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► **To cite this version:**

Amber Zandanel, Roland Hellmann, Laurent Truche, Vladimir Roddatis, Michel Mermoux, et al..
Geologically-rapid aqueous mineral alteration at subfreezing temperatures in icy worlds. *Nature Astronomy*, 2022, 10.1038/s41550-022-01613-2 . hal-03795029

HAL Id: hal-03795029

<https://hal.science/hal-03795029>

Submitted on 3 Oct 2022

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1 **Geologically-rapid aqueous mineral alteration at subfreezing temperatures in icy worlds**

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13 **The most active icy worlds like Europa or Enceladus are predicted to host extensive**
14 **aqueous alteration driven by water-rock interactions at elevated temperatures¹⁻³. On the**
15 **other hand, it is assumed that such alteration is kinetically inhibited at the sub-zero**
16 **temperatures of other icy worlds, such as the mid-sized moons of Saturn and Uranus or**
17 **Trans-Neptunian Objects^{1,4}. Here we perform aqueous alterations experiments on a**
18 **chondrite-analogue material (olivine) and find that chemical alteration processes are**
19 **still efficient at temperatures as low as -20 °C, as the presence of an unfrozen water film**
20 **still allows olivine to dissolve in partially frozen alkaline solutions. We infer that**
21 **aqueous alteration may be enhanced by salts and ammonia present in icy worlds, and**
22 **therefore remains a geologically rapid process even at sub-zero temperatures. Our**
23 **results imply that most icy bodies exceeding 400-500 km in diameter will be completely**
24 **altered to hydrous secondary minerals early in their evolutionary histories.**

25 Models of icy worlds evolution often anticipate the release of heat and chemical energy
26 through aqueous alteration or serpentinization of primary chondritic minerals when in contact
27 with fully melted water⁴⁻⁶. One fundamental question is whether bulk liquid water is a
28 necessary prerequisite to these processes, or can water-rock interactions still occur below the
29 freezing point in icy bodies? To address this, we determined the rates and mechanism of
30 olivine dissolution in alkaline solutions at -20, 4, and 22 °C from dissolution experiments that
31 lasted up to 442 days. The range of temperatures chosen corresponds to those that can be
32 achieved in mid- to large-sized icy worlds from radiogenic sources alone, in the absence of
33 extra heat due to tidal friction^{4,5,7}. Most icy worlds with diameters exceeding 400-500 km
34 cross this temperature threshold when their cores, comprised of ice and rock, undergo an
35 initial heating period. Three different solution chemistries were used at each temperature to
36 analyse the effect of NH₃ concentration (0, 0.8, 8.0 mass % - hereafter %) and pH in an
37 alkaline, dilute saline solution (H₂O-NaCl-KCl-NaHCO₃), such as is thought to evolve in

38 solutions interacting with a chondritic rock matrix^{8,9} and corroborated by analyses of vapour
39 and grains emitted in Enceladus' plumes². At -20 °C, some unfrozen solution existed in all
40 experiments as the NaCl-KCl-NaHCO₃-H₂O system has a eutectic temperature (solidus) of -
41 24 °C¹⁰, while the H₂O-NH₃ system has a eutectic temperature of -96 °C¹¹ (Supplementary
42 Information 4.1-4.2 and Supplementary Fig. 5). The amount of solution that remains unfrozen
43 increases with increasing NH₃ content (Table 1). At experimental conditions pure water ice
44 formed during freezing^{10,11}.

45 Optical microscope images of partially frozen 0.0, 0.8 and 8.0% NH₃ solutions illustrate
46 decreasing crystallinity and increasing porosity in the ice phase caused by increasing NH₃
47 content (Fig. 1a-c). Visual evidence of an unfrozen solution film at the olivine-ice interface
48 was obtained by imaging melt propagation from the ice-olivine boundary in a frozen sample
49 allowed to equilibrate to bench temperature (Fig. 1d), and an in-situ investigation of olivine
50 grains in frozen solutions (Fig. 1e). To identify solutes concentrated in the unfrozen film at
51 the olivine interface, Raman analyses were performed at -20 °C on an amalgam of olivine
52 grains, ice, and unfrozen solutions using a temperature-controlled stage. Raman spectra,
53 which probed the transition from ice to interfacial liquid water, show that the shape of the
54 broad symmetric and asymmetric OH-stretching band of water at 2900–3800 cm⁻¹ evolves
55 when approaching the olivine surface, characterized by an upward shift of the entire band and
56 a clear decrease in the intensity of the region <3325 cm⁻¹ that corresponds to symmetric OH-
57 stretching (Supplementary Figs. 3, 4). In addition, the intensities of NH₃ and CO₃²⁻ peaks
58 positively correlate with the broadening and intensity decrease of the spectral component
59 centred at 3138 cm⁻¹, which is clearly defined in ice. These observations corroborate the
60 accumulation of NH₃ and CO₃²⁻ in the unfrozen solution enveloping the olivine grains.

61 Increasing silica and magnesium concentrations with time indicate that olivine dissolution
62 occurred continuously at all experimental conditions (Fig. 2a-c). We derived separate

63 apparent olivine dissolution rates ($\text{mol m}^{-2} \text{s}^{-1}$) from aqueous [Si] and [Mg] (denoted r_{Si} and
64 r_{Mg}), and split them into two regimes based on reaction progress: initial rates (furthest from
65 equilibrium, $\Delta G_{\text{diss}} \ll 0$; 0-14d) and long-term rates (closer to equilibrium, $\Delta G_{\text{diss}} < 0$; 167d).
66 These rates are “apparent” as any sequestration of Mg or Si in secondary phases decreases
67 their respective aqueous concentrations, resulting in lower calculated olivine dissolution rates.

68 The initial apparent dissolution rates r_{Si} and r_{Mg} are relatively clustered at $-20\text{ }^{\circ}\text{C}$, indicating
69 nearly stoichiometric alteration (Fig. 2d). With increasing temperature r_{Si} and r_{Mg} increasingly
70 diverge from one another, with r_{Mg} generally lower than r_{Si} . The majority of the initial r_{Si} and
71 r_{Mg} also show a modest increase with increasing temperature from -20 to $4\text{ }^{\circ}\text{C}$, whereas from
72 4 to $22\text{ }^{\circ}\text{C}$, two of the r_{Si} rates and all of the r_{Mg} show no meaningful dependence on
73 temperature (Methods). Previous experimental studies that characterized olivine dissolution at
74 below $0\text{ }^{\circ}\text{C}$ focused on highly acidic solutions^{14,15}, and rapid dissolution rates were ascribed to
75 an acid concentration effect in an unfrozen fluid phase¹⁵. However, as the mechanism of
76 olivine dissolution is thought to change from acid to alkaline conditions¹², acid-pH olivine
77 dissolution rates cannot be directly applied to alkaline conditions. The overall trends from our
78 experiments show a weak inverse relation between pH and dissolution rates in the alkaline pH
79 range, consistent with published alkaline olivine dissolution rates at ambient temperatures^{12,13}.

80 In contrast, the individual r_{Si} show a positive correlation with ammonia concentration at a
81 given pH: despite having identical pH at $22\text{ }^{\circ}\text{C}$, r_{Si} is higher in all experiments with 0.8% NH_3
82 compared to 0% NH_3 (Fig. 2d).

83 Long-term apparent rates (ltr_{Si} and ltr_{Mg}) decrease with temperature from -22 to $4\text{ }^{\circ}\text{C}$ but are
84 roughly equivalent at 4 and $22\text{ }^{\circ}\text{C}$ (Fig. 2e). All rates appear to approach steady state at 167d,
85 while the experiments that lasted 442d (0.8% NH_3) show a curious increase in concentrations
86 (Fig. 2a-c; 167-443d), correlating to a slight transient increase in rates. In terms of
87 stoichiometry, $ltr_{\text{Mg}} > ltr_{\text{Si}}$ at $-20\text{ }^{\circ}\text{C}$, but at 4 and $22\text{ }^{\circ}\text{C}$ ltr_{Si} and ltr_{Mg} generally come close to

88 converging ($ltr_{Mg} \geq ltr_{Si}$). Long-term ltr_{Si} are relatively constant with increasing pH at 4 and 22
89 °C, with only a weak positive relation recorded at -20 °C.

90 All of the experiments displayed varying degrees of non-stoichiometric olivine alteration
91 behaviour, with $r_{Si} > r_{Mg}$ or $ltr_{Mg} \geq ltr_{Si}$. The increasing degree of non-stoichiometry in r_{Si} and
92 r_{Mg} with temperature, as well as very low activation energies, are evidence that released Mg
93 and Si were being pulled out of solution and incorporated into secondary authigenic phases
94 (Methods). Finally, the non-stoichiometric long-term rates at -20 °C indicate potential
95 secondary phase formation occurring even in the partially frozen experiments (Fig. 2e). Both
96 the initial (r_{Si} , r_{Mg}) and long-term (ltr_{Si} , ltr_{Mg}) apparent rates calculated at 4 and 22 °C cannot,
97 therefore, be considered equivalent to far-from-equilibrium olivine dissolution rates
98 (Supplementary Information 2.2). Our apparent rates rather describe an overall alteration
99 process occurring at conditions much closer to equilibrium, and thus more similar to the rates
100 expected on icy bodies.

101 Observation of olivine grains at the micron scale (SEM) revealed no visible alteration features
102 at the olivine surface (Fig. 3a). However, at the nanoscale, evidence of the formation of a non-
103 crystalline (amorphous) secondary phase at the olivine surface is apparent. In high-resolution
104 iDPC-STEM images (Fig. 3b), the olivine lattice fringes abruptly terminate at a surface
105 altered layer (SAL), here an irregular <1 nm-wide band of material without an ordered
106 structure (Fig. 3b). The long-term dissolution rates ($ltr_{Mg} > ltr_{Si}$; Fig. 2e) suggest possible
107 preferential sequestration of Si in this SAL. From the aqueous chemistry we further calculated
108 the theoretical thicknesses of SALs (Supplementary Information 2.3); typical values were
109 found to be <10 Å, consistent with our observations.

110 We propose that the mechanism for this alteration is the unfrozen film of solution at the ice-
111 olivine interface, which may also be enriched in ammonia due to its exclusion from the ice

112 phase. During melting/refreezing, the chemical potential at the solution-mineral interface
113 causes an interfacial liquid film to form around mineral grains that persists below the partial
114 freezing point (liquidus) and even the total freezing point (solidus) of the bulk solution^{16,17}.
115 The olivine alteration observed in our experiments validates a proposed mechanism for
116 aqueous mineral alteration signatures previously observed in chondrites¹⁸ and in extreme
117 environments in Antarctica¹⁹. Alteration at sub-zero temperatures at alkaline conditions has
118 far-reaching implications for interpreting the present day mineralogy of the rocky cores of icy
119 worlds, as exothermic mineral weathering is predicted at any temperature where this liquid
120 film forms, further enhanced by antifreeze agents (salts, NH₃) that increase the width of this
121 film and thus the liquid water-rock ratio¹⁷.

122 Based on long-term rates observed at -20 °C in our experiments (Fig. 2e), we assessed that the
123 heating rate generated by olivine dissolution (up to 2.3×10^{-8} to 4.6×10^{-7} W kg⁻¹, Methods) is
124 comparable to that generated by short-lived radioactive nuclides (e.g., ²⁶Al), and may provide
125 a heat pulse for periods of tens to hundreds of millions years after accretion^{4,5}. We posit that
126 during progressive radiogenic heating of initially frozen interiors, aqueous alteration should
127 commence at least when the first aqueous melts appear in the deepest regions (as low as -96
128 °C, depending on volatile and salt contents). Melting is expected to propagate throughout the
129 entire core at timescales ranging between a few tens to hundreds of millions of years,
130 depending on the body size and available heat sources^{4,5}. Given the relatively fast apparent
131 dissolution rates observed in our experiments, we predict that alteration will be controlled by
132 the outward propagation rate of melt front, resulting in alteration of most of the silicate core.
133 This process likely controlled the early evolution of most icy worlds, including Ceres,
134 Saturn's and Uranus' mid-sized moons (Mimas, Enceladus, Dione, Ariel, Oberon, Titania)¹,
135 and TNOs with diameters >500 km⁷. Low core densities of Ceres (2400-2900 kg m⁻³)²⁰,
136 Enceladus (2400-2500 kg m⁻³)²¹, and Dione (2400-2500 kg m⁻³)²² corroborate the hypothesis

137 that the rocky cores of these worlds are largely composed of altered hydrated minerals.

138 This initial period of geologically-rapid chemical alteration of primary ultramafic minerals
139 (Fe and Mg-rich silicates, such as olivine, pyroxene), associated with H₂ production²³, may
140 have produced potentially habitable rock-water-hosted environments even at relatively low
141 temperatures. After this first widespread alteration stage, active alteration of primary minerals
142 was likely limited to only a few bodies in the Solar system where fresh minerals are
143 continuously brought in contact with water, notably on Earth at mid-oceanic ridges, but also
144 possibly on Europa's seafloor²⁴.

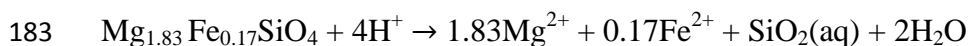
145 Even though our data support a new scenario where serpentinization reactions no longer play
146 a major role on icy moons, this does not imply that these bodies are geochemically quiescent.
147 For instance, chemical data from Enceladus should now be viewed within the framework of
148 water-rock interactions other than serpentinization of primary minerals: our results suggest
149 that the low yields of H₂ may be explained by oxidization of Fe(II) in secondary minerals
150 such as serpentine, siderite and Fe-bearing brucite². Alternatively, other processes may be
151 ongoing, such as hydrothermal pyrolysis of primordial organics or biotic methanogenesis, as
152 recently invoked to explain the rough equivalence of H₂ and CH₄ in the plumes of
153 Enceladus²⁵.

154 More generally, our results imply that secondary altered minerals should be ubiquitous in the
155 interiors of icy moons and parent bodies of carbonaceous chondrites. Altered mineral
156 assemblages in the samples retrieved by Hayabusa2 and OSIRIS-Rex, including detailed
157 investigations of SALs, will provide crucial information about past aqueous environments in
158 the parent bodies of Ryugu and Bennu²⁶. Similar to what was observed on Ceres with Dawn²⁷,
159 identification of alteration products by the upcoming observation campaigns using the James
160 Webb Spatial Telescope and the Lucy mission to the Trojan asteroids may confirm the
161 ubiquity of aqueous processes, even in distant icy worlds.

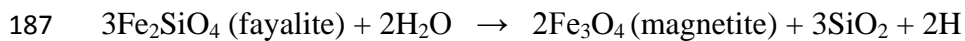
162 **Methods**

163 Batch reactor experiments were carried out at -20, 4 and 22 °C for variable periods of time
164 ranging from 41 to 442 days. Three experimental series were carried out at each temperature,
165 with each series being comprised of numerous Nalgene vials, each containing 0.3 g of San
166 Carlos olivine grains ($\text{Mg}_{1.83}\text{Fe}_{0.17}\text{SiO}_4$) sieved to 0.05-0.125 mm size range, and 30 mL of
167 saline fluid containing either 0.0, 0.8, or 8.0 mass % NH_3 (0.0 % NH_3 solution prepared with
168 NaOH). The starting $\text{pH}_{(25\text{ }^\circ\text{C})}$ values of the solutions were 10.8, 10.8, and 12.2, respectively.
169 Vials were then sequentially removed from the experiment at designated times and sampled
170 post-mortem (fluid chemistry shown in Fig. 2a-c). All experiments were carried out at
171 ambient pressure (1 bar). Pressure is not a crucial variable as pressures in mid-sized icy
172 bodies that maintain relevantly low temperatures will have correspondingly low pressures (for
173 example, <400 bar maximum in a core the size of Enceladus²⁸), at which pressure is not
174 known to have significant effects on olivine alteration processes²⁹. Mg-rich olivine (forsterite)
175 was selected for these experiments as a common and dominant primary mineral found in the
176 chondrites^{30,31} that are thought to make up icy worlds^{2,3,9}. In addition, olivine is of specific
177 interest as a primary mafic mineral that drives serpentinization reactions and the production of
178 H_2 ^{1,9}. The overall composition, ratios of salts, and NH_3 concentrations of the solution were
179 chosen to bracket the chemistry of solutions predicted to evolve from chondrite-fluid
180 interactions^{32,33}. Additional information on the experimental approach is discussed in
181 Supplementary Information 1.1-1.3.

182 The olivine dissolution reaction at our experimental conditions can be represented by:



184 This reaction is related but distinct from a serpentinization reaction. Based on the two olivine
185 solid solution end members, serpentinization reactions can be expressed as follows:



188 There is currently no consensus whether a lower temperature bound for serpentinization
189 exists. Studies postulate these reactions continue down to 10°C ²³, although recent field
190 studies of ophiolite weathering suggest that observed H_2 and CH_4 production at low
191 temperatures are attributable to later stages of water-rock interaction with secondary, rather
192 than primary, minerals³⁴. While our experiments were limited in time (max. 442 days), we can
193 speculate that over significantly longer time periods the amorphous SALs that formed on the
194 olivine grains could serve as a matrix for the in situ nucleation of poorly crystalline proto-
195 serpentine phase(s), especially in light of the chemical oversaturation with respect to
196 serpentine minerals in many of our experiments (Supplementary Information 4.3 and 4.4).
197 Such proto-serpentine have been observed as a precursor step in serpentinization reactions³⁵.
198 The major aqueous cations were analysed by inductively coupled plasma atomic emission
199 spectroscopy (ICP-AES). Apparent dissolution rates were calculated from the aqueous
200 concentrations of Mg and Si: initial apparent dissolution rates (r_{Si} and r_{Mg}) were calculated
201 based on linear regressions of the concentration data from $t = 0$ to 14 d; long-term apparent
202 rates (ltr_{Si} and ltr_{Mg}) were derived from the dc/dt slope of the aqueous concentration data at
203 167d (Supplementary Information 2.1 and Supplementary Fig. 1). Rates based on aqueous Fe
204 concentrations were not calculated as this element was generally below analytical detection
205 limits (Supplementary Information 6). As a reminder concerning mineral dissolution kinetics,
206 the concentrations of Si and Mg at a given time in a reactor reflect the dynamic relation
207 between two fundamental processes: their release from the olivine structure and their
208 subsequent incorporation into secondary authigenic phases (both crystalline and amorphous-
209 see details in Supplementary Information 2.3). The degree of incorporation into authigenic
210 phases is both element-specific and depends on temperature and other physico-chemical

211 parameters. Because the formation of authigenic phases decreases the aqueous concentrations
212 of the element(s) used to calculate the thermal activation energy E_a (Si, Mg), this decreases
213 the slope of the $\ln k$ vs $1/T$ relation used to calculate E_a (Supplementary Fig. 2). The
214 attenuated dependency of r_{Si} on temperature that we measured is therefore reflected in the
215 thermal activation energies ($E_a = 12\text{-}19 \text{ kJ mol}^{-1}$) determined from the initial apparent rates of
216 olivine dissolution at $T = -20, 4$ and $22 \text{ }^\circ\text{C}$. These values are lower than the average value of
217 $\sim 63 \text{ kJ mol}^{-1}$ from compiled rate data¹³. Further details on the calculation of E_a are given in
218 Supplementary Information 2.1-2.2; derived rates are listed in Supplementary Table 1.

219 The heating rate of olivine dissolution was calculated from the average ltr_{Si} ($1.2 \times 10^{-13} \text{ mol m}^{-2}$
220 s^{-1}) of all experiments at $-20 \text{ }^\circ\text{C}$ (Fig. 2), with a ΔH of 203 kJ mol^{-1} released during
221 dissolution³⁶. Heating rates can then be scaled to surface areas to calculate heating rates for a
222 mass unit of olivine having grain sizes different from those used in our experiments. The
223 range of heating rates presented above were calculated using geometric surface areas for
224 olivine grain sizes common to chondrites (0.05-1 mm radius, with surface areas of 18.5-0.923
225 $\text{m}^2 \text{ kg}^{-1}$)³¹.

226 To image olivine in partially frozen aqueous solutions we used optical microscopy (plain and
227 polarized light) to observe the nature of the olivine-ice interface and the porosity of the
228 enveloping adjacent ice. The microscopy work was done in a cold room at $-8 \text{ }^\circ\text{C}$. The physical
229 process of fluid melting at the olivine grain-ice interface was also studied with a mixture of
230 unreacted olivine grains (crushed, sieved and cleaned identically to olivine used in the
231 experiments, but not included in the experiments) and deionized water that was frozen with
232 liquid N_2 (77 K). The frozen mixture was then observed under an optical microscope at
233 ambient temperature so that we could record sequential images of the liquid solution front
234 propagating away from the olivine grain as the temperature gradually rose. Raman analyses of
235 olivine, ice, and unfrozen fluid were performed at the olivine-ice interface using a Renishaw®

236 InVia confocal Raman microscope. Samples (unreacted olivine grains and solution) were
237 placed in a quartz cell in a Linkam® THMS 600 heating/freezing stage and maintained at -20
238 °C during analyses. Measurements were performed at 532 nm using a 50x-long working
239 distance objective.

240 Post-reaction olivine grains were imaged by field emission scanning electron microscopy
241 (FEG SEM, Zeiss Ultra 55, CMTc, Univ. Grenoble Alpes) at 20 kV to characterize the
242 presence and degree of surface coverage of potential secondary phases (crystalline and/or
243 amorphous). Reacted olivine grains (10-15 grains total) originating from experiments in each
244 solution were used for EDX spot analyses. For all analyses, conchoidal fracture surfaces were
245 carefully selected to avoid any pre-existing alteration features on unaltered grains
246 (Supplementary Information 5.1). SEM images and EDX analyses of grain surfaces from all
247 grain sets did not reveal any dissolution features, such as etch pits, or surface precipitates.
248 EDX spot analyses of post reaction surfaces were not distinguishable from those measured on
249 unreacted olivine (in both cases, the nominal compositional stoichiometry of San Carlos
250 olivine was confirmed). Some remaining surface fines (micrometre-sized grain fragments
251 created during comminution) seem to have been present on both unreacted and reacted grains
252 (e.g., Fig. 3a).

253 Detailed high-resolution analyses by transmission electron microscopy (TEM) were centred
254 on three altered olivine grains subjected to 442 d of reaction at -20 °C in a 0.8 % NH₃ saline
255 solution, as this experiment was subject to the longest reaction times. Here, the purpose was
256 to examine structural and chemical changes to the near surface region, which included the
257 formation of secondary phases, in the form of mineral (crystalline) phases or amorphous
258 phases. We examined these samples in cross section with electron transparent foils prepared
259 by focused ion beam (FIB) milling (Supplemental Information 5.2) using standard preparation
260 techniques³⁷. These observations were then compared to samples from unreacted olivine

261 grains prepared in an identical manner (Supplementary Figs. 6-9). TEM analyses were
262 performed using a state-of-the-art Thermo Fisher Scientific Themis Z 3.1 operated at 300 kV,
263 and a Tecnai F20 operated at 200 kV, both housed at the GFZ-PISA facility, Potsdam. We
264 used standard bright and dark field (BF, DF), scanning TEM-high angle annular dark field
265 (STEM-HAADF), and integrated Differential Phase Contrast STEM (iDPC-STEM) imaging
266 techniques^{38,39}, while high resolution chemical analyses were carried out with EELS spectral
267 imaging in STEM mode (Supplemental Information 5.3). The chemical composition of the
268 very thin amorphous SALs (Fig. 3b) could not be measured because of their sensitivity to the
269 electron beam. It is interesting to note that the extreme thinness of the SALs indicates that
270 they would not have acted as a diffusion barrier to the release of Si and Mg from the olivine
271 structure. On the other hand, diffusion limitations can potentially occur for much thicker (up
272 to tens of nm) SALs⁴⁰.

273 Further details concerning methods, materials, instrumental parameters and techniques can be
274 found in the Supplementary Information.

275 **Data availability:** Additional data and complete analysed fluid chemistries are included in
276 Supplementary Information and Supplementary Tables 2-11.

277 **Corresponding author:** correspondence to A. Zandanel.

278 **Acknowledgments:** This study acknowledges the financial support from the French Agence
279 Nationale de Recherche, project ANR OASIS (grant N° ANR-16-CE31-0023-01). We thank
280 Y. Marrocchi for the raw San Carlos olivine and Selfrag AG (Kerzers, Switzerland) for the
281 high voltage pulsed power fragmentation of the original San Carlos olivine sample. The use of
282 equipment in the “Potsdam Imaging and Spectral Analysis Facility” (PISA) is acknowledged.
283 The authors especially thank the European Regional Development Fund and the State of
284 Brandenburg for the Themis Z TEM (part of PISA). Chemical analyses by ICP-AES and BET

285 surface area measurements were performed at the geochemistry-mineralogy platform of
286 ISTERre (UGA, Grenoble, France), partially funded by a grant from Labex OSUG@2020. We
287 also thank A. Schreiber (GFZ) for her help in developing the FIB technique used, N. Findling
288 (ISTERre) for assistance with the sub-zero alteration experiments.

289 **Author contributions:** L.T. designed the project. A.Z. performed the experiments, ICP-AES
290 analyses, and geochemical modelling. R.H. evaluated the kinetic behaviour of olivine
291 dissolution and interpreted TEM results with V.R. FIB and TEM work was carried out by
292 V.R. Raman analyses were performed and interpreted by M.M. The manuscript was written
293 by A.Z., R.H., G.T., and L.T., with contributions from all co-authors. All co-authors
294 contributed to the discussion and interpretation of the data.

295 **Competing interests:** The authors declare no competing interests.

296

297 **Tables**298 **Table 1**

Table 1: Physiochemical parameters									
Solution	NaOH (0 % NH ₃)			0.8 mass % NH ₃			8.0 mass % NH ₃		
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 NH ₃	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

299 **Table 1: Initial physiochemical characteristics of each experiment.**

300 “Fluid : Ice” indicates the mass ratio of unfrozen solution remaining to the moles of ice formed in each
 301 reactor. “Fluid : rock” indicates the mass ratio of unfrozen solution in each reactor to olivine, not
 302 including the mass of the unfrozen solution films at the mineral grain surface. Ionic strength, molal
 303 NH₃, and in-situ pH refer to properties of the in-situ unfrozen solution. In-situ pH was calculated with
 304 the code FREZCHEM¹⁰ from the measured bench temperature of each solution, and increases due to
 305 temperature effects at 4 °C, and due to temperature effect and solute exclusion from the ice phase at -
 306 20 °C. Note that at 22 °C the pH of the 0.8 % NH₃ solution is identical to the 0 % solution, but is
 307 lower than that of the 0 % solution at 4 °C and -20 °C.

308

309 **Display elements legends (Figures submitted separately)**310 **Fig. 1: Characterization of the ice, unfrozen solution, and ice-olivine interface.**

311 **a-c:** Images taken by an optical microscope in polarized transmission mode of the three solutions used
 312 in this study at -8°C: **a.** 0.0 % NH₃. **b.** 0.8 % NH₃. **c.** 8.0 % NH₃. Increased birefringence (highest
 313 birefringence visible as vivid blue) of the ice phase indicates increased crystallinity (Supplementary
 314 Information 3.1). Crystallinity of the ice phase increases with decreasing NH₃ content. **d.** Image of
 315 olivine crystals and deionized water flash-frozen with liquid N₂ and rapidly imaged under a
 316 microscope at room temperature to capture outward propagation of melt. **e.** Representative image of
 317 olivine in frozen solution taken with non-polarized light. **f.** Annotated compilation of three Raman
 318 spectra collected at -20 °C with spectral resolution 0.3-1 cm⁻¹. Two insets show the peaks unique to the
 319 spectra collected at the ice-olivine boundary. The gradual phase transitions recorded in the interfacial
 320 region are an instrumental artifact, the true gradients are much sharper (Supplementary Information
 321 3.2).

322

323

324 **Fig. 2: Measured [Si] and [Mg] concentrations over time and calculated olivine dissolution rates**
 325 **over temperature.**

326 **a. b. c.** Concentrations of Si (circles) and Mg (diamonds) ($\text{mmol L}^{-1} \times 10^{-2}$) in the fluid for the longest
327 running experiment sets (0.8 % NH_3) at each experimental temperature. Concentrations at -20°C (c)
328 are for the bulk (melted) solution. Error bars indicate instrumental error. **d.** Initial (0-14 day) apparent
329 dissolution rates r_{Si} and r_{Mg} over temperature. Divergence between values for r_{Si} and r_{Mg} in the same
330 experiment indicates that the rates become more non-stoichiometric with increasing temperature. **e.**
331 Long-term (167 day) dissolution rates ltr_{Si} and ltr_{Mg} with respect to temperature for all experiments
332 (two experiments were excluded due to reactor failure: see Supplementary Information 6). Error bars
333 show error calculated from summing standard errors of each sample used in the rate analysis and
334 standard deviations of the replicate samples at 167 h. In all panels, where error bars are not visible,
335 error is smaller than the symbols.

336

337

338 **Fig. 3: Solid-state analysis of an olivine grain reacted in 0.8 mass % NH_3 for 442 days at -20°C .**

339 **a.** SEM image of reacted olivine sample surface showing location where the FIB foil was cut (arrow).
340 Note the lack of any obvious surface precipitates or etch pits. **b.** FIB-prepared TEM foil of the same
341 altered sample imaged by iDPC-STEM. The interfacial region is characterized by lattice fringes of
342 unaltered olivine and an Au layer applied before FIB preparation (post-reaction surface). The two
343 phases are separated by a thin surface altered layer (SAL) lacking an ordered structure. The SAL
344 delimits the position of the solvent-olivine interface when the grain was removed from solution. The
345 colored atoms represent an atomic-scale overlay of the forsterite olivine structure.

346

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348 **References**

- 349 1. Vance, S. D. & Melwani Daswani, M. Serpentinite and the search for life beyond Earth. *Philos.*
350 *Trans. R. Soc. A* **378**, (2020).
- 351 2. Waite, J. *et al.* Cassini finds molecular hydrogen in the Enceladus plume: Evidence for
352 hydrothermal processes. *Science* **356**, 155–159 (2017).
- 353 3. Hsu, H.-W. *et al.* Ongoing hydrothermal activities within Enceladus. *Nature* **519**, 207–210 (2015).
- 354 4. Malamud, U. & Prialnik, D. Modeling Kuiper belt objects Charon, Orcus and Salacia by means of
355 a new equation of state for porous icy bodies. *Icarus* **246**, 21–36 (2015).
- 356 5. Malamud, U. & Prialnik, D. A 1-D evolutionary model for icy satellites, applied to Enceladus.
357 *Icarus* **268**, 1–11 (2016).
- 358 6. Palguta, J., Schubert, G. & Travis, B. J. Fluid flow and chemical alteration in carbonaceous
359 chondrite parent bodies. *Earth Planet. Sci. Lett.* **296**, 235–243 (2010).

- 360 7. Guilbert-Lepoutre, A., Prialnik, D. & Métayer, R. Internal structure and cryovolcanism on Trans-
361 Neptunian objects. in *The Trans-Neptunian Solar System* 183–201 (Elsevier, 2020).
- 362 8. Ohnishi, I. & Tomeoka, K. Hydrothermal alteration experiments of enstatite: implications for
363 aqueous alteration of carbonaceous chondrites. *Meteorit. Planet. Sci.* **42**, 49–61 (2007).
- 364 9. Sekine, Y. *et al.* High-temperature water–rock interactions and hydrothermal environments in the
365 chondrite-like core of Enceladus. *Nat. Commun.* **6**, 8604 (2015).
- 366 10. Marion, G. M. & Kargel, J. S. *Cold aqueous planetary geochemistry with FREZCHEM: from*
367 *modeling to the search for life at the limits.* (Springer Science & Business Media, 2007).
- 368 11. Marion, G., Kargel, J., Catling, D. & Lunine, J. Modeling ammonia–ammonium aqueous
369 chemistries in the Solar System’s icy bodies. *Icarus* **220**, 932–946 (2012).
- 370 12. Pokrovsky, O. S. & Schott, J. Kinetics and mechanism of forsterite dissolution at 25 °C and pH
371 from 1 to 12. *Geochim. Cosmochim. Acta* **64**, 3313–3325 (2000).
- 372 13. Rimstidt, J. D., Brantley, S. L. & Olsen, A. A. Systematic review of forsterite dissolution rate
373 data. *Geochim. Cosmochim. Acta* **99**, 159–178 (2012).
- 374 14. Hausrath, E. & Brantley, S. L. Basalt and olivine dissolution under cold, salty, and acidic
375 conditions: What can we learn about recent aqueous weathering on Mars? *J. Geophys. Res.*
376 *Planets* **115**, E12001 (2010).
- 377 15. Niles, P. B., Michalski, J., Ming, D. W. & Golden, D. Elevated olivine weathering rates and
378 sulfate formation at cryogenic temperatures on Mars. *Nat. Commun.* **8**, 998 (2017).
- 379 16. Anderson, D. M. The interface between ice and silicate surfaces. *J. Colloid Interface Sci.* **25**, 174–
380 191 (1967).
- 381 17. Barer, S., Churaev, N., Derjaguin, B., Kiseleva, O. & Sobolev, V. Viscosity of nonfreezing thin
382 interlayers between the surfaces of ice and quartz. *J. Colloid Interface Sci.* **74**, 173–180 (1980).
- 383 18. Rietmeijer, F. J. A model for diagenesis in proto-planetary bodies. *Nature* **313**, 293–294 (1985).
- 384 19. Dickinson, W. W. & Rosen, M. R. Antarctic permafrost: An analogue for water and diagenetic
385 minerals on Mars. *Geology* **31**, 199–202 (2003).
- 386 20. Park, R. *et al.* A partially differentiated interior for (1) Ceres deduced from its gravity field and
387 shape. *Nature* **537**, 515–517 (2016).

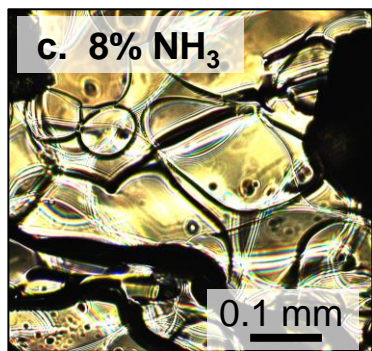
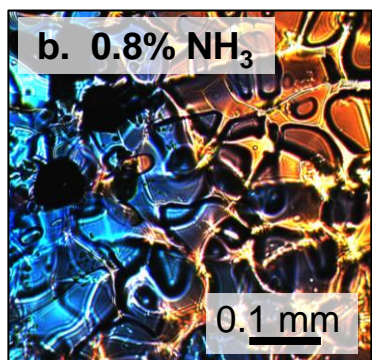
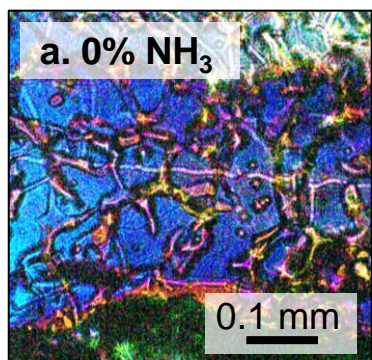
- 388 21. Iess, L. *et al.* The gravity field and interior structure of Enceladus. *Science* **344**, 78–80 (2014).
- 389 22. Zannoni, M., Hemingway, D., Casajus, L. G. & Tortora, P. The gravity field and interior structure
390 of Dione. *Icarus* **345**, 113713 (2020).
- 391 23. Bach, W. Some compositional and kinetic controls on the bioenergetic landscapes in oceanic
392 basement. *Front. Microbiol.* **7**, 107 (2016).
- 393 24. Běhounková, M. *et al.* Tidally Induced Magmatic Pulses on the Oceanic Floor of Jupiter’s Moon
394 Europa. *Geophys. Res. Lett.* **48**, e2020GL090077 (2021).
- 395 25. Affholder, A., Guyot, F., Sauterey, B., Ferrière, R. & Mazevet, S. Bayesian analysis of
396 Enceladus’s plume data to assess methanogenesis. *Nat. Astron.* 1–10 (2021).
- 397 26. Brunetto, R. & Lantz, C. Laboratory perspectives on sample returns from Hayabusa2 and OSIRIS-
398 REx. *Nat. Astron.* **3**, 290–292 (2019).
- 399 27. Marchi, S. *et al.* An aqueously altered carbon-rich Ceres. *Nat. Astron.* **3**, 140–145 (2019).
- 400 28. Choblet, G. *et al.* Powering prolonged hydrothermal activity inside Enceladus. *Nat. Astron.* **1**, 841
401 (2017).
- 402 29. O’Hanley, D. S. *Serpentinites: records of tectonic and petrological history.* (Oxford University
403 Press on Demand, 1996).
- 404 30. Rubin, A. E., Trigo-Rodríguez, J. M., Huber, H. & Wasson, J. T. Progressive aqueous alteration
405 of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **71**, 2361–2382 (2007).
- 406 31. Rubin, A. E. Size- frequency distributions of chondrules in CO₃ chondrites. *Meteoritics* **24**, 179–
407 189 (1989).
- 408 32. Zolotov, M. Y. An oceanic composition on early and today’s Enceladus. *Geophys. Res. Lett.* **34**,
409 L23203 (2007).
- 410 33. Glein, C. R., Baross, J. A. & Waite, J. The pH of Enceladus’ ocean. *Geochim. Cosmochim. Acta*
411 **162**, 202–219 (2015).
- 412 34. Miller, H. M. *et al.* Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and
413 implications for microbial habitability. *Geochim. Cosmochim. Acta* **179**, 217–241 (2016).

- 414 35. Lafay, R., Fernandez-Martinez, A., Montes-Hernandez, G., Auzende, A. L. & Poulain, A.
415 Dissolution-reprecipitation and self-assembly of serpentine nanoparticles preceding chrysotile
416 formation: Insights into the structure of proto-serpentine. *Am. Mineral.* **101**, 2666–2676 (2016).
- 417 36. Ball, J. & Nordstrom, D. *User's Manual for WATEQ4F, with Revised Thermodynamic Data Base*
418 *and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural*
419 *Waters*. 189 (1991).
- 420 37. Schaffer, M., Schaffer, B. & Ramasse, Q. Sample preparation for atomic-resolution STEM at low
421 voltages by FIB. *Ultramicroscopy* **114**, 62–71 (2012).
- 422 38. Lazić, I., Bosch, E. G. & Lazar, S. Phase contrast STEM for thin samples: Integrated differential
423 phase contrast. *Ultramicroscopy* **160**, 265–280 (2016).
- 424 39. Bosch, E. G. & Lazić, I. Analysis of HR-STEM theory for thin specimen. *Ultramicroscopy* **156**,
425 59–72 (2015).
- 426 40. Daval, D. *et al.* Influence of amorphous silica layer formation on the dissolution rate of olivine at
427 90 °C and elevated pCO₂. *Chem. Geol.* **284**, 193–209 (2011).
- 428
- 429
- 430

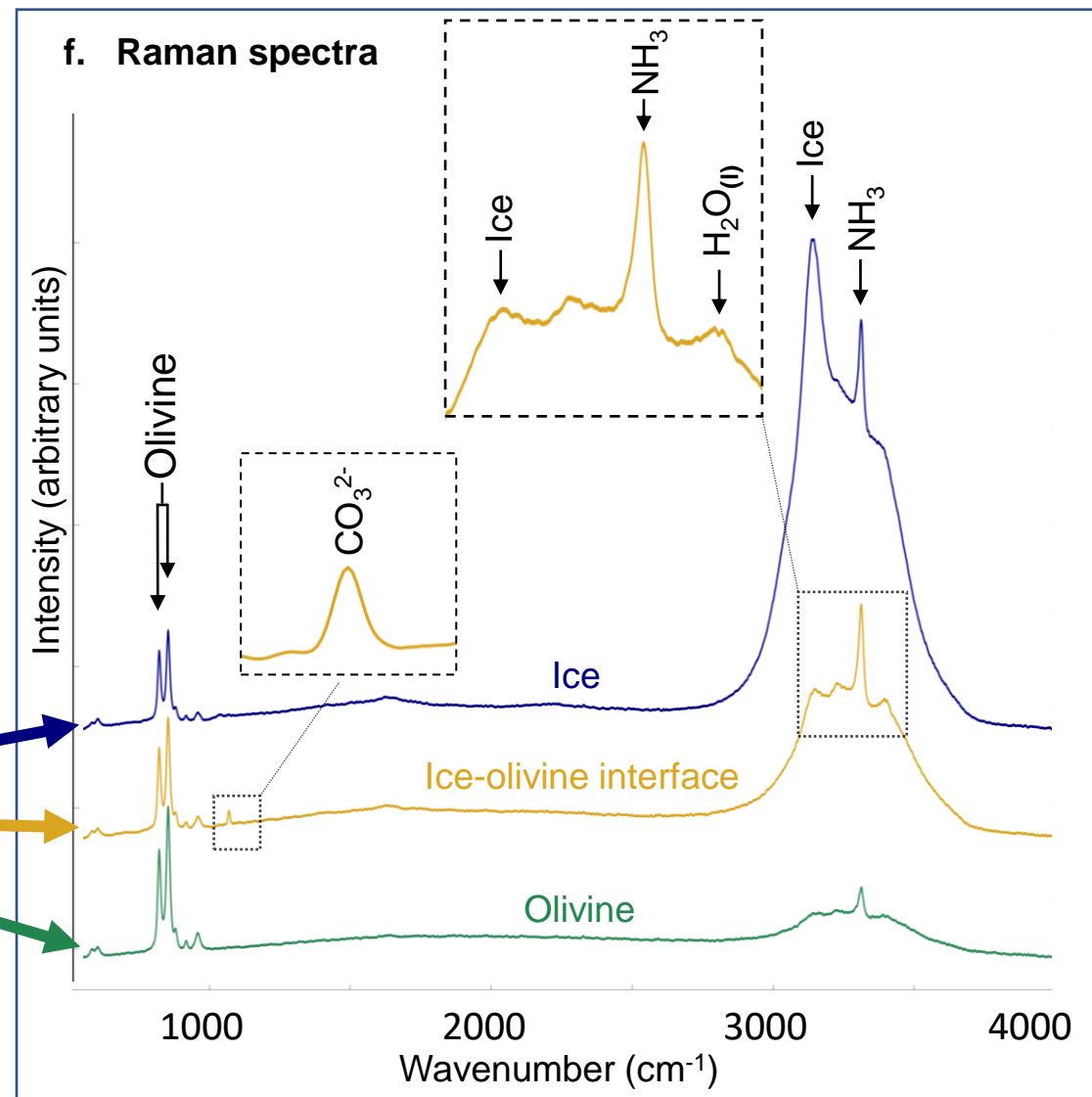
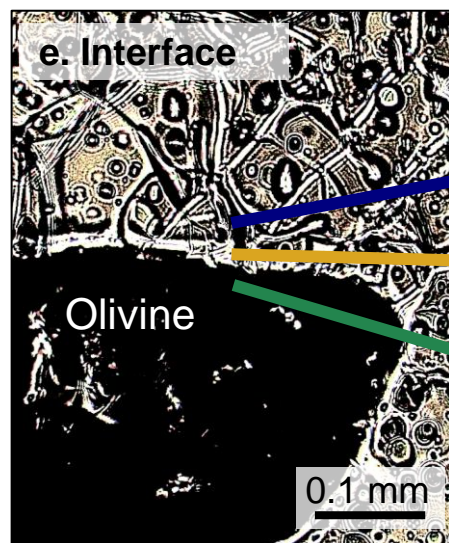
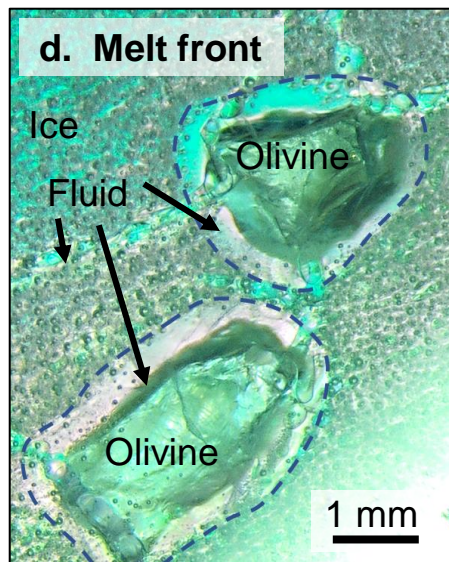
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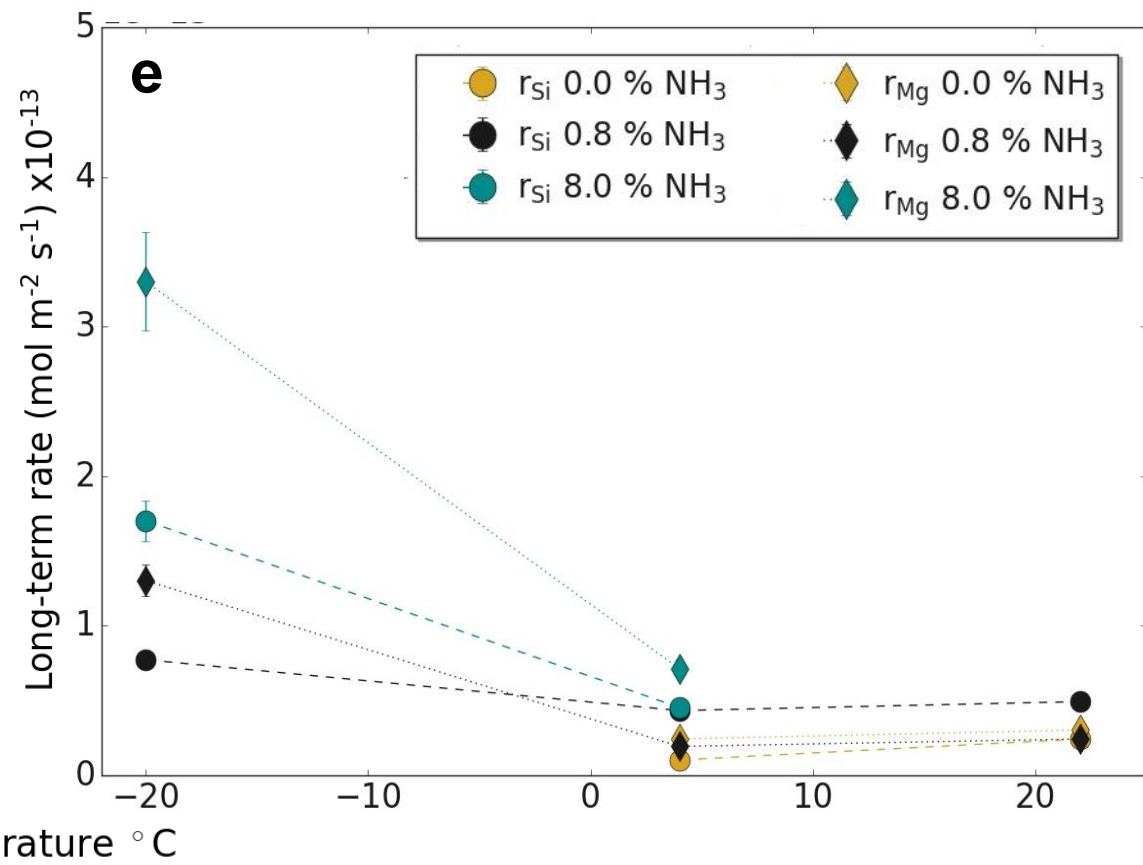
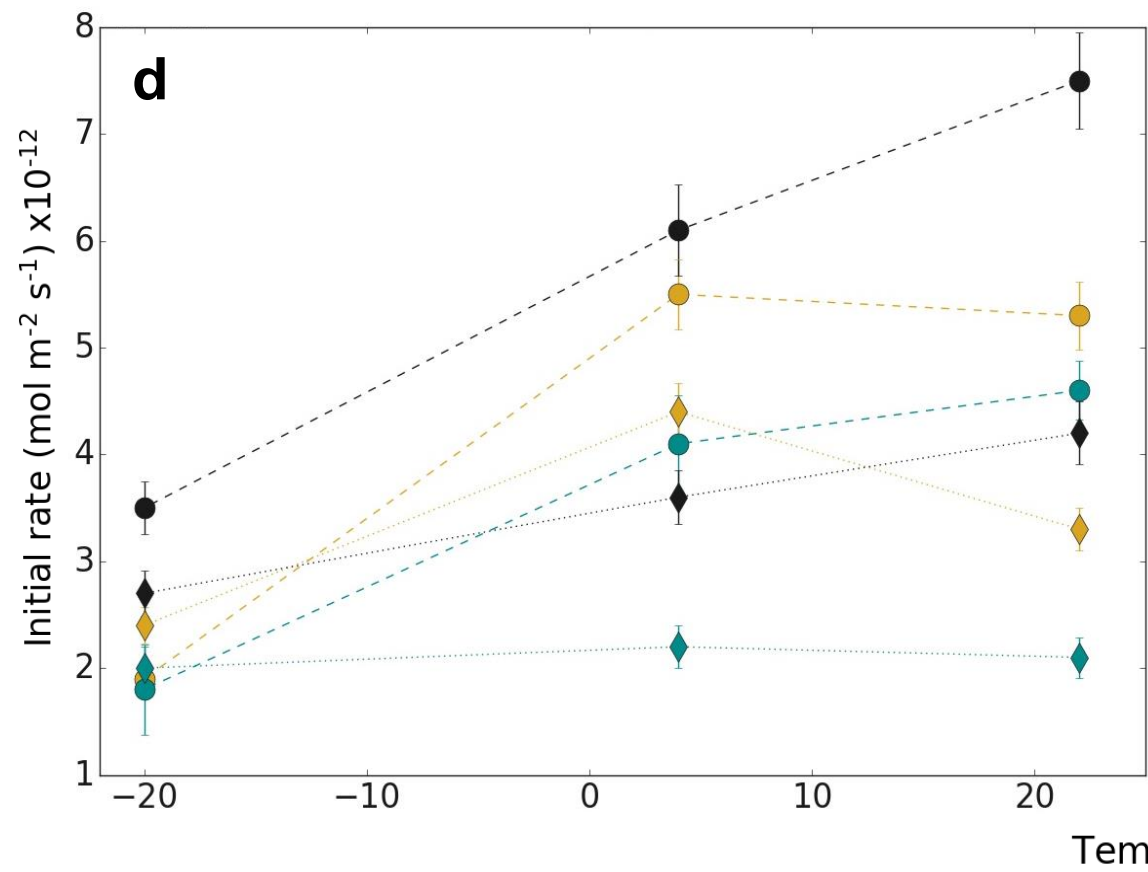
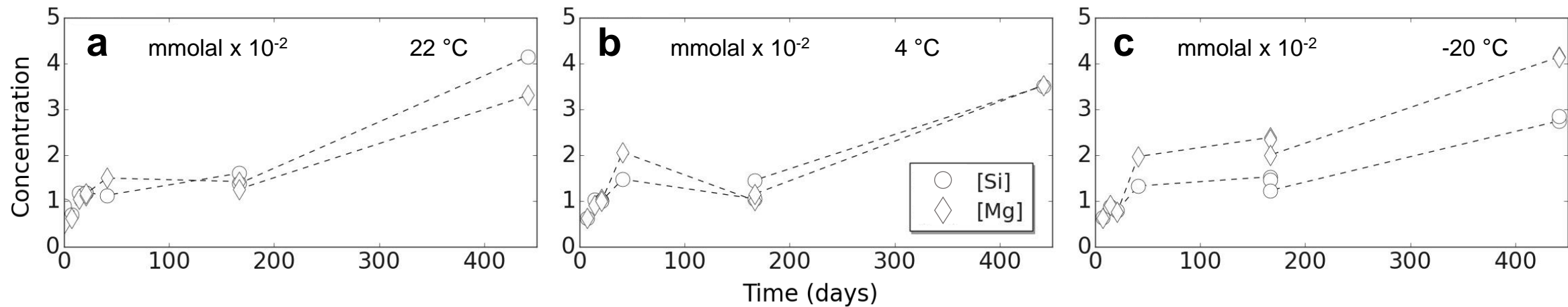
432

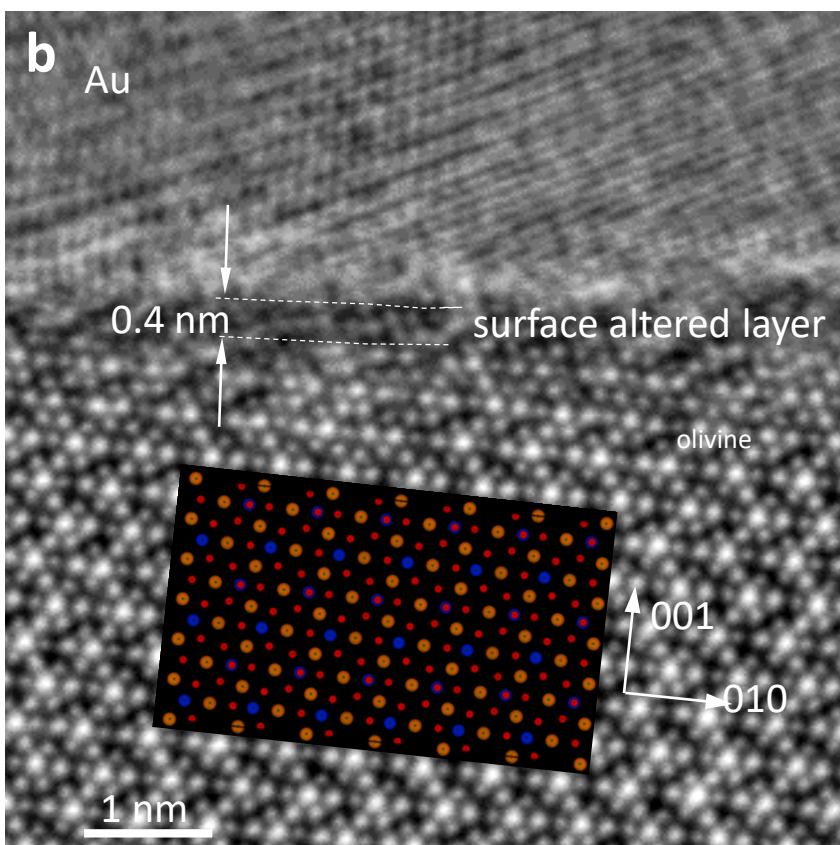
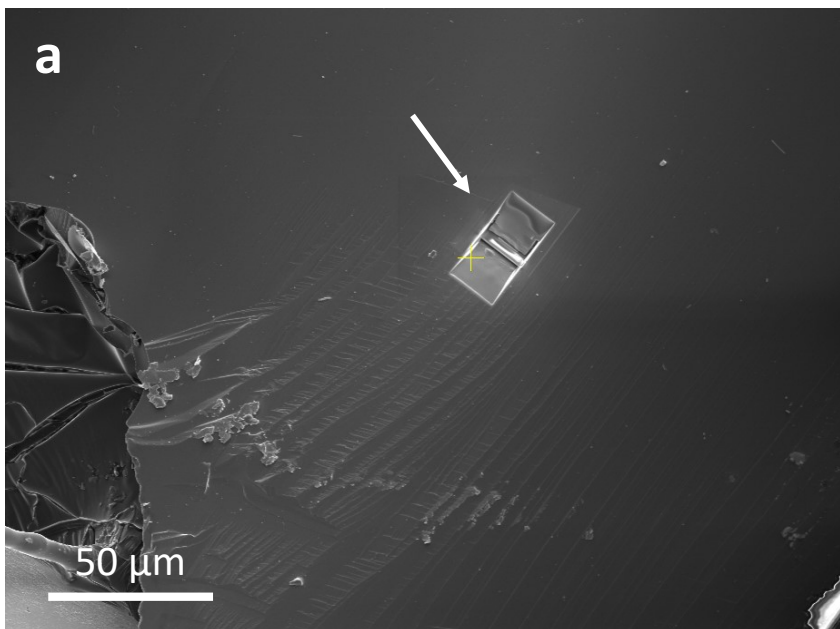
Increasing ice crystallinity / Decreasing NH_3 content



Fluid at the ice-olivine interface







● Si ● O ● Fe/Mg