxidation is not significant (Waite et al., 2009). For that reason, the nitrogen-bearing species were decoupled in our database to prevent thermodynamic equilibration of NH_3 to $N_2 + H_2O$. Similarly, H_2 was decoupled from carbonate species in the database to prevent complete reduction of CO_2 to CH_4 , which is incompatible with the elevated H_2 : CH_4 ratio measured in the plume (Waite et al., 2017).

The rate-controlled dissolution of olivine and the precipitation (or re-dissolution) of all secondary phases according to their chemical saturation in the fluid are treated as two separate steps in the 1-D model. Olivine dissolution in our model occurs by the following reaction:

$Mg_{1.82}Fe_{0.17}Al_{0.007}SiO_4 + 4 H^{+} = 1.82 Mg^{2+} + 0.17 Fe^{2+} + 0.007 Al^{3+} + SiO_2 + 2 H_2O \qquad \mbox{Equation 2.3}$

The dissolution process described in Eq. 3 can be considered an elementary reaction of the complex serpentinization reactions described in Eqs. 1 and 2. Rate data for Eq. 3 are readily available in the literature (Bandstra et al., 2008; Oelkers, 2001; Pokrovsky & Schott, 2000a; Rimstidt et al., 2012). Even though published kinetic data exist for serpentinization reactions at hydrothermal temperatures (Lamadrid et al., 2017; Malvoisin et al., 2012; McCollom et al., 2016, 2020), we used olivine dissolution rates rather than serpentinization rates because we are not aware of appropriate rate data for serpentinization reactions at the much lower temperatures used in our model. Lacking rate data at low temperatures, precipitation of secondary serpentinite minerals in our model (chrysotile, brucite, magnetite) is executed instantaneously as a separate step rather than as part of an integrated serpentinization process. Our model does not incorporate potentially competing alteration behaviors such as directly coupled dissolution-serpentinization reactions (Lafay et al., 2012) or kinetic retardation by secondary phases (Daval et al., 2011; Park & Fan, 2004). Instead, olivine dissolution functions as the rate-limiting reaction of serpentinization such as proposed by the experimental studies of Malvoisin et al. (2012) and Okamoto et al. (2011).

Aggregated empirical data for San Carlos olivine dissolution suggest that pH and temperature are responsible for up to 90% of the variability in empirically-derived dissolution rates (Rimstidt et al., 2012). The other 10% of variability is influenced by a number of factors, including water activities of <

0.9. The precipitation of hydrous minerals and the resulting concentration of soluble species in the remaining fluid results in water activities < 0.9 throughout the column in many of the runs. For this reason, we chose to use a specific dissolution rate law for olivine that includes terms for both pH and water activity (Olsen et al., 2015):

$$\log r = [6.05 - 3683 * (1/T)] - 0.52pH + 3.26 \log a_{H_{2}O}$$
 Equation 2.4

where log *r* is the dissolution rate of olivine in mol m⁻² s⁻¹ at 25 °C, and the temperature dependence (with T in Kelvin) is calculated as in the general kinetic rate law published in Rimstidt et al. (2012). As PHREEQC requires a non-zero water activity for computation, Eq. 4 also ensures convergence of the numerical method during long alteration timescales where the reactive transport model would otherwise allow the precipitation of hydrous minerals to consume all of the water in the column. No term relating the olivine dissolution rate to the Gibbs free energy of reaction ($\boxtimes G$) is included in Eq. 4: as less soluble secondary minerals are allowed to precipitate, the fluid-mineral system is always out of equilibrium (undersaturated) with respect to olivine, and therefore the far-from-equilibrium rate of Eq. 4 can be used. The pH term, as integrated in Eq. 4, assumes a linear decrease in the dissolution rate r with increasing pH; however, it is known that this dependence is less pronounced at pH > 6 (McCollom et al., 2020; Wogelius & Walther, 1992). Because of this, the dissolution rate law used in Eq. 4 then calculates slower rates of olivine dissolution than those calculated using dissolution rate laws resolved over the entire pH range (e.g. Pokrovsky & Schott, 2000b; Rimstidt et al., 2012).

The specific olivine dissolution rate expressed by Eq. 4 is embedded in a general reaction rate formula given by:

$$R_d = r \left(\frac{A_0}{V}\right) \left(\frac{m}{m_0}\right)^n$$
 Equation 2.5

where R_d is the overall reaction rate (mol L⁻¹ s⁻¹), r is the specific dissolution rate from Eq. 4, A_0 is the initial specific surface area of the olivine (m² kg⁻¹ rock, calculated geometrically from the selected grain size), V is the volume of solution in contact with the olivine grains (L kg⁻¹ rock); the A_0/V factor approximates the initial olivine surface area to fluid ratio. m_0 is initial moles of reactant, and m is the moles of reactant at the computational time (Appelo & Postma, 2004). In fact, m represents the moles of unaltered olivine at time step t, and m_0 is a term that normalizes the moles of olivine at time step t to a theoretical initial number of olivine moles (m_0 =100 in all runs). (m/m_0) can be considered an aging term that serves to decreases the general rate R_d during dissolution (Appelo & Postma, 2004; Christoffersen, 1976). n is a factor that scales (m/m_0) to simulate the decreases in reactive surface sites (reactive surface area) during aging, where n = 0.67 (or 2/3) represents a monodisperse grain size population (Dixon & Hendrix, 1993). As the effect of grain size is explicitly explored as a separate variable in this study, n = 0.67 was used in all models.

The rate expression given by Eq. 5 is employed by PHREEQC at each timestep to calculate olivine dissolution reaction progress. After each kinetically-controlled reaction step, thermodynamic mineral saturation indices are calculated from the final fluid composition in each cell. Where selected secondary phases reach chemical saturation in solution, these minerals are instantaneously precipitated in an amount proportional to their chemical saturation (or over-saturation). The secondary phases in our model includes those minerals that commonly occur during olivine alteration: chrysotile (serpentine), amorphous silica, Mg-smectite, brucite, gibbsite, magnesite, and magnetite.

These phases are allowed to precipitate, or even re-dissolve, based on their thermodynamic stability. Talc was included in the secondary mineral assemblage at 150°C. We note that although field studies have presented evidence that low-temperature serpentine minerals may form at temperatures of 25 °C or below in peridotites (Okland et al., 2012; Pfeifer, 1977), there is no consensus as to whether a minimum temperature for the formation of serpentine minerals exists. Chrysotile is nevertheless included as a secondary mineral in all models, as the long reaction times support the potential for its formation and sensitivity analyses show that its inclusion does not affect rates of olivine dissolution nor H_2 production.

Global rates of H_2 production are calculated by normalizing the total moles of H_2 produced in each time step in the entire column to the fixed value of the initial moles of olivine in the column, giving a rate of H_2 production: $mol_{H2} mol_{initial olivine}$ ⁻¹ year⁻¹. Annual H_2 production in the column can then be scaled to annual global production by estimating the quantity of moles of olivine initially present in the rocky core from the imposed O:W volume ratios, the molar volume of olivine, and the inferred volume of Enceladus' core (Table 2.1). Limitations of the code prevent exsolution of H_2 from the fluid during transport, but the complete exsolution of all H_2 produced would almost certainly not occur instantaneously at the low temperatures in downwelling regions. Moreover, some H_2 would remain dissolved in the fluid and percolate out of the core by fluid transport. An additional examination of the role of transport through the core after H_2 production is included in the discussion section.

2.3 Results and discussion

2.3.1 The 1-D transport model: water-limited alteration

The amount of olivine in the 1-D column initially decreases while interacting with the initial solution in the porous column (Fig. 2.2). This initial period of elevated water-rock interaction is analogous to an early phase of water-rock differentiation in small satellites. During this early phase water ice, initially homogeneously integrated with other solid phases, melts and migrates through the rock phase to form a liquid reservoir (ocean) differentiated from the rocky core (Malamud & Prialnik, 2016; Schubert et al., 2007; Vance et al., 2007). During this initial period in our models, olivine dissolution (Eq. 3) stoichiometrically releases Mg^{2+} , Fe^{2+} , Al^{3+} , and SiO_2 into the fluid at rates dictated by Eq. 5. After this initial period of dissolution, precipitation of secondary minerals causes consumption of the water in each cell (e.g. Eqs. 1 and 2). The decreasing water mass and increasing concentration of solutes in the remaining fluid causes the water activity to decrease from its original value of 1. As olivine dissolution is progressively retarded by decreasing water activity (Eq. 4), the dissolution rate slows during reactive transport until olivine dissolution becomes negligible (2 Myr or less). Without a mechanism to reintroduce water to the core, water-rock interaction would effectively halt after this period of water migration through (and reaction with) the rock core (see e.g. Malamud & Prialnik, 2013, 2016). The incorporation of tidally-driven water circulation through the core provides a mechanism for the reintroduction of water from the overlying liquid ocean: in our model, this is imposed through the fluid input and fluid transport in the column (Fig. 2.1). An alteration front then forms, where olivine dissolution and secondary precipitation occur only where water is reintroduced to the cells from fluid transport. Ongoing fluid input and transport through the column to the alteration front is what drives its progression in the direction of flow. The time duration for the dissolution of all the olivine in the

column (t_d) is then dependent on the rate of propagation of the alteration front (R_{front}), or stated another way, t_d is contingent upon the front passing completely through the column.

The general features of an alteration profile are illustrated in Fig. 2.2 based on a model run at 25 °C $(0:W = 4:1, \text{ grain size} = 0.1 \text{ mm}, \text{ flow rate} = 1 \text{ cm yr}^{-1})$. Fig. 2.2a shows that any given time, pH in the column increases in the direction of flow as the incoming fluid chemistry is progressively buffered by serpentinization reactions and equilibration with secondary brucite and chrysotile (Leong & Shock, 2020). Fig. 2.2b shows the moles of H_2 produced in the column as a function of depth. We identified three zones with distinct mineralogy and reactions: an "altered" sector upstream of active alteration, where olivine is completely dissolved (i.e. depleted) and secondary mineralogy is at equilibrium with the incoming fluid; an "alteration front" of active olivine dissolution and hydrous secondary mineral precipitation; and a "water-limited" sector downstream of the front where little olivine dissolution occurs due to low water activity (Fig. 2.2). The altered sector is dominated by the secondary paragenesis, predominantly chrysotile with small amounts of brucite, magnesite, and magnetite (Fig. 2.2c-d). pH remains equal to the pH of the incoming fluid. Within the alteration front, olivine actively dissolves and equilibration of the fluid in each cell at each time step causes Fe^{2+} oxidation to Fe^{3+} , H_2 production, pH increase, and precipitation of chrysotile, magnesite, and brucite (Fig. 2.2a-c). This is apparent from Fig. 2.2b, where H_2 production occurs only at the depth of the alteration front: at any given time, less olivine dissolves at the upstream trailing edge of the alteration front where olivine mass is decreased from previous fluid introduction; near the center of the alteration front, more olivine remains and more H₂ is produced; then at the downstream leading edge of the alteration front olivine dissolution and H₂ production decrease again as the increasing pH and decreasing water activity retard the olivine dissolution rate (Eq. 2.4). We define the leading edge of the alteration front as where olivine dissolution and H_2 production in the downstream edge of the front are near-zero, and the trailing edge as the first cell in the direction of flow to contain a non-zero amount of remaining olivine. In the waterlimited sector downstream of the alteration front, olivine remains the principal mineral component with some percent of secondary minerals that precipitated during the initial period of water-rock interaction. The pH in the water-limited zone is higher than that of the incoming seawater (Fig. 2.2a), having been buffered by the alteration process upstream.



Fig. 2.2: alteration front at 25 °C, 1 mm grain size, and 1 cm year⁻¹ flow rate after 12 Myr of reaction. a. pH of the fluid in each cell. b. H_2 production in total moles produced per cell in one time step. c. total moles of dissolved H_2 in the fluid phase in each cell: d. Mineralogy regimes in the column: "Minerals (% of total)" is calculated as a percent of the total moles of all minerals in a given cell, and " H_2O (% of initial)" represents what how much of the 20 % porosity is water-filled. e. Features of the alteration front. The leading and trailing edges of the alteration front are annotated.

The effect of the various parameters we explored in our models on the shape and the propagation rate of the alteration front through the core is shown in Fig. 2.3. Increasing the fluid flow rate has no effect on the shape of the alteration front but causes R_{front} to increase (Fig. 2.3a). In Fig. 2.3b it can be seen that the alteration front changes from a very sharp step function-like profile with a 5 km width (0.1 mm grain size) to a broad sigmoidal front with a width of 70 km (5 mm grain size). Grain size also affects the timing and depth of formation of the alteration front: larger grain sizes delay the formation of an alteration front as the proportionately smaller specific surface area slows local olivine dissolution rates, allowing water to continue flowing through the entire column without being completely consumed (Eq. 2). Once the alteration front is formed, however, changes to grain size have a relatively minor effect on R_{front} (Table 2.2). The initial O:W ratio (Fig. 2.3c) affects both the formation of an alteration front and the total olivine dissolution times (t_d) . Taking the case with low initial olivine content (case 3, O:W = 0.8:1, grain size = 0.1 mm, T = 1 °C, flow rate = 1 cm yr⁻¹), all of the initial olivine in the column is dissolved and converted to secondary minerals during the initial stage of water-rock interaction. In this case $t_d < 1$ Myr, and is not significantly affected by flow rate because an alteration front never forms. The dependency of the relative amounts of olivine remaining after the initial waterrock interaction stage on the initial O:W ratio is shown in Fig. 2.3c. The final parameter, temperature, alters the overall shape of the alteration front (Fig. 2.3d). At 1 °C, the sigmoidal front has a shallow gradient, extending over several tens of km, while at 150 °C, the front is sharp and resembles a step function.



Fig. 2.3: factors influencing the vertical rate of progress of the alteration front. a. Effect of flow rate (0:W = 4:1, grain size = 0.1 mm, T = 150 °C). b. Effect of grain size (0:W = 4:1, flow rate = 1 cm yr-1, T = 1 °C. c. Effect of the initial 0:W (grain size = 0.1 mm, flow rate = 1 cm yr-1, T = 1 °C). d and e. Effect of temperature from 1 to 150 °C (0:W = 4.1, grain size = 0.1 mm, flow rate = 1 cm yr⁻¹).

Once formed, the propagation of the alteration front through the core controls the time required for total alteration of olivine. The dependence of R_{front} on temperature and flow rate is graphically shown in Fig. 2.4. Figure 2.4a shows the depth of the alteration front over time, where the depth is defined by the trailing edge of the alteration front (as in Fig 2.2e). Six different cases are shown (all starting with O:W ratio = 4:1 and grain size = 0.1 mm): three cases at 150 °C with flow rates of 1, 10, and 100 cm yr⁻¹ to simulate upwelling (Fig 2.4a); and three additional cases with a 1 cm yr⁻¹ flow rate at temperatures of 1, 25, and 90 °C to simulate downwelling (Fig. 2.4b). By comparing Figs. 2.4a-b it is apparent that the R_{front} is much more sensitive to flow rate than temperature. By regressing R_{front} (km Myr⁻¹) as a function of flow rate and temperature, the sensitivity of the propagation rate with respect to these two parameters can be quantified (Figs. 2.4c, d). Figure 2.4c illustrates that R_{front} scales linearly with flow rate over the range of flow rates explored here. The effect of fluid flow rate on R_{front} (and therefore t_d) is pronounced: increasing the flow rate from 1 cm yr⁻¹ to 10 cm yr⁻¹ decreases t_d from 35 Myr to 4 Myr, which represents a relative decrease of more than 80 % (Fig. 2.4a). The overall effect of temperature on olivine alteration times is comparatively weak (Fig. 2.4b): increasing the temperature from 1 to 150°C decreases *t*_d by less than 5 Myr (< 15 % relative decrease). *R*_{front} scales logarithmically with respect to temperature (Fig. 2.4d).



Fig. 2.4: a. Depth of the alteration front as a function of time, where the depth is defined by the trailing edge of the alteration front (T = 150 °C for flow rate = 100 and flow rate = 10 cm yr⁻¹). b. inset from a. showing effect of temperature (flow rate = 1 cm yr⁻¹). c. R_{front} regressed over flow rate. d. R_{front} regressed over temperature.

The fixed temperatures and flow rates used here over the entire column length allow us to evaluate the effect of these parameters on the time window of active olivine alteration. In reality, temperature and flow rate are expected to vary with depth and time during Enceladus' evolution (Czechowski & Witek, 2015; Malamud & Prialnik, 2013). In upwelling fluid pathways a thermal gradient from seafloor to core center may vary by up to 10 °C, and slower fluid pathways during downwelling may have thermal gradients up to 100 °C (Choblet et al., 2017). Because of this, t_d may be overestimated by model cases that adopt low temperatures and slow water velocities throughout the entire column, and correspondingly underestimated by high-temperature, fast-flow rate model cases. The longest and shortest windows of active serpentinization in the model cases are respectively $t_d = 60$ Myr and $t_d = 380,000$ years (Table 2.2), These windows can then be considered end-member timescales that would encompass total serpentinization times of columns that included temperature or water velocity gradients.

Considering weathering along a circuit from seafloor to core and back to seafloor (Fig. 2.1), the limiting factor in the time needed to totally alter the core will be determined by the downwelling path due to slower water velocities (Fig. 2.1 and Table 2.2). The existence of upwelling fluids is dependent on there being enough downwelling fluid remaining, which is then heated in the core to create a hydrothermal upwelling fluid. While there is a high percentage of unaltered olivine remaining, the entire core would experience downwelling fluid circulation until some minimum water-filled porosity is established throughout the core. At that point, downwelling through the core and upwelling through fracture pathways at the poles can occur simultaneously, as considered in hydrodynamic models of water circulation in the core (Choblet et al., 2017; Liao et al., 2020) and as in the circuit described above. Upwelling paths in any circuit will then alter faster than their respective downwelling circuits, as they

are subject to higher temperatures and higher water flow rates (Table 2.2). Therefore, we consider that the downwelling cases represent the maximum t_d for an entire rocky core with a radius equal to the column length.

2.3.2 Model limitations

The dependency of t_d on the formation and propagation of an alteration front shows the importance of considering geochemical reactions over long distances, rather than applying small-scale models to macroscale processes. In the 140 km column models, olivine dissolution times were most sensitive to changes in flow rate and initial O:W ratios (Fig. 2.4). In contrast, the results of sensitivity analyses using a column comprising only a single 40 m cell (with O:W = 4:1, grain size = 0.1 mm) show that the time required for total olivine dissolution (t_d) is identical for flow rates at or above 1 cm yr⁻¹ (Fig. 2.5a). Tests with a 0.1 cm yr⁻¹ flow rate show that the residence time in a single cell at this flow rate (40,000 years) is long enough that the increased pH and decreased water activity noticeably affect decrease the olivine dissolution rate. Even in this case, however, t_d in the single-cell column is more sensitive to temperature than initial O:W ratio (Fig. 2.5b). The differences in the results based on the parameters used in a single-cell or batch reactor model, when compared to the importance of the same parameters in the 140 km model, highlights the importance of incorporating reactive transport modeling into interpretations of water-rock interactions in satellites.



Fig. 2.5: effect of a. flow rate and b. initial O:W ratio on olivine alteration in a single cell. "Years $(\times 10^3)$ " indicates the reaction time necessary to dissolve all olivine in the cell.

While modelling geochemical reactions over kilometer-scale distances provides insight into global processes, the use of the 1-D transport model requires necessary simplifications to water-rock interaction processes that would presumably occur in the core. Notably, volume increases of the solid phase during serpentinization are not considered by the code. In our model outputs the total calculated mass of precipitated secondary minerals would represent a volume increase of more than 30% compared to the initial olivine. These volume increases have been shown to drive reaction-induced cracking that can increase serpentinization times in batch reactions by up to an order of magnitude (Malvoisin et al., 2017). Similar reaction-induced fracturing has been proposed to form a reaction front that can advance at rates of tens of m yr⁻¹ in a peridotite having just 1 % preexisting fracture porosity (Kelemen et al., 2011; Rudge et al., 2010). Because the porosity of Enceladus' core is up to two orders of magnitude greater than porosities in terrestrial peridotites (0.8%, Hyndman and Drury 1976) and as the slowest imposed flow rate of 1 cm yr⁻¹ in our models is slower than the alteration front propagation anticipated from reaction-induced cracking, the addition of reaction-induced cracking to our model would be expected to accelerate $R_{\rm front}$ and increase the global serpentinization rate.

Another simplification in our model is that olivine dissolution and precipitation of secondary phases are treated as two separate steps. This ignores any effect of dissolution-precipitation coupling, which has been suggested to decrease long-term olivine dissolution rates by up to four orders of magnitude in acidic fluids (Daval et al., 2011). However, in alkaline fluids, this same coupled dissolutionprecipitation mechanism during serpentinization may in fact drive microfracturing at the olivine surface and promote olivine alteration (Lafay et al., 2018; Plümper et al., 2012). In light of these complexities, general quantitative models of how this factor influences dissolution rates over time are not readily available. Speculative inhibition of the dissolution rate over time is approximated by the aging term of Eq. 5, which decreases the rate by up to two orders of magnitude during runs.

2.3.3 Implications for Enceladus' core evolution

Despite the simplifying assumptions inherent to our model, the results are consistent with timescales of similar processes observed on Earth. The maximum t_d of olivine alteration in Enceladus' core based on our results would be 35-60 Myr (Table 2). This range overlaps the estimate of 54-240 Myr for serpentinization of a core the size of Enceladus' using the peridotite weathering rates proposed by Früh-Green et al. (2003). That our estimates are somewhat shorter is unsurprising given that we assume a porous, water-saturated core with a mechanism for active water flow within, as opposed to the low-porosity peridotite massifs that the terrestrial estimates are based from. Furthermore, our results are comparable to the timescales obtained by Malamud and Prialnik (2016) for reaching an almost complete core serpentinization during the early evolution of Enceladus. However, for the case of serpentinization that started early on during Enceladus' history, all olivine should have been exhausted now, and associated H₂ production by serpentinization should be extremely low. This suggests either that Enceladus formed very late, and/or that ice melting and hence water circulation have not developed until recently.

A comparison of the time windows of active H_2 production from our 1-D model with the amount of H_2 currently emitting from Enceladus can be used to estimate the maximum age of active water-rock interaction. The formation of an alteration front during reactive transport retards the rate of olivine alteration in the core. This means that the longest time windows of active olivine serpentinization are in scenarios with delayed alteration front formation and slow alteration front propagation. Olivine alteration times and corresponding H_2 production for the longest alteration cases (with O:W = 4:1, T = 1° C, flow rate = 1 cm yr⁻¹) are shown in Fig. 2.6 for all grain sizes. Complete alteration of all of the olivine in the core is achieved in 35, 37, and 58 Myr for grain sizes of 0.1 mm (case 1, Fig. 2.6a), 1 mm (case 4, Fig. 2.6b), and 5 mm (case 5, Fig. 2.6c), respectively. Thus, the slowest end-member case for alteration of the initial olivine, the window of H₂ production is just under 60 million years. During the entire 58 Myr period, H_2 production is several orders of magnitude larger than the minimum H_2 release rate calculated from the observed H₂ in the plume $(1-5 \times 10^9 \text{ moles yr}^{-1})$. Waite et al. 2017). During alteration of the initial olivine in the initial stage of water-rock interaction H_2 production rates peak at 3.5 ×10¹³ moles yr⁻¹, and subsequently plateau at over 2×10¹² moles yr⁻¹ as the alteration front propagates through the column (Fig. 2.6d-f). It is notable that in these models, decreasing the amount of initial olivine must decrease the total amount of H₂ produced, but it does not affect the rate of H₂ production. For example, case 2 (identical to 1, except for an initial O:W = 2.5:1) also has H₂ production rates that initially peak to > 1×10^{13} moles yr⁻¹ and plateau at over 2×10^{12} moles yr⁻¹, but olivine is completely exhausted within 6 Myr (Table 2.2) The result based on less initial olivine present in the column relative to water-filled porosity, which is analogous to starting with a partially altered rock phase, is that H_2 is produced at the same global annual rate only for a fraction of the time.



Fig. 2.6: Depth profiles of olivine dissolution and calculated global H_2 production as a function of time for a. grain size = 0.1 mm. b. grain size = 1 mm and c. grain size = 5 mm. Vertical dashed line indicates the time the leading edge of the alteration front reaches the column terminus. Panels d-f show the global H_2 production over the time corresponding to each of the cases above. Note the initial period of water-rock reaction is reflected in an initial spike in H_2 production. Horizontal dashed line indicates minimum global H_2 release rates from Enceladus.

To constrain our output to cases that might best reflect current processes in Enceladus, the model output and implications can be compared to the low core density and H₂ emission rates inferred from the data collected by the Cassini mission. We can evaluate the hypothesis that H_2 emitted from Enceladus is evidence of active primary mineral alteration by reviewing model scenarios where H₂ production occurs in a water-saturated column - where the column is not dominated by the waterlimited sector as described in Fig. 2.2. Contemporaneous H₂ production and water-filled porosity over the entire column length can occur in the 1-D reaction transport column in 4 scenarios: 1. imposed flow rates that always exceed the olivine dissolution rate (not modelled here, but as we discuss below, physically not possible); 2. low initial olivine percentage or large grain sizes that prevent the formation of an alteration front (cases 3 and 5, respectively); 3. in the initial phase of every run where the initial water-filled porosity interacts with the initial olivine (all cases); 4. during a period of time after an alteration front progresses through the entire column to intersect the outflow cell (cases 1, 2, 4, and 6-10). In our models, the 1^{st} scenario requires a flow rate of more than 100,000 cm yr⁻¹, which is not consistent with the physical constraints prescribed by tidal heating mechanisms (Choblet et al., 2017). Scenarios 2-4 are explored in our models and can be compared to observations of Enceladus' density and current global H₂ production.

The 2^{nd} scenario is described in our models by either a low initial olivine percentage available for dissolution or by low olivine specific surface area. A low initial olivine percentage (initial O:W = 0.8:1) completely prevents the formation of an alteration front even at slow reaction conditions (grain size = 0.1 mm, T = 1°C, flow rate = 1 cm yr⁻¹, case 3). At such a low O:W ratio, olivine dissolves before the available mass of water is completely consumed by secondary reactions. This process is relatively rapid and all of the primary olivine in the core is totally exhausted after 380,000 years of reaction time (Table 2.2). On the other hand, olivine with low specific surface area delays the production of an alteration

front. At large grain sizes (5 mm, case 5), water flow continues through the column contemporaneously with olivine dissolution for ~30 Myr before the formation of an alteration front. However, 5 mm is much larger than the reported average radius of chondritic olivine chondrules (0.1-0.2 mm, Rubin 1989) and even with moderate grain sizes (1 mm, case 4) an alteration front forms after only 2 Myr of reaction time (2.6c).

The 3^{rd} scenario is a feature of the initial alteration period, analogous to the initial water-rock interaction period defined by first contact of primary olivine with liquid water. This initial alteration period is marked by active olivine dissolution as well as water-filled porosity throughout the column. Ultimately, the H₂ production in this period is markedly high. Vigorous olivine alteration causes global H₂ production rates to reach values as high as $3-5 \times 10^{13}$ moles yr⁻¹ before an alteration front forms (Fig. 2.6d-f), which is significantly higher than the calculated minimum global H₂ release rate from Enceladus ($1-5 \times 10^9$ moles yr⁻¹, Waite et al. 2017). Overall, this period is geologically brief, as the column becomes mostly anhydrous and an alteration front is formed within 2 Myr. During this transient initial stage, the time span during which the modest rates of observed H₂ release from Enceladus are produced in the column is extremely short-lived in all models, making this scenario rather unlikely.

The 4th scenario corresponds to model cases 1, 2, 4, and 6-10 at the end of the run where the alteration front has progressed through the entire column so that it is near to, or intersecting, the end of the column. The time at which the alteration front reaches the end of the column is indicated in Fig. 2.6 as an orange dashed line. In the examples shown in Fig. 2.6 this corresponds to the last several million years of reaction time, where the majority of the column is composed of secondary hydrous minerals and the alteration front has reached the last part of the core (Fig. 2.6a-c, after ~25 Myr). This scenario is also most consistent with estimated annual H_2 release from Enceladus of 1 ×10⁹ moles yr⁻¹: after the leading edge of the alteration front reaches the end of the column, H_2 production decreases over several Myr from a plateau of 2 ×10¹² moles yr⁻¹ to zero after all olivine in the column is dissolved (Fig. 2.6d-f). The time window between the time where the alteration front first bisects the final cell of the column and $t_{\rm d}$ is dependent on the shape and the propagation rate of the alteration front. Considering an example case with a very diffuse sigmoidal alteration front and a slow R_{front} (case 5, O:W = 4:1, grain size = 5 mm, T = 1 $^{\circ}$ C, flow rate = 1 cm yr⁻¹), the alteration front reaches the outflow cell at ~26 Myr and $t_{\rm d}$ = 58 Myr (Fig. 2.6c). This represents 32 Myr of contemporaneous fluid flow throughout the entire column and active H₂ production. Again, case 5 is an endmember example. Even decreasing the grain radius to 1 mm at the same conditions (case 4, O:W = 4:1, grain radius = 5 mm, T = 1°C, flow rate = 1 cm yr⁻¹), the time window between the alteration front reaching the outflow cell and t_d decreases to ~6 Myr (Fig. 2.6b). This time window would be further shortened by increases in the propagation rate or a narrowing of the width of the alteration front (as a result of decreasing the initial O:W ratio, increasing the temperature, or increasing the flow rate).

According to our simulations, in both plausible scenarios (2 and 4) the current low H_2 release production rate from Enceladus thereby implies that olivine alteration in the core is very close to completion, if not already at completion (Fig. 2.6d-f). As aqueous alteration is very rapid ($t_d < 4$ Myr) in upwelling regions characterized by fast flow and elevated temperature, it is very likely that the olivine in these regions has long since been altered to secondary phases. The H_2 that we measure today in the plumes is then more likely to have been generated in the coldest parts of the rock core during downwelling (Fig. 2.7). This apparently contrasts with the model of H_2 generation in Enceladus proposed by Glein et al. (2018) and Glein & Waite, (2020) who concluded that the observed H_2 must be largely sourced by rocks at 250-350 °C in the deep core. This conclusion is not necessarily at odds with our results: as discussed for scenario 4 above, our model also suggests that if alteration is still ongoing it is more likely to be generated within the deeper part of the core (Fig. 2.6 d-f, Fig. 2.7). In addition, fluid circulation through a core with very low permeability (<10⁻¹⁶ m²) may generate temperatures of >200 °C when reaching the core center (Choblet et al., 2017). However, as olivine alteration rates increase with T until 250-310 °C (Lamadrid et al., 2020; Malvoisin et al., 2012; Wegner & Ernst, 1983), t_d in this case would be shorter than predicted by our models. We also note that the model of Glein et al. (2018) assumes that the fluid in the deep core is in redox equilibrium with serpentinizing mafic silicates, whereas the fluid nearer the seafloor is in redox equilibrium with secondary carbonate minerals. This is also consistent with our conclusion that seafloor alteration would occur rapidly, and current production is sourced from within an alteration front that has progressed to the inner core with downwelling fluid (Fig. 2.7)



Fig. 2.7: Conceptual sketch illustrating the fluid flow-driven chemical alteration and the resulting H_2 production and transport in Enceladus' porous core (adapted from Choblet et al. 2017). Most of the present H_2 production is expected to occur during downwelling (flow rate <1 cm yr⁻¹, T < 20 °C) from the oceanic seafloor to the core center. H_2 -rich aqueous fluids progressively heat up in the deep core due to tidal heating, until they become thermally unstable and rise, most notably in the polar regions, in the form of rapid hot water upwelling (flow rate >8 cm yr⁻¹, T >100°C). Hot water outflows are responsible for seafloor hotspots triggering oceanic thermal plumes that then transport H_2 rapidly to the jet sources in the ice shell. The whole cycle between the production of H_2 in cold regions and the release at the surface could take several millions of years.

Finally, it might also be possible that primary minerals are totally exhausted at present and that the observed H₂ is being produced by another process or is released over time from a previous production stage. For example, Glein et al. (2018) showed that the production of H_2 by organic pyrolysis can explain the observed H_2 given a high total tidal power within the core (> 50 GW). As for H_2 release over time, the observed high H₂:CH₄ ratios are thought to indicate that long-term H₂ storage is not occurring within Enceladus (Waite et al., 2017). However, the possibility of H_2 release from the core after active H_2 production has ceased is still possible by a process of flushing H₂-enriched fluids out of the porous core by fluid transport. During downwelling, the H₂ concentration increases in the aqueous fluid as olivine alteration proceeds. Warm aqueous fluids, enriched in H_2 , then become unstable and rise preferentially at the poles to feed seafloor hotspots as illustrated in the conceptual model of Fig. 2.7. According to the simulations of Choblet et al. (2017), the fluid velocity in hot upwellings is estimated between 8 and 80 cm yr⁻¹, for a rock permeability of 10⁻¹⁴-10⁻¹³ m² and a total tidal power between 10 and 30 GW. This would imply transport timescales from the center to the seafloor ranging from 0.2 to 2 Myr. As a consequence, it is possible that the H_2 being ejected into space today was produced a few millions of years ago and is not currently being produced. Considering the typical time for fluid parcels to go through the cold parts of the rock core during downwelling, today's H₂ may even have been produced ~10 Myr ago.

Taken together, these results indicate that the duration of active hydrothermalism on Enceladus, involving production of H_2 , is less than 100 Myr. The possibility of several successive hydrothermal episodes throughout the moon's history cannot be ruled out, with active hydrothermal stages whose cumulated duration is a few tens of Myr, interspersed by quiescent periods. The general trend of Saturn's moons' orbital expansion is nevertheless more consistent with a single stage of enhanced production of tidal power, involving the formation of an internal ocean and porous flow in the rocky core. While our results do not provide any constraints on the age of Enceladus, they suggest that the existence of global ocean and the water circulation in the porous core is geologically young, less than 100 Myr old.

2.3.4 Implications beyond Enceladus' core

The rates of propagation of the alteration front (Table 2.2) may also be applied to calculate alteration timescales within a longer or shorter column, this being equivalent to changing the radius of the core. For all model cases with a 1 cm yr⁻¹ flow rate (e.g. case 6, O:W = 4:1, grain size = 0.1 mm, T = 25 °C) the alteration front progresses at approximately 4 km yr⁻¹ (Fig. 2.4c). These alteration rates can then be adapted to the range of estimates for the radius Enceladus core, which vary from 185-190 km (Beuthe et al., 2016; Čadek et al., 2016; Hemingway et al., 2018). This gives a range of timescales of active serpentinization of 50-75 Myr given the propagation rates reported in Table 2.2. Additionally, we note that these rates could be adapted to estimate the duration of active serpentinization on other icy satellites where there is evidence of a past or current liquid ocean and an inner rocky core. For example, a column with a length consistent with the hypothesized rocky core of Saturn's smaller moon Mimas (< 100 km radius, Noyelles et al., 2019) would be totally serpentinized within 25 Myr. However, for satellites where current observations or models do not adequately constrain the physical parameters of water flow velocities within a core, these estimates remain speculative.

In icy satellites that do not experience tidally induced water flow throughout a rocky core, mechanicalor reaction-induced fracturing becomes particularly important. During alteration, the creation of void space where secondary mineral volume does not completely replace the water volume lost in hydration reactions may result in potentially irreversible core compaction (Malamud & Prialnik, 2016). This may leave fracturing as the main driver of introducing water from any liquid ocean to the core, rather than passive water flow through porous, unconsolidated media. Hydrothermal models of the dwarf planet Ceres (Neveu et al., 2015) and the Kuiper belt object Orcus (Malamud & Prialnik, 2015) suggest timescales of fracture propagation over time and maximum depths of fracturing within the rocky cores. The propagation rates described in these models are on the order of billions of years, timescales at which the reactions as described in our models would be instantaneous.

2.4 Conclusions

Using a 1-D reactive transport model, we simulated the serpentinization of Enceladus' core using olivine as an analog mineral. We investigated the effect of initial olivine percentage, grain size, temperature, and flow rate on the total time needed to completely alter the primary olivine in a rocky core the size and density of Enceladus'. In most cases, the alteration of olivine results in precipitation of hydrous secondary minerals and the formation of an alteration front that slows olivine alteration. For high (4:1) or medium (2.5:1) olivine:water ratios, representative of Enceladus' core, we have shown that the time of total olivine alteration is controlled by the rate of the vertical propagation of the alteration front, which separates a completely altered upstream sector from a water-limited downstream sector with little ongoing alteration. Active olivine dissolution and precipitation of secondary minerals starts at the leading edge of the alteration front.

Longer serpentinization times are obtained for slower fluid flow rates, lower temperatures and larger grain sizes. As a consequence, timescales of olivine alteration in regions characterized by rapid upwelling of hot water (> 8 cm yr⁻¹, > 100-150 °C) are geologically very short (< 500,000 year), while in regions where cold water slowly circulates (< 1 cm yr⁻¹, < 20 °C) timescales can be up to 60 Myr. The latter falls within the range of expected timespans for alteration of a mass of rock equivalent to Enceladus' rocky core based on chemical alteration rates of terrestrial peridotite massifs (Früh-Green et al., 2003).

In all model cases, olivine alteration results in an annual global rate of production of > 1×10^{12} moles yr^{-1} for almost the entire lifetime of active H_2 production. This rate is several orders of magnitude greater than Enceladus' minimum H₂ release rate $(1 \times 10^9 \text{ moles yr}^{-1})$ calculated from the H₂ measured in its vapor plumes (Waite et al., 2017). This implies that the present release rate corresponds to the tail end of the active H_2 production period with the current H_2 production rate (estimated at 1×10^9 moles yr⁻¹), compatible with exhaustion or quasi-exhaustion of the initial stock of olivine. In our models such low H₂ production is consistent with cases that either start with a small initial stock of unaltered olivine in the rock (olivine:water volume ratio < 0.8:1, or < 20 vol. % olivine in the rock phase). Alternatively, this low H_2 production may also correspond to the final stages of the alteration process where the alteration front has progressed through the majority of the column (Figs. 2.3, 2.6). The conclusion that alteration is nearing completion is also consistent with the inferred low density of Enceladus' core, as olivine is assumed to be replaced by lower-density, hydrous secondary minerals during alteration. Taken together, these results suggest that the liquid ocean on Enceladus is geologically young, developing during the last 100 Myr. If the H_2 currently being emitted from Enceladus can be positively attributed to inorganic production, the results of this study can further serve to constrain the possible length of time that the liquid ocean has existed on Enceladus.

A recent and short-lived duration of hydrothermalism on Enceladus does not reduce the astrobiological interest of this moon. The fact that the hydrothermal activity is recent on Enceladus indeed offer a unique opportunity to study hydrothermal environments during the early stage of planetary evolution. The hydrothermal activity observed today on Enceladus, even if declining, may be representative of various hydrothermal systems that may have active in many other icy bodies. Understanding the chemical complexity emerging in this young hydrothermal system is highly relevant to test the hypothesis that life possibly originated in alkaline hydrothermal vents on Hadean Earth (Martin & Russell, 2007; Russell et al., 2014; Sojo et al., 2016). Even if the geodynamic context on Enceladus is very different from Hadean Earth, Enceladus provides an independent test on the origin of life in hydrothermal environments, which may be addressed by future exploration missions (Choblet & Tobie, 2020). Infra-red mapping of Enceladus' surface revealed that outside the currently active south polar terrain, at least one other region in the northern hemisphere has been recently active (Robidel et al., 2020). This area may be the surface expression of another seafloor hotspot and may preserve chemical signatures of recent hydrothermal activities. Future characterization of the south polar plume activity together with compositional mapping of other recently active centers, such as the one recently identified by Robidel et al. (2020), may provide key insights on how hydrothermal activities involved through time and affected the chemical evolution of Enceladus's ocean.

2.5 References

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CHAPTER 3

Olivine dissolution in partially frozen ammonia-water-salt solutions

RESEARCH QUESTION

In icy worlds that do not have a liquid ocean, what are olivine alteration behaviors in contact with alkaline, partially frozen solutions?

Chapter 3. Olivine dissolution on icy worlds in partially frozen ammonia-water solutions

Abstract. The Cassini-Huygens and Dawn missions revealed surprising evidence of active ammoniawater-rock weathering on several icy worlds in the outer solar system. Mineral alteration by ammoniarich fluids opens new perspectives in the search for potentially habitable environments far from Earth. However, mineral alteration processes at relevantly low temperatures and in ammonia-rich solutions remain unconstrained. While directly measuring extraterrestrial weathering processes is technically challenging, experimental analogues may be used to determine alteration rates and reaction products that form in-situ. We designed and completed a set of batch experiments investigating olivine dissolution in partially frozen solutions. Batch experiments combined olivine with one of three solutions, having 0, 0.8, or 8 wt % ammonia, and monitored changes to solution chemistries from -20 to 22 °C for up to 442 days. We characterize a thin unfrozen film of solution at the ice-olivine interface that allows water-olivine interaction, and show that olivine dissolution reactions continue even in partially frozen solutions. Initial dissolution rates show a surprisingly weak dependence on changes in temperature, pH, and NH₃, while long-term rates show an apparent weak inverse relationship with temperature. Our findings imply that olivine dissolution is not significantly retarded at -20 °C compared to 22 °C, and that in high water-rock ratio environments olivine alteration is a geologically rapid process. In addition, high-resolution TEM analysis of the olivine surface after 442 days of reaction shows a thin (< 1 nm) surface altered layer at the olivine surface, unambiguously demonstrating that secondary reaction products can form in partially frozen solutions even at experimental timescales. Our olivine dissolution rates can be directly applied to models of mineral weathering in frozen or partially-frozen icy worlds such as Enceladus, (1) Ceres, or Uranus' moon Ariel, and extrapolated to lower temperatures within the partial-melt temperature range of the NH₃-H₂O system (0 to -96 °C).

3.1 Introduction

In-situ analyses of materials emanating from Saturn's moon Enceladus by the Cassini spacecraft, including detection of silica nanograins(Hsu et al., 2015) and hydrogen (Waite et al., 2017), provided the first evidence of ongoing hydrothermal activity outside of Earth. While these observations suggest hot water is venting from Enceladus' rock core (Sekine et al., 2015), model predictions (Choblet et al., 2017) indicate most of the rock core would presently experience interaction with mild- to lowtemperature (4-20 °C) aqueous fluids, and possibly much lower temperatures during periods of reduced tidal dissipation (Neveu & Rhoden, 2019). The Dawn mission additionally detected ammoniated phyllosilicates (M. C. De Sanctis et al., 2015) and hydrated salt deposits on the surface of dwarf planet Ceres (M. De Sanctis et al., 2020; Nathues et al., 2020), indicating aqueous weathering reactions may be occurring there at temperatures far below 0 °C. The examples of Enceladus and Ceres demonstrate that similar low-temperature aqueous processes may have operated in a variety of icy bodies of the solar system (Neveu et al., 2017). Pluto's moon Charon and Uranus' moon Ariel, where ammonia species have been identified at their surfaces (Cartwright et al., 2020; Dalle Ore et al., 2018), are other examples where low temperature ammonia-rich aqueous reactions may have played a key role in their evolution. During the early stages of satellite evolution, ammonia-rich aqueous fluids even may favor the generation of liquid oceans on small satellites (Malamud & Prialnik, 2013) by facilitating exothermic mineral dissolution reactions below 0 °C.

Mechanisms of silicate weathering in partially frozen solutions have been investigated for more than 50 years. During freezing, the chemical potential at the solution-mineral interface causes an interfacial

liquid film to form around mineral grains (D. M. Anderson, 1967; Drost-Hansen, 1969; Gilpin, 1979). The thickness of this film increases as a function of the freezing point depression (Barer et al., 1980), which is attributable to ammonia, salts, and volatiles(G. Marion et al., 2012). Silicate weathering within unfrozen solution films in natural environments is corroborated by a number of terrestrial weathering systems, including potentially authigenic clay minerals in extreme environments in Antarctica (Claridge & Campbell, 1984; Dickinson & Grapes, 1997) and evidence of silicate weathering in permafrost (Cuozzo et al., 2019; Dickinson & Rosen, 2003). Liquid films at mineral surfaces have similarly been proposed as a mechanism for mineral alteration observed in chondrites (Rietmeijer, 1985; Rietmeijer & Mackinnon, 1985; Young, 2001). However, dissolution rates and mechanisms in these unfrozen films are poorly constrained and still rely on extrapolated rates derived at 25 °C or higher (Gooding, 1978).

Two previous experimental studies have shown olivine dissolution continues below 0 °C in highly acidic solutions (Hausrath & Brantley, 2010; Niles et al., 2017), ascribing this phenomenon to an acid concentration effect in the unfrozen fluid phase(Niles et al., 2017). As the mechanism of olivine dissolution is thought to change from acid to alkaline conditions (Pokrovsky & Schott, 2000; Rimstidt et al., 2012), acid-pH olivine dissolution rates cannot be directly applied to chondrites or icy satellites where alkaline conditions are considered to predominate (Glein et al., 2015; Hsu et al., 2015; Ohnishi & Tomeoka, 2007; Sekine et al., 2015). Ammonia exclusion from ice and the resulting increase in pH may cause quite different behavior than expected at acid conditions, such as decreased dissolution rates or increased rates of secondary mineral precipitation (McCollom et al., 2020; Sekine et al., 2015). In the present study, we determined the rate and mechanism of olivine dissolution in alkaline solutions at -20, 4, and 22 °C using multiple replicate batch reactors, where textural and bulk (melted) solution chemical changes were monitored for up to 442 days. Three different solution chemistries were used at each temperature to analyze the effect of NH₃ concentration and pH. The rates and products of olivine dissolution measured in this study can be used to constrain alteration histories of chondrite parent-bodies and icy bodies in the outer solar system.

3.2 Methods

Batch experiments were carried out at -20, 4 and 22 °C for variable periods of time ranging from 41 to 442 days. Three experimental series were carried out at each temperature, with each series being comprised of numerous Nalgene vials, each containing 0.3 g of San Carlos olivine grains (Mg_{1.83}Fe_{0.17}SiO₄) and 30 mL of saline fluid containing either 0.0, 0.8, or 8.0 mass % NH₃ (0.0 % NH₃ solution prepared with NaOH). The starting pH values were 10.8, 10.8, and 12.2, respectively. The olivine-solution mixtures run at -20 °C were a frozen ice slush. The overall composition, ratios of salts, and NH₃ concentrations of the fluid were chosen to bracket the chemistry of solutions predicted to evolve from chondrite-fluid interactions (Glein et al., 2015; Zolotov, 2007). At certain designated times replicate vials were sequentially removed and sampled. The major cations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). To image olivine in partially frozen aqueous solutions we used optical microscopy (plain and polarized light) to observe the nature of the olivine-ice interface and the porosity of the enveloping adjacent ice layer. The microscopy work was done in a cold room at -8 °C. The physical process of fluid melting at the olivine grain-ice interface was also studied with a mixture of unaltered olivine grains and deionized water that was frozen with liquid N2 (77 K). The frozen mixture was then observed under an optical microscope at ambient temperature so that we could record sequential images of the liquid solution front propagating away from the olivine grain as the temperature gradually rose. Raman analyses of olivine, ice, and unfrozen fluid were performed at the olivine-ice interface using a Renishaw[®] InVia confocal Raman microscope. Samples (olivine grains and solution) were placed in a quartz cell in a Linkam[®] THMS 600 heating/freezing stage and maintained at -20 °C during analyses. Measurements were performed at 532 nm, using a 50x-long working distance objective.

Post-reaction olivine grains were imaged by field emission scanning electron microscopy (FEG SEM, Zeiss Ultra 55, CMTC, Grenoble) at 20 kV to characterize the degree of surface coverage by secondary precipitates. Further high-resolution analyses by transmission electron microscopy (TEM) were centered on three altered olivine grains subjected to 442 d of reaction at -20 °C in a 0.8 % NH₃ saline solution. Here, the purpose was to examine structural and chemical changes to the near surface region, which included the formation of surface altered layers and secondary crystalline precipitates. We examined this sample in cross section with electron transparent foils prepared by focused ion beam (FIB) milling using standard preparation techniques (Schaffer et al., 2012). TEM analyses were performed using a state-of-the-art Thermo Fisher Scientific Themis Z 3.1 operated at 300 kV, and a Tecnai F20 operated at 200 kV, both housed at the GFZ-PISA facility, Potsdam. We used standard bright and dark field (BF, DF), scanning TEM-high angle annular dark field (STEM-HAADF), and integrated Differential Phase Contrast STEM (iDPC-STEM) imaging techniques, while high resolution chemical analyses were carried out with EELS spectral imaging in STEM mode.

3.3 Results and discussion

3.3.1 The ice-olivine interface

Batch reactors were used to perform olivine dissolution experiments in a dilute H_2O -NaCl-KCl-NaHCO₃ "seawater" matrix containing one of three distinct NH₃ concentrations: 0.0 mass % (pH adjusted to 10.8 with NaOH), 0.8 mass % (pH 10.8), and 8.0 mass % (pH 12.2). "Mass %" is hereafter referred to as "%". At -20 °C, all solution compositions appeared solidly frozen inside the reactors. However, some unfrozen solution existed in all experiments as the NaCl-KCl-NaHCO₃-H₂O system has a eutectic temperature (solidus) of -24 °C (G. M. Marion & Kargel, 2007; Toner & Catling, 2017) and the H₂O-NH₃ system has a eutectic temperature of -96 °C(G. Marion et al., 2012). The amount of solution that remains unfrozen increases with increasing NH₃ content (Table 3.1). At experimental conditions pure water ice formed during freezing (Kargel, 1992; G. Marion et al., 2012). See Table 3.1 for amount of ice in each experiment, as well as the calculated pH, ionic strength, and solute concentrations in the remaining unfrozen solution. Note that the pH of the 0.8 % NH₃ solution, which is identical to the 0 % solution at 25 °C, is higher than that of the 0 % solution at 4 °C and -20 °C

Exp. ID	Α	В	С	D	Е	F	G	Н	Ι
Temp (°C)	22	4	-20	22	4	-20	22	4	-20
Fluid : Ice	30:0	30:0	1:29	30:0	30:0	2:28	30:0	30:0	13:17
Fluid : Rock	100:1	100:1	2:1	100:1	100:1	6:1	100:1	100:1	42:1
Ionic strength	0.1	0.1	5.1	0.11	0.11	1.89	0.09	0.09	0.22
Molal NH3	0	0	0	0.5	0.5	6.7	4.7	4.7	9.6
In-situ pH	10.8	11.1	11.5	10.8	11.5	11.9	12.1	12.8	13.7
Duration (days)	167	167	41	442	442	442	41	167	167

Table 3.1 Low-T olivine dissolution experiments

"Fluid : Ice" indicates the mass ratio of unfrozen solution remaining to the moles of ice formed in each reactor. "Fluid : rock" indicates the mass ratio of unfrozen solution in each reactor to olivine, not including the mass of the unfrozen solution films at the mineral surface. Ionic strength and NH_3 refer to in-situ properties of the unfrozen solution: -20 °C ionic strength and NH_3 concentration increase due to solute exclusion from the ice phase. In-situ pH is calculated in FREZCHEM and increases due to temperature effects at 4 °C and due to temperature effect and solute exclusion from the ice phase at -20 °C.

Optical microscope images of partially frozen 0.0, 0.8 and 8.0 % NH₃ solutions illustrate the decreasing crystallinity and increasing porosity in the ice phase caused by increasing NH₃ content (Fig. 3.1a-c). Sequential images taken of a frozen sample allowed to equilibrate to bench temperature revealed the propagation of a fluid melt away from the olivine-ice interface, consistent with melt propagation out from an unfrozen surface film (Fig. 3.1d). Visual evidence of an unfrozen solution film at the olivine-ice interface was also identified during in-situ investigation of olivine grains in frozen solutions (Fig. 3.1e) of all solution compositions.

To identify solutes concentrated in the unfrozen film at the olivine interface, Raman analyses were performed at -20 °C on an amalgam of olivine grains, ice, and unfrozen solutions using a temperature-controlled stage. Raman spectra show that the shape of the broad OH symmetric and asymmetric stretching band of water at 2900 – 3800 cm⁻¹ progressively evolves when approaching the olivine surface, characterized by both an upward shift of the entire band and a clear decrease in the intensity of the region below 3325 cm⁻¹ that corresponds to symmetric OH – stretching (Supplementary Figs. 3.2, 3.3). The gradual phase transitions recorded in the interfacial region are an instrumental artifact due to the low in-depth resolution of the technique when used with a long working distance, low numerical aperture, and objective relative to the real width of the interfacial water layer at -20 °C (Supplementary information). These spectral features probe the transition from ice to interfacial liquid water. In addition, the intensity of NH₃ and CO₃²⁻ peaks positively correlate with the broadening and intensity decrease of the spectral component centered at 3138 cm⁻¹, which is clearly defined in ice. These observations corroborate the accumulation of NH₃ and CO₃²⁻ in the unfrozen solution enveloping the olivine grains.



Fig. 3.1 Features of the ice, unfrozen solution, and ice-olivine interface. a-c: images taken by an optical microscope in polarized transmission mode of the three solutions used in this study at -8°C showing ice crustals and interstitial unfrozen solution. The increased birefringence (here visible as bright colors) of the ice phase indicates increased crystallinity. a. 0.0 % NH₃. b. 0.8 % NH₃. c. 8.0 % NH₃. d-e. Image the fluid phase at the ice-olivine interface. d. image of olivine crystals and DI water flash-frozen with liquid N₂ and rapidly imaged under a microscope at room temperature to capture melting. e. Representative image of olivine in frozen 0 % NH₃ solution taken with non-polarized light, where the difference in ice texture is visible at the olivine-ice interface. f. annotated compilation of three Raman spectra taken within the olivine (green), at the olivine-ice interface (yellow), and in the ice (blue): all spectra were collected at -20°C. Two insets show the peaks unique to the spectra collected at the ice-olivine boundary: a $CO_3^{2^\circ}$ peak at 1070 cm⁻¹ and a second feature showing the combined ice- NH₃-liquid water peak where a peak in the liquid water band (3405 cm⁻¹) is visible.



Fig. 3.2: Fluid chemistry evolution for 442-day experiments (0.8 wt % NH₃ solution). a-c: Si and Mg concentrations in the solution of each of the experiment sets, at each experimental temperature. Concentrations at -20 °C (panel c) were calculated by applying a concentration factor (15x) to the analyzed concentrations to account for solute exclusion from ice. Error bars indicate instrumental error: where error bars are not visible the error is smaller than the symbols. d-f: Chemical saturation indices of the solution with respect to forsterite (Mg-olivine) and select secondary minerals brucite (Mg(OH)₂) and sepiolite (low-T talc mineral, $Mg_4Si_6O_{15}(OH)_{2}$ •6H2O). Saturation indices at -20 C were calculated from the concentrations after applying the 15x factor as shown in panel c.

3.3.2 Olivine dissolution: effect of pH, NH₃, and T

Increasing silica and magnesium concentrations over time indicate olivine dissolution occurred at all experimental temperatures and NH₃ compositions (Fig. 3.2 a-c). From these concentrations, we derived separate apparent olivine dissolution rates (mol m⁻² s⁻¹) from aqueous [Si] and [Mg] (denoted r_{Si} and r_{Mg} , respectively). For each experiment we calculated initial rates at far-from-equilibrium olivine dissolution conditions (t = 0 to t = 14 d), where the solution is undersaturated with respect to Mg-olivine (Fig. 3.2d-f). Because initial r_{Mg} are generally lower than initial r_{Si} (Fig. 3.2a), for most experiments the initial r_{Mg} certainly underestimates the true olivine dissolution rate (Hausrath & Brantley, 2010; Oelkers et al., 2018). We note that r_{Si} may also underestimate the true olivine dissolution rate if Si is also sequestered in any secondary phase, and these rates are then considered to represent minimum possible olivine dissolution rates occurring in our experiments. Differences in initial r_{Si} between different experiments may then indicate possible effects of the experimental parameters (pH, NH₃, T) on reaction processes, while comparisons between r_{Si} and r_{Mg} help describe the processes occurring within the experiments over time.

Initial r_{Si} weakly decrease with increasingly alkaline pH, as evidenced by the slower initial r_{Si} in 8.0 % NH₃ (pH 12.2) solutions (Fig. 3.3a). Despite the weak inverse relationship between pH and dissolution rates in our own data and in the literature (Rimstidt et al., 2012; Wogelius & Walther, 1992), the 0.8 %

 NH_3 experiments have the fastest initial r_{Si} at any given temperature (Fig. 3.3a). The additional increase in NH_3 to 8 % does not result in higher initial r_{Si} .

The majority of the initial r_{si} show only a modest increase with increasing temperature from -20 °C to 4 °C, whereas from 4 °C to 22 °C nearly all of the calculated rates show no meaningful temperature dependence. Compared to extrapolated values from a global kinetic rate equation for forsterite dissolution (Rimstidt et al., 2012), our initial r_{si} are slower than predicted at 22 °C and faster than predicted at -20 °C (see Supplementary Material 2.1). This attenuated dependency of r_{si} on temperature is also reflected in the calculated thermal activation energies (E_a): our values, ranging from 12-19 kJ mol⁻¹, are lower than the average value of ~63 kJ mol⁻¹ from compiled rate data (Hänchen et al., 2006; Oelkers et al., 2018). The low E_a values based on our data suggest that secondary processes have removed Si and Mg from solution, thus interfering with the determination of the true rates from the aqueous [Si] and [Mg]. An alternative explanation is that in situ-formed surface altered layers (SAL) may impede dissolution. In any case, rates that have been calculated from the 4 °C data are potentially lower than the true olivine dissolution rate, this being even more true for those at 22 °C.

We also derived long-term apparent olivine dissolution rates after the solution has approached saturation with respect to Mg-olivine (Fig. 3.2d-f), titled ltr_{Si} and ltr_{Mg} (t = 167 d; Supplementary Material 2.1, Supplementary Fig. 3.1b). The long-term rates more closely reflect solution chemistry changes in a closed water-rock system nearing steady-state, such as would be found in a natural system (e.g. icy worlds). At 4 and 22 °C the values of ltr_{Si} and ltr_{Mg} generally come close to converging at 167 days ($ltr_{Si} \ge ltr_{Mg}$). Surprisingly, the long-term rates have an inverse relationship to T: rather than increasing with increasing T, as in the initial rates, the long-term rates decrease with increasing T and are highest in the -20 °C experiments. Comparing the initial and long-term apparent dissolution rates illuminates how the system evolves over time. Initial rates are decreasingly stoichiometric with increasing T, whereas long-term rates have reached near-stoichiometry at 4 and 22 °C and remain non-stoichiometric at -20. Further, initial rates show that $r_{Si} > r_{Mg}$, while long-term rates show $ltr_{Mg} > ltr_{Si} at -20 °C$. The experiments at 4 and 22 C then appear to have reached some steady state, which the experiments at -20 °C the experiments at -20 °C the secondary processes that prevent increasing [Si] and [Mg] in the solution at 4 and 22 °C, such as kinetic inhibition of secondary phase precipitation or of SAL formation.



Fig. 3.3: Apparent dissolution rates over temperature. a. short term (14 day) r_{Si} and r_{Mg} in mol m⁻² s⁻¹ over temperature. Divergence between values for r_{Si} and r_{Mg} in the same experiment indicates that the rates are non-stoichiometric. b. long term (167 day) apparent dissolution rates (ltr_{Si} and ltr_{Mg} , mol m⁻² s⁻¹) over temperature for all experiments (two experiments were excluded from the long-term rates due to reactor failure: see supplementary information).

3.3.3 Secondary alteration products

The concentrations of Si and Mg in solution at any time reflect the dynamic relation between two fundamental processes: their release from the olivine structure and their incorporation into secondary authigenic phases. All of the experiments, ranging in duration from 41 to 442 days, displayed varying degrees of non-stoichiometric (incongruent) olivine dissolution behavior, with $r_{\rm Si} > r_{\rm Mg}$ being the most prevalent. This non-stoichiometry suggests that authigenic phases formed during alteration even at -20 °C. In particular, while the initial apparent olivine dissolution rates appear to reflect stoichiometric dissolution at -20 °C, the non-stoichiometric dissolution apparent by comparing the long-term $ltr_{\rm Si}$ and $ltr_{\rm Mg}$ at -20 °C reveals that authigenic phases may even be forming in partially frozen solutions.

We investigated three different altered olivine grains reacted at -20 °C in 0.8 % NH₃ using scanning and transmission electron microscopy (SEM and TEM, Fig. 3.4a, b). At the micron scale in SEM, no alteration is visible at the olivine surface. The adjoining high-resolution integrated Differential Phase Contrast (iDPC, Bosch & Lazić, 2015; Lazić et al., 2016) STEM image shows very nicely how the olivine lattice fringes abruptly give way to an irregular < 1 nm wide band of material that no longer has an ordered structure. Even though its origin and composition are unknown, we speculate that the observed surface altered layer (SAL) is a consequence of chemical alteration. We may draw some insight from the aqueous chemistry, as the excess of Mg over Si seen in the long-term dissolution rates (Fig. 3.2c) shows possible preferential sequestration of Si in secondary phases. From the aqueous chemistry, we further calculated the theoretical thicknesses of SALs; typical values were found to be < 10 Å (see Supplementary Info), consistent with our observations (Fig. 3.4b). Because of its sensitivity to the electron beam, we were not able to obtain meaningful chemical analyses of the surface layer.



Fig. 3.4: Mineral analysis of an olivine grain reacted in 0.8 wt % NH3 for over 1 year at -20°C. a. SEM image of reacted olivine sample surface (0.8 % NH3, -20 °C) at the location where the FIB foil was cut (arrow). Note the lack of any obvious surface precipitates or etch pits. b. FIBprepared TEM foil of the same altered sample imaged by iDPC-STEM. The interfacial region is characterized by lattice fringes of unaltered olivine and an Au layer. The two are separated by a thin surface altered layer (SAL) lacking an ordered structure. The SAL delimits the position of the solvent-olivine interface when the grain was removed from solution. The colored atoms belong to an atomic-scale overlay of the forsterite olivine structure.

3.3.4 Implications for icy worlds

The unique kinetic and physico-chemical data we have collected from these experiments provide quantitative constraints on olivine dissolution in partially frozen solutions. This has implications for interpreting chemical weathering on icy bodies in the solar system, as solutions above the liquidus temperature are often considered a prerequisite in models of mineral weathering (Malamud & Prialnik, 2016; Palguta et al., 2010). Our results provide minimum olivine dissolution rates that can be used to model dissolution below 0 °C. The addition of excessive antifreeze to depress the liquidus temperature is not required to promote olivine dissolution, nor is highly concentrated acid solutions. Our data and kinetic analyses suggest two phenomena of critical interest for long-term chemical
weathering: first, the potentially amplifying effect of NH_3 on olivine dissolution, even above 0 °C; and second, the apparently small effect of temperature on dissolution rates as evidenced by relatively fast dissolution rates below 0 °C and low E_a values. Importantly, while the apparent olivine dissolution rates in our experiments represent a minimum olivine dissolution rate, this minimum rate at -20 °C is still faster than the dissolution rates predicted at low temperatures by existing dissolution rate laws (e.g. Rimstidt et al., 2012).

Small and cold icy bodies may be particularly susceptible to sustained mineral alteration in NH_3 -rich solutions over long time periods, since liquid reservoirs (in ice pores, grain surface films) are predicted to become more concentrated in ammonia as ice crystallization proceeds. In fact, as icy worlds such as Ceres (Castillo-Rogez et al., 2019) and Saturn's inner moons (Mimas, Enceladus, and Tethys, Neveu & Rhoden, 2019) may initially have spent millions or billions of years at an average temperature between the liquidus and solidus of the H_2O-NH_3 system (0 to -96 °C), NH_3 -rich fluids could have promoted the formation of unfrozen films at mineral surfaces, and mineral alteration within them, during much of their evolution.

In the case of Enceladus, even if the aqueous fluid is estimated to contain only 1-2% ammonia at present (Waite et al., 2017) and circulates in most of the rocky core at temperatures of 0-20 °C (Choblet et al., 2017), the interior may have been colder in the recent past. Even before the global ocean formed and Enceladus reached a hot and dissipative state⁴, low-temperature surface fluid films and poral liquids enriched in ammonia (5-10% of ammonia, assuming a core porosity of 20%) could have sustained aqueous processes over very long periods of time within the rocky core. In the case of Ceres, cold aqueous liquid reservoirs may have been preserved until today (Castillo-Rogez et al., 2019), which would permit low-temperature aqueous alteration to still operate at present. Our data allow us to infer that mineral alteration can continue in icy bodies throughout the universe wherever unfrozen liquids films are stable at mineral-grain interfaces.

3.4 Supplementary Methods and Results

3.4.1 Experimental approach.

Experimental protocol. The static reactions were carried out in Nalgene vials, each containing 0.3 g of olivine and 30 mL of fluid. Each set of vials was assembled at bench temperature and brought to experimental temperature within at most one hour of the olivine contacting the fluid. Three experimental series were run at $-20 (\pm 1)$, $4 (\pm 1)$, and $22 (\pm 2)$ °C, respectively (listed in Supplementary Table 3.1). Based on naked-eye observations, the -20 °C solutions with NaOH (0.0 %) and 0.8 % NH₃ appeared to be solidly frozen, whereas the 8.0 % NH₃ solutions resembled partially frozen slush. In all experiments, the vials were shielded from light. The vials were agitated once a week by hand to prevent agglomeration of the grains and to promote mixing, while still minimizing mechanical disruption of the ice in the experiments at -20 °C. At certain designated times (7, 14, 21, 41, 167 days) replicate vials were sequentially removed and sampled. Additional replicates for the 0.8% NH₃ experiments were reacted at each temperature for 442 d using 0.5 g olivine and 50 mL fluid. Fluid aliquots from all experiments were filtered (0.45 µm), diluted and acidified (2 vol. % HNO₃), and analyzed for major cations with matrix-matched standards using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Varian 720ES, ISTerre analytical geochemistry platform, Univ. Grenoble

Alpes). With respect to the vials held at -20 °C, they were first placed in a 30 °C water bath in order to completely melt the semi-frozen solutions (< 1 hr) before sampling the fluid. Fluid chemistries as analyzed and corrected only for acid dilution are reported in Supplementary Tables 3.2-10. After sampling the fluid, the olivine grains in each experiment were separated from the remaining fluid by vacuum filtration, then rinsed sequentially with DI water and ethanol and finally stored under an argon atmosphere.

Materials. Clear light-green grains of San Carlos olivine ($Mg_{1.83}Fe_{0.17}SiO_4$) having no visible inclusions were selected by hand and comminuted by Selfrag[®] high voltage pulse fragmentation. Grains were then sieved to the 0.05-0.125 mm size range. The sieved grains were repeatedly washed in ethanol in an ultrasonic bath until the supernatant was clear, after which they were dried under air at 50 °C. Powder X-ray diffraction analysis (XRD) of the prepared olivine before reaction was consistent with XRD diffraction patterns of a reference sample of pure San Carlos olivine with no secondary phases. Kr-BET analyses were performed with a Belsorp-Max volumetric gas sorption instrument, and a final specific surface area of $0.091 \pm 0.005 \text{ m}^2 \text{ g}^{-1}$ was adopted for calculations. XRD analyses were not performed on samples after reaction because the amount of sample in each experiment (0.3g) was too small to ensure a reproducible signal for even major mineral phases.

Aqueous solutions were prepared using Milli-Q water (18.2 M Ω •cm) degassed with Ar. Liquid NH₃ (Roth suprapure 20% NH₃ stock solution) was used to adjust the final concentrations to 0.8 and or 8 mass % NH₃. The NaOH (0 % NH₃) solution was pH-adjusted with analytical-grade sodium hydroxide ([NaOH] = 0.05 m). Analytical-grade NaCl, KCl, and NaHCO₃ salts were also added to each solution such that the final concentrations were: [NaCl] = 0.05 m, [KCl] = 0.0006 m, [NaHCO₃] = 0.05 m. All of the solutions were prepared under an Ar atmosphere in a dry glovebox (O_{2 (g)} < 1ppm). The starting pH values at ambient temperature of the 0.0 (NaOH), 0.8, and 8.0 wt % NH₃ solutions were 10.8, 10.8 and 12.2, respectively.

Reactor blanks and experiment replicates. Triplicate procedural blanks were performed with each fluid type to identify contamination in the experimental process. Nalgene vials were cleaned and prepared as for experiments, filled with one of the three solutions without olivine, and allowed to soak for one week at 22 °C. Fluid samples were then collected and processed as described for the experimental samples. In none of the vials did the [Mg] or [Si] increase in the solution after soaking. Results of these procedural blanks are reported in Supplementary Table 3.11. To quantify reproducibility of the experiments, 2-3 replicate vials at each fluid chemistry and each temperature were reacted for 167 days (4000 hours). Standard deviations for the triplicate samples in each fluid type are included in the error calculation for each elemental concentration reported in Supplementary Tables 3.2-10. For each experimental series, the initial solution (labeled as "S0" in Supplementary Tables 3.2-10) was collected immediately before contact with olivine.

3.4.2 Olivine dissolution.

Dissolution rate calculations. Each measured concentration ([Si], [Mg], mol L⁻¹) was corrected by subtracting the respective initial blank value (*S0*). In our calculations we have assumed a solution density of ~1 g cm³. Each corrected concentration value for either Si or Mg was calculated as follows:

$$[conc Si, Mg]_{corr} = \frac{(conc_{meas} - conc_{SO})V_{reac}/1000}{(SSA)(mass)(stoich factor)}$$

where the concentrations have units of mol L⁻¹ (*SO* denotes blank concentration), V_{reac} is the volume of the reactor (mL), *SSA* is the BET-measured specific surface area (m² g⁻¹), mass refers to the amount of olivine sample (g), and the stoichiometric factor (unitless) equals 1.0 for Si and 1.83 for Mg. The Si and Mg-corrected concentrations (mol olivine m⁻²) were then plotted as a function of time (s), allowing for the rates (in mol olivine m⁻² s⁻¹) to be determined as a function of the slope at a particular time *t*. The measured *SSA* can be used without adjustment at -20 °C because the unfrozen fluid film that envelopes each olivine grain prevents ice growth at the olivine surface from decreasing the olivine surface area available to interact with liquid water. Because of the possibility of secondary mineral precipitation that sequesters Si and Mg from the solution, thereby lowering the concentration, any rates calculated by this method may underestimate the "true" olivine dissolution rate. These apparent dissolution rates then represent a minimum olivine dissolution rate.

We determined two types of apparent dissolution rates, initial and long-term. Initial rates were determined using the initial rate method, which is based on a linear regression of the initial concentration vs time data. In our case, initial rates were based on the first three data (0, 7, and 14 d). Each linear regression was forced through the origin (Supplementary Fig. 3.1a).



Supplementary Fig. 3.1: Example fits of a. initial and b. long-term olivine dissolution rates for Exp. D (22 °C, 0.8% NH₃). [Corrected] mol m⁻² indicates the molar values of [Si] and [Mg] after subtracting the initial concentration of each element in the initial fluid (sample S0 in Supplementary Tables 3.2-10)

The long-term rates were calculated by fitting each set of experimental data (t = 0 to 167 d) with a hyperbolic mathematical equation (Michaelis-Menten), and then taking the derivative of the curve at 167 d (Supplementary Fig. 3.1b). This equation was used as a purely mathematical fit and does not assume any underlying reaction mechanism (Nordstrom, 1999). Given that it is known that secondary mineral precipitation is occurring in the experiments, it is even less likely that the long-term rates indicate an olivine dissolution rate. However, these rates may still be used to evaluate changes to fluid chemistry and non-stoichiometric behavior over time. 167 d was chosen as the longest duration for most of the experiments. In addition, many experiments converged to an apparent steady-state [Si] and [Mg] in the solution between 41 and 167 d. We note that while in most cases the maximum [Si] and [Mg] were measured at 167 d, this was not always the case. In a few experiments, maximum [Si] and [Mg] were measured at intermediate periods (t < 167 d, main text Fig. 3.2b and Supplementary Tables 2-10), before decreasing and then becoming more-or-less constant (i.e., achievement of steady-state concentration plateau). Further, in the three experiments that ran for > 1 year (0.8 % NH3), we measured the maximum [Si] and [Mg] in the final sample at 442 d (main text Fig. 3.2a-c), suggesting the observed steady-state concentration plateau from t = 41 to 167 d is a metastable phenomenon. Initial and long-term rates as calculated for each experiment are reported in Supplementary Table 3.1.

Thermal activation energy. The thermal activation energy was calculated using the classical Arrhenius relation:

$$k = Ae^{\frac{-E_a}{RT}}$$

In this equation, k is the rate constant (mol m⁻² s⁻¹), A is the pre-exponential factor (same units as k), E_a is the thermal activation energy (J mol⁻¹), R is the universal gas constant (J K⁻¹ mol⁻¹) and T is the absolute temperature (K). If we assume far-from-equilibrium conditions of dissolution at a basic pH, the overall rate R can be expressed as: $R = k(a_{OH-})^n$. Since it appears that in our range of alkaline pH there is only a weak dependence of the rate on [OH⁻], it is reasonable to assume $n \approx 0$, such that R = k.



Supplementary Fig. 3.2: Calculated activation energies based on [Si] and [Mg] after 14 days for experiments at each NH_3 concentration (a. 0.0, b. 0.8, and c. 8.0 mass %).

We separated the data into 3 groups: 0.0, 0.8 and 8.0 mass % NH₃, and then calculated the activation energies for each group. Each activation energy was determined by plotting ln k vs 1/T, and then multiplying the slope by -R (Supplementary Fig. 3.2). The ranges of E_a based on Si are 10.7-15.4 kJ mol⁻¹, and E_a based on Mg are 0.3 to 6.1 kJ mol⁻¹. Normally, the E_a should not depend on which element is chosen- but here this is clearly not the case. Note also the kink (break in slope) in the data going from 4 to 22 °C. This is an indication that the rates at 22 °C appear to be retarded. If the 22 °C rate data are omitted and the E_a are recalculated, then the range of E_a using Si is 11.5 to 22.6 kJ mol⁻¹; using Mg: 2.0-12.6 kJ mol⁻¹. This example underlines the sensitivity of E_a to the rate values used, in particular when the 22 °C rates are excluded. Even so, all of our E_a are too low, and we therefore estimate that these values do not represent true E_a . As a comparison, thermal activation values of forsterite in the literature are in the range 40- 60 kJ mol⁻¹ (Hänchen et al.(Hänchen et al., 2006) = 53 kJ mol⁻¹; Oelkers(Oelkers, 2001) = 64 kJ mol⁻¹; see also Table 1 in Rimstidt et al.(Rimstidt et al., 2012): E_a values range from 38 kJ mol⁻¹ to ~70 kJ mol⁻¹).

2.3 Aqueous stoichiometry of reaction vs. solid-state analyses. The overall reaction process was nonstochiometric, as evidenced by $r_{\rm Si} > r_{\rm Mg}$ for the duration of almost all experiments (e.g., see Supplementary Fig. 3.2 above). The main exception concerns the experiments at -20 °C. Nonetheless, in many of the long-term experiments, the rates started to converge towards stoichiometry at 4 and 20 °C. In general, non-stoichiometric rates are the chemical signature of the balance between two opposing processes, release of Mg and Si from the olivine structure, and their incorporation in secondary phases. This non-stoichiometry can express itself by the in-situ formation of surface altered layers (see, e.g., Hellmann et al., 2012, 2015), as well as classical precipitation (based on bulk solution chemical supersaturation) of secondary crystalline phases. Based on the aqueous data, the theoretical thickness of a SAL can be readily calculated by taking the absolute difference between the Mg and Si concentrations (normalized with respect to forsterite stoichiometry and total surface area, i.e., units of mol olivine m⁻²) measured at the end of an of experiment and then multiplying it by the molar volume of forsterite (43.790 cm³ mol⁻¹). This calculation gives a theoretical thickness of in situ surface alteration, assuming uniform coverage and a SAL with the same molar volume as olivine. We cannot, of course, exclude the possibility that we missed evidence for thicker SALs, which may have formed in a patchy manner or on specific crystallographic faces that were not examined.

The maximum SAL thickness that we calculated is ~ 10 Å (8 % NH₃, 25 °C). Most of the experiments that we ran yielded values in the 1-6 Å range. With respect to the particular grain examined by TEM (Fig. 4, main text), the calculated SAL thickness is ~ 1 Å, which comes close to the measured value of ~ 4 Å. Similar thicknesses were measured on the FIB-prepared TEM foils from the other 2 grains (Supplementary Figs. 6-8). Note that the calculated thicknesses would increase if we assume that the molar volume of the SAL is greater than that of olivine- this is in fact a realistic possibility. As already discussed in the main text, we were not successful in measuring the chemical composition of the very thin SAL, due mainly to the susceptibility of this material to the electron beam.

3.4.3 Characterization of the ice-olivine interface

Optical microscopy. We investigated olivine-ice interfaces that formed in various aqueous chemical environments at sub-zero temperatures with optical microscopy, using both plain and polarized light. To better understand the physical process of fluid melting at the olivine grain boundary, unaltered olivine grains and DI water were mixed and then flash-frozen with liquid nitrogen (77 K). Upon subsequent exposure to ambient temperature, sequential images were taken of the fluid front as it advanced from the solid interface into the enveloping ice. Images taken during the melt process show the fluid phase of the melt propagating away from the olivine-ice interface, consistent with melt propagation originating from an unfrozen film at the mineral surface (main text, Fig. 3.1d).

Because freezing rate has an effect on ice textures(Blackford, 2007), we also investigated ice textures and the olivine-ice interface in samples frozen slowly. Using the same 3 fluid compositions as in the -20 °C experiments, olivine-solution mixtures were frozen at -8 °C on glass slides in a cold room (note: the cold room could not achieve -20 °C). After 4 hours had elapsed, the frozen mixtures were observed under an optical microscope in situ at -8 °C. This allowed us to characterize the nature of the ice texture and ice-olivine interface in ice that formed slowly similar to experimental conditions.

Because crystalline ice is birefringent under polarized light, while amorphous ice and liquid water are not(Warren, 1984), the crystallinity of ice may be investigated using polarized light microscopy. Increasing birefringence of samples and visible grain boundaries of partially frozen 0.0, 0.8% NH₃, and 8.0% NH₃ solutions under polarized light show that increasing the NH₃ content results in ice with decreased crystallinity and increased porosity (main text Fig. 3.1a-c). A region of unfrozen solution at the olivine-ice interface visually identified by this method was used as a conceptual guide to Raman analyses of the chemistry at the olivine-ice interface.

Raman Spectroscopy. Raman analyses were performed at the olivine-ice interface using a Renishaw® InVia confocal Raman microscope. Measurements were performed using an excitation energy at 532 nm. The spectrometer was equipped with a visible-dedicated diffraction grating (2400 grooves/mm) and a CCD camera. Using this configuration, the spectral resolution is lower than ~1 cm⁻¹. Samples were placed in a quartz cell in a Linkam[®] THMS 600 heating/freezing stage that was maintained at -20 °C during analysis. A 50x long working distance objective (numerical aperture = 0.5) was used to focus and collect the incident and scattered beams. Graphed spectra in Fig. 3.1 (main text) and Supplementary Fig. 3.3 were smoothed using a 10-measurement simple rolling average to decrease noise. Measurements were collected in sequential profiles from near or within the olivine, to the surface (i.e., mineral-fluid interface), and into the ice. Profiles were collected in 8 wt % NH3 fluid at -10 and -20 °C, and in 0 % solution at -20 °C. In such a case, the 50 – 4000 cm⁻¹ range was systematically probed, giving information on both mineral and water phases. In addition, 2D spectral maps were collected at -20 °C in both 8 wt% NH₃ and 0 % solutions. Spectra were collected in a raster pattern over the selected range at the ice-olivine interface of a visually identified olivine grain with µm spatial resolution. In this last case, due to time constraints, a narrower spectral range centered on the water OH stretching modes region was probed. The Raman dataset were then analyzed using the manufacturer-supplied Wire 4 software. Maps were constructed either after visual inspection of the

whole data set, extracting some characteristic spectra, or using multivariate techniques such as PCA or multivariate curve resolution (MCR-ALS) techniques. In all cases, each individual spectrum is assumed to be a linear combination of model spectra. The intensity scale of the different images is then given by the coefficient that correspond to each model spectrum. All these methods gave the same trends, giving the same model spectra, and the same spatial distribution of the different signals.

Examining the spectra (Supplementary Fig. 3.3), it was possible to identify and use some of the characteristic lines from the following analytes of interest: olivine (820 and 850 cm⁻¹), CO_3^{2-} (1070 cm⁻¹), water-ice (broad peak from 3070-3200 that narrows with decreasing temperature: peak apex = 3139 cm⁻¹ at -20 °C), NH₃ (temperature causes the band to shift to lower wavenumbers with decreasing temperature: peak apex = 3312 cm⁻¹ at -20 °C) and liquid water (from the stretching band of liquid water from 3000-3724 cm⁻¹: peak apex = 3405 cm⁻¹ at 22 °C). Where the liquid water peak was not visible below -0 °C, the relative intensity of the ice band was used as a proxy to identify areas with less ice and more unfrozen solution. At below -0 °C conditions in all solutions, the intensity of the ice peaks decreases as the intensity of the olivine peaks increase. The NH₃ peak gains in relative intensity as CO_3^{2-} peaks are also identified in spectra with decreased intensity of the ice band, corroborating the modelled exclusion of those species from the ice phase and their concentration in the unfrozen solution surrounding the olivine grains.

Because the unfrozen film of solution at the olivine surface has greater width at higher temperatures (D. Anderson & Tice, 2012), the unfrozen film is better represented over the analytical path of the Raman spectrometer at -10 °C. The relative intensity of the bands at 820 and 850 cm⁻¹ (olivine) increases as more of the focal point, or more exactly the beam waist, is within the olivine grain, therefore also including the surface of the olivine. Decreasing intensity of the olivine peaks indicates the focal region is moving away from the surface of the olivine and includes more of the ice-olivine interface, including the unfrozen film, and in the most distal measurements water ice as well. Because of the low numerical aperture of the 50x objective used, the probing depth is rather high, most probably higher than approximately 10 µm. Thus, even within the olivine some signal contribution from the surrounding solution and ice-water mélange occurs: similarly, away from the olivine grain in the ice-solution coexistence region, a minor signal due to the olivine is still registered. With the exception of some specific conditions, i.e. a rather abrupt and vertical olivine/water interface, it is almost impossible to register a signal from the unfrozen film alone. Such a specific situation was nearly met, see Supplementary Fig. 3.4. In this case, mapping experiments have shown that it is possible to completely reconstruct the whole dataset using two different spectra corresponding to the frozen and unfrozen situations, respectively. The unfrozen region is then identified by the line shape of the O-H stretching modes regions, and the characteristic signal of ammonia.



Supplementary Fig. 3.3: Raman spectra in 8 % NH₃ at -10 °C, conditions approximating those of the optical microscopy images. The peaks in the wavenumber bands corresponding to olivine, CO₃²⁻, and ice are annotated.

We visually identified the thin film as having a thickness of >10 microns at -8 °C with an optical microscope in a cold room, and used a Raman spectral analysis to identify liquid and ice phases at the ice-olivine interface at -20 °C. Unfrozen water in contact with ice will behave as a normal Newtonian fluid in a fluid film with a thickness >1 nm(Gilpin, 1979). Because the unfrozen film at the olivine surface is thick enough to be identified as water from its characteristic O-H stretching bands in Raman analysis, we conclude that the unfrozen film at the olivine surface has a thickness that well exceeds 1 nm and that normal fluid dynamics apply to reactions in our experiments.



Supplementary Fig.3.4: Raman spectra in 8 % NH₃ at -20 °C, experimental conditions. The area analyzed is an 80 μ m square, this region was examined with a 2 μ m point spacing. The images on the left are 2D spatial maps determined by multivariate analysis techniques (PCA and multivariate curve resolution algorithms), that identified two characteristic spectra corresponding to water ice (red) and NH₃ in liquid water (black), see the two spectra on the right-hand side of the figure. These two spectra allowed a complete reconstruction of the whole dataset. Images were constructed assuming that each individual spectrum was a linear combination of the two model spectra, after normalization of the whole dataset.

3.4.4. Geochemical Calculations.

The formation of pure water ice in our experiments results in exclusion of solutes and NH₃, forming a concentrated brine. Because the eutectic temperature (freezing point of the entire solution) of the NaCl-H₂O system is -21.5 °C (Potter et al., 1978), all three solution types used in our experiments have some unfrozen solution at -20 °C, even after partial freezing and formation of pure water ice. This was verified in our own Raman analyses of the solutions at -20 °C, as discussed above. We found that NH₃ and carbonate species (here, CO3²⁻) were co-located with liquid water (Supplementary Fig. 3.3); and that ice and NH₃ signals were found exclusory of each other (Supplementary Fig. 3.4). Similarly, as the NH₃-H₂O system has eutectic temperature of -96 °C (177 K), the amount of NH₃ in the solution also affects the amount of unfrozen solution in experiments (Clegg & Brimblecombe, 1989; G. Marion et al., 2012). Calculations based on multicomponent NH₃-salt-water systems can then be used to calculate the ice:unfrozen solution ratio in each experiment.



Supplementary Fig. 3.5: ammonia-water phase diagram from 280 to 150 K (7 $^{\circ}$ to -123 $^{\circ}$ C) and initial NH₃ molality from 0 to 30. T_f indicates the freezing curve (partial freezing temperature) of the NH₃ - H2O system as a function of NH₃ content. T_e indicates the eutectic temperature of the NH₃ - H₂O system below which the entire system is frozen (solid). The chemistries used in our experiments are plotted at the experimental temperature 253 K (-20 $^{\circ}$ C). In the 0.0 % NH₃ (0 molal NH₃), 0.8 wt. % NH₃ (0.5 molal NH₃), and 8% NH₃ (5 molal NH₃) solutions, water ice starts forming at 273, 270, and 267 K, respectively. Within the "Solution + water ice" stability field, ice:water ratios increase with decreasing temperature (blue arrow) and with decreasing NH₃ content. Figure adapted from Marion et al., 2012.

For each sample we calculated in-situ pH, ionic strength, solute speciation, and saturation with respect to select minerals (brucite, sepiolite, chrysotile, amorphous SiO₂, and forsterite). We applied two complementary computational approaches to investigate the fluid chemistry: 1. PHREEQC v. 3.5.0 software (Parkhurst & Appelo, 2013), using the b-dot ion association model and the LLNL thermodynamic database (Johnson et al., 2000), was used to calculate in-situ pH, solute speciation, and corresponding saturation indices of secondary minerals; 2. FREZCHEM v. 15.2(G. M. Marion et al., 2010) thermodynamic freezing model was used to calculate the amount of ice formed and the chemistry of the remaining unfrozen solution in each experiment at -20 °C.

In-situ pH was calculated for each solution at each experimental temperature in PHREEQC. Solute speciation calculations and saturation indices were calculated by selecting an input solution chemistry for each sample and modelling the thermodynamic equilibrium for that input solution at the experimental temperature with PHREEQC. For samples from experiments at 22 and 4 °C, we simply

used the molar concentrations of solutes as analyzed by ICP and bench pH (Supplementary Tables 3.2-10) as the input solution parameters. For experiments at -20 °C, we used FREZCHEM to calculate the amount of water removed from each solution into the ice phase during the partial freezing process. Because ice forms as pure water ice under the experimental conditions, all solutes are concentrated in the remaining unfrozen solution and a concentration factor can be calculated from the amount of ice formed. This concentration factor was then applied to the analyzed solution chemistries for each experiment at -20 °C and the concentrated solution chemistry was used as the input solution to PHREEQC for each of these solutions to calculate the parameters listed above. For the 0.0 % NH₃ experiments, this represents a 30x increase in concentration over the original analyzed solute concentrations; for 0.8 % NH₃ experiments, a 15x concentration increase; and for 8.0 % NH₃ experiments, a 2.3x concentration increase.

3.4.5 Electron microscopy analyses

FEG-SEM. Scanning electron microscopy (SEM) was used to characterize alteration at the μ m-scale. Olivine grains from selected experiments were observed with a field emission gun scanning electron microscope (FEG-SEM: Zeiss Ultra 55, CMTC, Grenoble). Olivine grains from two long-term experiments were prepared for observation by FEG-SEM to identify any alteration visible at the micron scale. We selected at least 5 grains, respectively, from each of experiments B-28 (0.8% NH₃ reacted at 25 °C for 442 days) and B-5 (0.8% NH₃ reacted at -20 °C for 442 days). Using secondary electron (SE) and backscattered electron (BSE) imaging at 20 kV we analyzed olivine grains reacted at each temperature and found no obvious evidence for physical alteration at the sub- μ m-scale, such as the presence of etch pits. We also did not observe any authigenic secondary phases that potentially may have precipitated on the grain surfaces during alteration. Energy dispersive X-ray spectroscopy EDXS spot analyses on reacted surfaces also did not reveal any deviation from the nominal chemistry of the unaltered olivine.

FEG-SEM was also used to select suitable sites on specific grain surfaces from sample B-5 for focused ion beam (FIB) sampling. We specifically chose grain surfaces that displayed a clean conchoidal fracture for both FEG-SEM analyses and FIB sampling. This ensured that we were probing surfaces that had been freshly fractured during sample preparation before reaction. In this manner we avoided grain surfaces that had been previously exposed to natural weathering processes (i.e. at the original outcrop locality of San Carlos, AZ, USA).

FIB. One of the main advantages of focused ion beam (FIB) milling is that a specific area of interest on a sample surface can be chosen by the operator. Because FIB lamellae are in general milled from a cut oriented vertically and perpendicular to a sample surface, they afford a cross sectional view of the altered material. A FIB-prepared foil can then be analyzed using a sub-nm-sized TEM beam to measure chemical alteration-induced changes to the chemistry and structure of the near surface region. In our case, the FIB-prepared TEM foils reveal a sequence (from top to bottom) of distinct phases consisting of protective coatings (Pt, C, Au), potential secondary crystalline precipitates, a surface altered layer, and unaltered olivine. We used a dual beam instrument (FEI Helios G4 UC, GFZ, Potsdam) to fabricate the TEM foils from three selected grains from sample ESC-B5 (-20 °C, 1 % NH3 saline solution, 442 d)-see Supplementary Figs. 3.6a-c. We also fabricated a TEM foil by FIB from a 'blank' sample. This

pristine grain had not been altered in the experiments, and in addition, we chose a fresh conchoidal fracture surface to ensure it had not been exposed to previous natural weathering.

Before FIB milling, a ~20 nm C coating was deposited on all of the grains, which already had a layer of sputtered Au. The FIB procedure that we used starts with a ~120 nm layer of electron beam-deposited Pt, which in turn is overlain by 2 μ m of ion-deposited Pt (ion beam current of 230 pA). These two Pt layers constitute what is termed the Pt strap. Vertical trenches are then milled with a focused Ga ion beam at 30 kV and 9.5 nA. Once freed from the matrix, the foil is welded to a micromanipulator, enabling it to be transferred and welded to a post on a (Cu) TEM lift-out grid. The lamella is further thinned down in an incremental manner with a Ga ion beam (30 kV, 16 kV and 5 kV using ion beam currents of 230, 80, 41 and 25 pA). A final step consisted of cleaning the lamella with Ar+ ions with an energy of ~1 kV using a Gatan Duo Mill 600 ion milling device, which removes much of the amorphous material created at the lateral edges of the lamella. For more details on the FIB process, the interested reader is referred to ref (Schaffer et al., 2012).

TEM. Transmission electron microscopy (TEM) imaging and chemical analyses were performed with a Thermo Fisher Scientific (formerly FEI) state-of-the-art Themis Z 3.1 microscope operated at 300 kV, and a Tecnai F20 operated at 200 kV, both housed at the GFZ-PISA facility, Potsdam. The Themis TEM is equipped with an X-FEG electron source with a monochromator (energy resolution is < 300 meV at 300 kV) and a Cs S-CORR probe corrector (spatial resolution at 300 kV < 0.06 nm). It is also equipped with BF (bright field), DF2 and DF4 (dark field), and STEM-HAADF (scanning TEM-high angle annular dark field) detectors. High resolution chemical analyses were performed with a Gatan imaging filter Continuum 1065. Additional images of the TEM work performed on 3 altered olivine grains from experiment B-5 (0.8 % NH3, -20 °C) are presented below (Supplementary Figs. 3.6-3.8).



Supplementary Fig. 3.6: Altered olivine grain no. 1. a. SEM image b. location of FIB cut (arrow) c. high resolution iDCP-STEM image of olivine structure, with atomic-scale olivine model overlay (blue = Si, red = O, orange = Fe, Mg). The region beyond the dashed line is an amorphous surface altered layer (SAL). d. High-resolution TEM image of olivine, SAL, and overlying Au particles (C presumably occupies space between the Au and SAL). The image was collected using a FEI Tecnai F20 microscope operated at 200 kV.



Supplementary Fig. 3.7: Altered olivine grain no. 2. a. STEM-HAADF image of olivine structure, thin amorphous surface altered layer (SAL), and Au layer. The SAL is continuous along the interface, but is only partially delimited by dashed lines in image. b. iDCP STEM image of the same interface, but at much higher spatial resolution. Note the distinct 4 Å-thick SAL. This grain is also portrayed in the main text (Fig. 4b).



Supplementary Fig. 3.8: Altered olivine grain no. 3. a. SEM image of grain and FIB location (red arrow). b. STEM-HAADF image of olivine structure, thin amorphous surface altered layer (SAL), and Au layer. The SAL is semi-continuous along the interface and is delimited by dotted lines. c. iDCP STEM image of the same interface. In both panels, the lower left area shows evidence of electron beam damage during focusing.

3.5 References

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3.6 Aqueous chemistry tables

Supplementary table 3.1 lists experimental parameters and dissolution rates, where "Exp. ID" indicates the experiment name, "Solution" indicates solution type. Initial pH at bench (ambient conditions) and calculated in-situ pH are listed for all experiments. In-situ pH at -20 °C is calculated for the unfrozen portion of the solution in the experiments based on thermodynamic freezing of pure water ice and OH⁻ solute exclusion into the unfrozen solution as calculated with FREZCHEM. Final pH values for all experiments varies from initial pH by less than 0.1 pH units (less than the instrumental error for the pH probe) and are therefore not listed. The "initial rate" and "final rate" values are calculated as described in Supplementary section 2.1.

Supplementary tables 3.2-3.10 present results from ICP-AES analyses of the fluid aliquots from each reactor in each experiment set. For all tables 2-10: the column "Sample ID" indicates the reactor identifier during the experiment set; "Days" indicates the total time of reaction in days (number of days from initial contact of solution with olivine grains in the reactor, and experiment quench); "[element]" is the concentration of each element measured in a fluid aliquot from the indicated reactor (mmol L⁻¹). Uncertainties for the elemental concentrations (mmol L⁻¹) includes from instrumental error, systemic error from pipetting (during initial allocation of solution in experiments and acid dilution for analysis), and the standard deviation between 3 replicates of experiments reacted for 167 days. Null values ("--") indicate concentrations below detection limits or meaningless values (for example, uncertainty in saturation index estimates).

Supplementary table 3.11 presents fluid analyses from blanks, where fluid was allowed to soak in the reactor vials with no olivine.

Exp. ID	Solution	T (°C)	pH (bench)	in-situ pH	Initial rate (Si)	Final rate (Si)	Initial rate (Mg)	Final rate (Mg)
Exp.A	0.0% NH ₃	22 ± 2	10.79 ± 0.05	10.8	5.3x10 ⁻¹²	2.4x10 ⁻¹⁴	3.3x10 ⁻¹²	3.0x10 ⁻¹⁴
Exp.B	0.0% NH ₃	4 ±1	10.79 ± 0.05	11.1	5.5x10 ⁻¹²	9.9x10 ⁻¹⁵	4.4x10 ⁻¹²	2.4x10 ⁻¹⁴
Exp.C	0.0% NH ₃	-20 ± 1	10.79 ± 0.05	11.5	1.9x10 ⁻¹²		2.4x10 ⁻¹²	
Exp.D	0.8% NH ₃	22 ± 2	10.82 ± 0.05	10.8	7.5x10 ⁻¹²	4.9x10 ⁻¹⁴	4.2x10 ⁻¹²	2.4x10 ⁻¹⁴
Exp.E	0.8% NH ₃	4 ±1	10.82 ± 0.05	11.5	6.1x10 ⁻¹²	4.3x10 ⁻¹⁴	3.6x10 ⁻¹²	1.9x10 ⁻¹⁴
Exp.F	0.8% NH ₃	-20 ± 1	10.82 ± 0.05	11.9	3.5x10 ⁻¹²	7.7x10 ⁻¹⁴	2.7x10 ⁻¹²	1.3x10 ⁻¹³
Exp.G	8.0% NH ₃	22 ± 2	12.21 ± 0.05	12.2	4.6x10 ⁻¹²		2.1x10 ⁻¹²	
Exp.H	8.0% NH ₃	4 ±1	12.21 ± 0.05	12.8	4.1x10 ⁻¹²	4.5x10 ⁻¹⁴	2.2x10 ⁻¹²	7.1x10 ⁻¹⁴
Exp I	8.0% NH ₃	-20 ± 1	12.21 ± 0.05	13.7	1.8x10 ⁻¹²	1.7x10 ⁻¹³	2.0x10 ⁻¹²	3.3x10 ⁻¹³

Supplementary table 3.1: List of experiment parameters and dissolution rates.

Supplementary table 3.2: Exp. A (0.0 mass % NH $_3$ at 22 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
NaOH S0	0	0.0006	0.560	0.002	129	0.004	-1.3	-12.5	-4.9	-4.3	-0.2
NaOH-1	7	0.0006	0.524	0.008	122	0.008	-0.8	-8.6	-3.6	-4.0	2.0
NaOH-7	14		0.729	0.008	151	0.009	-0.8	-8.5	-3.5	-4.0	2.1
NaOH-8	21		0.929	0.011	145	0.012	-0.7	-7.3	-3.2	-3.9	2.6
NaOH-2	41	0.0019	0.629	0.024	118	0.017	-0.3	-4.6	-2.3	-3.6	4.1
NaOH-0-C	167	0.0010	0.494	0.013	125	0.011	-0.6	-6.6	-2.9	-3.8	3.0
Uncertainty		± 0.000002	± 0.01	± 0.0001	± 1	± 0.0003					

Supplementary table 3.3: Exp. B (0.0 mass % NH $_3$ at 4 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SI _{Forsterite}	SI _{SiO2}	SI Chrysotile
NaOH S0	0	0.0006	0.560	0.002	129	0.004					
NaOH-3	7	0.0005	0.517	0.007	123	0.007	-1.9	-9.2	-5.6	-3.8	0.3
NaOH-10	14	0.0003	0.614	0.012	132	0.011	-1.7	-7.2	-4.9	-3.6	1.3
NaOH-12	21		0.885	0.010	142	0.010	-1.7	-7.6	-5.0	-3.7	1.2
NaOH-4	41	0.0014	0.595	0.020	114	0.014	-1.4	-5.2	-4.2	-3.4	2.4
0-D	167	0.0007	0.534	0.013	131	0.008	-1.6	-7.6	-4.9	-3.7	1.3
0-B	167	0.0007	0.552	0.013	134	0.009	-1.6	-7.4	-4.9	-3.7	1.4
Uncertainty		± 0.000002	± 0.01	± 0.0001	± 1	± 0.0003					

Supplementary table 3.4: Exp. C (0.0 mass % NH₃ at -20 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
NaOH S0	0	0.0006	0.560	0.002	129	0.004					
NaOH-5	7	0.0007	0.550	0.007	126	0.006	-0.2	-3.9	-2.3	-4.0	4.9
NaOH-14	14		0.704	0.006	147	0.006	-0.2	-4.5	-2.4	-4.1	4.7
NaOH-15	21	0.0001	0.873	0.007	140	0.007	-0.2	-3.7	-2.3	-3.9	5.0
NaOH_6	41	0.0013	0.464	0.016	103	0.011	0.1	-0.4	-1.4	-3.6	6.6
Uncertainty		± 0.000002	± 0.01	± 0.0001	± 1	± 0.0003					

Supplementary table 3.5: Exp. D (0.8 mass % NH $_3$ at 22 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
0.8% NH ₃ S0	0	0.0004	0.442	0.002	92	0.003	-1.0	-9.1	-3.9	-3.9	1.5
1-1	7	0.0006	0.530	0.006	108	0.007	-0.9	-9.1	-3.8	-4.0	1.6
1-7	14		0.762	0.010	129	0.012	-0.7	-7.2	-3.2	-3.8	2.7
1-8	21	0.0001	0.906	0.011	120	0.012	-0.6	-6.9	-3.1	-3.8	2.8
1-2	41	0.0012	0.464	0.015	77	0.011	-0.6	-5.8	-2.8	-3.7	3.3
1-E	167	0.0006	0.489	0.014	105	0.016	-0.6	-5.5	-2.7	-3.6	3.4
1-A	167	0.0006	0.488	0.012	105	0.014	-0.6	-6.1	-2.9	-3.7	3.1
B-28	442	0.0015	0.731	0.033	107	0.041	0.0	-1.4	-1.3	-3.3	5.7
Uncertainty		± 0.00002	± 0.01	± 0.001	± 1	± 0.001					

Supplementary table 3.6: Exp. E (0.8 mass % NH $_3$ at 4 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
0.8% NH ₃ S0	0	0.0004	0.442	0.002	92	0.003					
1-3	7	0.0004	0.480	0.006	102	0.006	-1.1	-8.5	-4.5	-4.2	1.8
1-10	14		0.771	0.009	130	0.010	-1.0	-6.9	-4.0	-4.0	2.6
1-12	21		0.880	0.010	118	0.010	-0.9	-6.6	-3.8	-4.0	2.8
1-4	41	0.0016	0.601	0.020	100	0.015	-0.6	-4.1	-3.0	-3.8	4.1
1-I	167	0.0005	0.515	0.010	107	0.010	-0.9	-6.4	-3.8	-4.0	2.8
1-F	167	0.0007	0.595	0.011	124	0.014	-0.9	-5.5	-3.6	-3.9	3.2
B-30	442	0.0015	0.703	0.035	104	0.035	-0.4	-1.0	-2.2	-3.4	5.5
Uncertainty		± 0.00005	± 0.03	± 0.0005	± 6	± 0.001					

Supplementary table 3.7: Exp. F (0.8 mass % NH₃ at -20 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SI _{Forsterite}	SI _{SiO2}	SI Chrysotile
0.8% NH ₃ S0	0	0.0004	0.442	0.002	92	0.003					
1-5	7	0.0005	0.487	0.005	103	0.005	0.1	-4.8	-2.0	-4.3	5.2
1-14	14		0.742	0.007	126	0.007	0.3	-3.7	-1.5	-4.3	5.9
1-18	21	0.0001	0.811	0.006	110	0.006	0.2	-4.1	-1.7	-4.3	5.6
1-6	41	0.0014	0.615	0.016	102	0.011	0.6	-0.9	-0.6	-4.0	7.4
1-H	167	0.0014	0.644	0.019	106	0.012	0.7	-0.3	-0.4	-4.0	7.7
1-D	167	0.0014	0.603	0.019	101	0.012	0.7	-0.3	-0.5	-4.0	7.7
1-B	167	0.0013	0.456	0.016	77	0.010	0.5	-0.5	-0.6	-3.9	7.4
B-16	442	0.0022	0.684	0.033	107	0.022	0.9	2.2	0.3	-3.7	9.0
B-5	442	0.0020	0.689	0.033	105	0.023	0.9	2.3	0.3	-3.7	9.0
Uncertainty		± 0.00004	± 0.05	± 0.001	± 8	± 0.001					

Supplementary table 3.8: Exp. G (8.0 mass % NH $_3$ at 22 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SI _{Forsterite}	SI _{SiO2}	SI Chrysotile
8% NH ₃ S0	0	0.0001	0.456	0.002	96	0.004	-1.5	-12.8	-5.1	-4.2	-0.5
10-1	7	0.0000	0.469	0.003	99	0.006	1.5	-8.0	-0.3	-5.4	6.1
10-7	14		0.669	0.006	122	0.009	1.8	-6.3	0.4	-5.3	7.1
10-8	21		0.830	0.011	119	0.012	2.0	-4.4	1.0	-5.2	8.2
10-2	41	0.0014	0.382	0.020	68	0.015	2.3	-2.0	1.7	-4.9	9.4
Uncertainty		± 0.0005	± 0.04	± 0.004	±2	± 0.004					

Supplementary table 3.9: Exp. H (8.0 mass % NH $_3$ at 4 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
8% NH ₃ S0	0	0.0001	0.456	0.002	96	0.004					
10-3	7	0.0000	0.424	0.003	93	0.005	1.1	-8.3	-1.3	-5.6	5.7
10-10	14		0.682	0.006	121	0.008	1.4	-6.5	-0.6	-5.5	6.8
10-11	21		0.838	0.011	118	0.011	1.6	-4.8	0.0	-5.4	7.7
10-4	41	0.0019	0.568	0.032	98	0.024	2.1	-0.6	1.3	-5.0	9.9
10-F	167	0.0030	0.614	0.013	128	0.013	1.7	-4.2	0.2	-5.3	8.0
10-E	167	0.0010	0.605	0.011	125	0.009	1.6	-5.5	-0.1	-5.5	7.5
10-D	167	0.0024	0.749	0.027	122	0.014	2.0	-2.6	0.9	-5.3	9.1
Uncertainty		± 0.0005	± 0.04	± 0.004	± 2	± 0.004					

Supplementary table 3.10: Exp. H (8.0 mass % NH₃ at -20 °C)

Sample ID	Days	[Fe]	[K]	[Mg]	[Na]	[Si]	SIBrucite	SI _{Sepiolite}	SIForsterite	SI _{SiO2}	SI Chrysotile
8% NH ₃ S0	0	0.0001	0.456	0.002	96	0.004					
10-5	7	0.0000	0.336	0.002	71	0.003	2.8	-9.7	0.9	-7.0	8.2
10-14	14		0.648	0.006	117	0.006	3.3	-6.8	2.0	-6.8	9.9
10-15	21	0.0001	0.818	0.007	119	0.007	3.3	-6.0	2.2	-6.6	10.2
10-6	41	0.0017	0.553	0.026	94	0.016	3.7	-2.2	3.3	-6.3	12.1
10-C	167	0.0028	0.699	0.029	117	0.015	3.7	-2.5	3.2	-6.3	12.0
10-A	167	0.0029	0.742	0.031	123	0.016	3.7	-2.4	3.3	-6.3	12.1
Uncertainty		± 0.00004	± 0.02	± 0.001	± 2	± 0.0003					

Supplementary table 3.11: reactor soak results

Replicate ID	Days	рН	[Fe]	[K]	[Mg]	[Na]	[Si]
0.0% NH ₃ S0	0	10.8		0.805	0.005	212	0.0
0.0 rep 1	7	10.8		0.740	0.004	151	0.0
0.0 rep 2	7	10.8		0.886	0.005	140	0.0
0.0 rep3	7	10.8		0.786	0.005	140	0.0
0.8% NH ₃ S0	0	10.8		0.801	0.005	128	0.0
0.8 rep 1	7	10.8		0.749	0.005	127	0.0
0.8 rep 2	7	10.8		0.891	0.005	117	0.0
0.8 rep 3	7	10.8		0.654	0.004	87	0.0
8.0% NH ₃ S0	0	12.2		0.839	0.005	132	0.0
0.8 rep 1	7	12.2		0.540	0.003	90	0.0
0.8 rep 1	7	12.2		0.821	0.006	115	0.0
0.8 rep 1	7	12.2		0.812	0.006	114	0.0



0 %, 90 °C (6 mo)

0.8 %, 90 °C (5 mo) 8 %, 90 °C (6 mo)

CHAPTER 4

Experimental insights into of olivine dissolution in ammonia-salt-water solutions from 0-150 °C

RESEARCH QUESTION

Does an ammonia-bearing solution affect olivine dissolution rates, or otherwise influence olivine alteration behavior through interactions with dissolved species or secondary phases?

<u>Chapter 4. Experimental insights into of olivine dissolution in NH₃-salt-water solutions</u> <u>from 0-150 °C</u>

Abstract. The presence of NH_3 , salts, silica nanoparticles, and H_2 in emissions from Saturn's moon Enceladus, as well as geophysical observations consistent with a liquid ocean beneath its icy crust, has been interpreted as evidence that hydrothermal activity and active serpentinization of primary ultramafic minerals is occurring within an NH₃-bearing ocean at present day. However, if hydrothermal vents have formed in an H₂O-NH₃ ocean on this or other icy worlds, the impact of NH₃ on mineral alteration in this environment is virtually unknown. Specifically, inhibiting effects on olivine alteration could conceivably increase the time windows of active serpentinization on icy worlds, and the presence of NH₃ may affect the formation of NH₃-bearing minerals in secondary mineral assemblages. Conversely, enhancing effects of NH₃ on olivine dissolution may decrease the expected time windows of active serpentinization on icy worlds. In conceptually and numerically modelling primary mineral alteration in these exotic environments, defining any effect of NH₃ on olivine dissolution rates and its alteration products is of critical importance to interpreting the geochemical observations of these icy worlds. To address this, we designed and completed two complementary sets of experiments that seek to characterize Mg-rich olivine dissolution and alteration in 0, 0.8, or 8 wt % NH₃ solutions, at a range of relevant temperatures. We carried out continuous-flow stirred-tank reactor (CFSTR) experiments at 0-150 °C to measure dissolution rates, as well as closedsystem batch reactor experiments at 90 and 150 °C to enhance secondary mineral precipitation and characterize alteration products in NH₃. The calculated apparent olivine dissolution rates show no significant impact of NH₃, as well as a surprisingly weak dependence on temperature. In fact, the apparent dissolution rates at 0 °C are the fastest of any temperature in the CFSTR experiments. In addition, our results agree with other studies that have found that olivine dissolution rates are not sensitive to increasing pH at highly alkaline conditions. The effect of NH₃ on the formation of secondary products turns out to be more complicated, however. Secondary precipitation is observed to be more abundant and secondary products more crystalline in experiments with NH₃, especially those conducted at 90 °C; however, no NH₃-minerals or NH₄⁺-clays were found among the secondary products. These results suggest new research directions for fundamental mechanisms of mineral precipitation in aqueous fluids rich in NH₃. To our knowledge, the CFSTR experiments reported here represent the first continuous-flow measurements of olivine dissolution in alkaline solutions at 0 °C, and join a growing number of studies in showing faster-than-anticipated dissolution rates of minerals at or below 0 °C. These results suggest a potential change in the dissolution mechanism of olivine at low temperatures that is not reflected by our current knowledge of the olivine dissolution system. It may also reflect less inhibition of rates due to precipitates or surface altered layers.

4.1 Introduction

Observations of Saturn's small moon Enceladus by the recent Cassini-Huygens mission found geophysical evidence consistent with a global subsurface liquid ocean underneath an icy crust, surrounding a rocky core 360-400 km in diameter (Čadek et al., 2016; Thomas et al., 2016). Even more surprising was both the discovery of geyser-like plumes of water vapor that emitted from Enceladus' south pole (Hansen et al., 2006), and the finding that the E-ring of Saturn is possibly comprised largely of the particulates from these plumes (Spahn et al., 2006). This offered the unforeseen possibility of indirectly sampling this ocean using the Cosmic Dust Analyzer (CDA) and Ion and Neutral Mass

Spectrometer (INMS) instruments already on board the Cassini spacecraft (Schneider et al., 2009; Waite et al., 2006). The resulting analyses of both the plumes and the E-ring show salts and NH₃ that have been cited as evidence of a salty, NH₃-bearing aqueous liquid ocean beneath the icy crust (Postberg et al., 2011, 2009; Waite et al., 2009). The discovery of H₂ in the plume (Waite et al., 2017) and silica nanoparticles in the E-ring (Postberg et al., 2013) have been used to argue that regions of the rockocean interface must reach at least 90 °C (Hsu et al., 2015; Sekine et al., 2015). Geophysical models of heterogenous tidal heating within the core additionally suggest mechanisms that drive hydrothermal vents at the polar hot spots at temperatures up to 150 °C (Choblet et al., 2017; Liao et al., 2020). This discovery is of great interest for astrobiological research, as low-temperature hydrothermal systems are among the environments thought to be able to act as a host for the origins of life on early Earth (Choblet and Tobie, 2020; Martin et al., 2008). However, mineral alteration processes in the presence of NH₃-rich aqueous fluids, such as in extraterrestrial environments, have no relevant modern terrestrial analogues (Hazen et al., 2008). The exotic fluid composition of Enceladus' ocean may impact alteration by 1) affecting the rates or mechanisms of primary mafic mineral dissolution or 2) by modifying the type or abundance of secondary phases that form. Enceladus' rocky core is thought to have a chondritic composition (Sekine et al., 2015), with olivine being the most abundant ultramafic mineral. Expanding the range of experimentally derived data on how NH₃ affects olivine dissolution and alteration can then be used to understand the possible evolution of hydrothermal vents and the composition of the ocean on Enceladus, as well as on other small icy satellites, and even on primitive Earth. Alteration rates may also be used to constrain the timespan of active water-rock interaction and associated H₂ generation until complete serpentinization of the ultramafic rocky core occurs.

Small, icy satellites that receive little solar radiation outside the frost line of the solar system represent a primitive chemical environment potentially comparable to early Earth. Previous suppositions about the energy that could be generated by such small satellites were that they would remain frozen solid, being too small to generate the heat needed to create liquid water. However, it is now thought that endogenic activity, specifically tidal heating, may be sufficient to create and maintain a liquid ocean in these small satellites. The cores of Saturn's moons, including Enceladus, are thought to originate from aggregated ice and carbonaceous chondrites of an initially mafic or ultramafic mineralogy (Sekine et al., 2015). Aqueous alteration of olivine and pyroxene are thought to be especially vigorous during periods where water and volatiles melt and differentiate from the silicate and metal fraction (Malamud and Prialnik, 2016; Vance et al., 2007; Vance and Melwani Daswani, 2020). These hydration processes, analogous to serpentinization, may continue as long as there is liquid water and primary minerals available to be altered. In small icy satellites, exothermic primary mafic mineral alteration may represent a significant fraction of the total heat flux that can theoretically lead to a 'reaction runaway', where heat from the exothermic reaction prompts the melting of water ice, which in turn allows further primary mineral alteration (Jewitt et al., 2007; Malamud and Prialnik, 2013). The rates of these reactions are then crucial to models describing evolution of Enceladus' rocky core and other icy worlds that may harbor oceans underneath their surfaces, and possibly even possess rocky cores of silicate rocks that may possess ocean-rock interfaces (e.g. Europa (Carr et al., 1998), Mimas (Noyelles et al., 2019), Ceres (Castillo-Rogez et al., 2019), and Pluto (Dalle Ore et al., 2019). How the presence of NH₃ might affect primary mineral alteration in these systems remains unconstrained at present.

Olivine is one of the most important primary minerals composing chondrites, and is often considered in icy moon alteration studies. Specifically, Mg-rich olivine provides a convenient analogue to studying

extraterrestrial processes involving water (Buseck and Goldstein, 1969; Komatsu et al., 2001; Oelkers et al., 2018) as it benefits from decades of field and laboratory studies to understand weathering of Mg-Fe-silicates (for example, Oelkers, 2001; Olsen et al., 2015; Pokrovsky and Schott, 2000). The effect of NH₃ on both pH and dissolved element speciation/complexation are expected to be the most significant factors influencing olivine dissolution (Rimstidt et al., 2012). Olivine dissolution rate studies have found that water activity and ionic strength have little effect on olivine dissolution for water activities > 0.9 or ionic strengths < 12 M (Olsen et al., 2015). A dilute seawater containing 0.8 wt % NH₃ has little impact on water activity and ionic strength (water activity is calculated to decrease from ~0.99 to ~0.98, and ionic strength to increase by ~1 × 10⁻⁵ mol kg⁻¹ water). However, NH₄⁺ conspicuously resembles H₂O in several respects (specifically, it has similar molar mass, bond angles, interatomic distances, partial molar volumes, and hydrogen bond strengths) and may stabilize dissolved species owing to its tetrahedral shape and its ability to form hydrogen bonds (Brugé et al., 1999; Perrin and Gipe, 1987, 1986), or via redox processes in with dissolved elements solution (Chivers and Elder, 2013). These effects on the rate constants of olivine dissolution have not explicitly been explored.

In addition to the importance of H_2 as a source of energy for the deep biosphere and as a reducing agent for organic molecule abiotic synthesis (Truche et al., 2020), origin-of-life theories also focus on the importance of secondary products of primary mineral alteration: specifically, brucite and phyllosilicates. In particular, ferromagnesian phyllosilicates such as those found as secondary products in hydrothermal vents, are known to adsorb nucleotides and other prebiotic organic molecules at their surfaces (Feuillie et al., 2013; Pedreira-Segade et al., 2016). Brucite may act as precursor to semi-permeable hydrothermal structures that provide a mechanism for chemical gradients that can concentrate organic molecules (Barge et al., 2015; Barge and White, 2017). Charged clay mineral surfaces can provide a mechanism for concentrating organic molecules in hydrothermal environments where conditions might otherwise favor their decomposition (Hazen and Sverjensky, 2010; Shock, 1992). The type and abundance of secondary minerals formed during olivine alteration are then of interest in evaluating the habitability of modern or relict ocean worlds. The composition of both the rocky core and liquid ocean are critical to predicting secondary mineralogy and may change greatly over the life of a given satellite (Hazen et al., 2008; Schoonen et al., 2004). Currently, the role of NH₃ on the evolution of secondary precipitates in hydrothermal seafloor environments is not well known. NH_3 and NH_4^+ concentrations are known to have stabilizing effects on nesquehonite (MgCO₃·3H₂O), and especially roguinite ((NH₄)₂Mg(CO₃)₂•4H₂O), which has been proposed to be a metastable Mg-carbonate precursor phases to brucite (Zhu et al., 2017). In light of this, experimental studies of the growth and morphology of secondary mineralogy in the presence of NH₃-rich aqueous solutions are of interest in modelling the evolution of hydrothermal seafloor vents on icy worlds.

This chapter presents experimental data on the aqueous geochemistry and mineralogical relationships in water–olivine \pm NH₃ systems through two different experimental sets: a first set of constant-flow experiments designed to identify potential effects of NH₃ on olivine dissolution rates at 0, 23, 90, and 150 °C; and a second set of closed-system batch experiments designed identify effects of NH₃ on the type and abundance of secondary phases formed during olivine alteration at 90 and 150 °C (Fig. 4.1). Olivine alteration experiments provide a starting point for understanding fluid–rock interactions that may be influenced by the presence of NH₃ at both seafloor conditions, as well as more confined conditions within water-saturated rocky cores on icy ocean worlds. Our experimental results are then discussed in light of data from Enceladus, as well as with respect to mineralogical data from the surfaces of Ceres and Pluto, which are known to host NH₃-bearing minerals.





Fig. 4.1. a. Conceptual model of water-rock reactions within Enceladus, including diameter of the moon and core. Depths of the ice crust and liquid ocean are less well-constrained. b. Illustration of batch and c. continuously-stirred flow-through experimental systems. Pressure is maintained in the batch experiments from a pressurized headspace, and pressure is maintained in flow-through experiments by an in-line back-pressure regulator (BPR).

4.2 Methods

The experimental approach for this study uses two complementary experimental setups to explore kinetic parameters of olivine reaction in NH_3 -rich fluids. A first set of flow-through dissolution experiments used continuous-flow stirred tank reactors (CFSTR) to measure olivine dissolution rates in NH_3 -water solutions at far-from-equilibrium conditions. A second set of batch experiments used titanium batch reactors equipped for periodic gas and liquid sampling, to observe reaction products and secondary minerals from olivine dissolution in NH_3 -water solutions. All experiments are based on the interaction of San Carlos olivine and a dilute $Na-K-Cl-HCO_3$ solution with varying NH_3 concentrations

4.2.1 Materials

Single mineral San Carlos olivine ($Mg_{1.83}Fe_{0.17}SiO_4$) was used for all experiments. Olivine grains of 0.5-3 cm were selected by hand for light-green color and transparency. The selected olivine grains were then comminuted by Selfrag[®] high voltage pulse fragmentation. or with an agate rotary mortar. The grains were sieved to 0.05-0.62 mm and 0.63-1.25 mm size fractions. Each size fraction was sonicated in an ethanol bath. The ethanol was repeatedly poured off and replaced until the supernatant was clear (5-10 washes). After sonication the olivine was dried overnight in air at 50 °C. The washed and dried size fraction was identified as pure San Carlos olivine by XRD; however, as the detection limits for the XRD analysis are ~1 % of the sample by mass, a small fraction of other phases may escape detection by this method. Despite careful selection to prevent additional phases in the initial mineral assemblage, we visually and chemically identified minute (< 50 µm) grains of feldspar and interbedded pyroxene grains during pre- and post-mortem FEG-SEM imaging of the olivine. Specific surface area (Kr BET) measurements were made for each size fraction after crushing, sieving and cleaning, and an average of at least 3 measurements is reported as the surface area for each size fraction. Surface area was measured at 0.014 ± 0.002 m² g⁻¹ for the olivine size fraction of 0.65-1.25 mm, and 0.035 ± 0.005 m² g⁻¹ for the olivine size fraction 0.05-0.65 mm.

Solutions comprised ultrapure Milli-Q[®] water (18 MΩ cm), degassed with argon, and combined with research-grade NaCl, NaHCO₃ and KCl. All experiments used a dilute NaCl solution (78 ×10⁻³ mol L⁻¹) with lesser amounts of NaHCO₃ (39×10^{-3} mol L⁻¹) and KCl (0.6 ×10⁻³ mol L⁻¹). These salt ratios are consistent with the range of solution chemistries predicted both by Zolotov (2007) and from the chemistry of Enceladus' ocean, as estimated from chemical analyses of salts in Saturn's E ring (Postberg et al., 2011, 2009). Varying amounts of liquid NH₃ (stock solution: Roth suprapure 20 % NH₃) were added to reach the desired NH₃ wt % (where 0 wt % = 0 mol L⁻¹, 0.8 wt % = 0.47 mol L⁻¹, and 8 wt % = 4.7 mol L⁻¹). For ease of use, "%" will hereafter be used in place of "wt %" when referring to the NH₃ content of solution. While the NH₃ concentrations in Enceladus' ocean were calculated to not exceed 1 wt %, based on measured concentrations in the plumes, we used 8 % NH₃ as an extreme end-member solution to accentuate the potential effects of NH₃ on olivine alteration. In the 0 % NH₃ experiments, up to 3.5×10^{-3} mol L⁻¹ NaOH was added to adjust the pH to a value equivalent to the bench pH of 0.8 % NH_3 (pH = 10.8). Despite using analytical-grade materials, both Mg and Si were present in the initial fluids, due to trace Mg present in the NaCl salt, as well as Si contamination due to preparing the basic solutions in glass volumetric flasks. The initial concentrations of Si in the synthesized fluids were lower than the subsequently measured concentrations in samples from both the batch and CFSTR

experiments. In the batch experiments, the initial concentrations of Mg were often the highest measured Mg values. In the CFSTR experiments, Mg concentrations in the fluid represented a significant proportion of the total concentrations measured later on in the outlet solutions sampled during the experiments; in some cases, they were even higher than the concentrations measured in the outlet solution. The reason for this strange behavior is not immediately clear. The measured concentrations of the inlet solutions are included in Supplementary Tables 4.1-4.11. Initial parameters for all experiments are listed in Tables 1 (batch) and 2 (flow-through).

4.2.2 CFSTR experiments

Flow-through experiments (EF-C, -D, -F, -G, -H, -I, -J, -K, -L, -M, -N, -O; parameters listed in Table 5.1) were conducted using flow-through tank reactors (volume = 50, 100, or 300 mL, see Table 5.1) that were continuously stirred with an internal impeller. San Carlos olivine in the size range of 0.65-1.25 mm was used in the experiments to mitigate the loss of small grains from the system during agitation. Input solutions were introduced at constant flow rate during each experiment (0.05-0.06 mL min⁻¹, see table 2) with an HPLC pump. The hydrostatic pressure of the water (<10 bar) in the reactor was set by a back-pressure regulator downstream of the reactor. Output solutions were collected continuously from the outlet of the back-pressure regulator. Sampling times and chemistries are tabulated in Supplementary Tables 4.12-4.23.

Flow-through experiments were conducted at 0, 23, 90, and 150 °C. At 0 °C, temperature was maintained by submerging a Teflon-lined reactor in a continuously chilled glycol-water bath (Fig. 4.2). A Teflon-coated stir bar was placed inside the reactor and a stir plate was placed below the glycol-water bath to stir the contents. Parr^{*} stirred hydrothermal reactors made of pure titanium (Ti grade 4) were used for all experiments from 23 to 150 °C. At 23 °C, the reactor temperature was allowed to fluctuate with room temperature (± 2 °C). For experiments at 90 and 150 °C, jacket furnaces surrounding the reactors were used to control the temperature, which was monitored by an internal thermocouple (± 1 °C).



Fig. 4.2: CFSTR experiment setup at 0 °C. a. Setup with the reactor and reservoir inside the glycol bath. The batch reactor is cooled through a closed-loop radiator that circulates chilled fluid from inside the chiller through copper tubing submerged in the glycol. An arrow indicates where a stir plate sits below the bath (not visible in this image). After the final experiment (ESC-0), Teflon flakes from apparent mechanical damage were visible inside the reactor (b) and in the solid filtrate (c).

4.2.3 Batch experiments

Experimental set ESC (Enceladus Static) comprises experiments ESC-1, -2, -4, -5, -6, -7 and -8. These experiments were conducted at 90 or 150 °C in Parr^{*} batch titanium (Ti grade 4) autoclave reactors with a 300- or 500-mL internal volume. Two experiments had ramped-temperature runs that started at 90 °C and later the temperature was increased to 150 °C (Table 5.2). The reactors are equipped with several ports that enabled periodic on-line sampling of reaction fluids (liquid and gas) to monitor reaction progress. All reactors were fitted with internal pressure and temperature sensors and an exterior jacket furnace to control temperature. The aqueous fluid inside the reactor is stirred by an impeller driven by an external magnetic driver. Olivine (0.05-0.65 mm) and seawater solution were weighed and added directly to the pressure vessel and then flushed with argon for at least half an hour to remove dissolved oxygen. The experiments were conducted at ~20 bar Ar pressure. This positive overpressure allowed leak detection during the run (loss of pressure cannot be detected at vapor saturation pressure until the reactor is dry). The reactor was then heated to the experimental temperature within 15 min to minimize olivine alteration at lower temperatures. Solution samples were taken regularly throughout the experiments to characterize changes to the fluid chemistry over time. A 1 µm titanium frit installed within the sampling tube prevented escape of fine olivine grains. At the end of each experiment the reactor was quickly cooled (quenched) and reacted olivine grains were immediately recovered, rinsed sequentially with Milli-Q and ethanol, and then dried and stored in a glove box under anoxic conditions.

4.2.4 Analytical Methods

Fluid samples from both experiment sets were analyzed for pH and major cations (Si, Mg, Fe). Fluid samples from experiments were filtered at $0.2 \,\mu$ m and acidified with 30 % suprapure nitric acid before analysis by ICP-OES. After reaction, the solid fraction was separated from the remaining fluid by vacuum filtration through and rinsed sequentially with Milli-Q water to remove adhering salts, and then with ethanol to remove any remaining surface water films from the mineral grains. The reacted mineral samples were then stored in glove box under argon ([O₂] <1 ppm) before conducting textural and mineralogical analyses. Solids were analyzed using optical microscopy, field emission scanning electron microscopy (FEG-SEM), and X-ray diffraction (XRD).

Scanning electron microscopy (SEM) was used to characterize alteration at the μ m-scale. Olivine grains from selected experiments were observed with a field emission gun scanning electron microscope (FEG-SEM: Zeiss Ultra 55, CMTC, Grenoble). FEG-SEM was also used to select suitable sites on specific grain surfaces from samples ESC-1, ESC-2, ESC-4, ESC-5 and ESC-6 for focused ion beam (FIB) sampling. To minimize the possibility of sampling grain surfaces that had been exposed to natural weathering processes before our experiments, we selected grain surfaces that displayed a clean conchoidal fracture textures for both FEG-SEM analyses and FIB sampling. Using secondary electron (SE) and backscattered electron (BSE) imaging at 20 kV we analyzed olivine grains reacted at each temperature and solution chemistry. Energy dispersive X-ray spectroscopy EDXS spot analyses on reacted surfaces did not reveal any deviation from the chemistry of the unaltered olivine. This result reflects very thin alteration phases on the grain surfaces.

Electron-transparent TEM foils were fabricated from an olivine grain selected from each of the listed experiments by focused ion beam (FIB) milling. The FIB lamellae were fabricated using standard techniques with two dual beam instruments (FEI Helios 600 NanoLab, CP2M Lab, Univ. Aix-Marseille; FEI Helios G4 UC, GFZ, Potsdam) by the method detailed in Chapter 2 and described by Wirth (2009). Additionally, dispersed samples were prepared by sonicating several mg of olivine in ethanol from experiments ESC-2, ESC-5, and ESC-6. Each sample suspended in ethanol was then placed on a carbon grid and allowed to dry at room temperature before analyses. Transmission electron microscopy (TEM) imaging and chemical analyses were performed using a FEI Tecnai G2 F20 X-twin FEG TEM (GFZ, Potsdam) operating at 200 kV, as further detailed in Chapter 2. We additionally used a Thermo Fisher Scientific Themis Z G3 S/TEM operating at 80 kV (Institut des Matériaux Jean Rouxel, Nantes) for electron dispersive spectroscopy (EDS) chemical mapping; and a Jeol TEM (Aix-Marseilles) for additional clay dispersion sample imaging.

4.2.5 Dissolution rates

Olivine dissolution rates were calculated from the Si and Mg concentrations for each of the flowthrough experiments using the following equation:

$$r_i = \frac{C_i * v}{\partial * A}$$
 Equation 1

where r_i is the olivine dissolution rate (mol m⁻² s⁻¹) calculated from the concentration of solute *i*, C_i is the change in concentration (mol L⁻¹) of solute *i* from inlet to outlet, *v* is the solution flow rate through the reactor (L s⁻¹), ∂ is the (unitless) stoichiometric coefficient *i* (where ∂ =1 for Si and ∂ =1.8 for Mg), and *A* is the total initial olivine surface area in the reactor (m²). With this equation, r_{Si} equals r_{Mg} when the overall alteration process is stoichiometric (congruent). Reported dissolution rates for r_{Si} and r_{Mg} are an average of rates calculated after the first 10 days (240 h) of each experiment- we did not consider rates at t < 10 d since dynamic steady state was not achieved. An exception is experiment EF-H that had a run time of < 10 d: in this case, only the last three samples of the experiment were used to calculated the average value. The standard deviations for these averages are reported as the error for the rates.

Initial dissolution rates were also determined for samples taken over the first 24 hours from each batch experiment- see reported values in Table 1. While these values do not represent far-from-equilibrium or steady-state dissolution rates, the results are useful in evaluating and comparing the initial rates of reaction between our own batch experiment sets. This is particularly valuable given the wide range of values for olivine dissolution rates reported in the literature, highlighting the difficulties in directly comparing experimental results between labs (Ostertag-Henning et al., 2014). To calculate dissolution rates from the batch reactors, we used the following equation to correct the concentration of each sample:

$$[conc Si, Mg]_{corr} = \frac{(conc_{meas} - conc_{SO})V_{reac}/1000}{(SSA)(mass)(stoich factor)}$$
 Equation 2

where the concentrations have units of mol L⁻¹ (*SO* denotes blank concentration), V_{reac} is the volume of the reactor (mL) adjusted for the volume lost from sampling, *SSA* is the BET-measured specific surface area (m² g⁻¹), mass refers to the amount of olivine sample (g), and the stoichiometric factor (unitless) equals 1.0 for Si and 1.83 for Mg. This gives a corrected concentration in units of mol m⁻², or of moles of dissolved olivine per unit surface area of the initial olivine. The Si and Mg-corrected concentrations were then plotted as a function of time (s) and apparent dissolution rates was derived from the slope between the initial samples, giving an olivine dissolution rate calculated from Si concentrations (r_{Si}) and a second rate calculated from Mg concentrations (r_{Mg}) in mol m⁻² s⁻¹. As Mg concentrations generally did not increase during the initial part of the experiments positive r_{Mg} were not derived, and only r_{Si} are reported in Table 1.

We note that especially in cases where fluid chemistry is non-stoichiometric with respect to the olivine composition $(r_{Si} \neq r_{Mg})$, dissolution rates calculated from the fluid chemistry may fail to capture the "true" olivine dissolution rate as additional phases that may release or sequester these elements are not accounted for in the rate calculation of Eq. 2. r_{Si} and r_{Mg} calculated from these conditions may then at best be viewed as apparent, or minimum, olivine dissolution rates. The impact of this is further considered in the results and discussion sections of this chapter.

4.2.6. Thermal activation energy

Where there is a positive correlation between temperature and r_{Si} or r_{Mg} in the flow-through experiments, a thermal activation energy for olivine at these conditions can be calculated using the Arrhenius relation:

$$k = Ae^{\frac{-E_a}{RT}}$$

Equation 3

where k is the rate constant (mol m⁻² s⁻¹), A is the pre-exponential factor (mol m⁻² s⁻¹), E_a is the thermal activation energy (J mol⁻¹), R is the universal gas constant (J K⁻¹ mol⁻¹) and T is the absolute temperature (K). If we assume far-from-equilibrium conditions of dissolution at a basic pH, the overall rate r can be expressed as: $r = k(a_{OH-})^n$. In the range of alkaline pH used in these experiments, there is no apparent dependence of the observed rates on [OH⁻]. We therefore assume $n \approx 0$, such that r = k. Based on this assumption, we calculated a separate E_a from the data from each solution set (0, 0.8, and 8 % NH₃). Each E_a was then determined from the Si-derived rates by plotting ln k vs 1/T (K), and then multiplying the slope by -R. No thermal activation energy was calculated using r_{Mg} , since there is no positive correlation between temperature and r_{Mg} .

4.2.7 Geochemical Calculations: in situ pH & saturation indices

Geochemical codes were used to determine in-situ pH reported for each experiment, based on the measured bench pH and internal temperature. Mg and Si concentrations at chemical saturation with respect to select minerals (brucite and sepiolite) were also calculated for experimental conditions of select experiments. All calculations were performed using the PHREEQC version 3.5.0 (Parkhurst and Appelo, 2013) with the b-dot ion association model, and the resident thermodynamic database llnl.dat (Johnson et al., 2000, chosen for internal consistency).

Table 5.1	CFSTR	experiments
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ID	NH ₃	T (°C)	Hrs	pH (in)	pH (at T)	Olivine (g)	V (mL)	Flow (mL min ⁻¹)	Log r _{si}	SD r _{si}	Log <i>r</i> _{Mg}	SD r _{Mg}
EF-N	0	0	484	10.8	11.1	3.30	100	0.06	-9.1	0.08	-9.1	0.08
EF-K	0	23	380	10.8	10.8	4.56	300	0.06	-10.8	0.16	(negative)	
EF-D	0	90	507	10.7	10.0	3.00	50	0.06	-10.0	0.11	-9.7	0.47
EF-G	0	150	382	10.7	9.6	4.52	300	0.05	-10.5	0.08	(negative)	
EF-J	0.8	0	800	10.8	11.5	3.16	100	0.06	-9.7	0.17	-10.4	0.27
EF-M	0.8	23	478	10.8	10.8	3.12	50	0.06	-10.3	0.12	(negative)	
EF-I	0.8	90	478	10.8	9.6	4.50	300	0.05	-10.4	0.33	-10.6	0.07
EF-C	0.8	150	508	10.8	9.3	4.52	300	0.05	-9.9	0.06	-10.9	0.06
EF-O	8	0	522	12.2	13.1	3.00	100	0.06	-9.4	0.15	(negative)	
EF-F	8	23	532	12.3	12.3	3.16	50	0.06	-10.7	0.20	-10.9	0.22
EF-H	8	90	240	12.2	10.6	3.30	50	0.06	-10.3	0.06	-11.0	0.04
EF-L	8	150	400	12.2	9.9	3.26	50	0.06	-9.7	0.11	-10.7	0.24

NH₃ is in weight %; "Time" indicates experiment duration in hours, pH (in) is of the input solution at bench; pH (at T) is the calculated in-situ pH of the solution at the experimental T; V is the reactor volume; flow is the flow rate of the input solution; log r_i indicates the apparent olivine dissolution rate (in mol m⁻² s⁻¹) calculated from solute i, and SD r_i indicates the standard deviation of the log r_i as described in section 4.2.1.

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	ID	\mathbf{NH}_3	T (°C)	Hrs	рН (i)	pH (at T)	Olivine (g)	V (mL)	W/R	r _{si}	<i>r</i> (h)
	ESC-4	0	90	4152	10.7	10.0	4.50	295	65.6	-8.4	2
	ESC-5	0	150	1643	9.9	9.3	3.02	195	64.6	-8.8	24
	ESC-8	0	90-150	1056	10.8	10.0-9.6	3.05	195	64.0	-8.7	2
	ESC-9	0	90	915	10.8	10.1	3.01	195	64.8	-8.3	18
	ESC-11	0	150	413	10.9	9.7	3.03	197	65.0	-8.0	19
	ESC-1	0.8	90	4367	10.7	9.6	3.13	195	62.3	-9.4	1
	ESC-2	8	90	3849	12.0	10.5	4.53	295	65.1	-7.7	1
	ESC-6	8	150	1642	11.9	9.7	4.50	295	65.6	-8.8	1
	ESC-7	8	90-150	1010	12.4	10.8-10.0	4.02	295	73.4	-8.8	1
	ESC-10	8	90	915	11.9	10.4	4.50	295	65.5	-9.0	1
	ESC-12	8	150	413	12.1	9.9	4.50	295	65.5	-8.7	1

Table 5.2 Batch experiments

NH₃ is in weight %, experiment duration is in hours, pH (i) is the initial solution pH at bench, W/R is the initial water-rock ratio by mass, r_{si} is the apparent olivine dissolution rate (in mol m⁻² s⁻¹) by the method described in section 4.2.5, including samples taken over the experiment time (since start) indicated in hours by r(h).
4.3 Results

4.3.1 Flow-through experiments

In all experiments at and above 23 °C, concentrations of Si and sometimes of Mg displayed an initial increase during the flow-through experiments, followed by a decrease to a relatively steady-state concentration (Fig. 4.3a). The relative concentrations of Si and Mg were rarely stoichiometric with respect to their ratio in olivine (with Mg:Si being 1.8:1). In the experiments at 0 °C a clear trend in dissolution behavior does not emerge between the three solutions. In 0 % NH₃ (EF-N), both [Si] and [Mg] increase in the outlet solution throughout the experiment; in 0.8 % NH₃ (EF-J), [Si] and [Mg] concentrations increase and slowly decrease for the entire experiment duration, and in 8 % NH₃ (EF-O) no trend increasing or decreasing is apparent in either [Si] or [Mg] (Fig. 4.3b). Although other literature at high pH reports steady-state stoichiometric dissolution is achieved after at most ~200-300 h (Hänchen et al., 2006; Pokrovsky and Schott, 2000b), most of our experiments do not achieve stoichiometric dissolution even after 400-500 h: r_{Si} is generally higher than r_{Mg} throughout the experiments (Fig 4.4a and 4.4b). It follows that the calculated r_{Mg} almost certainly under-estimate the true dissolution rates, although the calculated r_{Si} will also under-estimate the true rate of olivine dissolution rates if Si is incorporated into a secondary phase(s) within the reactor system. In addition, even where stoichiometric dissolution was achieved (EF-F, 8 % NH3 and 23 °C; and EF-N, 0 % NH3 and 0 °C), a true steady-state dissolution rate value was not reached even after 500 hours, as rates are still decreasing. In the one experiment run for 800 hours (EF-J, Fig. 4.3b and 4.4b), an apparent steady-state was achieved after 600 hours; however, the trend is only in 5 samples and the r_{si} is still decreasing. Because of these complicating factors, we emphasize that the rates reported here represent apparent (or minimum) alteration rates, as we cannot exclude the possibility of the incorporation of Si into secondary authigenic phases.



Fig. 4.3a. Si and Mg concentrations over time, for all flow through experiments at 23, 90, and 150 °C. Both measured concentration values and corrected values (Δ) (subtracting the blank ([Si] and [Mg] in the input solutions) are shown. Letters in title indicate experiment name (Table 2); volume in title indicates reactor volume in mL.



Fig. 4.3b. Si and Mg concentrations over time, for all flow through experiments at 0 °C. Both measured concentration values and values corrected for the blank ([Si] and [Mg] in the input solutions) are shown. Note that the x axis scale varies between plots, and the y axis scale differs from Fig. 4.3a, above. Letters in title indicate experiment name (Table 2); volume in title indicates reactor volume in mL.



Fig. 4.4a. Olivine dissolution rates calculated from [Si] and [Mg] (r_{Sl} and r_{Mg} , respectively) over time, for all flow through experiments at 23, 90, and 150 °C. The Mg:Si ratio is included as point values, with a dashed line where Mg:Si=1.8, or stoichiometry. Rates are calculated as discussed in section 4.2.4. Letters in title indicate experiment name (Table 2); volume in title indicates reactor volume in mL.



Fig. 4.4b. Olivine dissolution rates calculated from [Si] and [Mg] (r_{Si} and r_{Mg} , respectively) over time for experiments at 0 °C. The Mg:Si ratio is included as point values, with a dashed line where Mg:Si=1.8, or stoichiometry. Letters in title indicate experiment name (Table 2); volume indicates reactor volume in mL. Note that the x axis scale varies between subplots, and the y axis scale differs from Fig. 4.4a above.

4.3.1 Batch experiments

In all batch experiments at all temperatures, Si concentrations increase over time. In the rampedtemperature experiments, increasing the temperature from 90 to 150 °C is followed by a rapid increase in Si concentration and decrease in Mg concentration (Fig. 4.5). The rate of increase slows (see additional discussion below), and in most experiments the concentrations reach an apparent steadystate concentration (Fig. 4.6). In contrast, Mg concentrations initially decrease in most experiments before coming to an apparent steady-state. As these results imply, Mg:Si ratios are non-stoichiometric at all sampling times in all batch experiments, with [Si] >> [Mg]. The stoichiometric ratio of Mg:Si in San Carlos olivine is approximately 1.8, while experimental [Mg]:[Si] ratios range from of 0.1 to 0.01. Geochemical trends from select experiments are shown in Figs. 4.5 and 4.6, and full fluid chemistry results from all experiment sets are included in Supplementary Tables 4.1-4.11. In the 8 % NH₃ experiment, pH decreases after ramping up the temperature to 150 °C (Fig. 4.5); in the rest of the batch experiments, the pH does not significantly change over time (Fig. 4.5, 4.8). In one experiment, ESC-5 with 0 % NH₃ at 150 °C, the pH decreases immediately to a new lower pH (from 10 to 9.5) and remains at this pH for the duration of the experiment. The initial (surface-area normalized) $r_{\rm Si}$ calculated during the batch experiments generally 1-2 orders of magnitude faster than observed in the CFSTR experiments (Table 1). However, we note that these are not directly comparable as the rates from the batch experiments are calculated from samples collected during the first 24 hours or less of experiments, whereas the rates reported by CFSTR experiments specifically exclude results collected in this time period.



Fig. 4.5: Mg and Si concentration from ramped-T (90-150 °C) experiments at 0 and 8 % NH₃. T is increased at ~ 550 h in both experiments (vertical dashed line). The concentration of Si at sepiolite saturation (SI_{sep}) and Mg at brucite saturation (SI_{bruc}) are plotted as horizontal lines with [Si] (top) and [Mg] plot (center), respectively (0 wt% NH₃ = solid line; 8 wt% NH₃ = dashed line). pH (lower) is at bench T.



Fig. 4.6: [Mg] and [Si] results from single-T batch experiments at 90 and 150 °C. Values represent concentration in the reactor fluid, uncorrected for initial [Mg] and [Si], or normalized to olivine stoichiometry or surface area. Colors indicate experiments at the same conditions (replicate experiments).



Fig. 4.7: Bench-temperature pH over time for batch experiments at 90 and 150 °C. Colors indicate experiments at the same conditions (replicate experiments).

4.3.2 Olivine alteration and secondary mineral precipitation

After the CFSTR experiments, no secondary minerals or dissolution textures (such as etch pits) were identified, either by XRD characterization or by SEM observations. After the batch experiments, SEM imaging of olivine grains from select experiments showed a layer of phyllosilicate-like secondary minerals at the olivine surface after all of the experiments reacted at 150 °C, and from the experiments reacted with NH₃ at 90 °C (Fig. 4.8). BSE analyses of these precipitates were not able to identify a chemical signature other than olivine. Similarly, XRD results did not identify any secondary minerals

after experiments, indicating that any secondary minerals represent less than 1-2 % of the mineral content by mass. In general, the amount of secondary precipitate identifiable at the olivine surfaces after the experiments increased with increasing NH₃ and temperature.

The experiments with NH₃ at 90, 150 °C and ramped-T (90-150 °C) had more visible secondary alteration products than the 0 % NH₃ experiments (Fig. 4.8). At 90 °C, olivine reacted in 0.8 % NH₃ also had secondary minerals of greater abundance and crystallinity at the olivine surface. At 150 °C, this effect is less pronounced, showing a slightly increased amount of alteration products at the olivine surfaces reacted in 8 % NH₃ as compared to 0 % NH₃. Both experiments at 150 °C had shorter run times than those at 90 °C. This may explain the lesser apparent abundance of secondary phases in the 150 °C than in the NH₃-bearing experiments at 90 °C (which ran for ~ 6 months). In the ramped-temperature experiments, there is more alteration visible at the olivine surfaces in the experiment with 8 % NH₃ than with 0 % NH₃. The secondary phases are also less well-developed on the olivine grains reacted in the ramped temperature experiments, consistent with their shorter run times (Fig. 4.8 and Table 1).



Fig. 4.8: SEM images from representative batch experiments, with reaction time indicated in months (mo), and unreacted olivine. Subplots: a. ESC-4; b. ESC-2; c. ESC-1; d. ESC-5; e. ESC-6; f. ESC-8; g. ESC-7; h. Unreacted olivine. Insets are of the same samples at higher magnification.

FIB-prepared TEM foils from ESC-1, ESC-2, ESC-4, ESC-5, and ESC-6 (Table 2) were also used to isolate and identify the secondary phases at the olivine surface, as well as to provide information on the mechanism of dissolution at the olivine surface (Fig. 4.9). We analyzed the olivine surface with respect to three distinct zones of the FIB section: 1. unaltered bulk olivine, 2. an alteration layer comprising secondary minerals found on the olivine surface, and 3. the interface between the bulk olivine and the alteration layer. A FIB lamella of olivine from ESC-1 (90 °C, 0.8 % NH₃) distinctly shows the sheet-like secondary phases protruding from the olivine surface (Fig. 4.9c). EDS element mapping in STEM mode of the olivine bulk-alteration interface on ESC-1 in several places showed a Si enrichment and Mg depletion relative to the olivine bulk (Fig. 4.9e). In this sample no d-spacing was visible from their orientations (Fig. 4.10a) and high-magnification imaging of the interface at the interface was complicated by focus issues due to the thickness and orientation of the FIB section (see section 4.6.2). Two FIB lamellae were made from olivine grains reacted in 8 % NH₃ at 90 °C (ESC-2) as this experiment had the most abundant crystalline secondary phases identifiable at the olivine surface in FEG-SEM. In TEM the secondary phases were not readily characterized (Fig. 4.10b) as the morphology of the alteration products in both FIB sections was damaged or destroyed during preparation. That the secondary phases were so sensitive to damage during FIB preparation indicates their fragility, which was corroborated through TEM imaging of a clay dispersion sample from ESC-2 (see discussion below). FIB section images of olivine grains from ESC-4 (0 % NH₃, 90 °C) reveal that while no secondary phases are visible from this sample by FEG-SEM, an apparent amorphous alteration layer formed at the olivine interface during the experiment (Fig. 4.10c). EDX acquisition of this layer suggests the Mg:Si ratio is indistinguishable from that of the olivine bulk. FIB sections from two experiments carried out at 150 °C at 0 and 8 % NH₃ (ESC-5 and ESC-6, respectively) successfully captured the surface alteration phases and the olivine-alteration interface. In the FIB section from ESC-5 (0 % NH₃), phyllosilicates at the olivine surface are visible, as well as a non-continuous amorphous layer (Fig. 4.10d). EDX acquisition of the more crystalline areas has a greater Mg:Si ratio than the olivine bulk. The crystal structure of the secondary minerals on the surface of ESC-6 are also clearly visible in the FIB cross-section, although again their orientation prevented clear identification of any d-spacing of those minerals. Notably, while most of the alteration minerals at the surface of ESC-6 morphologically resembled the phyllosilicates seen in the ESC-2 and ESC-5, we also identified regions of lower density (bright regions in Fig. 4.10e and dark regions in Fig. 4.10f). EDX analysis of this region revealed that it is relatively enriched in Fe and C.



Fig. 4.9: process of selecting, preparing and analyzing FIB thin sections. a. SEM image of the olivine surface of ESC-1 (90°, 0.8 % NH₃), where the FIB section was prepared. b. the FIB section after separation from the olivine surface. c. TEM image of FIB section showing a cross-section of the phyllosilicate-like alteration phases seen at the olivine surface. d. TEM image of the transect (dashed line) shown in subplot e. the chemical information along the transect from the olivine bulk to the olivine-alteration boundary.



Fig. 4.10: Bright-field TEM images from a. ESC-1 (0.8 % NH₃, 90 °C); b. ESC-2 (8 % NH₃, 90 °C); c. ESC-4 (0 % NH₃, 90 °C); d. ESC-5 (0 % NH₃, 150 °C); e. ESC-6 (8 % NH₃, 150 °C); dark-field TEM of image ESC-6 (8 % NH₃, 150 °C) showing an Fe-C rich secondary phase (red point where EDX was acquired).

TEM analysis of alteration products in the clay dispersion sample from ESC-2 was performed to identify the chemistry and structure of the alteration products formed in high-NH₃ conditions. ESC-2 was chosen as this experiment (8 % NH₃, 90 °C, 5.3 months reaction time; see Table 2 for details) had the most abundant secondary mineralogy, as apparent from the FEG-SEM images. In analyses of dispersed clay particles, the secondary minerals were identified by d-spacing and morphology as lizardite, brucite, and smectite. EDX analyses of the dispersed sample showed that the clays were rich in Si and Mg, with some Al and little or no N (and therefore, little or no NH₃ or NH₄). Unfortunately, the electron beam, both during imaging as well as EDX chemical analyses, rapidly caused structural damage to these clays (Fig. 4.9c).

4.4 Discussion

In all of our experiments, both flow-through and batch, stoichiometry between Si and Mg (with respect to the San Carlos olivine composition) was generally not achieved. In flow-through experiments, rates of olivine dissolution (r) were faster when calculated from [Si] than from [Mg]. In many cases, the r_{Mg} was negative, making it a meaningless rubric by which to evaluate olivine dissolution. As r_{Mg} almost certainly underreports the true rate of olivine dissolution in our experiments, we focus the following discussion of effects of NH₃, temperature, and pH on differences in r_{Si} . We again note, however, that r_{Si} may also underestimate the true olivine dissolution rate. The calculated rates then reflect changes in fluid chemistry that are responsive to dissolution as well as precipitation or sequestration of the elements into secondary phases. Comparisons between the apparent dissolution rates from different experiments may illuminate potential differences in reaction processes between experiments where differences in the calculated rates exist; however, where no differences between rates exist, competing reaction processes may still be at play. For example, an increased dissolution rate may be obfuscated by a contemporaneous increase in secondary mineral precipitation, thus resulting in a fluid chemistry identical to an experiment with both slower dissolution rates and slower precipitation rates. The following discussion is then focused on where trends can be identified.

4.4.1 Olivine dissolution rates as deduced from flow-through experiments

Result from the CFSTR experiments show that there is no significant effect of NH_3 on the apparent olivine dissolution rates. As the 0 and 0.8 % NH_3 solutions have the same pH at bench conditions, any effect of NH_3 would be most visible between the experiments conducted at 23 °C. However, at all temperatures > 0 °C, the apparent rates from the 0 and 0.8 % NH_3 experiments plot within, or nearly within error, of each other (Fig. 4.11). We note here that the error bars ascribed to the rates are the deviation from an average of samples taken from a single experiment and do not represent averages of multiple CFSTR experiments. The point has been well made by multiple publications that because of the difficulties in replicating experimental results (e.g. Ostertag-Henning et al., 2014; Rimstidt et al., 2012), arriving at any true effect of a ligand or solution constituent on the dissolution rate may require many replicate experiments and benefits from characterization in different laboratories and experiment set-ups. Despite these caveats, these results show that any impact of NH_3 on the olivine dissolution rate, being smaller than the variance observed within our own experiments, is certainly smaller than the variance seen in experiments between sources (where dissolution rates vary by as much as three orders of magnitude). Our initial results from this study then show that even if a

relationship may be determined in multiple studies that is not seen here, any effect is likely to be insignificant when considering the impact of other factors on olivine dissolution.

The relationship between the apparent CRSTR dissolution rates and temperature is also weak compared to that predicted by existing rate equations. Excluding the rates at 0 °C (discussed below), there is an apparently linear increase in dissolution rates with increasing temperature in all the solution types (Fig. 4.11a). However, this increase is orders of magnitude less than that predicted by existing rate laws and comparable experimental studies. For example, in our 8 % NH₃ solutions with a bench pH = 12.2 we find a log *r* of -10.3 and -9.7 at 90 and 150 °C, respectively. Using a similar experiment design in a solution of bench pH = ~12.2, Hänchen et al. (2006) reported a log *r* of -8.7 at 90 °C and of -8.5 at 120 °C. Calculated rates from existing rate laws are even higher: for a solution pH = 12.2, the rate law proposed by Rimstidt et. al. (2012) predicts a log *r* of -8.6 and -7.2 at 90 and 150 °C, respectively (Fig. 4.11b). In general, the r_{Si} from our experiments at 90 and 150 °C are closer to the predicted rate at 25 °C than their respective predicted values at higher temperatures (4.11b). This may well reflect an increase in secondary precipitation at higher temperatures in our experiments, rather than a truly depressed olivine dissolution rate.



Fig. 4.11: average log R_{si} (in mol m⁻² s⁻¹) from each flow-through experiment. a. Rates regressed over 1000/T (K): marker border colors correspond to temperatures on the x axis. b. Rates regressed over (bench-T) pH: marker border colors indicate temperature as in subplot a; lines indicate the rate law from Rimstidt et al. (2012) at 25, 90, and 150 °C. Grey shaded area indicates the error of the linear rate law at 25°C reported by Rimstidt et al. (2012), approximately ± 0.5 log units.

The slower rates at high temperatures in our experiments are not attributable to increased salinity or decreased water activity, as the ionic strength in our experiments is well below the minimum ionic strength known to affect olivine dissolution rates (Olsen et al., 2015). These slower-than-expected rates also cannot be attributed solely to pH as it occurs with all solution types, regardless of initial or in-situ pH. In fact, the change in pH from the 0 and 0.8 % NH₃ experiments (~10.8 at bench T) to the 8 % NH₃ experiments (12.2 at bench T) has no discernable effect on r_{Si} (or, for that matter, r_{Mg}). While the rate equations as proposed by Pokrovsky and Schott 2000b and Rimstidt et al. 2012 find a weak inverse

relationship between pH and olivine dissolution rates at pH > 6.5, we note that other studies (e.g. Palandri and Kharaka, 2004) show little or no decrease in olivine dissolution rates with pH in alkaline solutions. This lack of consensus is likely due in part to the comparatively high variances between studies increases in alkaline conditions (\pm 0.5 log units, Fig. 4.11, based on the data compiled by Rimstidt et al. 2012). This observation may be due to a number of phenomena. First, the very low dissolution rates in alkaline conditions mean that analytical errors and biases are proportionately larger to the measured concentration values. Second, the long experimental times (several weeks) needed to reach stoichiometry may result in sampling during preferential release of Si (Pokrovsky and Schott, 2000b). Finally, there are simply less olivine dissolution studies in alkaline conditions: for example, in solutions with pH > 9, the temperature dependency of the rate equation of (Rimstidt et al., 2012) is based on only three experiments (performed by Hänchen et al., 2006), including two experiments at 90 and one at 120 °C.

The calculated thermal activation energies for each experiment set also reflect the weak dependence of the observed r_{Si} on temperature. We calculated that $E_a = 8.1$, 7.5, and 18.9 kJ mol⁻¹ in 0, 0.8, and 8 % NH₃ solutions, respectively. All of these calculated E_a are extremely low in comparison to accepted values: thermal activation values of forsterite in the literature are around 40-60 kJ mol⁻¹ (Hänchen et al. (2006) = 53 kJ mol⁻¹; Oelkers et al. (2018) = 64 kJ mol; see also Table 1 in Rimstidt et al. (2012), including E_a values ranging from 38 kJ mol⁻¹ to 70 kJ mol⁻¹). This comparison reinforces the likelihood that the r_{Si} in our experiments do not reflect the true olivine dissolution rate. We note that true dissolution rates can be considerably skewed if released elements (which are used to establish rates) are incorporated into authigenic secondary phases. We also stress that all the listed activation energies from the literature have been derived in acidic to circumneutral conditions. A change in the dissolution mechanism from acidic to circumneutral to alkaline pH may also explain these discrepancies. Indeed, one has to keep in mind that activation energy calculations rely on the strong assumption that the reaction mechanism is constant at all temperatures investigated. In general, the best Ea are derived from conditions where dissolution occurs at very far-from-equilibrium conditions, such that secondary phases don't perturb the signal of the element(s) used to determine the rate.

There are several additional issues with comparing the results of these experiments directly to the existing literature. First and foremost, very few of our experiments achieved stoichiometric dissolution during their run times (Fig. 4.4a and 4.4b). It has been noted that at alkaline pH, the time to achieve stoichiometric dissolution can be as long as 250-300 hours (Pokrovsky and Schott, 2000b), although other experimental studies report stoichiometric dissolution in less than 24 hours at a pH as high as 12.5 (Hänchen et al., 2006). In many of our experiments, Mg:Si ratios are well below the stoichiometric ratio of 1.8:1 even after 500 hours. This is important as most aggregated rate laws from flow-through experiments are based on stoichiometric dissolution to ensure that the rates do not reflect a transient period of increased Si or Mg release. At alkaline pH, the mechanism of olivine dissolution has been postulated to involve the formation of Mg(OH)₂ at the olivine surface, due to preferential Si release into solution during the initial phase of dissolution (Pokrovsky and Schott, 2000a). Unusually high rates of olivine dissolution previously reported in alkaline solutions (Wogelius and Walther, 1991) have since been speculated to be due to potential artifacts from sampling during an initial period of increased Si release during in our experiments (Fig. 4.4a and 4.4b); however, even during this peak the rates in

our high-T experiments are less than those observed at later "steady-state" conditions reported by Hänchen et al. (2006).

Another point of interest is the apparent r_{si} in the majority of our CFSTR experiments continue to decrease even until the end of the experiments, at 500 h of reaction time. Surface-area normalized olivine dissolution rates are known to decrease over time, for a several reasons. Batch experiments of olivine alteration in neutral or acid solutions have shown the formation of an amorphous silica surface layer on the olivine surface that may slow olivine dissolution (Béarat et al., 2006; Sissmann et al., 2013). This secondary surface altered layer may start forming almost immediately upon the interaction of aqueous fluid with the olivine grains (Daval et al., 2011). The same type of layer has been found in olivine reacted in flow-through experiments, implying that surface-scale processes are controlling the formation of this secondary phase even where it is not predicted by the bulk fluid chemistry (Hellmann et al., 2012). Even more fundamentally, olivine dissolution is known to proceed quickly at first along dislocations to the crystal lattice (Grandstaff, 1978), and preferentially along some crystallographic axes and faces even of the same crystal (Awad et al., 2000; King et al., 2014). The decrease of these preferential dissolution sites and faces over time means that surface-normalized dissolution rates will also decrease over time. However, the quantification of this decrease is elusive, as phenomena such as the occurrence and rate of growth of passivating surface layers or the relative dissolution rates of different crystallographic faces are not themselves quantified. We recognize that at the longer timescales of our experiments (240-800 h) compared to that of the experiments used to derive current rate laws (6-300 h) means that the decrease may be more easily identified over time. This highlights the transient quality of quantitative dissolution rates and the difficulty in comparing dissolution rates from experiments with even slightly varying olivine preparation methods, experimental designs, and protocols.

Finally, the apparent r_{si} observed in the 0 °C CFSTR experiments are surprisingly high. One explanation may simply be that at 22 °C and higher, Si and Mg sequestration in secondary phases results in apparent rates (r_{Si} and r_{Mg}) that are lower than their respective true olivine dissolution rates, while at 0 °C these processes are comparatively kinetically inhibited. Another possible factor may lie in that the reactor system at 0 °C was a different design in our experiments than those used for the higher-temperature flow-through experiments (see section 4.3.1). Specifically, the different stirring mechanism could have further inhibited secondary mineral formation in this reactor. However, olivine dissolution rates in general are not well characterized at low temperatures. For example, the rate equation of Rimstidt et al. plotted in Fig. 4.11 includes experiments from just two sources below 23 °C, both using solutions with pH < 6 (Eriksson, 1982; Grandstaff, 1986). Several recent studies have shown that olivine dissolution at and below-0 °C temperatures have faster dissolution rates than anticipated by existing rate laws (Hausrath and Brantley, 2010; Niles et al., 2017). In Chapter 2 of this manuscript, we presented experimental results from batch experiments that also displayed faster-than-predicted olivine dissolution rates at -20 °C (although we note the batch experiment results of Chapter 2 are not directly analogous to the CFSTR results presented here). To the best of our knowledge, these are the first continuous-flow olivine dissolution rate values given in alkaline solutions at < 25 °C, and that along with the low-temperature batch experiments discussed in Chapter 2, represent some of the first olivine dissolution experiments of any design in alkaline conditions at temperatures below < 25 °C. This is important because the fundamental parameters of aqueous solutions - such as density, viscosity, heat capacity, conductivity, and the activity coefficients of dissolved species - are highly dependent on temperature (Akinfiev et al., 2001; Light, 1984; Pitzer, 1995), and their combined impact on mineral dissolution and precipitation kinetics at near-0 °C temperatures often relies on extrapolation of the equations that describe far above-0 °C properties (Gooding, 1978). Future studies should build a more complete understanding of the mechanisms of dissolution in alkaline conditions, especially with regard to the effect of temperature.

4.4.2 Secondary mineral saturation during batch experiments

The fluid chemistry from the batch experiments shows that magnesium concentrations approach brucite saturation at steady-state. Amorphous silica remains significantly undersaturated for the entire duration of all experiments. Conversely, chrysotile and magnesite are significantly oversaturated for the entire duration of all experiments. An analysis of the saturation indices for select minerals shows that both clay minerals and brucite are saturated at lower Si and Mg concentrations in the 8 % NH₃ experiments (at higher pH) than in the lower NH_3 (lower pH) experiments. An illustration from the ramped-temperature experiments (ESC-7 and -8) shows the magnitude of these differences at 90 and 150 °C (Fig. 4.5). At 90 °C, the sepiolite saturation in both 0 and 8 % NH₃ solutions is almost identical, showing a lower dependency on the difference pH at lower temperature. At 150 °C, Si concentration at sepiolite saturation is notably higher in the experimental conditions of the 0 % NH₃ experiment. While at 150 °C neither experiment reaches saturation with respect to sepiolite, the Si concentration is higher in the 0 % NH₃ experiment at 150 °C and continues to increase throughout the experiment. An opposite trend is seen with brucite saturation. At 90 °C, the Mg concentration in equilibrium with brucite in the 8 % NH₃ experiment is lower than in the 0 % NH₃ experiment. Similarly, the measured Mg concentrations are lower in the 8 % NH₃ experiment than in the 0 % NH₃ experiment. At 150 °C, the Mg concentration in equilibrium with brucite is near identical for the two solutions, as are the measured concentrations from the experiments.

4.4.3 Mineral formation in NH₃-rich fluids

While no effect of NH_3 on the apparent dissolution rates was identified from the batch experiment (or CFSTR) fluid chemistry, the presence of NH_3 in batch experiments had an apparently promoting effect on secondary mineral precipitation. This effect is not merely a pH effect: while the pH of the solution with 8 % NH_3 is still higher than that of the 0 % NH_3 solutions at both 90 and 150 °C, the pH of the 0.8 % solution is actually lower than that of the 0 % solution at 90 and 150 °C due to the different pH-buffering effects of NH_3 and NaOH (Fig. 4.12). The abundant ammonium clays on Ceres (De Sanctis et al., 2015) suggest that phyllosilicates in the rock fraction of the satellite have interacted with aqueous NH_3 at some point in their past



Fig. 4.12: calculated pH evolution of each idealized seawater solution with temperature.

(Castillo-Rogez et al., 2018). Experimental data suggest that these are largely comprised of smectites with NH₄⁺ incorporated into the interlayers. The preferential order of cation incorporation in clays with exchangeable cation interlayer sites (as for example presented in Stumm, 1992 or in McBride, 1994) is as follows:

 $Al^{\scriptscriptstyle 3+} > Ca^{\scriptscriptstyle 2+} > Mg^{\scriptscriptstyle 2+} > \mathbf{NH_4^+} > \mathrm{K^+} > \mathrm{Na^+} > \mathrm{Li^+}$

The availability of Mg^{2+} in the fluid then suggests that NH_{4^+} may not preferentially occupy the interlayer space in any clays forming during the experiments. This is corroborated by chemical analyses of crystalline clays found in clay suspensions investigated by TEM. Even after experiments with 8 % NH_3 in the fluid, no peaks at the wavelengths associated with nitrogen could be positively identified above the baseline (Fig. 4.13).



Fig. 4.13: TEM images and analyses of clay suspensions from ESC-2 (90 °C, 8 % NH₃). a. interstratified lizardite and brucite identified from d-spacings. b. smectite, identified by dspacing and morphology. c. smectite: inset shows an EDX chemical analysis of the circled region n 4.13c with the nitrogen peak location labelled.

If there are no NH₃ or NH₄⁺ clays in our experiments, we may ask the question as to the reason for the greater abundance of secondary phases seen in experiments run with NH₃ at 90 °C? As the initial fluids include relatively high concentrations of carbonate species (included 39 ×10⁻³ mol L⁻¹ NaHCO₃) and trace amounts of Mg from contamination (~0.005 ×10⁻³ mol L⁻¹), the solutions are slightly supersaturated with respect to magnesite in all experiments. Empirical research has shown that olivine carbonation may cause magnesite formation in temperatures as low as 50 °C (Miller et al., 2018), and kinetic rates of the carbonation process increase up to 185-200 °C (Miller et al., 2019). Zhu et al. (2017) recently illustrated the combined role of carbon and nitrogen in solution to stabilizing often transient or metastable phases that may then be converted to brucite, such as nesquehonite (MgCO₃·3H₂O) and roguinite ((NH₄)₂Mg(CO₃)₂•4H₂O). This study also showed that NH₄-bearing roguinite was the dominant secondary phases in experiments with higher NH₃ concentrations (6.7 mol kg⁻¹). Roguinite may then be a mineral of interest in this system, if its stability increases with increasing NH₃ as the experiments of Zhu et al. (2017) suggest. Of additional interest is that olivine carbonation rates increase dramatically at around 90 °C (Miller et al., 2019), purportedly caused by a change in the mechanism of magnesite

growth (Saldi et al., 2009). We note that no magnesium carbonate minerals of any kind were identified after our experiments, and the mineral identity of the Fe-C rich phase found after reaction with 8 % NH_3 (ESC-6, Fig. 4.10) was not ascertained. While reliable thermodynamic information for the relevant minerals are scarce, we speculate that the greater secondary mineralogy seen in the 90 °C experiments with NH_3 may be due to the early nucleation of a metastable NH_3 -bearing precursor phase, such as roguinite, or teschemacherite (NH_4HCO_3) that is especially pronounced at < 150 °C where more conventional olivine carbonation pathways proceed slowly.

4.4.4 Interface dissolution-precipitation and the TEM results

The close proximity of amorphous phases and phyllosilicates at the olivine surface, seen especially in ESC-5 (0 % NH₃, 150 °C: Fig. 4.10d), suggests that secondary clay minerals may actually start to crystallize within and after formation of an amorphous surface altered layer (ESC-5 shows this nicely). HRTEM images of olivine grains from ESC-4 (0 % NH₃, 90 °C- Fig 4.10c) are illustrative of the alteration processes that can be inferred from the fluid chemistry: while no secondary phases are visible from this sample by FEG-SEM, nanoscale analysis indicates a possible amorphous altered layer, with no phyllosilicates, at the surface of ESC-4 (0 % NH₃, 90 °C). Further, we found that while the secondary phases (lizardite, brucite, and smectite) at the surface of olivine reacted at 90 °C (ESC-1 and ESC-2) appear distinctly crystalline at the micron scale, their sensitivity to damage both during preparation of FIB sections and TEM analysis of the dispersed clays indicates that they are in fact very thin and/or poorly crystalline. That the secondary minerals occurring at the surface of olivine reacted at 150 °C (ESC-5 and ESC-6) appeared to be less damaged during the FIB section preparation suggests that despite their shorter run times (2 months as compared to 5-6 months), the secondary minerals formed are more structurally robust than those formed after reaction at 90 °C (ESC-1 and ESC-2). At 150 °C, this is true of samples reacted both with and without NH₃.

4.4.4 Significance for chondrites and icy satellites

The batch and flow-through experiments presented here represent idealized analog reactions that could be happening on icy satellites. From the CFSTR experiments completed for this study, we do not see any significant or reproducible effect of NH₃ on the fluid chemistry at any temperature. Specifically, we do not see a difference in the apparent dissolution rates between 0.8 % NH₃ and pHcontrolled 0 % NH₃ experiments. This suggests against NH₃ having any catalyzing or retarding effect on olivine dissolution in planetary fluids. Moreover, the initial r_{si} observed in this study from the batch experiments can be regressed against temperature along with the r_{Si} from batch experiments as presented in Chapter 3 (Fig. 4.14). Regressing the r_{Si} from each solution type over the entire temperature range (1000/T (K) for all batch experiments from -20 to 150 °C yields thermal activation energies of E_a = 47.6, 36.2, and 45.0 kJ mol⁻¹ in 0, 0.8, and 8 % NH₃ solutions, respectively. That these E_a values are much closer to the accepted values (40-60 kJ mol⁻¹) additionally support the extension of these rates to low temperatures (Fig. 4.14). This is a particularly interesting result given the weak dependency on temperature for each of the individual experiment sets of -20 to 23 °C, and 90-150 °C. The attenuated dependency of dissolution rates on temperature in the -20 to 22 °C batch experiments of Chapter 2 yielded E_a values of at most 20 kJ mol⁻¹. No E_a values were derived from the batch experiment results presented in this chapter, as they only encompass two temperatures; only a weak positive relationship exists between the r_{Si} from our experiments at 90-150 °C.

As different slopes are then described between temperature and r_{Si} at high temperatures vs. low temperatures, this additionally gives credit to the conclusions from the CFSTR experiments: that there is a potential change in the dissolution mechanism between low temperatures, at least in alkaline solutions. Alternatively, the processes that increasingly inhibit olivine dissolution – such as the presence of passivating surface altered layers – may be significantly retarded at low temperatures, indirectly promoting olivine dissolution. This has potentially significant implications for icy worlds: if continuing decreases in temperature have no profound effect on decreasing olivine dissolution rates, then alteration of primary olivine could proceed faster than anticipated in the low-temperature, alkaline solutions that are hypothesized to exist in chondrites and icy worlds.



Fig. 4.14: initial *r*_{Si} from all single-temperature batch experiments from this chapter, additionally presented with the initial *r*_{Si} at from batch experiments at -20, 4, and 23 °C presented in Chapter 3.

Further, the increased abundance and crystallinity in experiments with NH_3 has implications for the habitability of hydrothermal vents in NH_3 -bearing oceans. While our CFSTR experimental results show apparent dissolution rates that at best represent a minimum olivine dissolution rate, the high value of this minimum rate at 0 °C complements several other recent studies that reveal high rates of olivine serpentinization in alkaline conditions (Lamadrid et al., 2020, 2017; McCollom et al., 2020). Further, our batch experiment results showing that NH_3 may promote the rate of formation of brucite and smectite in low-temperature hydrothermal conditions supports models of secondary olivine alteration products forming at lab timescales even at low temperatures, where NH_3 is present. The rate at which secondary products can form may be particularly important in small icy satellites, where the endogenic activity that creates hydrothermal systems may be transient and short-lived. Brucite is of particular interest, as it forms in part the membranous chimneys at the low-temperature Lost City Hydrothermal Field (Kelley et al., 2005; Ludwig et al., 2006). In these structures, minute chemical gradients form over cm-scales are thought to promote prebiotic reactions (Barge et al., 2015; Russell et al., 2014). In addition, phyllosilicates such as smectite are known to adsorb and concentrate organic molecules in hydrothermal conditions (Gautier et al., 2017; Pedreira-Segade et al., 2018), and even to

catalyze amino acid synthesis in the presence of precursor compounds (Vinogradoff et al., 2020). It is interesting that our experiments already show that even at lab time scales (several months), crystalline secondary minerals including brucite and smectite may form faster in the presence of NH₃.

4.5 Conclusions

This chapter presents the results of two complementary experimental setups: a. continuously-flow stirred tank reactor (CFSTR) olivine dissolution experiments at 0, 23, 90, and 150 °C were performed to identify possible effects of NH_3 on olivine dissolution rates; b. static batch reactor olivine alteration experiments at 90 and 150 °C designed to promote secondary mineral formation after reaction with NH_3 -bearing aqueous solutions in a closed-system. The main results are as follows:

- No significant effect of NH_3 on the apparent olivine dissolution rates is identified from the CFSTR experiments. We also evaluated the effect of pH and found that decreasing the pH from 10.8 to 12.2 does not result in slower olivine dissolution rates.
- Notably, the CFSTR experiments also showed a weak relationship with temperature from 23-150 °C. Thermal activation energies calculated from our experiments were in the range of 7.5-18.9 kJ mol⁻¹, significantly lower than the values of 40-60 kJ mol⁻¹ given for acid to circumneutral conditions in the literature.
- In general, our measured rates at 23 °C are within error of the rate predicted by existing rate equations (specifically Rimstidt et al. 2012), but at 90 and 150 °C our observed rates are 1-3 orders of magnitude lower than that predicted by these rate equations. Given that there is a large variance (+- 0.5 log units) between data even the well-studied conditions of 25 °C and pH > 6.5, this may in part be due to the fact that the current rate equations incorporate very few experimental data at alkaline conditions. This highlights the need for further empirical study of olivine dissolution in alkaline solutions.
- The CFSTR apparent olivine dissolution rates at 0 °C are also surprisingly higher than the rates calculated from experiments at 23 or 90 °C. To the best of the author's knowledge, these are the first continuous-flow reactor experiments of olivine dissolution at T < 25 °C under alkaline conditions and more insights will certainly be gained by additional exploration in this topic. Moreover, our study is not the first to show higher than expected olivine dissolution rates at ≤ 0 °C. Future work should focus on identifying if there is a change in the primary or secondary processes that affect olivine dissolution rates over time between 25 and 0 °C.
- While no effect on fluid chemsitry is observed, NH₃ is correlated with greater abundance and crystallinity of secondary phases in batch experiments, specifically brucite, smectite, and lizardite. This is not solely a pH effect, as this is observed in both 1 and 10 % NH₃ experiments at 90 °C, while not in a pH-controlled 0 % NH₃ experiment. As no NH₃-carbonates or -clays were identified, we speculate that the mechanism for this greater abundance is the formation of NH₃-bearing metastable precursor phases that promote the growth of the more stable secondary phases identified in our experiments.

These results can be summarized by stating that while the presence of NH_3 has no significant effect on fluid chemistry, NH_3 does promote the formation of secondary minerals during olivine alteration. The effects of NH_3 can then largely be ignored in planetary evolution models that seek to evaluate olivine dissolution times. However, the rapid formation of secondary minerals is of interest to evaluating the

potential habitability of hydrothermal vent systems, in particular with respect to conceptual models seeking to characterize low-T hydrothermal vents in icy worlds that may harbor NH_3 -bearing oceans. In addition, these results highlight the specific need for more empirical exploration of olivine dissolution in alkaline systems, particularly with respect to the effect of temperature. Specifically, and intriguingly, our results point to a possible change in the olivine dissolution mechanism between 0 and 25 °C. This could mean that olivine dissolution is not significantly retarded by low temperatures, and will proceed rapidly in icy worlds as soon as water-rock interaction has begun.

4.6 Cautionary tales

Any progress this project has made represents just a small part of the work done, due to the minor setbacks and ongoing improvements that are seemingly inherent to experimental work. The focus here is not to dwell on the tedious functional issues that limit any short-term project, but rather to remark briefly on how resolving (or even just identifying) several of these issues led to a better understanding of the fundamental processes that underlie the results presented here.

4.6.1 The particularities of FIB sections

Issues with preparation of several FIB lamellae resulted in ambiguous results that required further study to arrive at the conclusions presented in this chapter and Chapter 3. First, in preparing a thin section from ESC-2 (90 °C, 10 % NH₃) with its abundant secondary phases visible at the surface by FEG-SEM, the process of milling with the Ga ion beam apparently destroyed the secondary phases. When the FIB-milled foil was viewed by TEM at the µm to nm-scale, a gap was visible at the surface- in fact, there was no evidence of the phyllosilicate crystals that had populated the surface and that had been so clearly observed by FEG-SEM (Fig. 4.15). Initially, we hypothesized that this could have occurred from the orientation of the FIB lamella: the plate-like secondary phases at the FIB location have a clear orientation at the surface, and the lamella is oriented parallel to this directional orientation. Instead of taking a cross-section of these secondary phases, then, the parallel orientation destabilized the secondary material or made it impossible to image. However, as discussed above in section 4.3.2, two other FIB lamellae later taken from olivine reacted in ESC-2 also were significantly damaged during the FIB-milling. The secondary phases seen in the FIB section from ESC-1 (90 °C, 8 % NH₃) were similarly difficult to image. Together, it suggests that the secondary phases themselves are very thin, delicate, poorly crystalline, or otherwise more susceptible to damage than the secondary phases formed at 150 °C.



Fig. 4.15: first FIB section prepared from ESC-2 (90 °C, 10% NH₃). Left: FIB section is aligned parallel with the alignment of the crystalline secondary phases. Right: initial TEM images of the FIB section even at a large scale show a gap of missing material between the olvine and the platinum.

Second, during the course of this work, improvements to the FIB milling procedure process were made at GFZ Potsdam (PISA facility, see additional information in section 4.2.4 and Chapter 3) that prompted a reevaluation of our interpretation of specific results. Specifically, in Chapter 3 the results of a possible surface alteration layer < 1 nm thick at the surface of the olivine was shown after reaction in 0.8 % NH₃ at -20 °C for one year. The thickness of this layer is consistent with the fluid chemistry results from those experiments (see Chapter 3 for additional discussion). However, the first set of analyses of the interfacial region of this sample yielded a different interpretation. In Fig. 4.16a, a TEM image of the first FIB section taken from this experiment clearly shows an apparent amorphous surface altered layer of 10-15 nm thick. Chemical analyses (TEM-EDX spot analysis) of this layer further showed that it appeared to be enriched in Si and depleted in Mg relative to the bulk olivine phase. This led to the reasonable conclusion that this was an amorphous silica layer that formed during alteration. The intervening methodological developments in FIB section milling (considerable decrease in milling voltage and beam current) later showed that this layer could in fact be formed as an artifact of the FIB section process. Three additional FIB sections were produced on three different grains, and the results in each case were the same. For this reason, we now believe that the layer is considerably thinner than at first assumed, as presented in Chapter 3. Because of its extreme thinness and susceptibility to electron beam damage, we were not able to correctly measure the chemical composition of the surface altered layer. This calls into question the results from some of the other FIB lamellae that were prepared using the older method, including those presented in this chapter. While the presence of crystalline secondary phases is not an artifact, the presence (and thickness) of amorphous material between the unaltered olivine structure and secondary crystalline phases may require a more conservative intepretation. For example, the FIB section of ESC-4 (Fig. 4.16b) shows a visually similar amorphous alteration layer, also seemingly enriched in Si and depleted in Mg as compared to the olivine bulk. As time and budget constraints prevent thorough re-analyses of all of the many FIB sections and TEM analyses presented in this chapter, the true nature or thickness of any surface altered layer in this specific sample cannot be verified.



Fig. 4.16: TEM images of two different FIB section showing an apparent Si-rich amorphous phase at the olivine sufrace. a. FIB section prepared from B-5 (-20 °C, 0.8 % NH₃, reacted for > 1 year). b: FIB section of ESC-4 (90 °C, 0 % NH₃, reacted for 6 months).

We also note that very thin suface altered layers would be expected after alteration at basic pH conditions. This follows from the fact that the solubility of silica is very high at basic pH. It is well known that the solubility of silica is constant in the acid to neutral pH regime, but then sharply increases at basic pH. Several published studies have also found amorphous layers as thin as 5-50 nm on altered olivines (Béarat et al., 2006; Daval et al., 2011). However, these aforementioned studies are based on experiments at acid pH conditions, where silica is relatively insoluble (as compared to basic pH), such that these results are likely to be real. However, it cannot be discounted that some minor degree of FIB-induced artefacts also occurred in these studies.

While it is known that FIB section preparation can result in a near-surface amorphized layer in silicates that may be as much as 17-34 nm thick (Engelmann et al., 2003; Wirth, 2004), FIB section best-practices (such as reducing the beam voltage and current during preparation of the section) already exist that attempt to mitigate the potential for creating artifacts (Wirth, 2004). Overall, these examples show the difficulties associated with careful TEM foil preparation, as this is perhaps the most difficult step in all TEM studies.

4.6.2 Complexities in interpretation of high resolution TEM images

After the FIB section preparation, analyses of the resulting samples with TEM also presents challenges, especially in identifying alteration features at the interfacial boundary between the unaltered olivine structure and secondary surface phases, be they amorphous or crystalline. There is no reason to assume that the interface is either perfectly flat or perfectly vertical (i.e. perfectly parallel to electron beam). In fact, highly oblique and uneven boundaries are quite common place, and this can also lead to possible misinterpretations of high resolution images. As an example, in Fig. 4.17 an apparent alteration layer and a crenulated boundary characterize the olivine interface with a protective C-coating (sample ESC-1: 90 °C, 0.8 % NH₃). However, by changing the depth of focus, the nature of the interfacial boundary changes dramatically- the 'alteration layer' is no longer present, and the boundary appears to be more linear. Another common problem is delocalization when using TEM instruments without aberration correction. This phenomenon results in lattice fringes appearing where they

physically do not occur. An example of this can be seen in Fig. 4.16a. In conclusion, these examples point out that detailed, high resolution TEM work is far from routine, and that extreme care must be taken in the interpretation of TEM data.



Fig. 4.17: TEM images from the FIB section from ESC-1 (90 °C, 0.8 % NH₃) Left: olivine boundary appears to have an irregular trace, with a possible SAL (elongated vertical feature). However, upon changing the depth of focus (panel b), the lattice fringes extend further to the left and define a more regular boundary. The apparent surface altered layer has disappeared and actually appears to be a part of the olivine structure

4.7 References

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Aqueous chemistry: supplementary data.

Supplementary tables 4.1-4.10 present results the batch reactions, including ICP-AES analyses of the fluid aliquots from each reactor in each experiment set. For all tables 2-10: the column "ID" indicates the sample number; "Hours" indicates time of reaction in hours (number of hours from initial contact of solution with olivine grains in the reactor), "element mol" is the concentration of each element measured in a fluid aliquot from the indicated reactor (mol L⁻¹). Uncertainties for the elemental concentrations (mol L⁻¹) includes from instrumental error and systemic error from pipetting (during acid dilution for analysis). Null values ("--") indicate concentrations below detection limits.

		mL						
Sample ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC1 S00	-10	200	10.68		5.9E-04	2.0E-06	0.12	1.2E-05
ESC1 S01	24	195	10.61	2.3E-07	5.9E-04	8.6E-06	0.12	3.9E-05
ESC1 SO2	40	190	10.60	3.0E-06	5.9E-04	1.2E-05	0.13	7.1E-05
ESC1 SO3	120	185	10.60	4.7E-07	5.8E-04	1.1E-05	0.12	1.1E-04
ESC1 SO4	169	180	10.61	0.0E+00	6.1E-04	7.3E-06	0.12	8.7E-05
ESC1 SO6	382	170	10.47	4.7E-07	6.0E-04	8.6E-06	0.13	1.5E-04
ESC1 S07	693	165	10.58	-7.4E-09	7.4E-04	7.5E-06	0.15	1.2E-04
ESC1 SO8	1626	160	10.58	4.5E-07	5.8E-04	7.2E-06	0.12	1.6E-04
ESC1 S10	3224	150	10.57	-6.4E-08	6.0E-04	0.0E+00	0.17	1.9E-04
ESC1 S11	4367	145	10.58		7.5E-04	3.1E-06	0.15	1.9E-04
Uncertainty		± 1	± 0.5	± 7.2E-09	± 4.8E-06	± 1.3E-07	± 6.3E-04	± 5.6E-07

Supplementary table 4.1: ESC 1 (90 C, 0.8 % NH₃)

Supplementary table 4.2: ESC 2 (90 °C, 8 % NH₃)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC2 SOO	0	300	12.01	-5.0E-07	5.8E-04	5.0E-06	0.17	1.3E-05
ESC2 SO1	2.32	295	12	-6.1E-07	6.7E-04	3.4E-06	0.19	1.2E-04
ESC2 SO2	167.17	290	11.77	4.0E-06	5.5E-04	6.2E-05	0.15	2.0E-04
ESC2 SO3	225.17	285	11.88	9.3E-07	4.2E-04	2.2E-05	0.12	1.6E-04
ESC2 SO4	321.17	280	11.83	9.2E-07	5.6E-04	2.7E-05	0.16	2.1E-04
ESC2 SO6	2337.17	270	11.79	-6.9E-07	5.2E-04	-8.7E-07	0.13	2.4E-04
ESC2 SO6	2337.17	270	11.79	-6.9E-07	5.2E-04	-8.7E-07	0.13	2.4E-04
Uncertainty		±1	± 0.5	± 7.2E-09	± 4.8E-06	± 1.3E-07	± 6.3E-04	± 5.6E-07

Supplementary table 4.3: ESC 4 (90 $^{\circ}\text{C},$ 0 % $\text{NH}_{3}\text{)}$

		mL						a i 1
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC4 S00	0	300	10.78	7.7E-07	3.7E-03	1.3E-05	0.15	1.4E-05
ESC4 S02	18	290	10.31	1.3E-06	6.9E-04	1.2E-05	0.16	1.9E-04
ESC4 S03	48	285	10.4	4.7E-08	8.8E-04	4.4E-07	0.19	3.3E-04
ESC4 S04	121	280	10.51	8.6E-07	6.9E-04	8.3E-06	0.16	3.7E-04
ESC4 S05	645	275	10.45	2.6E-05	6.1E-04	3.4E-04	0.14	3.6E-04
ESC4 S06	1057	270	10.55	2.5E-06	6.2E-04	2.9E-05	0.14	3.4E-04
ESC4 S08	3000	260	10.53	-6.2E-08	5.8E-04	-2.0E-09	0.19	3.3E-04
ESC4 S09	4032	250	10.51	6.3E-06	7.9E-04	6.4E-05	0.16	4.0E-04
Uncertainty		±1	± 0.5	± 7.2E-09	± 4.8E-06	± 1.3E-07	± 6.3E-04	± 5.6E-07

Supplementary table 4.4: ESC 5 (150 °C, 8 % NH₃)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC5 S00	0	200	9.9	-3.4E-07	6.6E-04	4.5E-06	0.13	1.4E-06
ESC5 S01	19	200	9.53		4.3E-04	3.3E-06	0.16	7.0E-05
ESC5 S02	329	195	9.4		5.1E-04	3.4E-06	0.18	1.2E-04
ESC5 S03	954	180	9.5		6.0E-04	2.0E-05	0.13	1.7E-04
ESC5 S04	1643	185	9.16	-1.2E-07	6.5E-04	1.2E-06	0.13	1.4E-04
ESC5 S05	1652	180	9.11	-2.3E-07	6.3E-04	3.7E-06	0.13	1.4E-04
Uncertainty		±1	± 0.5	± 9.7E-08	± 1.7E-05	± 3.0E-07	± 1.6E-03	± 6.3E-07
ESC5 S03 ESC5 S04 ESC5 S05 Uncertainty	954 1643 1652 	180 185 180 ± 1	9.5 9.16 9.11 ± 0.5	 -1.2E-07 -2.3E-07 ± 9.7E-08	6.0E-04 6.5E-04 6.3E-04 ± 1.7E-05	2.0E-05 1.2E-06 3.7E-06 ± 3.0E-07	0.13 0.13 0.13 ± 1.6E-03	1.7E-04 1.4E-04 1.4E-04 ± 6.3E-07

Supplementary table 4.5: ESC 6 (150 °C, 0 % NH₃)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC6 S00	0	300	12.2		6.0E-04	3.9E-06	0.13	1.1E-06
ESC6 S01	19	295	12.2		4.1E-04	7.4E-07	0.14	6.6E-05
ESC6 S02	329	290	12.4		5.5E-04	1.3E-06	0.18	1.2E-04
ESC6 S03	954	285	12.2		5.6E-04	1.8E-05	0.11	1.1E-04
Uncertainty		±1	± 0.5	± 9.7E-08	± 1.7E-05	± 3.0E-07	± 1.6E-03	± 6.3E-07

Supplementary table 4.6: ESC 7 (90-150 $^{\circ}\text{C},$ 8 % $\text{NH}_{3}\text{)}$

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC7 SOO	0	300	12.4	4.1E-07	5.0E-04	2.4E-06	0.11	5.5E-06
ESC7 S01	1	295	12.65	7.0E-08	5.0E-04	2.1E-06	0.10	1.1E-05
ESC7 S02	4	290	12.39	6.5E-08	5.1E-04	1.7E-06	0.10	1.2E-05
ESC7 S03	16	285	12.97	5.7E-08	5.1E-04	2.0E-06	0.12	2.0E-05
ESC7 S04	28	280	12.87		4.9E-04	2.1E-06	0.12	2.8E-05
ESC7 S05	90	275	12.89	6.7E-08	5.0E-04	2.0E-06	0.11	3.0E-05
ESC7 S06	193	270	12.78	2.3E-08	5.0E-04	1.9E-06	0.11	3.5E-05
ESC7 S07	548	265	12.62	6.7E-08	5.1E-04	2.0E-06	0.10	3.8E-05
ESC7 S08	549	260	12.37	7.5E-07	4.8E-04	7.3E-07	0.10	3.2E-05
ESC7 S09	551	255	12.21	1.3E-06	5.0E-04	8.2E-07	0.10	3.1E-05
ESC7 S10	555	245	12.19	1.5E-08	3.9E-04	-4.7E-08	0.09	4.4E-05
ESC7 S11	570	240	12.28	3.1E-08	4.7E-04	-2.2E-07	0.11	4.4E-05
ESC7 S12	604	235	12.14	7.0E-07	5.2E-04	4.4E-07	0.11	4.5E-05
ESC7 S13	668	230	12.21	9.8E-08	5.2E-04	3.4E-07	0.11	4.5E-05
ESC7 S15	937	220	12.31	4.5E-07	5.7E-04	4.2E-07	0.11	4.5E-05
ESC7 S16	1009	215	12.22	9.2E-07	5.2E-04	7.3E-07	0.11	4.7E-05
Uncertainty		± 1	± 0.5	± 3.0E-09	± 1.4E-06	± 1.7E-07	± 1.6E-03	± 2.6E-07

Supplementary table 4.7: ESC 8 (90-150 °C, 8 % NH₃)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC8 SOO	0	200	10.71	1.0E-06	5.5E-04	5.9E-06	0.12	5.5E-06
ESC8 S01	1	195	10.8	9.2E-07	5.7E-04	4.5E-06	0.13	9.1E-06
ESC8 S02	2	190	10.83	1.0E-06	5.1E-04	3.7E-06	0.12	1.0E-05
ESC8 S03	14	185	10.83	8.2E-07	5.0E-04	3.3E-06	0.12	1.7E-05
ESC8 S04	26	180	10.49	1.2E-06	5.1E-04	3.6E-06	0.12	2.1E-05
ESC8 S05	87	175	10.75	5.6E-07	4.8E-04	3.1E-06	0.11	2.6E-05
ESC8 S06	191	170	10.71	6.1E-07	5.5E-04	3.4E-06	0.12	3.5E-05
ESC8 S07	547	165	10.62	9.8E-06	5.1E-04	3.1E-06	0.12	4.3E-05
ESC8 S08	547	160	10.69	8.5E-06	5.8E-04	2.5E-06	0.13	5.1E-05
ESC8 S09	549	155	10.74	1.5E-05	5.1E-04	1.6E-06	0.12	4.6E-05
ESC8 S10	551	150	10.92	7.8E-07	5.2E-04	1.2E-06	0.12	5.3E-05
ESC8 S11	568	145	10.44	7.9E-07	4.8E-04	9.8E-07	0.11	5.2E-05
ESC8 S12	602	140	10.92	7.1E-07	4.7E-04	8.5E-07	0.11	5.6E-05
ESC8 S13	666	135	10.87	6.6E-07	5.0E-04	8.6E-07	0.12	6.3E-05
ESC8 S14	800	130	10.85	1.0E-06	5.2E-04	8.5E-07	0.12	6.9E-05
ESC8 S15	935	125	10.87	6.8E-07	5.7E-04	9.6E-07	0.13	7.6E-05
ESC8 S16	1007	120	10.92	5.7E-07	5.6E-04	5.3E-07	0.13	7.5E-05
ESC8 S17	1056	115	10.75	6.8E-07	5.6E-04	5.9E-07	0.13	7.7E-05
Uncertainty		±1	± 0.5	± 3.0E-09	± 1.4E-06	± 1.7E-07	± 1.6E-03	± 2.6E-07

Supplementary table 4.8: ESC 9 (90 °C, 0 % NH₃)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ESC9 SO	0		10.68	1.4E-06	4.3E-04	1.2E-05	0.13	9.0E-06
ESC9 S01	1	195	10.8	9.5E-07	4.1E-04	4.2E-06	0.13	1.6E-05
ESC9 S02	1	190	10.79	9.3E-07	3.9E-04	3.4E-06	0.12	1.7E-05
ESC9 S03	6	185	10.8	9.0E-07	4.0E-04	3.0E-06	0.13	2.2E-05
ESC9 S04	20	180	10.8	1.2E-06	5.0E-04	3.8E-06	0.16	3.5E-05
ESC9 S05	30	175	10.73	1.1E-06	4.6E-04	3.9E-06	0.15	3.6E-05
ESC9 SO6	50	170	10.78	1.2E-06	5.5E-04	4.1E-06	0.17	4.5E-05
ESC9 S07	78	165	10.83	1.2E-06	4.7E-04	4.0E-06	0.15	4.1E-05
ESC9 S08	148	160	10.72	1.2E-06	5.6E-04	3.8E-06	0.18	5.1E-05
ESC9 S09	212	155	10.67	1.8E-07	5.5E-04	3.7E-06	0.18	6.5E-05
ESC9 S10	312	150	10.72	8.5E-07	5.6E-04	3.9E-06	0.18	6.8E-05
ESC9 S11	406	145	10.79	1.7E-05	5.8E-04	4.2E-06	0.18	7.3E-05
ESC9 S12	720	140	10.97	1.9E-07	5.5E-04	3.6E-06	0.17	7.3E-05
ESC9 S13	862	135	10.78	1.8E-07	6.4E-04	3.3E-06	0.20	8.3E-05
Uncertainty		±1	± 0.5	± 3.0E-09	± 1.4E-06	± 1.7E-07	± 1.6E-03	± 2.6E-07

Supplementary table 4.9: ESC 10 (90 $^\circ C,$ 8 % NH_3)

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ES10 S0	0.0		12.17	2.2E-07	3.5E-04	2.2E-06	0.09	1.1E-05
ES10 S1	0.5	295	12.17	1.4E-07	3.6E-04	9.4E-07	0.09	1.1E-05
ES10 S2	1	290	12.16	9.6E-08	3.9E-04	4.2E-07	0.09	1.3E-05
ES10 S3	6	285	12.28	1.4E-07	3.3E-04	1.0E-07	0.09	1.4E-05
ES10 S4	20	280	12.53	1.3E-07	4.1E-04	2.2E-07	0.11	2.5E-05
ES10 S5	30	275	12.3	1.3E-07	4.5E-04	6.1E-07	0.12	2.9E-05
ES10 S6	50	270	12.64	1.1E-07	4.2E-04	5.6E-07	0.11	3.3E-05
ES10 S7	78	265	12.39	1.2E-07	4.9E-04	8.5E-07	0.12	3.6E-05
ES10 S8	148	260	12.6	2.2E-07	4.4E-04	6.2E-07	0.12	4.0E-05
ES10 S9	212	255	12.6	8.0E-08	4.9E-04	4.0E-07	0.13	5.8E-05
ES10 S10	312	250		5.0E-08	5.0E-04	5.0E-07	0.13	5.9E-05
ES10 S11	406	245	12.54	7.3E-08	5.0E-04	6.8E-07	0.12	6.2E-05
ES10 S12	720	240	12.35	5.0E-08	5.3E-04	8.2E-07	0.12	6.2E-05
ES10 S13	862	225	12.72	1.0E-07	5.4E-04	1.6E-06	0.13	6.7E-05
Uncertainty		± 1	± 0.5	± 3.0E-09	± 1.4E-06	± 1.7E-07	± 1.6E-03	± 2.6E-07

Supplementary table 4.10: ESC 11 (150 °C, 0 % $\rm NH_3)$

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ES11 S00	0	200	10.65	3.7E-07	6.2E-04	5.0E-06	0.18	1.8E-05
ES11 S01	0.1	197	10.66	5.7E-07	5.9E-04	2.2E-06	0.17	3.7E-05
ES11 S02	1	194	10.69	5.1E-07	4.4E-04	2.0E-06	0.13	4.0E-05
ES11 S03	6	191	10.68	4.8E-07	4.8E-04	2.3E-06	0.14	4.4E-05
ES11 S04	12	188	10.68	3.5E-07	4.8E-04	2.1E-06	0.14	4.3E-05
ES11 S05	19	185	10.63	4.3E-07	5.4E-04	2.6E-06	0.16	5.1E-05
ES11 S06	51	182	10.68	6.0E-07	6.2E-04	3.6E-06	0.18	5.8E-05
ES11 S07	77	179	10.62	2.6E-07	6.3E-04	2.2E-06	0.18	5.9E-05
ES11 S08	148	176	10.63	5.6E-07	5.0E-04	1.9E-06	0.15	3.6E-05
ES11 S09	197	173	10.6	2.5E-07	5.8E-04	1.8E-06	0.17	5.5E-05
ES11 S10	246	170	10.67	4.0E-07	6.1E-04	2.1E-06	0.17	5.7E-05
ES11 S11	316	167	10.7	5.3E-07	6.3E-04	3.4E-06	0.18	6.0E-05
ES11 S12	413	164	10.72	3.0E-07	6.2E-04	1.8E-06	0.17	5.6E-05
Uncertainty		±1	± 0.5	± 3.2E-08	± 7.2E-06	± 1.9E-07	± 1.2E-03	± 4.9E-07

Supplementary table 4.11: ESC 12 (150 °C, 8 % $\rm NH_3)$

		mL						
ID	Hours	remaining	рН	Fe mol	K mol	Mg mol	Na mol	Si mol
ES12 S00	0		12.11	1.4E-07	5.8E-04	2.0E-06	0.13	2.6E-05
ES12 S01	0.1	297	12.31	1.0E-07	5.8E-04	1.4E-06	0.13	3.0E-05
ES12 S02	1	294	12.31	8.5E-08	5.0E-04	2.8E-07	0.11	3.3E-05
ES12 S03	7	291	12.19		3.7E-04	8.6E-08	0.09	3.4E-05
ES12 S04	20	288	12.14		4.6E-04	5.1E-07	0.11	3.8E-05
ES12 S05	30	285	12.01		5.7E-04	6.0E-07	0.13	5.4E-05
ES12 S06	52	282	12.06		5.0E-04	5.6E-07	0.11	4.1E-05
ES12 S07	78	279	11.9		5.2E-04	3.2E-07	0.12	4.4E-05
ES12 S08	149	276	12.01		4.9E-04	4.7E-07	0.11	4.3E-05
ES12 S09	198	273	11.97		5.8E-04	4.5E-07	0.13	4.8E-05
ES12 S10	247	270	11.83		5.9E-04	3.3E-07	0.13	4.6E-05
ES12 S11	317	267	11.96		6.3E-04	1.6E-06	0.14	5.4E-05
ES12 S12	414	264	11.96	2.8E-07	5.0E-04	1.5E-07	0.12	4.2E-05
Uncertainty		±1	± 0.5	± 3.2E-08	± 7.2E-06	± 1.9E-07	± 1.2E-03	± 4.9E-07

Supplementary tables 4.12-4.23 show fluid chemistry results from CFSTR experiments. Sample ID indicates the number of the sample taken, where "Input" indicates the chemistry of the input fluid. Hours is the time after initially combining solution with olivine (experiment start). ICP-AES analyses of the fluid aliquots from each reactor in are given in mol L⁻¹. Uncertainties for the elemental concentrations (mol L⁻¹) includes from instrumental error and systemic error from pipetting (during acid dilution for analysis). d indicates the concentration (in mol L⁻¹) of the Si and Mg in the output solution minus that of the input solution. Mg/Si is a molar ratio. r_{Si} and r_{Mg} are the calculated rates in mol m⁻² s⁻¹. % error for the rates was calculated from the % error associated the molar concentrations, Kr BET surface area, and mass measurements: % error was calculated at 15 % for r_{Si} and 14 % for r_{Mg} (not given in the tables below). Null values ("--") indicate concentrations below detection limits or meaningless values (dissolution rate of the input fluid), or where uncertainty is not given.

Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-C Input	0		1.5E-03	0.21		1.3E-05	-1.9E-06	3.1E-06	-1.68		
EF-C 01	3		1.6E-03	0.21	7.2E-06	1.5E-05	6.9E-06	4.7E-06	0.69	1.1E-10	4.2E-11
EF-C 02	5		1.6E-03	0.22	1.9E-05	1.4E-05	1.9E-05	3.5E-06	0.18	3.0E-10	3.1E-11
EF-C 03	6		1.4E-03	0.20	1.8E-05	1.1E-05	1.8E-05	6.8E-07	0.04	2.8E-10	6.0E-12
EF-C 04	8		3.7E-04	0.05	5.9E-06	2.8E-06	5.5E-06	-7.5E-06	-1.36	8.7E-11	-6.6E-11
EF-C 05	9		1.6E-03	0.22	2.8E-05	1.1E-05	2.8E-05	6.4E-07	0.02	4.4E-10	5.6E-12
EF-C 06	23		1.7E-03	0.23	3.7E-05	1.1E-05	3.7E-05	8.5E-07	0.02	5.8E-10	7.5E-12
EF-C 07	27		2.1E-03	0.28	4.9E-05	1.4E-05	4.9E-05	3.3E-06	0.07	7.8E-10	2.9E-11
EF-C 08	48		1.7E-03	0.23	4.0E-05	1.2E-05	4.0E-05	1.2E-06	0.03	6.3E-10	1.1E-11
EF-C 09	55		1.7E-03	0.23	4.0E-05	1.1E-05	3.9E-05	8.3E-07	0.02	6.2E-10	7.3E-12
EF-C 10	71		1.4E-03	0.20	3.4E-05	1.0E-05	3.3E-05	-2.5E-07	-0.01	5.3E-10	-2.2E-12
EF-C 11	79		1.7E-03	0.23	3.6E-05	1.2E-05	3.6E-05	1.5E-06	0.04	5.7E-10	1.4E-11
EF-C 12	143		1.7E-03	0.23	3.2E-05	1.3E-05	3.2E-05	2.3E-06	0.07	5.0E-10	2.0E-11
EF-C 13	199		1.7E-03	0.24	2.6E-05	1.4E-05	2.5E-05	3.6E-06	0.14	4.0E-10	3.2E-11
EF-C 14	240		1.6E-03	0.22	2.0E-05	1.3E-05	2.0E-05	2.8E-06	0.14	3.1E-10	2.4E-11
EF-C 15	482		1.7E-03	0.23	2.1E-05	1.4E-05	2.1E-05	3.9E-06	0.19	3.3E-10	3.5E-11
EF-C 16	488		1.7E-03	0.23	1.7E-05	1.4E-05	1.7E-05	4.2E-06	0.25	2.7E-10	3.7E-11
EF-C 17	503		1.8E-03	0.24	1.8E-05	1.5E-05	1.8E-05	5.0E-06	0.28	2.8E-10	4.4E-11
EF-C 18	505		1.7E-03	0.23	1.6E-05	1.5E-05	1.6E-05	4.5E-06	0.28	2.5E-10	3.9E-11
EF-C 19	508		1.7E-03	0.24	1.4E-05	1.1E-05	1.4E-05	6.0E-07	0.04	2.2E-10	5.3E-12
Uncertainty			1.1E-04	1.9E-03	2.3E-06	3.3E-08	2.3E-06	3.3E-08			

Supplementary table 4.12: EF-C (150 °C, 0.8 % NH₃)

Supplementary table 4.13: EF-D (90 $^\circ C,$ 0 % $NH_3)$

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-D Input	0	1.1E-08	1.2E-02	0.10	1.1E-06	5.3E-06	4.7E-08	1.2E-06	25.19		
EF-D 01	0.3	6.3E-09	1.2E-02	0.10	2.1E-06	6.0E-06	1.1E-06	1.9E-06	1.79	2.1E-11	2.1E-11
EF-D 02	2	5.4E-09	1.2E-02	0.10	4.8E-06	4.2E-06	3.8E-06	4.6E-08	0.01	7.5E-11	5.1E-13
EF-D 03	3	3.6E-09	9.8E-03	0.08	1.3E-05	2.4E-06	1.2E-05	-1.7E-06	-0.14	2.4E-10	-1.9E-11
EF-D 04	4	4.1E-09	1.2E-02	0.10	2.8E-05	2.0E-06	2.7E-05	-2.1E-06	-0.08	5.4E-10	-2.3E-11
EF-D 05	9	3.0E-09	1.2E-02	0.10	3.6E-05	1.2E-06	3.5E-05	-2.9E-06	-0.08	7.0E-10	-3.2E-11
EF-D 06	23		1.2E-02	0.10	3.4E-05	1.1E-06	3.3E-05	-3.0E-06	-0.09	6.6E-10	-3.3E-11
EF-D 07	26		1.2E-02	0.10	3.1E-05	1.4E-06	3.0E-05	-2.7E-06	-0.09	5.9E-10	-3.0E-11
EF-D 08	31	8.7E-07	1.2E-02	0.10	3.1E-05	1.0E-04	3.0E-05	9.7E-05	3.27	5.9E-10	1.1E-09
EF-D 09	47	5.6E-09	1.2E-02	0.10	2.5E-05	2.1E-06	2.4E-05	-2.0E-06	-0.08	4.8E-10	-2.2E-11
EF-D 10	55	6.3E-09	1.0E-02	0.08	1.8E-05	1.5E-06	1.7E-05	-2.6E-06	-0.16	3.3E-10	-2.9E-11
EF-D 11	72	1.5E-09	1.2E-02	0.10	1.9E-05	2.1E-06	1.8E-05	-2.0E-06	-0.11	3.6E-10	-2.2E-11
EF-D 12	76	4.5E-09	1.2E-02	0.10	1.7E-05	2.5E-06	1.6E-05	-1.6E-06	-0.10	3.1E-10	-1.8E-11
EF-D 13	144	1.8E-07	1.3E-02	0.11	1.7E-05	1.8E-05	1.6E-05	1.4E-05	0.85	3.3E-10	1.5E-10
EF-D 14	166	2.1E-08	1.4E-02	0.11	2.2E-05	5.6E-06	2.1E-05	1.4E-06	0.07	4.1E-10	1.6E-11
EF-D 15	177	3.1E-08	1.3E-02	0.11	1.6E-05	7.4E-06	1.5E-05	3.3E-06	0.22	3.0E-10	3.6E-11
EF-D 16	192	2.5E-08	1.3E-02	0.11	1.4E-05	7.2E-06	1.2E-05	3.1E-06	0.24	2.5E-10	3.4E-11
EF-D 17	248	1.9E-07	1.3E-02	0.11	1.3E-05	2.6E-05	1.2E-05	2.2E-05	1.82	2.3E-10	2.4E-10
EF-D 18	312	2.4E-07	1.4E-02	0.11	1.2E-05	3.2E-05	1.1E-05	2.8E-05	2.61	2.1E-10	3.1E-10
EF-D 19	364	2.3E-07	1.4E-02	0.11	9.3E-06	2.7E-05	8.2E-06	2.3E-05	2.83	1.6E-10	2.6E-10
EF-D 20	412	1.7E-07	1.4E-02	0.11	8.1E-06	2.5E-05	7.0E-06	2.0E-05	2.92	1.4E-10	2.3E-10
EF-D 21	487	1.6E-07	1.2E-02	0.10	6.9E-06	2.4E-05	5.9E-06	2.0E-05	3.46	1.2E-10	2.2E-10
EF-D 22	507	2.6E-06	1.4E-02	0.11	1.1E-05	3.2E-04	9.4E-06	3.1E-04	33.20	1.9E-10	3.5E-09
Uncertainty			1.1E-04	1.9E-03	2.3E-06	3.3E-08	2.3E-06	3.3E-08			
Supplementary table 4.14: EF-F (23 $^\circ C,$ 8 % $NH_3)$

Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-F Input	0		5.8E-04	0.13	2.8E-05	4.1E+00	2.3E-05	-1.4E-06	-0.06	5.0E-10	-1.7E-11
EF-F 01	2		6.0E-04	0.11	5.7E-06	3.8E-06	1.8E-06	-3.6E-07	-0.20	4.0E-11	-4.5E-12
EF-F 02	5		5.9E-04	0.11	8.4E-06	3.4E-06	4.5E-06	-6.7E-07	-0.15	1.0E-10	-8.5E-12
EF-F 03	18	4.9E-08	6.9E-04	0.12	9.4E-06	5.4E-06	5.5E-06	1.3E-06	0.24	1.2E-10	1.7E-11
EF-F 04	22		5.9E-04	0.10	9.5E-06	4.5E-06	5.6E-06	4.3E-07	0.08	1.3E-10	5.4E-12
EF-F 05	25		6.1E-04	0.11	8.9E-06	4.4E-06	5.0E-06	3.2E-07	0.06	1.1E-10	4.1E-12
EF-F 06	29		5.9E-04	0.10	8.2E-06	4.2E-06	4.3E-06	4.0E-08	0.01	9.6E-11	5.1E-13
EF-F 07	43		6.4E-04	0.11	7.3E-06	3.7E-06	3.4E-06	-3.7E-07	-0.11	7.6E-11	-4.6E-12
EF-F 08	48		6.1E-04	0.11	6.8E-06	3.4E-06	2.9E-06	-6.9E-07	-0.24	6.5E-11	-8.6E-12
EF-F 09	53		6.0E-04	0.11	6.1E-06	3.3E-06	2.2E-06	-8.3E-07	-0.38	5.0E-11	-1.0E-11
EF-F 10	68	9.0E-08	7.5E-04	0.12	6.1E-06	3.6E-06	2.2E-06	-5.2E-07	-0.23	5.0E-11	-6.5E-12
EF-F 11	69		6.9E-04	0.12	5.6E-06	3.7E-06	1.7E-06	-3.9E-07	-0.23	3.9E-11	-4.9E-12
EF-F 12	72		6.0E-04	0.10	4.0E-06	3.7E-06	7.2E-08	-4.5E-07	-6.29	1.6E-12	-5.7E-12
EF-F 13	77		6.2E-04	0.11	5.1E-06	3.7E-06	1.2E-06	-3.9E-07	-0.32	2.8E-11	-4.9E-12
EF-F 14	137	7.8E-08	7.6E-04	0.13	4.8E-06	4.2E-06	8.7E-07	9.5E-08	0.11	2.0E-11	1.2E-12
EF-F 15	163	5.9E-08	7.8E-04	0.13	5.6E-06	4.8E-06	1.7E-06	6.4E-07	0.39	3.8E-11	8.1E-12
EF-F 16	186	5.3E-08	8.0E-04	0.13	5.4E-06	5.0E-06	1.5E-06	8.4E-07	0.57	3.3E-11	1.1E-11
EF-F 17	211	1.1E-07	7.6E-04	0.12	7.2E-06	5.5E-06	1.5E-06	1.4E-06	0.93	3.3E-11	1.7E-11
EF-F 18	243	1.3E-07	7.6E-04	0.13	7.2E-06	5.3E-06	1.5E-06	1.2E-06	0.80	3.4E-11	1.5E-11
EF-F 19	307	8.9E-08	7.9E-04	0.13	7.3E-06	5.5E-06	1.6E-06	1.4E-06	0.92	3.5E-11	1.8E-11
EF-F 20	357	1.0E-07	8.1E-04	0.13	6.6E-06	5.7E-06	9.2E-07	1.6E-06	1.71	2.1E-11	2.0E-11
EF-F 21	410	1.2E-07	8.1E-04	0.13	8.0E-06	5.9E-06	2.3E-06	1.8E-06	0.78	5.2E-11	2.2E-11
EF-F 22	478	1.5E-07	9.0E-04	0.14	8.1E-06	7.2E-06	2.4E-06	3.1E-06	1.27	5.5E-11	3.9E-11
EF-F 23	532	2.0E-07	1.0E-03	0.15	9.0E-06	8.7E-06	3.3E-06	4.6E-06	1.38	7.5E-11	5.8E-11
Uncertainty		7.2E-09	4.8E-06	6.3E-04	5.6E-07	1.3E-07	5.6E-07	1.3E-07			

Supplementary table 4.15: EF-G (150 $^\circ C,$ 0 % NH_3)

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-G Input	0	2.3E-07	7.1E-04	0.14	1.0E-05	5.5E-06	3.4E-07	1.4E-06	4.07		
EF-G 01	4	1.2E-07	7.2E-04	0.14	7.9E-06	4.4E-06	-1.7E-06	2.7E-07	-0.16	-2.6E-11	2.3E-12
EF-G 02	5	2.9E-07	6.9E-04	0.14	1.4E-05	3.9E-06	3.9E-06	-1.8E-07	-0.04	6.2E-11	-1.5E-12
EF-G 03	7	8.7E-08	6.9E-04	0.14	1.6E-05	3.2E-06	6.7E-06	-9.2E-07	-0.14	1.1E-10	-8.1E-12
EF-G 04	9	4.4E-08	7.1E-04	0.14	1.9E-05	3.2E-06	9.7E-06	-9.2E-07	-0.09	1.5E-10	-8.1E-12
EF-G 05	22	6.1E-09	7.2E-04	0.14	2.3E-05	2.6E-06	1.3E-05	-1.5E-06	-0.11	2.0E-10	-1.3E-11
EF-G 06	25	2.4E-08	7.0E-04	0.14	2.4E-05	2.5E-06	1.4E-05	-1.7E-06	-0.12	2.3E-10	-1.4E-11
EF-G 07	28	2.5E-08	7.0E-04	0.14	2.4E-05	2.6E-06	1.5E-05	-1.6E-06	-0.11	2.3E-10	-1.4E-11
EF-G 08	30	6.6E-08	7.0E-04	0.14	2.4E-05	2.5E-06	1.4E-05	-1.6E-06	-0.11	2.3E-10	-1.4E-11
EF-G 09	46	1.4E-08	6.9E-04	0.14	2.3E-05	2.5E-06	1.3E-05	-1.6E-06	-0.12	2.1E-10	-1.4E-11
EF-G 10	49	3.7E-08	7.1E-04	0.14	2.3E-05	2.5E-06	1.3E-05	-1.6E-06	-0.12	2.0E-10	-1.4E-11
EF-G 11	54	3.6E-08	6.8E-04	0.13	2.2E-05	2.4E-06	1.2E-05	-1.7E-06	-0.14	2.0E-10	-1.5E-11
EF-G 12	70	5.2E-08	7.0E-04	0.14	2.1E-05	2.5E-06	1.2E-05	-1.7E-06	-0.14	1.8E-10	-1.4E-11
EF-G 13	78	2.8E-08	7.0E-04	0.14	2.0E-05	2.5E-06	1.0E-05	-1.7E-06	-0.16	1.6E-10	-1.4E-11
EF-G 14	142	2.9E-08	6.9E-04	0.14	1.6E-05	2.4E-06	6.5E-06	-1.7E-06	-0.26	1.0E-10	-1.5E-11
EF-G 15	167	8.8E-08	7.4E-04	0.14	1.6E-05	2.6E-06	6.1E-06	-1.5E-06	-0.25	9.6E-11	-1.3E-11
EF-G 16	192	3.8E-08	7.0E-04	0.14	1.5E-05	2.4E-06	5.1E-06	-1.7E-06	-0.34	8.1E-11	-1.5E-11
EF-G 17	218	3.3E-08	7.3E-04	0.14	1.7E-05	2.4E-06	7.8E-06	-1.7E-06	-0.22	1.2E-10	-1.5E-11
EF-G 18	238	1.3E-07	7.0E-04	0.14	1.0E-05	2.7E-06	5.3E-06	-9.9E-07	-0.19	8.3E-11	-8.7E-12
EF-G 19	245	3.5E-08	6.9E-04	0.14	7.9E-06	2.6E-06	2.9E-06	-1.1E-06	-0.37	4.6E-11	-9.4E-12
EF-G 20	313	3.8E-08	7.0E-04	0.14	8.8E-06	2.5E-06	3.8E-06	-1.2E-06	-0.31	6.0E-11	-1.0E-11
EF-G 21	382	1.3E-07	7.2E-04	0.14	8.7E-06	2.4E-06	3.7E-06	-1.3E-06	-0.35	5.9E-11	-1.2E-11
Uncertainty		7.2E-09	4.8E-06	6.3E-04	5.6E-07	1.3E-07	5.6E-07	1.3E-07			

Supplementary table 4.16: EF-H (90 $^\circ C,$ 8 % $NH_3)$

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-H Input	0		5.7E-04	0.10	1.8E-06	5.7E-06	-3.2E-06	3.6E-06	-1.15		
EF-H 01	1		6.9E-04	0.12	2.4E-05	5.2E-06	1.9E-05	3.1E-06	0.16	3.4E-10	3.1E-11
EF-H 02	3		7.0E-04	0.11	2.1E-05	7.6E-06	1.6E-05	5.5E-06	0.35	2.8E-10	5.5E-11
EF-H 03	4		6.8E-04	0.11	2.9E-05	7.4E-06	2.4E-05	5.4E-06	0.22	4.4E-10	5.4E-11
EF-H 04	7		6.7E-04	0.11	3.3E-05	6.5E-06	2.8E-05	4.4E-06	0.16	5.0E-10	4.4E-11
EF-H 05	22		7.0E-04	0.12	3.3E-05	7.1E-06	2.8E-05	5.1E-06	0.18	5.1E-10	5.1E-11
EF-H 06	24		6.4E-04	0.11	2.9E-05	7.3E-06	2.4E-05	5.2E-06	0.21	4.4E-10	5.2E-11
EF-H 07	26		6.6E-04	0.11	2.9E-05	7.1E-06	2.5E-05	5.1E-06	0.21	4.4E-10	5.1E-11
EF-H 08	30		6.4E-04	0.11	2.7E-05	7.1E-06	2.3E-05	5.1E-06	0.23	4.1E-10	5.1E-11
EF-H 09	45		7.6E-04	0.13	2.6E-05	6.1E-06	2.1E-05	4.0E-06	0.19	3.8E-10	4.0E-11
EF-H 10	50		6.3E-04	0.11	2.2E-05	7.5E-06	1.7E-05	5.5E-06	0.33	3.0E-10	5.5E-11
EF-H 11	54		6.6E-04	0.11	2.8E-05	7.2E-06	2.3E-05	5.1E-06	0.22	4.1E-10	5.1E-11
EF-H 12	70		6.9E-04	0.12	2.6E-05	8.3E-06	2.1E-05	6.2E-06	0.29	3.8E-10	6.2E-11
EF-H 13	75		6.2E-04	0.11	2.3E-05	7.1E-06	1.8E-05	5.0E-06	0.28	3.3E-10	5.1E-11
EF-H 14	79		7.2E-04	0.12	7.5E-06	6.0E-06	2.5E-06	3.9E-06	1.58	4.5E-11	4.0E-11
EF-H 15	149		6.5E-04	0.11	2.1E-05	8.5E-06	1.6E-05	6.4E-06	0.41	2.8E-10	6.4E-11
EF-H 16	172		6.7E-04	0.12	2.1E-05	8.3E-06	1.6E-05	6.2E-06	0.40	2.8E-10	6.3E-11
EF-H 17	196		7.2E-04	0.12	1.2E-05	4.1E-06	7.0E-06	2.0E-06	0.29	1.3E-10	2.0E-11
EF-H 18	222		7.2E-04	0.12	1.0E-05	4.4E-06	5.5E-06	2.3E-06	0.42	9.9E-11	2.3E-11
EF-H 19	240		7.1E-04	0.12	1.2E-05	4.4E-06	6.9E-06	2.4E-06	0.35	1.2E-10	2.4E-11
Uncertainty			4.8E-06	6.3E-04	5.6E-07	1.3E-07	5.6E-07	1.3E-07			

Supplementary table 4.17: EF-I (90 $^\circ\text{C},$ 0.8 % $\text{NH}_3)$

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-I Input	0	1.8E-07	7.1E-04	0.12	4.5E-06	6.5E-06	2.4E-07	1.6E-06	6.40		
EF-I 01	3	1.2E-07	7.0E-04	0.12	1.5E-05	3.9E-06	1.1E-05	-9.9E-07	-0.09	1.7E-10	-8.7E-12
EF-I 02	5	1.6E-07	6.9E-04	0.12	2.1E-05	4.5E-06	1.6E-05	-4.4E-07	-0.03	2.6E-10	-3.8E-12
EF-I 03	8	1.0E-07	7.0E-04	0.12	2.2E-05	4.4E-06	1.8E-05	-4.9E-07	-0.03	2.8E-10	-4.4E-12
EF-I 04	23	4.6E-08	7.4E-04	0.12	2.7E-05	5.2E-06	2.3E-05	2.3E-07	0.01	3.7E-10	2.1E-12
EF-I 05	26	1.8E-08	7.3E-04	0.12	2.6E-05	5.6E-06	2.2E-05	7.0E-07	0.03	3.4E-10	6.1E-12
EF-I 06	28	1.8E-08	7.3E-04	0.12	2.7E-05	5.9E-06	2.3E-05	9.6E-07	0.04	3.6E-10	8.5E-12
EF-I 07	46	4.5E-09	7.2E-04	0.12	2.7E-05	5.9E-06	2.3E-05	9.3E-07	0.04	3.6E-10	8.2E-12
EF-I 08	51	3.2E-08	7.4E-04	0.12	2.8E-05	6.6E-06	2.4E-05	1.6E-06	0.07	3.8E-10	1.4E-11
EF-I 09	54	1.6E-08	7.5E-04	0.13	2.9E-05	6.9E-06	2.5E-05	2.0E-06	0.08	4.0E-10	1.8E-11
EF-I 10	71	4.6E-08	7.0E-04	0.12	3.0E-05	6.8E-06	2.6E-05	1.8E-06	0.07	4.2E-10	1.6E-11
EF-I 11	75	3.8E-08	6.9E-04	0.12	3.0E-05	6.9E-06	2.5E-05	1.9E-06	0.08	4.0E-10	1.7E-11
EF-I 12	76	1.2E-08	7.3E-04	0.12	2.9E-05	7.2E-06	2.4E-05	2.3E-06	0.09	3.9E-10	2.0E-11
EF-I 13	143	2.1E-06	7.3E-04	0.12	2.1E-05	7.4E-06	1.7E-05	2.4E-06	0.15	2.6E-10	2.1E-11
EF-I 14	168	2.5E-07	6.7E-04	0.12	1.9E-05	7.3E-06	1.5E-05	2.3E-06	0.16	2.3E-10	2.1E-11
EF-I 15	175	3.0E-08	7.2E-04	0.12	1.8E-05	8.2E-06	1.4E-05	3.3E-06	0.23	2.2E-10	2.9E-11
EF-I 16	190	1.9E-08	7.0E-04	0.12	1.9E-05	8.0E-06	1.4E-05	3.0E-06	0.21	2.3E-10	2.7E-11
EF-I 17	198	2.2E-08	7.3E-04	0.12	1.9E-05	8.3E-06	1.5E-05	3.4E-06	0.23	2.3E-10	3.0E-11
EF-I 18	213		7.0E-04	0.12	1.6E-05	8.2E-06	1.2E-05	3.3E-06	0.27	1.9E-10	2.9E-11
EF-I 19	223		7.1E-04	0.12	1.6E-05	8.3E-06	1.2E-05	3.3E-06	0.27	1.9E-10	2.9E-11
EF-I 20	238		6.9E-04	0.12	1.5E-05	8.0E-06	1.1E-05	3.1E-06	0.28	1.8E-10	2.7E-11
EF-I 21	245		8.7E-04	0.13	1.6E-05	8.2E-06	1.2E-05	3.3E-06	0.28	1.9E-10	2.9E-11
EF-I 22	311	1.9E-07	7.1E-04	0.12	1.8E-05	1.1E-05	1.4E-05	6.0E-06	0.43	2.2E-10	5.3E-11
EF-I 23	318	8.5E-08	6.2E-04	0.13	1.6E-05	9.1E-06	1.2E-05	4.2E-06	0.34	1.9E-10	3.7E-11
EF-I 24	336	6.0E-08	6.2E-04	0.13	1.6E-05	9.0E-06	1.2E-05	4.1E-06	0.35	1.9E-10	3.6E-11
EF-I 25	343		6.7E-04	0.13	1.3E-05	7.8E-06	9.1E-06	2.8E-06	0.31	1.5E-10	2.5E-11
EF-I 26	360		6.2E-04	0.13	1.2E-05	7.6E-06	8.1E-06	2.7E-06	0.33	1.3E-10	2.3E-11
EF-I 27	366		6.3E-04	0.13	1.2E-05	7.4E-06	8.2E-06	2.5E-06	0.31	1.3E-10	2.2E-11
EF-I 28	413		6.2E-04	0.13	1.2E-05	7.5E-06	7.6E-06	2.5E-06	0.33	1.2E-10	2.2E-11
EF-I 29	479		6.8E-04	0.13	1.1E-05	7.3E-06	7.2E-06	2.4E-06	0.33	1.1E-10	2.1E-11
EF-I 30	506		5.5E-04	0.18	3.2E-05	7.6E-06	2.7E-05	2.7E-06	0.10	4.3E-10	2.4E-11
EF-I 31	837		5.7E-04	0.18	1.3E-05	9.6E-06	8.4E-06	4.7E-06	0.56	1.3E-10	4.1E-11
EF-I 32	839		5.6E-04	0.18	9.0E-06	8.8E-06	4.7E-06	3.9E-06	0.83	7.5E-11	3.4E-11
EF-I 33	914		5.3E-04	0.18	1.8E-05	8.6E-06	1.4E-05	3.7E-06	0.26	2.3E-10	3.3E-11
Uncertainty		9.7E-08	1.7E-05	1.6E-03	6.3E-07	3.0E-07	6.3E-07	3.0E-07			

Supplementary table 4.18: EF-J (0 $^{\circ}\text{C},$ 0.8 % $\text{NH}_{3}\text{)}$

Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-J Input	0	1.6E-07	7.1E-04	0.12	4.6E-07	5.2E-06	-9.5E-06	-8.5E-07	0.09		
EF-J 01	1	2.5E-08	1.6E-04	0.03	1.3E-05	1.4E-06	2.9E-06	-4.6E-06	-1.61	6.5E-11	-5.8E-11
EF-J 02	3	1.1E-07	6.8E-04	0.12	1.2E-04	4.6E-06	1.1E-04	-1.4E-06	-0.01	2.5E-09	-1.8E-11
EF-J 03	19	1.5E-07	7.0E-04	0.12	7.9E-05	6.5E-06	6.9E-05	4.3E-07	0.01	1.6E-09	5.3E-12
EF-J 04	26	1.8E-07	7.1E-04	0.12	9.2E-05	9.3E-06	8.2E-05	3.3E-06	0.04	1.9E-09	4.1E-11
EF-J 05	42	1.7E-07	7.0E-04	0.12	9.2E-05	1.2E-05	8.2E-05	5.9E-06	0.07	1.8E-09	7.4E-11
EF-J 06	45	1.9E-07	7.0E-04	0.12	9.3E-05	1.2E-05	8.3E-05	6.1E-06	0.07	1.9E-09	7.7E-11
EF-J 07	49	5.6E-07	7.0E-04	0.12	9.4E-05	1.2E-05	8.4E-05	5.6E-06	0.07	1.9E-09	7.0E-11
EF-J 08	63	2.0E-07	7.4E-04	0.13	9.5E-05	1.2E-05	8.5E-05	5.9E-06	0.07	1.9E-09	7.4E-11
EF-J 09	74	1.9E-07	7.2E-04	0.12	9.8E-05	1.3E-05	8.8E-05	7.4E-06	0.08	2.0E-09	9.3E-11
EF-J 10	139	2.1E-07	7.6E-04	0.13	9.7E-05	3.0E-05	8.7E-05	2.4E-05	0.27	2.0E-09	3.0E-10
EF-J 11	163	2.4E-07	7.4E-04	0.13	8.4E-05	4.9E-05	7.4E-05	4.3E-05	0.58	1.7E-09	5.4E-10
EF-J 12	187	2.0E-07	7.9E-04	0.14	8.4E-05	4.7E-05	7.4E-05	4.1E-05	0.55	1.7E-09	5.1E-10
EF-J 13	211	1.9E-07	7.3E-04	0.13	7.6E-05	4.6E-05	6.6E-05	4.0E-05	0.60	1.5E-09	5.0E-10
EF-J 14	235	1.7E-07	7.5E-04	0.13	7.8E-05	5.4E-05	6.8E-05	4.8E-05	0.72	1.5E-09	6.1E-10
EF-J 15	336	1.5E-07	6.7E-04	0.12	7.5E-05	7.6E-05	6.5E-05	7.0E-05	1.08	1.5E-09	8.8E-10
EF-J 16	410		6.2E-04	0.13	8.8E-06	7.7E-06	-1.2E-06	1.6E-06	-1.41	-2.6E-11	2.1E-11
EF-J 17	497	1.5E-07	6.7E-04	0.12	4.3E-05	3.2E-05	3.3E-05	2.6E-05	0.78	7.5E-10	3.3E-10
EF-J 18	507	1.4E-07	6.6E-04	0.12	4.0E-05	2.6E-05	3.0E-05	2.0E-05	0.69	6.7E-10	2.6E-10
EF-J 19	521	1.5E-07	6.8E-04	0.12	3.9E-05	2.3E-05	2.9E-05	1.7E-05	0.60	6.5E-10	2.2E-10
EF-J 20	545	1.4E-07	6.7E-04	0.12	3.3E-05	1.8E-05	2.3E-05	1.2E-05	0.53	5.2E-10	1.5E-10
EF-J 21	572	1.5E-07	7.1E-04	0.12	3.2E-05	1.4E-05	2.2E-05	8.4E-06	0.37	5.1E-10	1.1E-10
EF-J 22	577	1.6E-07	7.5E-04	0.13	2.9E-05	1.4E-05	1.9E-05	8.2E-06	0.44	4.2E-10	1.0E-10
EF-J 23	642		6.3E-04	0.13	2.1E-05	8.5E-06	1.1E-05	2.5E-06	0.22	2.6E-10	3.1E-11
EF-J 24	673		6.2E-04	0.13	2.2E-05	9.6E-06	1.3E-05	3.5E-06	0.28	2.8E-10	4.4E-11
EF-J 25	697		6.2E-04	0.13	2.2E-05	8.7E-06	1.2E-05	2.7E-06	0.22	2.7E-10	3.3E-11
EF-J 26	722		6.1E-04	0.13	2.1E-05	8.2E-06	1.1E-05	2.1E-06	0.20	2.4E-10	2.7E-11
EF-J 27	745		6.2E-04	0.13	2.0E-05	8.9E-06	1.0E-05	2.8E-06	0.27	2.4E-10	3.5E-11
EF-J 28	839		6.0E-04	0.13	2.7E-05	1.9E-05	1.7E-05	1.3E-05	0.76	3.8E-10	1.6E-10
EF-J 29	864		5.5E-04	0.18	2.3E-05	1.1E-05	1.3E-05	5.4E-06	0.42	2.9E-10	6.8E-11
EF-J 30	912		4.4E-04	0.14	3.2E-05	3.0E-05	2.2E-05	2.4E-05	1.09	5.0E-10	3.0E-10
EF-J 31	1003		2.9E-04	0.09	3.3E-05	4.0E-05	2.3E-05	3.4E-05	1.52	5.1E-10	4.3E-10
EF-J 32	1055		5.0E-04	0.17	2.2E-05	1.2E-05	1.2E-05	6.1E-06	0.49	2.8E-10	7.6E-11
Uncertainty		9.7E-08	1.7E-05	1.6E-03	6.3E-07	3.0E-07	6.3E-07	3.0E-07			

Supplementary table 4.19: EF-K (23 $^\circ C,$ 0 % $\rm NH_3)$

Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-K Input	0		7.0E-04	0.14	4.5E-07	5.3E-06	-9.5E-06	-8.5E-07	0.09		
EF-K 01	2		5.2E-04	0.15	3.4E-06	3.4E-06	3.1E-06	-2.0E-06	-0.64	4.8E-11	-1.7E-11
EF-K 02	4		4.9E-04	0.14	3.7E-06	4.2E-06	3.4E-06	-1.2E-06	-0.35	5.3E-11	-1.0E-11
EF-K 03	19		4.9E-04	0.14	3.7E-06	4.8E-06	3.3E-06	-5.9E-07	-0.18	5.2E-11	-5.1E-12
EF-K 04	23		4.9E-04	0.14	4.2E-06	4.7E-06	3.8E-06	-6.0E-07	-0.16	5.9E-11	-5.3E-12
EF-K 05	27		4.6E-04	0.14	3.8E-06	4.6E-06	3.5E-06	-7.5E-07	-0.22	5.4E-11	-6.6E-12
EF-K 06	44		4.7E-04	0.14	3.8E-06	4.7E-06	3.4E-06	-6.1E-07	-0.18	5.4E-11	-5.3E-12
EF-K 07	47		4.6E-04	0.14	3.7E-06	4.6E-06	3.3E-06	-7.9E-07	-0.24	5.2E-11	-6.8E-12
EF-K 08	52		4.4E-04	0.13	3.6E-06	4.3E-06	3.2E-06	-1.0E-06	-0.32	5.0E-11	-8.8E-12
EF-K 09	65		4.4E-04	0.13	3.3E-06	4.4E-06	3.0E-06	-9.8E-07	-0.33	4.7E-11	-8.5E-12
EF-K 10	70		4.2E-04	0.13	3.0E-06	4.2E-06	2.6E-06	-1.2E-06	-0.45	4.1E-11	-1.0E-11
EF-K 11	75		4.3E-04	0.13	3.3E-06	4.0E-06	3.0E-06	-1.3E-06	-0.44	4.7E-11	-1.1E-11
EF-K 12	141		4.6E-04	0.14	3.2E-06	4.3E-06	2.8E-06	-1.0E-06	-0.35	4.5E-11	-8.7E-12
EF-K 13	149		4.7E-04	0.14	3.0E-06	4.2E-06	2.6E-06	-1.2E-06	-0.44	4.1E-11	-1.0E-11
EF-K 14	164		4.5E-04	0.13	2.9E-06	4.2E-06	2.6E-06	-1.2E-06	-0.46	4.0E-11	-1.0E-11
EF-K 15	169		6.1E-04	0.15	4.9E-06	4.8E-06	2.4E-06	-1.2E-06	-0.50	3.8E-11	-1.0E-11
EF-K 16	171		6.3E-04	0.16	4.7E-06	5.0E-06	2.3E-06	-1.1E-06	-0.48	3.5E-11	-9.4E-12
EF-K 17	218		6.4E-04	0.16	4.7E-06	5.0E-06	2.2E-06	-1.1E-06	-0.49	3.4E-11	-9.2E-12
EF-K 18	244		6.3E-04	0.16	4.6E-06	5.1E-06	2.1E-06	-9.9E-07	-0.47	3.3E-11	-8.6E-12
EF-K 19	316		6.2E-04	0.15	3.3E-06	4.6E-06	8.3E-07	-1.4E-06	-1.72	1.3E-11	-1.2E-11
EF-K 20	312		6.5E-04	0.16	4.4E-06	4.6E-06	1.9E-06	-1.4E-06	-0.74	3.0E-11	-1.3E-11
EF-K 21	316		6.4E-04	0.16	4.4E-06	4.6E-06	1.9E-06	-1.5E-06	-0.76	3.0E-11	-1.3E-11
EF-K 22	337		3.7E-04	0.15	4.9E-06	3.1E-06	2.4E-06	-3.0E-06	-1.22	3.8E-11	-2.6E-11
EF-K 23	369		3.9E-04	0.16	4.7E-06	3.2E-06	2.2E-06	-2.9E-06	-1.30	3.5E-11	-2.5E-11
EF-K 24	380		4.9E-04	0.20	5.7E-06	3.9E-06	3.2E-06	-2.1E-06	-0.65	5.1E-11	-1.8E-11
Uncertainty			1.7E-05	1.6E-03	6.3E-07	3.0E-07	6.3E-07	3.0E-07			

Supplementary table 4.20: EF-L (150 $^\circ C,$ 8 % NH_3)

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-L Input	0		5.0E-04	0.18	2.9E-05	4.0E-06	2.3E-05	-1.4E-06	-0.06	5.0E-10	-1.7E-11
EF-L 01	2		5.3E-04	0.19	3.1E-05	4.0E-06	2.6E-05	-1.3E-06	-0.05	5.6E-10	-1.6E-11
EF-L 02	17		5.7E-04	0.21	5.5E-05	5.6E-06	4.9E-05	2.7E-07	0.01	1.1E-09	3.3E-12
EF-L 03	20		5.4E-04	0.20	6.0E-05	6.2E-06	5.4E-05	8.8E-07	0.02	1.2E-09	1.1E-11
EF-L 04	25		5.4E-04	0.20	5.7E-05	6.8E-06	5.1E-05	1.4E-06	0.03	1.1E-09	1.7E-11
EF-L 05	41		5.8E-04	0.21	5.4E-05	1.0E-05	4.8E-05	4.6E-06	0.10	1.1E-09	5.7E-11
EF-L 06	45		5.4E-04	0.20	5.0E-05	1.2E-05	4.4E-05	7.0E-06	0.16	9.7E-10	8.5E-11
EF-L 07	51		5.6E-04	0.20	4.8E-05	1.4E-05	4.3E-05	8.4E-06	0.20	9.4E-10	1.0E-10
EF-L 08	63		5.7E-04	0.21	4.8E-05	1.3E-05	4.3E-05	7.2E-06	0.17	9.4E-10	8.8E-11
EF-L 09	68		5.7E-04	0.21	5.0E-05	7.5E-06	4.4E-05	2.1E-06	0.05	9.6E-10	2.6E-11
EF-L 10	72		5.7E-04	0.20	5.0E-05	6.5E-06	4.4E-05	1.2E-06	0.03	9.7E-10	1.5E-11
EF-L 11	139		6.4E-04	0.23	4.3E-05	9.2E-06	3.7E-05	3.9E-06	0.10	8.2E-10	4.7E-11
EF-L 12	146		6.1E-04	0.22	3.5E-05	1.6E-05	2.9E-05	1.0E-05	0.36	6.3E-10	1.3E-10
EF-L 13	162		5.4E-04	0.21	3.0E-05	9.9E-06	2.5E-05	4.5E-06	0.19	5.4E-10	5.5E-11
EF-L 14	168		5.7E-04	0.21	3.2E-05	5.0E-06	2.6E-05	-3.1E-07	-0.01	5.8E-10	-3.7E-12
EF-L 15	193		5.6E-04	0.21	2.7E-05	7.5E-06	2.1E-05	2.2E-06	0.10	4.7E-10	2.7E-11
EF-L 16	218		5.8E-04	0.22	3.5E-05	6.2E-06	3.0E-05	8.9E-07	0.03	6.5E-10	1.1E-11
EF-L 17	242		5.7E-04	0.21	3.6E-05	4.3E-06	3.1E-05	-1.0E-06	-0.03	6.7E-10	-1.3E-11
EF-L 18	335		6.8E-04	0.24	3.6E-05	8.4E-06	3.0E-05	3.0E-06	0.10	6.7E-10	3.7E-11
EF-L 19	402		6.1E-04	0.22	2.2E-05	1.2E-05	1.6E-05	6.8E-06	0.41	3.6E-10	8.2E-11
EF-L 20	384		6.2E-04	0.23	2.8E-05	3.4E-06	2.2E-05	-2.0E-06	-0.09	4.9E-10	-2.4E-11
EF-L 21	402		6.4E-04	0.23	3.3E-05	4.3E-06	2.7E-05	-1.1E-06	-0.04	5.9E-10	-1.3E-11
Uncertainty			1.7E-05	1.6E-03	6.3E-07	3.0E-07	6.3E-07	3.0E-07			

Supplementary table 4.21: EF-M (23 $^\circ C$, 0.8 % $\rm NH_3)$

Sample ID	Hours	Fe mol	к	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-M Input	0		6.3E-04	0.12	1.0E-06	5.5E-06	-9.5E-06	-8.5E-07	0.09		
EF-M 01	2		5.3E-04	0.12	1.5E-05	1.7E-05	1.5E-05	1.2E-05	0.79	3.4E-10	1.5E-10
EF-M 02	5		5.6E-04	0.12	2.1E-05	1.8E-05	2.0E-05	1.2E-05	0.60	4.7E-10	1.6E-10
EF-M 03	20		5.8E-04	0.12	1.9E-05	2.1E-05	1.8E-05	1.5E-05	0.83	4.2E-10	1.9E-10
EF-M 04	25		5.9E-04	0.13	1.6E-05	2.0E-05	1.6E-05	1.4E-05	0.92	3.6E-10	1.8E-10
EF-M 05	29		6.0E-04	0.13	1.5E-05	2.0E-05	1.5E-05	1.4E-05	0.97	3.4E-10	1.8E-10
EF-M 06	44		7.8E-04	0.16	2.5E-05	4.1E-06	2.5E-05	-1.3E-06	-0.05	5.7E-10	-1.6E-11
EF-M 07	54		9.5E-04	0.18	2.5E-05	4.2E-05	2.5E-05	3.6E-05	1.47	5.7E-10	4.6E-10
EF-M 08	69		1.1E-03	0.19	2.5E-05	4.4E-05	2.5E-05	3.9E-05	1.57	5.7E-10	5.0E-10
EF-M 09	76		1.1E-03	0.20	2.5E-05	4.7E-05	2.5E-05	4.2E-05	1.67	5.7E-10	5.3E-10
EF-M 10	142		8.6E-04	0.17	2.4E-05	4.0E-06	2.4E-05	-1.3E-06	-0.06	5.4E-10	-1.7E-11
EF-M 11	243	6.1E-06	4.1E-04	0.09	3.5E-05	6.5E-05	1.0E-05	3.3E-06	0.33	2.3E-10	4.2E-11
EF-M 12	310	6.1E-06	5.3E-04	0.11	3.3E-05	6.4E-05	8.7E-06	1.7E-06	0.19	2.0E-10	2.1E-11
EF-M 13	317	6.1E-06	6.1E-04	0.12	3.3E-05	6.5E-05	8.7E-06	2.4E-06	0.28	2.0E-10	3.1E-11
EF-M 14	317	6.0E-06	6.2E-04	0.12	3.4E-05	6.4E-05	9.2E-06	2.2E-06	0.24	2.1E-10	2.8E-11
EF-M 15	357	6.4E-06	6.3E-04	0.12	3.5E-05	6.7E-05	1.0E-05	4.4E-06	0.43	2.4E-10	5.6E-11
EF-M 16	363	1.8E-07	6.6E-04	0.13	6.0E-06	8.3E-06	5.6E-06	2.9E-06	0.52	1.3E-10	3.7E-11
EF-M 17	411		7.0E-04	0.13	3.5E-06	3.8E-06	3.1E-06	-1.5E-06	-0.49	7.2E-11	-2.0E-11
EF-M 18	477		6.6E-04	0.13	3.6E-06	3.5E-06	3.3E-06	-1.9E-06	-0.58	7.5E-11	-2.4E-11
EF-M 19	524		6.4E-04	0.12	3.6E-06	2.7E-06	3.2E-06	-2.7E-06	-0.83	7.4E-11	-3.4E-11
Uncertainty		3.0E-09	1.4E-06	1.6E-03	2.6E-07	1.7E-07	2.6E-07	1.7E-07			

Supplementary table 4.22: EF-N (0 °C, 0 % NH₃)

Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-N Input	0		6.2E-04	0.15	2.5E-05	4.3E-05	9.0E-09	9.7E-09	1.08		
EF-N 01	4		4.4E-04	0.19	1.1E-05	1.6E-05	-1.4E-05	-2.6E-05	1.88	-3.0E-10	-3.2E-10
EF-N 02	22		4.6E-04	0.19	2.1E-05	3.9E-05	-3.4E-06	-4.1E-06	1.20	-7.3E-11	-4.9E-11
EF-N 03	28		4.4E-04	0.18	4.3E-05	8.4E-05	1.9E-05	4.1E-05	2.20	4.0E-10	4.9E-10
EF-N 04	28		4.5E-04	0.19	6.2E-05	1.2E-04	3.8E-05	8.1E-05	2.14	8.1E-10	9.7E-10
EF-N 05	95		4.9E-04	0.20	7.3E-05	1.4E-04	4.8E-05	9.6E-05	2.00	1.0E-09	1.2E-09
EF-N 06	98		5.0E-04	0.19	1.0E-04	2.0E-04	7.9E-05	1.5E-04	1.93	1.7E-09	1.8E-09
EF-N 07	103		5.2E-04	0.20	1.0E-04	1.9E-04	7.6E-05	1.5E-04	1.90	1.7E-09	1.7E-09
EF-N 08	119		5.5E-04	0.21	1.1E-04	2.0E-04	8.2E-05	1.6E-04	1.95	1.8E-09	1.9E-09
EF-N 09	126		5.4E-04	0.21	1.0E-04	1.9E-04	7.9E-05	1.5E-04	1.88	1.7E-09	1.8E-09
EF-N 10	142		5.4E-04	0.21	9.4E-05	1.8E-04	6.9E-05	1.4E-04	1.97	1.5E-09	1.6E-09
EF-N 11	150		6.8E-04	0.26	1.1E-04	2.1E-04	8.8E-05	1.7E-04	1.93	1.9E-09	2.0E-09
EF-N 12	198		6.3E-04	0.15	9.8E-05	1.7E-04	7.4E-05	1.3E-04	1.74	1.6E-09	1.5E-09
EF-N 13	265		6.1E-04	0.15	1.4E-04	2.3E-04	1.1E-04	1.9E-04	1.69	2.4E-09	2.2E-09
EF-N 14	340		6.1E-04	0.15	1.5E-04	2.6E-04	1.3E-04	2.2E-04	1.70	2.7E-09	2.6E-09
EF-N 15	431		6.1E-04	0.16	1.7E-04	3.0E-04	1.5E-04	2.6E-04	1.72	3.2E-09	3.1E-09
EF-N 16	485		6.5E-04	0.16	1.2E-04	2.1E-04	9.7E-05	1.6E-04	1.68	2.1E-09	2.0E-09

Supplementary table 4.23 EF-O (0 °C, 8 % NH ₃)
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Sample ID	Hours	Fe mol	К	Na	Si	Mg	d Si	d Mg	Mg/Si	r Si	r Mg
EF-O Input	0		1.6E-02	0.11	6.3E-06	1.8E-06	-3.6E-05	-2.1E-05	0.60		
EF-O 01	3		5.1E-04	0.10	9.3E-05	7.9E-05	5.1E-05	5.6E-05	1.10	1.2E-09	7.1E-10
EF-O 02	13		6.0E-04	0.12	5.8E-05	1.7E-05	1.6E-05	-5.9E-06	-0.37	3.7E-10	-7.6E-11
EF-O 03	25		4.8E-04	0.11	6.6E-05	7.3E-05	2.4E-05	5.0E-05	2.13	5.4E-10	6.4E-10
EF-O 04	27		5.9E-04	0.12	3.8E-05	1.5E-05	-4.3E-06	-8.1E-06	1.88	-9.9E-11	-1.0E-10
EF-O 05	42		4.3E-04	0.10	5.5E-05	6.4E-05	1.3E-05	4.1E-05	3.14	3.0E-10	5.3E-10
EF-O 06	51		6.2E-04	0.13	1.4E-04	2.1E-05	1.0E-04	-2.0E-06	-0.02	2.4E-09	-2.5E-11
EF-O 07	70		4.4E-04	0.10	7.6E-05	6.9E-05	3.4E-05	4.6E-05	1.33	7.9E-10	5.9E-10
EF-O 08	75		4.9E-04	0.11	7.6E-05	7.4E-05	3.4E-05	5.0E-05	1.49	7.8E-10	6.5E-10
EF-O 09	139	7.6E-06	5.1E-04	0.11	4.3E-05	8.1E-05	8.2E-07	5.8E-05	70.24	1.9E-11	7.4E-10
EF-O 10	241		6.3E-04	0.13	1.0E-04	2.1E-05	6.2E-05	-1.6E-06	-0.03	1.4E-09	-2.1E-11
EF-O 11	307		6.2E-04	0.12	8.7E-05	1.9E-05	4.5E-05	-3.8E-06	-0.09	1.0E-09	-4.9E-11
EF-O 12	355		6.3E-04	0.13	4.0E-05	1.8E-05	-2.4E-06	-4.7E-06	1.94	-5.6E-11	-6.1E-11
EF-O 13	361	9.2E-07	6.4E-04	0.13	9.0E-05	2.0E-05	4.8E-05	-2.6E-06	-0.05	1.1E-09	-3.4E-11
EF-O 14	409		5.2E-04	0.11	6.4E-05	8.7E-06	2.2E-05	-1.4E-05	-0.67	5.0E-10	-1.8E-10
EF-O 15	475		5.8E-04	0.12	7.8E-05	1.3E-05	3.6E-05	-1.0E-05	-0.28	8.4E-10	-1.3E-10
EF-O 16	523		6.4E-04	0.13	8.3E-05	2.1E-05	4.1E-05	-2.3E-06	-0.06	9.4E-10	-2.9E-11
Uncertainty		3.0E-09	1.4E-06	1.6E-03	2.6E-07	1.7E-07	2.6E-07	1.7E-07			



CHAPTER 5

Experimental insights into ammonia-olivineorganic interaction and applications to Enceladus and exploration of icy worlds

RESEARCH QUESTION

At the seafloor-hydrothermal conditions in icy ocean worlds, do ammonia and olivine facilitate prebiotic reactions by stabilizing or catalyzing complex organic molecules?

<u>Chapter 5. Experimental insights into NH₃-olivine-organic alteration: applications to Enceladus</u> <u>and exploration of icy worlds</u>

In addition to inorganic chemistry, the Cassini mission found organic compounds in particles emitted from Enceladus that are comparable to those found in carbonaceous chondrites (Waite et al., 2009). Carbonaceous chondrites can contain as much as 2-3 % by mass of organic carbon, including hundreds of different types of organic compounds (Sephton, 2002). In terrestrial systems, these compounds are considered a possible rich source of prebiotic chemistry in seafloor hydrothermal vents (Gold, 1985; Sephton and Hazen, 2013). The presence of an NH₃-bearing ocean in Enceladus (Waite et al., 2009), in addition, suggests interesting possibilities for prebiotic chemistry in hydrothermal vents at its seafloor. The impact of combined mineral co-alteration and NH₃-rich aqueous fluids on the stability and polymerization of these organic compounds inherited from carbonaceous chondrites is then of particular interest in evaluating the habitability within the hydrothermal vents at the Enceladus' seafloor. However, little experimental data exist that explore the potential effects of an NH₃-water ocean on mineral and organic co-alteration in hydrothermal environments. Specifically, to identify organic compounds that were altered in hydrothermal vents, it may be useful to characterize the chemical signatures of chondritic organic material that were exposed to these environments. This chapter presents the results of two experiment sets that test the stability of organic compounds in the presence of NH₃, olivine, or a combination of the two. A first experiment set tested glycine alteration in a dilute salt-water solution as a monomolecular proof-of-concept that olivine and NH₃ may have a combined effect on the alteration of nitrogen-bearing compounds. These experiments reacted a glycine-salt-water solution with NH_3 and/or olivine in batch reactors at 150 $^{\circ}$ C for 45 days and measured glycine and inorganic species concentrations in solution. Initial results from this experiment set show that glycine is more stable in solution with NH_{3} , but that this effect is diminished in the presence of olivine. A second experiment set adapted the batch experiment approach to observe the alteration of a complex chondrite-like organic matter synthesized to simulate a pristine chondritic organic matter. This second experiment was not designed to quantify concentrations of specific molecules, but rather to statistically define alteration signatures of a complex organic mixture from semi-quantitative ultrahigh-resolution mass spectrometry. These kinds of results may be compared to mass spectrometry measurements from Cassini, as well as potential future missions. The second experiments reacted a synthesized chondrite organic matter (SCOM) in pure water with NH₃ and/or olivine for 70 days. Soluble organic compounds were then extracted and analyzed by high-resolution mass spectrometry (Orbitrap) to statistically characterize the change in size and complexity of the organic constituents. From initial interpretations of the analyses of the organic by-products, we see specific compounds that occur only in experiments with olivine. These compounds then make good target compounds for identifying water-mineral-organic interaction in hydrothermal environments, and may inform interpretation of data collected by the Cassini mission and in planning future missions to icy ocean worlds.

5.1 Introduction

Data collected by the Cassini-Huygens mission returned several surprising observations from Saturn's moon Enceladus. First, the mission returned geophysical and geochemical evidence of an NH₃-bearing aqueous ocean beneath the icy crust (Čadek et al., 2016; Postberg et al., 2011, 2009; Thomas et al., 2016; Waite et al., 2009). Second, molecular hydrogen and silica nanoparticles emitted from Enceladus were further interpreted as evidence of hydrothermal activity within the internal ocean (Hsu et al., 2015;

Postberg et al., 2013; Sekine et al., 2015; Waite et al., 2017). Third, in addition to inorganic chemistry, the Cassini mission found organic compounds in particles emitted from Enceladus, comparable to those found in in carbonaceous chondrites (Waite et al., 2009). In-situ mass spectra analyses of Saturn's E-ring, sourced from Enceladus' emissions, found evidence of break-up compounds consistent with hydrocarbons (Postberg et al., 2008) as well as macromolecular organic compounds of up to 200 atomic mass units (Postberg et al., 2018). Because these organic compounds were found embedded in the same populations of E-ring ice grains that also host salts, this in-situ observation was interpreted as promising evidence of complex organic compounds being hosted in Enceladus' ocean. More recent analyses of the measurements taken from Enceladus' plume emissions by Cassini's Cosmic Dust Analyzer (CDA) identified aromatic nitrogen- and oxygen-bearing compounds of low atomic mass (Khawaja et al., 2019).

The evidence of potential hydrothermal activity on Enceladus is exciting for its astrobiological implications, as hydrothermal systems have been proposed as a potential environment for the emergence of life on Earth (Hazen and Sverjensky, 2010; Holm, 1992; Miller and Bada, 1988). Originof-life theories are generally based on the need for environments with both water and reduced organic species (Martin et al., 2008). On Earth as well as on icy worlds, low-temperature seafloor hydrothermal vents are considered among the likely environments that might meet these criteria. The serpentinization reactions that oxidize iron in primary ultramafic minerals provide a source of chemical and thermal energy (Truche et al., 2020) and also a source of reducing fluids and H₂ that may stabilize the reduced carbon of organic molecules (Holm and Andersson, 1995). In evaluating habitability of the icy satellites, it is then of interest to know the co-alteration products of minerals and organic compounds of carbonaceous meteorites in the NH₃-bearing hydrothermal fluids as may exist on Enceladus.

The importance of NH_3 as a prebiotic ingredient is well-recognized, as a parent of the amine group (- NH_2) that defines amino acids. While amino acids generally tend to decompose in hydrothermal conditions (Bada et al., 1995), the presence of NH_3 may increase the stability of certain organic molecules, specifically amino acids (Cox and Seward, 2007; Klingler et al., 2007). NH_3 is a common byproduct of amino acid alteration, and it follows that solutions enriched in NH_3 may have higher equilibrium concentrations of amino acids. In more favorable conditions (i.e. more reducing, cooler, or with high concentrations of precursor compounds), NH_3 may react to form amino acids as well as stabilize them. Indeed, the original hypotheses of submarine hydrothermal systems as a potential origin site of life on Earth proposed a sequence of reactions that started with synthesis of amino acids from NH_3 , CH_4 , and H_2 (Corliss et al., 1981; Fox, 1971). Numerous studies have characterized the hydrothermal synthesis of amino acids via reactions between NH_3 or NH_4^+ and commonly occurring simple carbon compounds, such as formaldehyde (Hennet et al., 1992; Marshall, 1994; Oró et al., 1959), cyanide (Ferris et al., 1978; Lowe et al., 1963), and CH_4 (Yanagawa and Kobayashi, 1992).

As water-soluble prebiotic molecules (such as amino acids and precursors) suffer the problem of extreme dilution if considered to exist in a liquid water ocean, the presence of minerals and inorganic constituents are considered valuable as mechanisms for concentrating as well as synthesizing organic molecules (Deamer and Damer, 2017; Oparin, 1938; Russell et al., 2014). The role of clays in adsorbing and concentrating organic species is well known (Feuillie et al., 2013; Mortland, 1970; Pedreira-Segade et al., 2016) and may even promote amino acid synthesis in the presence of NH₃ (Ménez et al., 2018; Vinogradoff et al., 2020). Other proposed pathways of abiotic organic synthesis in natural systems are

Fischer-Tropsch-type (FTT) reactions (Hazen and Sverjensky, 2010; McCollom and Seewald, 2007, 2006; Potter et al., 2004) that form hydrocarbons from hydrogen and carbon compounds in aqueous solutions:

$(2n+1)H_2 + nCO \rightarrow CnH(2n+2) + nH_2O$	Equation 5.1
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2$	Equation 5.2

Field studies at both mid-oceanic ridges and off-axis hydrothermal vents (Charlou et al., 2010; Proskurowski et al., 2008) have concluded that the fluids at these vents carry abiotic CH₄ and straightchain hydrocarbons that may have been formed by FTT reactions (including the Fischer-Tropsch reaction of Eq. 5.1 and the Sabatier reaction of Eq. 5.2). On recent experimental study seeking to recreate hydrothermal conditions on meteorites found that in NH₃-water solutions, hydrothermal alteration of aldehydes resulted in longer alkyl-chain reaction products when the solution was reacted with olivine than without (Naraoka et al., 2015). This suggests that olivine specifically has a previously unexplored mechanism that affects the alteration and synthesis of organic molecules in NH₃. Select analyses of organic alteration of complex organics in NH₃ from chondrite histories, however, have suggested that co-alteration of complex organic matter (OM) in with mineral assemblages in fact favors decomposition reactions over polymerization (e.g. Botta et al., 2007; Herd et al., 2011).

To evaluate the stabilization and potential synthesis reactions of organic matter in an NH₃-bearing hydrothermal system, we conducted two sets of experiments simulating organic reaction in the $H_2O\pm NH_3\pm olivine$ system. First, we completed a batch experiment test of glycine alteration in NH₃-saltwater solutions with and without olivine as a monomolecular proof of concept. Glycine was chosen as a simple amino acid that is known to occur naturally in carbonaceous chondrites (Sephton, 2002). Second, we designed and completed an experiment set to explore alteration of synthetic chondrite organic material (SCOM) in aqueous solutions, with NH₃ and/or olivine. The purpose of these experiments was to identify alteration signatures of a complex organic matter, as may have been inherited in icy worlds from chondritic parent bodies. Using high-resolution mass analysis, we can compare the resulting ~10,000 peaks of mass spectra to molecules that can be detected in the emissions of Enceladus from the data collected by Cassini or even by future missions. These results could then be used to constrain chemical alteration histories on chondrites as well as to identify molecules that may indicate active water-rock interaction in icy worlds.

5.2 Glycine alteration experiments

5.2.1 Methods

A monomolecular glycine alteration experiment (E-Gly: Enceladus-seawater Glycine) was performed in the presence of NH_3 and olivine. The purpose of this experiment was to refine analytical methods at ISTerre and test the hypothesis that NH_3 and olivine in combination affect organic molecule alteration. For this experiment set, small batch experiments were completed reacting glycine at 150 °C for 6 weeks, with and without olivine, either in a dilute Enceladus-seawater solution free of ammonia (pH = 9.2) or in the same seawater solution additionally containing 0.8 wt % NH_3 (pH = 10.8).

The experiments used San Carlos olivine ($Mg_{1.83}Fe_{0.17}SiO_4$), hand-selected to be free of visual defects or inclusion of secondary minerals. These grains were then crushed by a agate rotary mortar and sieved to the 50-125 µm size fraction. After sieving, the grains were sonicated repeatedly in an ethanol bath

where the supernatant was periodically poured off until the supernatant was clear (at least 5 washes), and then dried in an oven at 50 °C. Surface area analyses (Kr BET) of the cleaned olivine yielded a surface area of 0.0087 (\pm 0.006) m² g⁻¹.

The dilute Enceladus-seawater solutions were synthesized by adding analytical-grade salts to Milli-Q[®] water (18 M Ω cm) degassed with argon such that concentrations (mol L⁻¹) were equal to: [NaCl] = 78 × 10⁻³, [KCl] = 0.6 × 10⁻³, [HCO₃] = 39 × 10⁻³. The salt concentrations were selected to be within the range of solution chemistries in Enceladus' ocean estimated in thermodynamic models by Zolotov (2007) and from chemical analyses of salts in Saturn's E ring (Postberg et al., 2011, 2009). Glycine was added to selected solutions to equal an initial concentration of 60 mmol. In NH₃ experiments, suprapure liquid NH₃ was additionally included so that the concentration was equal 0.47 mol L⁻¹ (0.8 wt %). In experiments with olivine, the water/rock mass ration was equal to 10. Reactants were prepared and sealed in a Teflon-lined 6mL Parr bomb in a glove box under argon ([O₂] <1 ppm). The reactors were then placed in an oven at 150 ^oC for 6 weeks (Fig. 5.1).



Fig. 5.1: Parr bombs containing glycine in a dilute salt water ± olivine, NH₃.

After reaction, the solutions were sampled, filtered (0.45 μ), and acidified with 30% suprapure nitric acid. The acidified samples were analyzed for major cations with matrix-matched standards using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Varian 720ES, ISTerre analytical geochemistry platform, Univ. Grenoble Alpes). The solid fraction was then separated by vacuum filtration and rinsed sequentially with Milli-Q and ethanol. Glycine concentrations were analyzed after reaction by high performance liquid chromatography (HPLC: Département de Chimie Moléculaire, Univ. Grenoble Alpes). Because the samples were acidified and measured by anion exchange, all dissolved glycine is measured. The speciation of glycine in solution (discussed below) is not measured by this method.

5.2.2 Results and discussion

Initial results show that some glycine remained in all experiments after 45 days (6 weeks) of reaction. Generally, higher concentrations of glycine remained in experiments with NH_3 ; this effect is much more pronounced in experiments without olivine (Fig. 5.2). Replicate experiments show remarkably similar results in the amount of glycine remaining after reaction at each experimental condition, indicating that the results from these conditions are reproducible. In general, the experiments with NH_3 and without olivine have approximately a 50 % reduction in the glycine concentration from (from 60 to ~30 mmol L⁻¹), while all other experimental conditions result in an 90-80 % reduction, or final glycine concentrations of 6-10 mmol L⁻¹.

After reaction, Si and Mg also increase in the experiments with olivine, consistent with olivine dissolution during the experiments. In the experiments with olivine, final Si concentrations in experiments with NH₃ are over twice that of Si concentrations in experiments without NH₃. Slightly higher concentrations of Si also exist in the final experiments with NH₃ and no olivine, from Si contamination during preparation of the solutions. The silica and magnesium concentrations at the end of the experiments are also similar in replicate experiments.

ID	Set #	Olivine (g	$\mathbf{NH}_3 \mathbf{mm}$	mL	Glycine	K	Mg	Na	Si
)	ol L ⁻¹	solution					
EGly 1	1	0.99	470	6.02	9.89	1.16	0.006	99.15	0.9
									8
EGly 5 2	2	0.62	470	6	8.7	1.06	0.009	101.38	0.6
	-								2
EGly 2	1	0.62		6.04	6.07	1.14	0.013	99.18	0.3
									6
EGly 6	2	0.61		6.07	6.99	0.92	0.028	102.28	0.2
									6
EGly 3	1		470	5.93	28.85	0.74	0.002	99.78	0.0
									4
EGly 7	2		470	6.06	30.91	0.71	0.002	103.02	0.0
-									3
EGly 4	1			6.02	6.11	0.72	0.003	101.12	0
EGly 8	2			6.02	6.34	0.7	0.004	99.79	0

Table 5.1 Glycine alteration experiments carried out at 150°C for 45 days

Set # indicates replicates: set 2 are replicates of set 1. Glycine, K, Mg, Na and Si concentrations are in mmol L⁻¹ after reaction. '--' indicates a null value, where no reactant (olivine or NH₃) was present in the experiment.

 NH_3 is a common reaction product of glycine decomposition (Klingler et al., 2007), for example as by the following conversion of glycine to glycolic acid:

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NH_3CH_2COOH (glycine) + H_2O \rightarrow HOCH_2CO_2H (glycolic acid) + NH_3 Equation 5.3
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The conservation of glycine in the NH_3 -water solution experiments was then expected due to the excess of the reaction product NH_3 . However, this does not explain the why glycine is not conserved at similar concentrations in the experiments with both NH_3 and olivine. In experiments without NH_3 , no such difference in glycine concentration is seen between experiments with and without olivine. Considering the question of why there is an effect of olivine on glycine concentrations in NH_3 -bearing solutions, but no significant effect of olivine in non- NH_3 -bearing solutions, may then be used to deduce what the effect itself might be.

A major difference between the two solutions that may explain the selective role of olivine is the pH. The speciation of glycine in solution at 20 °C can be summarized as follows:

⁺ NH ₃ CH ₂ COOH (glycinium cation) \rightleftharpoons ⁺ NH ₃ CH ₂ COO ⁻ + H ⁺ (pK _a = 2.34)	Equation 5.4		
⁺ NH ₃ CH ₂ COO ⁻ \Rightarrow NH ₂ CH ₂ COO ⁻ (glycinate) + H ⁺ (pK _b = 9.78)	Equation 5.5		

The pH at pK_b (9.78) falls between the pH of the seawater solution without NH_3 (9.2 at bench) and that of the NH_3 -seawater solution (10.8 at bench). The speciation of glycine during our experiments may then favor the glycinate anion in the NH_3 -bearing solutions (at higher pH), and the glycine zwitterion in non- NH_3 -bearing solutions. This suggests a reaction specifically between olivine (and/or its dissolution products) and the glycinate anion that does not occur between olivine and glycine in its neutral (or more accurately, zwitterionic) form. Glycinate is well known to act as a bidentate ligand with metal ions (including Mg and Fe, see e.g. Smith et al., 2004) to form metal chelates. The irreversible formation of Mg- or Fe-chelates could then at least partly explain the decrease of glycine concentrations in olivine-bearing experiments, where Mg and Fe is present from olivine dissolution. Alternatively, the results could suggest that olivine (and/or its dissolution products) interact with NH_3 in a way that decreases its efficiency at stabilizing glycine, although no such interaction between the inorganic constituents of olivine and NH_3 or NH_4^+ has been identified so far.



Fig 5.2: glycine, Si and Mg concentrations in mmol L⁻¹ after reaction at 150 ^oC for six weeks. Both graphs are ordered from lowest to highest glycine concentrations in final solution. Orange star on the Si axis indicates the approximate Si concentration (0.05-0.08 mmol L⁻¹) in the 150 ^oC inorganic olivine dissolution experiments of Chapter 4.

Another notable result from the glycine reaction experiments is that in experiments with olivine, the final concentrations of Si are significantly (> 2x) greater in the experiments with NH_3 . This is in contrast to the results of inorganic olivine dissolution experiments discussed in Chapter 4, where at 150 °C, Si concentrations are lower in experiments with NH_3 (and higher pH) than in experiments with no NH_3 (and lower pH) after ~ 6 weeks reaction time (see for example Fig. 4.5). We propose that the presence of glycine enhances olivine dissolution or precludes secondary mineral precipitation under alkaline pH condition. This demonstrates that glycine may in fact interact with olivine surface or its dissolution (solid and aqueous) by-products. We note that the presence of organic ligands is known in some cases to increase olivine dissolution rates (e.g. Grandstaff, 1986; Hänchen et al., 2006; Wogelius and Walther, 1991), but as all of the experiments in this set have the same duration with no intervening samples, we are not able to draw conclusions about kinetic processes occurring in our experiments. Future work to conclude these experiments is planned to characterize surface alteration of the olivine through FEB-SEM or TEM analyses.

5.3 Synthetic chondritic organic matter alteration experiments

The second experimental series explored hydrothermal alteration of a synthesized complex organic matter. The purpose of these experiments was to identify the signature of organic alteration by-products in NH_3 -rich aqueous solutions, and especially to identify signatures of hydrothermal coalteration of organic compounds with minerals. The approach of this experimental series differs from the glycine experiments (above) by the use of gold capsule reactors, using a salt-free pure water solution to simplify organic compound analyses, and heating the reactants to 100 °C to be directly comparable to previous studies (at CRPG Nancy, unpublished) with the goal of building a comprehensive dataset between laboratory approaches.

5.3.1 Methods: synthetic chondrite organic matter alteration experiments

Materials. Synthetic chondritic organic material (SCOM) was synthesized by plasma ionization of a H_2 -CO gas mixture (e.g. Kuga et al., 2015). Briefly, the SCOM was synthesized by flowing the reactant gasses through glass vacuum tubes to a quartz reactor, where microwave energy (2.45 GHz) is applied from the outside of the reactor to ionize the gas ("Nebulotron" system, CRPG, Nancy). The ionized gas rapidly polymerizes on cooling, condensing on the reactor walls. The condensed solid is then recovered by disconnecting the quartz reactor and gently scraping the interior. No N_2 was used in the gas mixture in order to synthesize a low-nitrogen SCOM similar to that found in chondrites.

The experiments used San Carlos olivine (Mg_{1.83}Fe_{0.17}SiO₄) of the 50-125 μ m size fraction with a surface area of 0.0087 (± 0.006) m² g⁻¹ (Kr BET), prepared as described in section 5.2.1 above. Solutions are comprised of MilliQ water degassed with argon for 2 hours and, in NH₃ experiments, suprapure liquid NH₃ added so that the final concentration was 4.7 mol L⁻¹ (~ 10 wt %). Aside from the reactor type and nature of the organic reactant, these experiments differ from the glycine alteration experiments discussed in section 5.2 in several ways. First, a higher concentration of NH₃ (4700 instead of 470 mmol L⁻¹, or 8 wt % rather than 0.8 wt %) was used in these experiments to amplify the signal of any NH₃-SCOM alteration products. No salts were added to the solutions in this experiment, to ensure exclusion of any analytical signal from inorganic salts during Orbitrap analyses of the samples. In addition, the lower temperature of 100 °C was chosen to be consistent with low-temperature hydrothermal systems, in order to promote slower decomposition of the SCOM, and to be comparable with initial hydrothermal alteration experiments of similar SCOM in water, performed at CRPG, Nancy (Bekaert, Touche; personal communication).



Fig 5.3: "Nebulotron" gas ionization system in use. The quartz reactor is visibly illuminated from the radiation applied to the exterior of the reactor.

Design and protocol. Reactants were combined in gold capsules and heated at 100 °C for 6 weeks. Capsules were annealed in flame for 2-3 minutes to prepare the gold for welding and to combust any organic residue on the metal. The Au capsules (volume of ~0.2 mL) were filled under anoxic condition inside a glove box under Ar ($[O_2] < 1$ ppm), and their extremities were pinched. The capsules were immediately welded outside the glove box and placed inside an oven at 90°C overnight to ensure the absence of leakage (the mass of the capsules was weighed before and after heating). Capsules were heated in a titanium reactor with a water-saturated argon headspace. The reactor pressure was maintained at 25 bars to allow leakage detection during the run. Because the gold capsules are malleable, this also maintained the interior of the capsules at 25 bars during the experiments. Duplicate capsules were run for each of the combinations including Nebulotron organic material in an H₂O-NH₃ solution, H₂O-NH₃ solution with olivine, and H₂O with olivine (Table 5.2). A single capsule was also run containing Nebulotron material and H₂O-NH₃ and olivine (Table 5.2).

After reaction within the titanium reactor, the gold capsules were recovered and their external surfaces were rinsed with ethanol prior to opening in order to remove external organic contaminants. Specific olivine-bearing capsules selected for gas chromatography (GC) analyses of H₂, CO, CO₂, and CH₄ were then processed by the method given below. After GC analyses, all capsules were rinsed again in a 30-70 distilled methanol-toluene mixture. The capsules were then cut open and the solution was allowed

to evaporate under argon for 3 days to concentrate the soluble (dissolved) and insoluble OM in the solid fraction. Each of the gold capsules, with the solid fraction of the reactants, were then placed within a centrifuge tube with distilled methanol-toluene and soaked for 1 week at 4 °C to extract the soluble OM into the solvent. Tubes were then centrifuged and solvent extract was sampled for analysis. The two "blank" capsules underwent the same procedure and the extract from these capsules was analyzed for contaminants from the gold, olivine, and solutions. After analyses of the methanol-toluene extract, the remaining extract was evaporated and the solid fraction (olivine+OM) recovered.

Analyses. The pure San Carlos olivine was analyzed by XRD prior to reaction. The masses used in each experiment (~0.02 g, Table 2) were too small for reliable post-reaction XRD analysis. Olivine grains from selected experiments were imaged at the μ m-scale both by secondary (SE) and backscattered (BSE) electrons (SEM: TESCAN VEGA3, ISTerre, Grenoble). Gas chromatography (GC) analyses were done on the experiments containing olivine to identify in-situ H₂, CO, CO₂, and CH₄ production or release during the experiments. The Au capsules were weighed to ensure the absence of leakage, and immediately analyzed for gas concentration. A syringe equipped with an indenter and a three-way valve was used to pierce the gold capsules and release the produced gas. The syringe was previously flushed with Ar to remove air. The gas mixture (Ar + released gases) was sampled through a septum placed on the three-way valve and analyzed by gas chromatography for H₂, CO₂ and CH₄. The details of this procedure are described by Malvoisin et al. (2013) (Fig. 5.4).

Ion-trap high-resolution mass spectrometry measurements were done on the methanol-toluene extract from each capsule, along with extracts from the unreacted SCOM and a process blank (Thermo LTQ Orbitrap XL instrument coupled with an Electrospray ionization (ESI) source. IPAG, Univ. Grenoble Alpes). The direct infusion technique was used to identify protonated compounds in the m/z range of 150–800. The positive ions were analysed with a resolving power of $m/\Delta m \sim 100000$ at m/z = 400u.



Fig 5.4: Gas-tight syringe fitted for puncturing gold capsules and sampling the gas for analysis.

Cable 5.2 Synthetic chondritie	c organic matter ex	periments
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ID	NH₃ mmol L⁻¹	Solution (µL)	Olivine (mg)	SCOM (mg)	Leak ?	H ₂ 1	CO2 2
Blank_NH ₃	4700	76			Yes		
Blank_NH ₃ _Ol	4700	76	7.71				
Neb_Ol_2		103	18.79	2.00		1.5×10 ⁻⁵	0
Neb_Ol_1		103	20.14	2.24	Yes	0	5.3×10 ⁻⁴
Neb_NH ₃ _Ol_1	4700	103	20.35	2.26	Yes		
Neb_NH ₃ _Ol_2	4700	103	21.77	2.17		1.13×10-6	0
Neb_NH ₃ _1	4700	103		2.32			
$Neb_NH_{3}_2$	4700	103		2.32	Yes		
$Neb_H_2O_1$		103		2.36			

Reactants in each gold capsule. "—" values indicate no value. "Blank" sample IDs indicate gold capsule reactors with no SCOM. NH_3 is noted where the solution includes NH_3 : where NH_3 concentration is not listed the solution is pure degassed MilliQ water. SCOM refers to the synthesized organic matter used in the experiments. Where the capsule lost weight or otherwise showed apparent signs of leakage it is marked in the "Leak" column. Two GC analyses were done for each measured sample, only H_2 and CO_2 results are reported (total moles within each capsule at the time of analysis). "0" indicates where a sample was analyzed and was below detection limits for the GC; "—" indicates where no sample was taken.

5.3.2 Initial results and discussion: synthetic chondrite organic matter alteration experiments

Orbitrap analyses of the unreacted SCOM also show that despite using no N_2 in the initial gas mixture and storage under argon, a fraction of the sample included N-bearing organic species. As the Nebulotron synthesis process relies on first evacuating air from the synthesis chamber before flushing the entire system with the synthesis gas mixture (CO and H₂), the nitrogen in the initial samples may be a result of imperfect vacuum during synthesis or adsorption during storage.

Comparison of the sample weights pre- and post-experiment show that at least three of the samples had lost mass greater than attributable to measurement error, indicating weld failure during the experiments and loss of water and/or reactants from the capsules. These samples are indicated in Table 5.2 and their results are excluded from the following discussion. The samples selected for further analysis and discussed in the rest of the chapter are then: Neb_H₂O_1, Neb_NH₃_1, Neb_Ol_2, and Neb_NH₃_Ol_2. However, we note that the results from the leaked experiments were similar to their respective replicate experiments, giving confidence that the results from the reported samples are replicable. This also implies that although mass may have been lost from the interior, the reactions occurring within the capsules were not significantly affected by the mass loss. Water-organic reactions could certainly have still occurred within a capsule with a failed weld, as the water in the reactor ensured that the argon atmosphere inside the reactor was saturated with water vapor at 100 °C and the interior of the gold capsules would not have completely dehydrated under these conditions.

During GC analyses (calibrated for H_2 , CO, CO₂, and CH₄), only H_2 and CO₂ were identified in any sample. H_2 was measured in samples from two capsules, and CO₂ was measured from a third capsule which is attributed to exposure to air (leak) that occurred during sampling (Table 2). These results demonstrate an initial proof of concept for analyses by this method. Future work using this method could be used to identify and quantify sources of H_2 release (i.e. from organic decomposition or from olivine hydrolysis) in organic and mineral co-alteration experiments.

After reaction, the olivine showed alteration features at the surface. To identify alteration that occurred during the experiments, we focused the investigation on clean, freshly-fractured olivine surfaces (Fig. 5.5a). Dissolution features were visible in several olivine grains from Neb_NH₃_Ol_1 (reacted with NH₃) at edges of the fractured regions (Fig. 5.5b). Similar dissolution textures were observed in the replicate sample reacted with NH₃ and SCOM, as well as the olivine reacted in pure water and SCOM (not shown). In addition to dissolution textures, we also identified possible secondary minerals at the surface of at least one olivine grain from Neb_NH₃_Ol_1 (Fig. 5.5c). These possible secondary alteration products appear morphologically similar to smectite or other phyllosilicates identified at olivine surfaces after alteration (e.g. Chapter 4 of this manuscript). BSE analyses of the feature on the reacted samples did not return a chemical signature distinct from olivine, which is not surprising given their minute size and the interaction volume of the BSE measurements. Due to the mechanical damage introduced to the SCOM during preparation (see Section 5.3.1, Materials) no unambiguous alteration or dissolution textures were identified in the solid organic compounds by SEM.



Fig 5.5: SEM images of the olivine surface. a. Unreacted olivine, showing a clean fractured face characteristic of the olivine grains before reaction. b. Insoluble organic matter (IOM) and dissolution textures at the olivine surface (Neb_NH₃_Ol_1). c. Possible secondary minerals forming at the surface of olivine (Neb_NH₃_Ol_1), seen as sheet-like structures overlaying the rippled fracturing features at the olivine surface.

The results of the Orbitrap analyses reports the molecular masses and semi-quantitative intensities of thousands of species. Using these highly accurately determined molecular masses and charges, a chemical formula could be assigned to the individual peaks of the mass spectra. The assigned chemical formulas were then used to infer a number of properties about the sample: the number of C, H, N, and O atoms in a each of the molecules; the amount of unsaturation (number of double bonds) those molecules possess; and how distributions of these species populations vary from one sample to another by means of statistical analyses. While errors due to weighing and dilution means that quantitative comparisons of the concentrations of select compounds are not supported at this step of the data reduction, we can characterize overall differences between the samples and the unreacted SCOM by focussing on distributions of compounds relative to the entire sample.

First, we can compare the number of nitrogen atoms contained in the compounds in each SCOM sample to identify any effect of NH_3 on synthesizing N-bearing compounds. The number of C, H, N, and O atoms in the molecules at each peak are identified by fitting the mass of the peak to known atomic weights. The initial results show that the percentage of molecules from each sample that have more than one N in their formulas increases in experiments after reaction with NH_3 . However, this preliminary result has not been examined with respect to the possibility of post-experimental amination (adduction of an amine group) of organic compounds during the fluid evaporation stage of sample preparation (see section 5.3.1, "Design and protocol"), or for matrix effects of dissolved NH_4^+ on the analysis itself (see also section 5.3.3, "Ongoing work").

Molecules in the post-reaction samples where N atoms = 1 (including peaks from compounds with one nitrogen atom) were then evaluated in terms of their overall saturation. This was achieved by calculating the double-bond equivalent (DBE) and comparing the resulting data from each experiment to the initial sample. The DBE is an index for molecular unsaturation, calculated by the following relation:

$$DBE = C + 1 - \frac{H}{2} + \frac{N}{2}$$
 Equation 5.4

where C is carbon, H is hydrogen, and N is nitrogen. Traditionally the relation also includes a term subtracting the total halides; however, as no such species were identified in our samples, this term

equals zero and is not included in the calculations. The value of the DBE then represents the number of double bonds or rings present in the organic compound in question. Note especially where that DBE = 0 this indicates saturated hydrocarbons.

Regressing the DBE over the C in the molecules of the sample then gives a visual representation of the overall tendency toward saturation of organic molecules at all molecular weights. Where saturation increases linearly with number of C, a linear trend emerges as seen in the results from the unreacted SCOM (Fig. 5.6). This can be compared to results of the the same analyses performed on the reacted SCOM. Intensity differences (point size in Figs. 5.6 and 5.7) in these initial analyses may be due to differences in dilution. However, a significant trend appears after reaction with olivine. While all samples show a linear trend in the point cloud of increasing DBE with increasing number of C in the molecular structure, samples reacted with olivine also have a marked trend of molecules at DBE = 0, even with increasing number of C in the molecular structure. These molecules were not seen in a analysis of an extract of Blank_NH₃_Ol, that reacted just olivine with solution in a gold capsule. This excludes the possibility of contamination and strongly suggests that these compounds are being created from SCOM interaction with olivine or its dissolution products.



Fig. 5.6: Unreacted sample including data from all peaks where N = 1. Y axis shows the double bond equivalency (DBE: lower numbers indicate greater saturation) over number of carbon in each analyzed molecule for the unreacted synthesized SCOM. Color indicates number of oxygen in the molecule and size indicates intensity (a relative measure of abundance).



Fig. 5.7: Double bond equivalency (DBE) over number of carbon atoms for post-reaction samples. Note box in the two graphs from experiments with olivine indicating the suite of saturated hydrocarbons that do not occur in experiments without olivine.

To evaluate the compounds seen specifically after reaction with olivine, the spectra where DBE = 0 (Fig. 5.7) can further be selected and compared to theoretical distributions of organic molecules from different abiotic synthesis regimes. To compare the semi-quantitative results from each of the samples, we fit the data to two different mathematical distributions: first, the Schuls-Zimm (SZ) distribution that

represents a most-probable distribution from chain-growth type organic molecule polymerization ; second, the Schulz-Flory (SF) distribution that models step-growth type organic molecule polymerization. This latter SF distribution is often used to describe naturally occuring abiotic hydrocarbons produced from FTT reactions, such as those observed in terrestrial hydrothermal fields (Etiope and Sherwood Lollar, 2013; McCollom, 2013). Comparing the distribution of molecules where DBE = 0 from the OM+H₂O+Olivine sample (Neb_Ol_2, Table 2) to the SZ distribution show that the distribution of saturated hydrocarbons produced during reaction with olivine matches well with the SZ distribution. (Fig. 5.8a). Conversely, the molecular distribution in the sample does not match the SF distribution. (Fig. 5.8b). This indicates that the mass distribution of saturated hydrocarbons (DBE = 0) observed after our experiments with olivine is not consistent with the mass distribution expected from abiotic hydrocarbons synthesized by FTT reactions.



Fig. 5.8: comparison of Schulz-Zimm and Schulz-Flory distributions as applied to the results from Neb_Ol_2 for peaks where DBE = 0. a. normalized intensity of each peak over the carbon number. The blue line follows the Schulz-Zimm distribution. b. Mass fraction of the same data shown in Fig. 5.8a over carbon number. Red line follows the Schulz-Flory distribution that indicates possible abiotic hydrocarbon synthesis as through FTT reactions.

Finally, the goodness of fit between our data and a selected distribution can be used to distinguish overall changes to the SCOM during alteration in the experiments. To do this, peaks from each sample were grouped by CH_2 family and fit to the SZ distribution (similar to the case illustrated for the group DBE = O in Fig. 5.8a). The residual of the fit of each CH_2 group of each sample (where a residual of 0 indicates a perfect fit) is then regressed over its size diversity index. The size diversity index is calculated using Shannon's diversity index, a measure of entropy, by the following equation:

$$H_{CH_2 \text{ family}} = -\sum P_i \ln P_i$$

Equation 5.5

where *H* is the size diversity index, P_i is probability given by the fitted SZ distribution values for a given number of carbons in a CH₂ family; and *i* is the number of carbons in a CH₂ family. Lower index values indicate lower size diversity, or in this case, lower entropy. The unreacted SCOM ("before") has a relatively large size diversity and good fit to the SZ distribution. In general, after reaction both the size diversity and the goodness of fit (indicated by increasing residual values) decrease during the experiments (Fig. 5.9). The amount of modification is tiered, where modification of SCOM + H_2O < SCOM + H_2O + NH_3 < SCOM + H_2O + olivine < SCOM + H_2O + NH_3 + olivine. The most modified condition, therefor, was SCOM alteration with olivine in an NH_3 solution.



Fig 5.9: graphical representation of the Schulz-Zimm distribution fit for all the CH₂ families. Size diversity index indicates Shannon's diversity index, i.e. entropy, with $H_{CH_2 \text{ family}} = -\sum P_i \ln P_i$ where P_i is probability given by the fitted SZ distribution values for a given number of carbons in a CH₂ family; and *i* is the number of carbons in a CH₂ family.

5.3.3 Ongoing work

Sample analyses, data reduction and interpretation are still ongoing as part of a collaboration with IPAG. Specifically, additional analyses of the unreacted sample are being pursued, as well as tests to identify possible amination of the organic compounds during evaporation of NH₃-bearing reactant solutions during sample preparation, or matrix effects of NH₃ within the analytical instrument. Further data reduction to adjust for differences in dilution factors may support a more quantitative analysis of the data presented in this chapter, especially with regard to comparing the concentrations of select

species in the unreacted and reacted SCOM. Identification of specific species may allow us to evaluate specific synthesis pathways of N-bearing compound, most relevantly the Strecker synthesis of amino acids from ammonium chloride and cyanide that is thought to occur in chondrites (Botta et al., 2002), and Friedel-Crafts reactions of amino acid synthesis that may be sustained in hydrothermal systems by the presence of Fe-bearing clays and oxyhydroxides (Barge et al., 2019; Baross, 2018; Ménez et al., 2018).

Capillary electrophoresis methods are also being developed (ISTerre) for amino acid analysis, and for reaction products of amino acids including formic acid, glycolic acid, propionic acid, and NH_3 . Unreacted SCOM extracted in H_2O was analyzed by this method, and by comparing the sample to several amino acid standards we were able to determine that the sample may contain alanine, and does not contain detectable amounts of glycine, L-glutamine, L-cysteine, or L-asparagine. However, several unidentified species are seen by this method, which are being compared with standards for other forms of the amino acids (such as aspartic acid). Further development may allow the identification of some of the N-bearing organic species in the unreacted and reacted synthesized SCOM. Their identity is of interest, as their use as an indicator of hydrothermal water-olivine interaction depends in part on their lifespan in the oceans of icy worlds. If identified, the kinetic rate constants for their decomposition may be compared against the conditions of icy worlds (as in Truong et al., 2019) to evaluate how recently water-rock-organic interaction must have occurred.

5.4 Initial conclusions

As the work on processing the samples and interpreting data continues, the conclusions from the results of these experiments are very preliminary. However, we can draw some initial conclusions both from the glycine alteration experiments and the synthesized chondritic organic material (OM) experiments.

From the glycine alteration experiments, we can conclude that NH_3 does in fact stabilize glycine at hydrothermal conditions, and that olivine inhibits this mechanism. On its own, olivine seems to have little or no effect on glycine stability, as experiments in salt water with and without olivine had virtually identical glycine concentrations at the end of the experiments. Conversely, the effect of glycine on olivine alteration is being explored through further identification of alteration at the mineral surface.

The results of the SCOM alteration experiments results can be viewed in terms of: 1) comparison of all reacted SCOM with the unaltered SCOM; 2) comparison of NH_3 -bearing experiments to non- NH_3 -bearing experiments; and 3) comparison of olivine-bearing experiments to non-olivine-bearing experiments. These comparisons can be summarized as follows:

- 1) After all synthetic chondritic organic matter (SCOM) alteration experiments, organic molecules decreased both in diversity and in size compared to molecules in the initial synthesized SCOM. The decreased entropy of the sample sizes implies that polymerization or synthesis of macromolecules is not the dominant reaction at these conditions.
- 2) Mass analysis of protonated ions (in the positive mode of analysis) indicate that there may be more N-bearing molecules after reaction with NH₃-bearing fluids than are present in SCOM reacted with non- NH₃-bearing fluids, or in unreacted SCOM. This a preliminary result, as further analyses are needed in the negative analysis mode as well as to test matrix effects of NH₃ on the analysis. We note that N per molecule in this case does not mean larger molecules

(overall); the overall size of molecules in NH_3 -bearing experiments is not statistically different from those without.

3) Reaction with olivine results in an abundance of saturated organic compounds not seen in experiments without olivine. The reactions that produce these molecules have no identifiable effect on the decrease in entropy during the experiment (Fig. 5.10). In addition, the presence of NH₃ either slightly enhances or does not affect this reaction.

As the addition of multiple reactants does not have any unique, combined effect on the SCOM alteration as characterized here, it suggests that the alteration mechanisms of SCOM driven by H_2O , NH_3 , and olivine are independent of, and not significantly affected by, the other alteration pathways (Fig. 5.10).



Results are independent and additive No unique results are attributable to reactant combinations

Fig. 5.10: conceptual model of hydrothermal alteration in the synthesized chondritic OM (SCOM) experiments. Each reactant has distinct reproducible effect on the alteration of the OM that is seen even on combination with other reactants (NH₃ or olivine).

While preliminary, these initial conclusions have the potential to be developed for application to icy worlds exploration. Measurements from Enceladus' plume have ignited speculation of that organicmineral hydrothermal interactions may be currently occurring within the satellite. However, because of the analytical complexities in interpreting results of chemical data from Enceladus, interpretation of the organic constituents has so far been limited to identifying a few select compounds (Khawaja et al., 2019; Postberg et al., 2018, 2015). The most important result from our initial study is that there is a specific compound distribution from complex SCOM that was hydrothermally altered in the presence of olivine. This molecular signature may then be of interest in developing analytical approaches to determining active water-rock-organic interactions on future missions, or to fitting analyses of the existing data from the Cassini mission to similar distributions.

5.5 References

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CHAPTER 6

Conclusions and perspectives

SUMMARY

What is the importance of the main findings from this work, and how can they be applied to ongoing research on the subject of icy worlds?

Chapter 6. Conclusions and Perspectives

6.1 Conclusions

6.1.1 How long can serpentinization processes be sustained in a small icy satellite?

Chapter 2 presents a 1-D reactive transport model that evaluates the possibility that the H_2 emitting from Saturn's moon Enceladus may be produced by active, in-situ serpentinization processes. This model is based on a simulation of kinetically-controlled olivine dissolution along 1-D stream lines using the PHREEQC code. The initial parameters of this model satisfy key geophysical constraints of Enceladus' core: the existence of a liquid water ocean; a low-density, water-saturated porous core; and constant, tidally-driven circulation of liquid water within the core at temperatures ranging from 0 to 150 °C (Choblet et al., 2017). The main findings of this chapter are as follows:

- If the primary mineral (olivine) composes >30 vol % of the initial rock phase, olivine alteration results in precipitation of hydrous secondary minerals and the formation of an alteration front, arresting continuous water flow within the entire core. Water delivered to the alteration front by tidal forcing is quickly consumed by serpentinization processes at the front. This result is then inconsistent with our stated assumptions about the current conditions in Enceladus, which require constant water circulation throughout the entire core to generate the heat that maintains the liquid ocean.
- This model additionally shows that even small amounts of initial olivine in the core may produce H_2 at global rates of ~1 × 10¹² mol yr⁻¹, or 4-5 orders of magnitude higher than the estimated H_2 emission rate from Enceladus (1-5 × 10⁹ mol yr⁻¹).
- H₂ from olivine alteration is produced at rates consistent with the estimations from Enceladus occur in our models only where the entire 1-D column is already largely serpentinized and primary olivine alteration is nearing completion. This implies that the core may have already been largely serpentinized before water could begin freely circulating within the core.
- Even assuming no prior olivine alteration, our models indicate that serpentinization of a core the size of Enceladus' would reach completion in < 100 Myr (Fig. 6.1). This suggests either that the ocean of Enceladus is geologically young, or that the currently observed H₂ is produced from sources other than serpentinization (such as organic pyrolysis, or later alteration of secondary minerals).

6.1.2 What are olivine dissolution behaviors in contact with partially frozen NH₃-rich solutions?

Chapter 3 presents the results of batch experiments reacting olivine with NH₃-salt-water solutions at -20, 4, and 20 °C for up to one year. These long-term experiments are designed to show alteration rates and reaction products in partially frozen solutions as may occur on icy satellites in the outer solar system. Our conclusions can provide insight into planetary evolution processes and specifically in icy satellites without a liquid ocean:

- Olivine dissolution continues in partially frozen solutions to at least -20 °C by the mechanism of an unfrozen thin film of solution that envelopes the mineral surfaces (Fig.
6.1). In addition, this phenomenon is not reliant on the presence of NH₃: dissolution similarly continues in pH-controlled experiments without NH₃.

- **The olivine dissolution rates show a surprisingly weak dependence on temperature**, as rates at 25 °C are lower than predicted by existing rate laws, and rates at -20 °C are higher. While our rates at 25 °C may in part be low due to comparing results from batch experiments to existing rate laws based on continuous-flow experiments, combined with the comparatively high rates at -20 °C this suggests that different dissolution processes are at play in temperatures at and below 0 °C.
- **Based on these results, we can extrapolate that dissolution may continue to temperatures as low as -97 °C, the freezing point of the H**₂**O-NH**₃ **system**. Without extrapolation, these rates can already be incorporated in models to include alteration in partially frozen solutions, expanding on alteration models that do not initiate water-rock interaction until enough heat can be generated to reach the total melting point of the local solution

6.1.3 Can we exclude the possibility that NH₃ might affect olivine dissolution rates or otherwise alter olivine dissolution behavior through interactions with dissolved species or mineral phases?

The results of experiments reacting olivine in NH_3 -salt-water solutions at 0 to 150 °C are presented in Chapter 4: including continuous-flow reactor experiments at 0, 23, 90 and 150 °C; and closed-system batch experiments at 90 and 150 °C. These latter experiments were conducted to identify NH_3 effects on olivine dissolution, either through interactions with the olivine directly or with secondary products in the fluid or at the mineral surface, that may occur if hydrothermal vents form in an H_2O-NH_3 ocean where unaltered olivine persists. From these data we draw the following conclusions:

- The lack of identifiable effect of NH₃ on olivine dissolution rates suggests that, in fact, we can rule out significant effects of NH₃ on olivine dissolution rates. In addition, the observed dissolution rates are not sensitive to pH at highly alkaline conditions.
- As there is some (albeit weak) effect of temperature on the batch dissolution rates, these results can also be used to extend the regression of olivine dissolution rate over temperature as presented in Chapter 3. We can show that from -20 to 150 °C there is an apparent break in slope between 23 and 90 °C, due to the anomalously low rates at 23 °C compared to those at 4 and -20 °C (see in-depth discussion in Chapter 3). We posit this break in slope may be due a change in the dissolution mechanism at below-23 °C temperatures, or an apparently-low dissolution rate at 23 °C due to secondary mineral precipitation.
- Results of batch experiments at 90 and 150 °C show that NH₃ has an enhancing effect on the formation of secondary reaction products. Secondary precipitation of brucite, lizardite, and smectite is observed to be more abundant in experiments with NH₃, especially those conducted at 90 °C. However, as no NH₃-minerals or NH₄⁺-clays were found among the secondary products, the mechanism behind this effect is currently unidentified.
- We note that the flow through rates show a remarkable lack of sensitivity to temperature, NH_3 , or pH. At T > 23 °C are generally 1-3 orders of magnitude lower than those predicted by existing rate laws. In addition, dissolution rates from flow-through experiments at 0 °C were higher than those from 23 and 90 °C, and in some cases higher than those at 150 °C. The role of NH_3 in affecting apparent dissolution rates through promoting Si and Mg sequestration is a topic of investigation in our results. However, this effect of NH_3 on secondary minerals does not

explain the similar dissolution rates seen in pH-controlled experiments with no NH_3 . The complexity of these results highlights the relative scarcity of literature on olivine dissolution in alkaline conditions, especially at temperature above and below ~25 °C.

6.1.4 Does NH₃ or olivine facilitate prebiotic interactions by stabilizing or catalyzing complex organic molecules?

Chapter 5 discusses the initial results from experiments reacting organic matter with NH₃ and olivine in low-temperature hydrothermal conditions (100 °C). An initial experiment set reacted glycine with and without olivine and NH₃ in order to evaluate how these two parameters affect glycine stability. A second experiment set reacted a synthesized complex organic material (OM) that simulates a pristine chondritic OM (Kuga et al., 2015) with and without olivine and NH₃, and measured the soluble organic assemblage extracted from the reacted solids by high-resolution mass spectrometry (Orbitrap). While the conclusions are still preliminary, they can already be applied to questions of organic alteration in icy moons:

- In the first experiment, hydrothermal alteration of glycine with olivine and/or NH_3 shows a general trend toward glycine decomposition that is diminished in the presence of NH_3 . The stabilizing effect of NH_3 on glycine largely negated when olivine was also present in the experiment.
- In the second experiment, hydrothermal alteration of pristine synthesized chondritic organic material (SCOM) similarly shows a trend toward decomposition reactions under all hydrothermal conditions. This includes with pure water, as well as with NH₃, with olivine, and with both NH₃ and olivine.
- Initial results from high-resolution mass spectrometry (Orbitrap) of the SCOM in positive mode (protonated) show that the reacted OM may have a larger proportion of molecules with more N atoms after reaction with NH₃ than without. Given the nature of the analyses the identity of these species was not identified, and the specifics of this result (in light of matrix effects or reactions during sample preparation) are still being explored.
- Orbitrap analyses further show a distinctive trend of long-chain unsaturated carbon species, identified after reaction with olivine, that are not seen in samples reacted without olivine (Fig. 6.1).



Fig. 6.1: Main modelling and experimental conclusions from this manuscript. Enceladus image credit: NASA/JPL-Caltech.

6.2 Perspectives

Even if hydrothermal water-rock interactions on Enceladus are very recent or short-lived, this may in itself offer a unique opportunity to study hydrothermal environments during the early stage of planetary evolution. Additional studies characterizing the chemical complexity that may emerge in this young hydrothermal system is highly relevant to test the hypothesis that life possibly originated in alkaline hydrothermal vents on Hadean Earth (Martin & Russell, 2007; Russell et al., 2014; Sojo et al., 2016). The results of the studies presented in this thesis suggest several paths of inquiry: by expanding geochemical modelling, experimental investigations, and even combining these approaches to evaluate already available data of icy worlds, and constrain future observations from upcoming space missions.

6.2.1 Future directions for geochemical modelling of icy worlds

Chapter 2 presents a robust geochemical exploration of the parameters that affect outcomes of olivine alteration in a 1-D column within an icy satellite. The results from this model show the sensitivity of kinetically-controlled olivine alteration to parameters that affect the known dissolution rate in a multikilometer 1-D profile having the unusual constraints thought to exist in icy satellites. A linear extension of these results would be to add complexity to the framework provided by this model. Limitations to the PHREEQC 1-D model mean that changes in porosity, permeability, and mineral volumes during alteration are ignored. However, the importance of fracturing both in terrestrial serpentinization processes and as a potentially significant driver of alteration in icy satellites is well known (Malvoisin et al., 2017, 2020; Vance & Melwani Daswani, 2020). Within the existing PHREEQC framework, static zones of lower or higher porosity that might result from fracturing can be included. Incorporation of the PHREEQC model into a coupled geochemical-geophysical framework (e.g. Myagkiy et al., 2019) could greatly expand this approach by adding hydrodynamic feedbacks following volume changes, fracturing, and 2-D fluid flow responsive to the geochemical changes dictated by the PHREEQC program.

The results of the PHREEQC model point to a major question in evaluating the current geochemistry in Enceladus: what is the source of the observed H_2 emissions in Enceladus' plume? The high H_2 :CH₄ ratios suggest an inorganic source, but the results of the model of Chapter 2 suggest that primary mineral alteration is unlikely to continue to the present day. The release of H_2 from secondary minerals, as from the silicification of Fe(II)-bearing brucite (Tutolo et al., 2018) or conversion of siderite to magnetite (Glein et al., 2018), is then of specific interest in fitting geochemical models to current observations. Incorporating these or similar reactions into the reactive transport model of Chapter 2 could then prove to be useful. Specifically, a database of well-defined kinetic rate constants both for a) the incorporation of Fe(II) into secondary minerals and b) reactions oxidizing Fe(II) contained in those secondary minerals, such as those recently discussed by Ray et al. (2020), would be needed to estimate global rates of H_2 production from the secondary paragenesis by this approach.

Finally, the experimental results from Chapters 3 and 4 can be directly integrated into modelling applications. The dissolution rates from low-temperature weathering of olivine in NH₃ can be applied to models of mineral weathering in partially frozen solutions, specifically between the liquidus and solidus of the H₂O-NH₃ system. This is important because planetary evolution models often consider

mineral alteration to start the liquidus of H_2O or H_2O -NH₃ (Fig. 6.2 "total melt"). This work provides mineral alteration rates below the liquidus of the H_2O -NH₃ system (Fig. 6.2 "partial melt"), extending the empirical rates that can be used in models to partially frozen systems. Applying these principles to models would increase the amount of heat provided by serpentinization processes during early satellite evolution and greatly reduce the amount of primary minerals available later on. For example, in Fig. 6.2, including mineral weathering as proposed by our dissolution rates in the "partial melt" duration of Enceladus' evolution (0-0.8 Gyr) would decrease the amount of unaltered primary mineral extant when "total melt" temperatures are achieved at 2.8 Gyr of evolution.



Fig. 6.2: Thermal evolution of Enceladus (modified from Neveu and Rhoden, 2019). Legend indicates color for temperatures -273 to 327 $^{\circ}$ C (0-600 K), with a blue marker at 0 $^{\circ}$ C (liquidus of the NH₃-H₂O system). Panel shows the modelled thermal evolution of Enceladus over time. Yellow arrows indicate time spans for when some or all of the core is > -97 $^{\circ}$ C, or above the solidus ("Partial melt") of the NH₃-H₂O system; and where some or all of the core is > -0 $^{\circ}$ C ("Total melt"), or above the liquid of the NH₃-H₂O system, and a differentiated liquid ocean forms.

6.2.2 Perspectives on low-T olivine dissolution

The surprising conclusions from the olivine alteration experiments presented in Chapters 3 and 4 immediately present several avenues of inquiry. The work of Chapter 3 is only the second study to date of olivine dissolution in partially frozen solutions, with the single previous study being in highly acid solutions (Niles et al., 2017). However, the unfrozen thin film of solution at mineral surfaces that allows the dissolution observed in these experiments is a physical mechanism that should also occur in pure water solutions (Anderson, 1967; Gilpin, 1979; Rietmeijer, 1985). It follows that the presence of salts, NH_3 , or acid in solution is not strictly necessary to continue altering minerals at sub-zero temperatures as long as this thin unfrozen film forms. Additional characterization of mineral-liquid-ice system at extreme temperatures, such as by the Raman spectroscopy method introduced in Chapter 3 or by other in-situ measurements such as cryogenic atomic force microscopy (AFM) or cryogenic TEM, could further identify mineral alteration mechanisms. Future studies may even approach this process as conceptually analogous to interface-coupled dissolution-precipitation (Fig. 6.3). By this model, where the unfrozen film becomes very thin (as thin as ~ 6 Å at -80 °C, Rietmeijer, 1985) it may promote

secondary mineral formation even at kinetically inhibiting low temperatures by concentrating solutes within the unfrozen film at the mineral surface. While increasing solutes in the solution film may eventually retard primary mineral dissolution by reaching equilibrium with respect to the primary mineral of interest, greater absolute amounts of primary mineral might still be expected to dissolve in in a frozen mélange due to the decreasing stability (and increasing solubility) of primary ultramafic minerals with decreasing temperature (e.g. Goldich, 1938).



Fig. 6.3: water films at mineral surfaces. a. Model of an equilibrium liquid water film between ice and substrate (adapted from Gilpin, 1979). b. A conceptual model of interface-coupled dissolution-precipitation (adapted from Hellmann et al., 2012), that proposes a fluid film between the dissolving front of a mineral surface and the precipitate at the surface.

The surprisingly fast dissolution of olivine in partially frozen solutions discussed in Chapter 3 calls for further inquiry, but it is already supported by the relatively fast dissolution rates at 0 °C reported in Chapter 4, as well as two other previous studies of olivine dissolution at and below 0 °C that also reported faster-than-anticipated dissolution rates (Hausrath & Brantley, 2010; Niles et al., 2017). Due to the rapidly changing properties of water and solutes in solution with changing temperature (e.g. maximum water density is at 4°C and not 0°C as one may expect), this may even indicate a change in the olivine dissolution mechanism between 0 and 25 °C. In addition, or in conjunction, this effect may reflect a retardation in the formation of secondary minerals at low temperatures and a resulting impact on the apparent mineral dissolution rate. Additional studies are needed to better define the dissolution processes at play in the poorly investigated 0 to 25°C temperature window, as scientific surprises may await researchers exploring this range of temperatures, just outside the range in temperatures (T >= 25 °C) that have already been explored in exceedingly numerous studies. Such investigations would provide a more extensive database for mineral alteration processes in cold environments, applicable to the Moon, Mars, and icy worlds, as well as the polar regions of Earth.

The role of NH_3 in promoting secondary mineral alteration at the olivine surface at 90 °C was another unexpected result from our experiments that bears further investigation. While we speculate that the reason for the greater abundance of secondary minerals in the presence of NH_3 is the emergence of metastable secondary phases that quickly stabilized into the observed brucite, smectite, or lizardite, such transient phases were not directly identified after the several months of reaction time of our experiments. Studies that focus specifically on the stability and transition series for secondary phases of interest may be necessary to identify the true effect of NH_3 in this system. In-situ analyses with high temporal resolution, such as in-situ Raman spectroscopy (Guren et al., 2020; Montes-Hernandez & Renard, 2016) or X-ray diffraction (Miller et al., 2018; Schaef et al., 2011), might be used to identify the nucleation and growth of specific secondary phases stable in NH_3 -rich solutions, such as the NH_4 -carbonate roguinite. Identification of the mechanism of secondary mineral production may also shed light on the potential effects of these secondary minerals on long-term olivine dissolution rates.

6.2.3 Ongoing directions for organic-olivine-NH3 interactions

Whether or not the chemical alteration of primary minerals within Enceladus has come to completion, the existence of a liquid ocean with localized emissions of tidally-heated water from the rocky core suggests the existence of hydrothermal vents at Enceladus' seafloor (Choblet et al., 2017; Liao et al., 2020; Porco et al., 2006). Low-mass nitrogen-bearing organic compounds, macromolecular organics, and NH₃ are all possible constituents of this ocean, constrained by geochemical evidence of these species found in Enceladus' plume and Saturn's E-ring (Khawaja et al., 2019; Postberg et al., 2015, 2018). While the emitted organics may be sourced from a concentrated organic layer at the boundary between the liquid ocean and the icy crust (Khawaja et al., 2019), their origin as part of the chondritic parent bodies of Enceladus indicates that they may still be present within the crust.

Given the preliminary nature of the results from the experiments presented in Chapter 5, it is not surprising that they still present more questions than they do answers. Some of these questions may be resolved by ongoing work with the data from Chapter 5, while some may still present avenues for future research. A major question that drives current data interpretation is identifying the reaction mechanism(s) that produced the saturated hydrocarbons in experiments reacting complex synthesized OM with olivine. Reduced organic compounds are deeply sensitive to redox conditions in solutions (McCollom, 2013; McCollom & Seewald, 2003; Shock et al., 1998), which suggests that the oxidation of iron during olivine serpentinization may be critical to our results. The presence of secondary phyllosilicates, as seen at the olivine surface reacted in the complex OM alteration experiments, may also affect organic compounds' synthesis and stability (Barge et al., 2019; Ménez et al., 2018; Pedreira-Segade et al., 2016). Evaluating the data from our experiments especially in light of these known reactions may then reveal the dominant reaction pathways during co-alteration of complex OM and minerals in hydrothermal systems.

Finally, our initial conclusion that the presence of NH₃ during organic alteration may result in more nitrogen-bearing molecules can be expanded in light of the findings from Chapter 4, that secondary phases during olivine alteration are more abundant in NH₃-bearing solutions. The secondary minerals brucite and smectite are of particular interest for their adsorptive properties of nitrogen-bearing organic compounds (e.g. Feuillie et al., 2013; Vinogradoff et al., 2020). This raises an interesting conceptual possibility for hydrothermal vents in an NH₃-bearing ocean, where high concentrations of amino acids and other nitrogen-bearing compounds may be stabilized by the NH₃ in the ocean as well as concentrated by the quickly forming, abundant clays. In short, while the period of hydrothermal mineral alteration in icy worlds may be brief, the results of this manuscript suggest that their unique geochemical properties mean that they continue to be a curious source of newly-considered habitable environments in the solar system.

6.3 References

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