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3   Simulated Diagenesis of the Iron-Silica Precipitates in Banded Iron Formations

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9

10   **Abstract**

11   Banded Iron Formations, or BIFs, are chemically precipitated sediments that can record Archean

12   ocean geochemistry. BIFs are laminated silica- and iron-rich deposits that host a range of iron(II,

13   III) minerals, including hematite, magnetite, siderite, greenalite, minnesotaite, and stilpnomelane.

14   This diverse mineralogical assemblage reflects secondary mineralization reactions due to

15   diagenesis and/or post-depositional alteration. While petrographic observations of BIFs sparingly

16   contain the iron silicate greenalite, recent evidence of greenalite nanoparticles preserved in early-

17   mineralizing BIF chert suggest this mineral was a primary phase in BIF progenitor sediments.

18   Therefore, it is critical to investigate the formation and alteration of greenalite to constrain the

19   Archean ocean environment and help unravel post-depositional processes. To examine how iron

20   silicates precipitate and then crystallize and/or transform during diagenesis, we simulated these

21   two processes under Archean ocean conditions. We first precipitated a poorly ordered Fe-rich

22   serpentine with subsidiary ferrihydrite at neutral pH by performing in situ Fe(II) oxidation

23   experiments at 25 °C in the presence of silica. Subjected to simulated diagenesis at 80 °C, the

24   rudimentary Fe- phyllosilicate transformed into a crystalline phyllosilicate characterized as 30%

25   cronstedtite-70% greenalite accompanied by magnetite and persistent ferrihydrite. At

26   temperatures ≥ 150 °C, we continued to observe ferrihydrite, increased magnetite formation, and

27   elevated incorporation of Mg into the phyllosilicate as it further recrystallized into Mg-

28   greenalite. Our findings demonstrate a possible formation mechanism of early silicates through

29   partial Fe(II) oxidation and support petrographic observations that magnetite likely mineralizes

30   during diagenesis. Additionally, we suggest that Mg contents in BIF iron phyllosilicates could

31   serve as a tracer for diagenesis, with Mg signaling phyllosilicate-fluid interactions at elevated

32   temperatures. Ultimately, our experiments help reveal how initial iron-silica coprecipitates are

33   altered during diagenesis, providing novel insights into the interpretation of greenalite and

34   magnetite in ancient BIF assemblages.

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39   Keywords: greenalite, crystallization, magnesium substitution, magnetite, serpentine

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Introduction

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42   Chemical sediments provide an archive of (bio)geochemical processes. The oceans on

43 Archean [4.0-2.5 billion years ago, Ga] Earth were actively precipitating and depositing

44 authigenic chemical sediments, which can therefore serve as a proxy for the ancient marine

45 (bio)geochemistry and signals of the evolution of life (Derry and Jacobson 1990). A prominent

46 example of such sediments are the banded iron formation (BIF) deposits, laminated sedimentary

47 deposits that contain at least 15% iron and commonly also host a high silica content (James

48 1954). BIFs provide the best record of ancient marine conditions in the Archean ocean, with their

49 chemistry interpreted as reflecting an iron and silica rich system (Klein 2005; Bekker et al.

50 2014).

51   The presence of BIF deposits in ancient oceans require a mechanism to initially induce

52 chemical precipitation (Holland 1984). Minerals recorded in BIFs contain Fe(II) and Fe(III) with

53 an average oxidation state of $Fe^{2.4+}$ (Klein and Beukes 1992). This is indicative of a partially

54 oxidative environment, the result of biotic and/or abiotic processes in Archean oceans and

55 sediments. Extensive BIF deposition occurred in the Archean ocean, which had little to no

56 molecular oxygen until the Great Oxygenation Event at ~2.3 Ga (Gumsley et al. 2017; Farquhar

57 et al. 2011; Poulton et al. 2021; Johnson and Molnar 2019). Estimates place atmospheric O_2 prior

58 to this rise in oxygen as < 1 ppm or less than $\sim10^{-5.7}$ atm (Pavlov and Kasting 2002; Farquhar et

59 al. 2011). A popular hypothesis for the deposition of precursor BIF sediments invoked low levels

60 of dissolved O_2 in the ocean reacting with dissolved Fe^{2+} to consume marine oxygen and form

61 insoluble Fe^{3+} precipitates such as ferric (oxyhydr)oxides (Cloud 1973; Bekker et al. 2014;

62 Konhauser et al. 2017). Others have attributed the generation of BIF progenitor precipitates to

63 anoxygenic Fe^{2+}-oxidizing photosynthesis (Hartman 1984; Kappler et al. 2005; Konhauser et al.

64   2002) or reactions between Fe^{2+} and ultraviolet light (Cairns-Smith 1978; Braterman et al. 1983;

65   Bekker et al. 2010).

66   To identify the potential processes responsible for their formation, the iron-rich muds and

67   cherts in BIFs have been intensely investigated. However, the primary BIF sediments

68   experienced physical and chemical alteration as they transformed into sedimentary rock through

69   the process of diagenesis, and most of these rocks were then subject to subsequent post-

70   depositional alteration, fluid flow, and metamorphism (Beukes 1984; Fischer and Knoll 2009;

71   Trendall 2002). Consequently, none of the minerals in BIFs are considered the initial

72   precipitates and BIF deposits are composed of a mineral mixture of chert, hematite, magnetite,

73   iron-rich carbonates, and iron silicates at disequilibrium   (Klein 2005; Bekker et al. 2014;

74   Konhauser et al. 2017). This complexity has led to an ongoing debate to determine the most

75   primary   mineral(s) associated with BIFs, as only the original precipitates would accurately

76   reflect Archean marine geochemistry and potentially biology.

77   The effects of diagenesis and later alteration complicates the detection of the initial

78   amorphous and/or metastable phases precipitated in Archean oceans, and competing hypotheses

79   suggest two different original BIF precipitates. Earlier models, supplemented by numerous

80   observations of BIFs, pointed to ferric oxides or hydroxides being the primary iron precipitate

81   (James 1954; Cloud 1973; Klein and Beukes 1989; Beukes and Gutzmer 2008; Sun et al. 2015).

82   However, recent studies examined early-mineralizing chert within BIFs that can serve as a

83   barrier to diagenesis, preserving the early assemblage of minerals. These investigations

84   discovered inclusions of iron-rich silicate nanoparticles and suggested these iron silicates were

85   primary minerals from the Archean ocean (Muhling and Rasmussen 2021; Rasmussen et al.

86   2015; Rasmussen et al. 2019). Further characterization of the iron silicate nanoparticles

87   concluded they contained undetectable to < 0.5 atomic% (at.%)   quantities of magnesium and

88   ~10-25% Fe(III) (Johnson et al. 2018; Rasmussen et al. 2018). The primary silicates are thus

89   within the solid solution space between greenalite [$(Fe^{2+},Mg)_3Si_2O_5(OH)_4$] and cronstedtite

90   [$(Fe^{2+},Fe^{3+},Mg)_3(Si,Fe^{3+})_2O_5(OH)_4$]), two serpentine group iron silicates with 7 Ångstrom (Å)

91   lattice spacing.

92   These recent observations call for an understanding of the geochemical conditions and

93   mechanism(s) required to form iron silicates under plausible Archean ocean conditions. Previous

94   anoxic ex periments conducted at low temperatures of 20-25 °C reported the formation of

95   amorphous to poorly crystalline iron(II)-silica precipitates, proposed to be precursor silicates,

96   when pH was ≥ 7.5 (Farmer et al. 1991; Tosca et al. 2016). The analyses performed on these

97   iron-silica precipitates could not definitively conclude whether these precipitates were a

98   heterogeneous mix of Fe(II) and Si-rich phases or homogenous Fe(II)-silicates (Francisco 2020).

99   However, similar experiments in another study demonstrated that the initial Fe(II)-Si

100   coprecipitates at pH 7.5 could be hydrothermally aged into greenalite-like phases with ~7 Å

101   lattice spacing (Hinz et al. 2021). Another concern with the relevance of these experiments is

102   that the pH of ≥ 7.5 used in these experiments was higher than the hypothesized pH of the

103   Archean ocean, which was constrained to pH ~6.5-7.0 by two independent marine and

104   atmospheric geochemical models (Halevy and Bachan 2017; Krissansen-Totten et al. 2018) and

105   considerations of authigenic clay formation (Isson and Planavsky 2018). An additional issue with

106   Fe(II)-silicate precipitation generating the initial BIF sediments is that this Fe(II)-silica saturation

107   mechanism would not account for the low levels of Fe(III) detected in the BIF iron silicate

108   inclusions.

109   To address whether ferric iron can in fact induce precipitation of iron silicates at a more

110   plausible Archean ocean pH of 6.5-7.0, we previously examined the precipitate products

111   resulting from the addition of low amounts of aqueous (aq) Fe(III) to ferrous iron- and silica-rich

112   conditions (Hinz et al. 2021). We found that Fe(III) (aq) triggered the low-temperature

113   precipitation of an amorphous iron- and silica-rich phase accompanied by rare layered silicate-

114   like structures at these more relevant pH values. Earlier studies have simulated diagenesis by

115   hydrothermally aging iron and/or magnesium and silica suspensions at ≥ 60 °C to promote the

116   crystallization of silicates (Baldermann 2014; Mizutani et al. 1991; Tosca et al. 2011). When we

117   hydrothermally aged our Fe(II,III)-silica precipitates at 150 °C, we identified the crystalline

118   products as ~7 Å iron phyllosilicates, similar to BIF greenalite but more magnesium-rich, along

119   with additional green rust carbonate, magnetite, hematite, and magnesite (Hinz et al. 2021).

120   The highly oxidized and heterogeneous assemblage that we observed after Fe(III) (aq)

121   additions and 150 °C aging motivated us to explore an alternative precipitation mechanism and

122   hydrothermal aging scheme at several temperatures. In this study, we induced in situ partial

123   Fe(II) oxidation at pH 7 in the presence of silica by bubbling low concentrations of oxygen gas

124   into simulated Archean ocean conditions. The partially-oxidized iron-silica precipitates that

125   formed at room temperature (25 °C) aimed to recreate phases that formed in the Archean water

126   column. To promote crystallization and simulate chemical reactions, we hydrothermally aged

127   these precipitates over the typical diagenetic temperature interval of surface temperatures to 200

128   °C (Brenner et al. 1991; Siever 1986). Similar to previous experimental studies of silicate

129   systems, we aged our initial iron-silica precipitates within anoxic, sealed vessels in sequential

130   steps at 80 °C (Pignatelli et al. 2013; Vacher et al. 2019), 150 °C (Baldermann et al. 2014;

131   Mizutani et al. 1991) and 220 °C (Janecky and Seyfried 1986) and compared these precipitates to

132   low-temperature (25 °C) products. We measured solution chemistry over the course of the

133   simulated diagenesis and characterized the resultant precipitates as they crystallized and

134   transformed.

135

136   **Methods**

137   **Experimental Solution Setup**

138   All experiments originated from bulk uniform solutions prepared in 4 L wide mouth jugs

139   at room temperature with 18.2 MΩ-cm ultrapure water. The ultrapure water was boiled before

140   being covered with aluminum foil and purged with pure N_2 gas to deoxygenate the water. Next,

141   the water was brought into a MBraun glovebox consisting of an N_2 atmosphere (< 0.1 ppm O_2)

142   where it was stirred uncapped for at least 72 hours to release any residual oxygen in solution. All

143   solid chemical reagents were weighed outside the glovebox before being transported into the

144   glovebox to be dissolved in deoxygenated water used in experimentation.

145   We prepared a 3.6 L solution in duplicate where first sodium orthosilicate (Na_4SiO_4) was

146   dissolved in the anoxic ultrapure water to a final concentration of 1.1 mM Si. Estimated

147   dissolved silica in Archean seawater was expected to be between ~0.67 mM to an upper limit at

148   amorphous SiO_2 saturation of, ~1.9 mM (Siever 1992; Maliva et al. 2005; Stefurak et al. 2015;

149   Gunnarsson and Arnórsson 2000); we therefore chose an intermediate level between these

150   constraints and below amorphous silica precipitation. The solution was stirred, and the pH was

151   measured with a ThermoFisher Orion Star A221 pH meter outfitted with a Fisherbrand accuCap

152   spear tipped capillary junction pH probe while being adjusted to pH 7 by dropwise additions of 1

153   M hydrochloric acid (HCl). The solution was continuously stirred in the glovebox for 24 hours to

154   allow for the depolymerization of the dissolved silica in solution (Dietzel 2000) before we added

155   other Archean seawater salts.

156   Assuming similar salinity over time, our Archean solution (Table 1) had 400 mM sodium

157   chloride and 7 mM potassium chloride, comparable to the   modern ocean   (Riley and Chester

158   1971). Archean ocean models have estimated ammonium to be 0.03-10 mM (Stüeken 2016);

159   therefore, we added 10 mM ammonium chloride at the upper end of this range as this reductant

160   may   help maintain   reducing conditions. The magnesium content in Archean oceans has

161   been estimated to be 10-30 mM (Jones et al. 2015), with processes associated with hydrothermal

162   seawater-oceanic crust interactions decreasing dissolved magnesium in ocean water from today's

163   concentration of ~50 mM (Spencer and Hardie 1990; Halevy and Bachan 2017; Izawa et al.

164   2010). We used the lower estimate and added 10 mM magnesium chloride. A maximum

165   concentration of ~2 mM Fe(II) in Archean oceans has been suggested to be constrained by the

166   supersaturation of ferrous silicates (Jiang and Tosca 2019); we thus set Fe(II) to 1.1 mM.

167   Archean oceans have been estimated to contain 5-30 mM of dissolved inorganic carbon

168   (DIC) (Blättler et al. 2017), and we assume initial pore fluids would have similar concentrations.

169   Additionally, the presence of common organic buffers (HEPES & MOPS) has been shown to

170   impact iron oxidation (Buchholz et al. 2011). Therefore, we added the highest estimate for

171   bicarbonate, 30 mM (Table 1), to both maximize inorganic buffering and account for potential

172   increases in DIC due to organic carbon respiration in the sediments (e.g., Heimann et al, 2010).

173   See Supplemental Materials (SM) for more details.

174   We then mixed the solutions to homogenize any slight chemical differences before

175   apportioning the solution into twelve 610 mL borosilicate glass bottles, wrapped in aluminum

176   foil to prevent any possible ultraviolet (UV) photooxidation of Fe(II). Six of the newly sealed

177   experiments remained in the glovebox to act as ferrous controls. The remaining six identical

178   bottles were removed from the glovebox to be bubbled with low O_2.

179   To partially oxidize the Fe(II) (aq) in situ under simulated Archean ocean conditions, six

180   sealed experimental bottles were equilibrated with N_2 mixed with 49.1 ± 0.9 ppm O_2. Each

181   solution was continuously bubbled with this gas mixture at 3 psi at 25 °C for 90 minutes while

182   outgassing through a separate needle (expanded description in SM). The bottles were transported

183   back into the glovebox and remained resting on their side wrapped in aluminum foil.

184

Initial Fe(II) Oxidation and pH

186   The bubbled and control experiments were allowed to react and equilibrate horizontally

187   in the glovebox at 25 °C. Each bottle was shaken horizontally three times a week to homogenize

188   the solution. After 19 days, we observed that increases in precipitate quantity had stopped for > 4

189   days and deemed that the Fe(II) (aq) had fully reacted with O_2. We then measured the pH of each

190   control and bubbled experiment (Table 2).

191   To measure the extent of Fe(II) oxidation (reported as Fe(III)/FeT), one of each of the

192   bubbled and control experimental bottles were unsealed and completely acidified with anoxic 4

193   M HCl to a pH of 3 for > 12 hours, after which all visible precipitate was dissolved.

194   Subsequently, the dissolved experimental solutions were analyzed by the ferrozine assay

195   (Stookey 1970; Viollier et al. 2000) to determine the bulk Fe(III)/FeT (Table 3) after

196   equilibration for 19 days at 25 °C. In addition, two precipitate subsamples from the bubbled

197   experiments after 19 days at 25 °C (Fig. 1) were removed and washed three times between

198   centrifuging. One subsample was acidified following the same protocol as described above to

199   complete dissolution before being analyzed by the ferrozine assay (Table 4) while the other

200   subsample was stored and later dissolved and analyzed for its Fe(II) content by the Wilson

201   vanadate method (Tables S1,S2); more details on these assays are below and in SM.

202

203   **Hydrothermal Aging and Subsampling**

204   The remaining four control and four bubbled experiments were mixed to homogenize

205   each condition's solution. The solution, along with any precipitate present, was equally

206   distributed in 15 mL increments into eight separate 22 mL stainless steel gas-tight Parr vessels fit

207   with a PTFE gasket and anoxically sealed. Each bubbled vessel contained ~1-2 grams of

208   precipitate while the control solution had no apparent solids. One of the control and bubbled

209   experiments remained sealed in a Parr vessel within the glovebox at 25 °C for the duration of

210   simulated diagenesis (total of 40 days). Three control and three bubbled experiments in Parr

211   vessels were taken out of the glovebox and placed into a Thermo Scientific™ Heratherm™ oven

212   set at 80 °C to undergo hydrothermal aging.

213   After 7 additional days of hydrothermal aging at 80 °C, one of the control and bubbled

214   Parr vessels were removed from the oven and transferred to the glovebox (Fig. 1). The

215   hydrothermally aged 80 °C vessels were allowed to cool to 25 °C before a pH measurement of

216   the solution was taken (Table 2). If a precipitate was present, the precipitate slurry was

217   centrifuged three times and rinsed with anoxic water with a pH ± 0.1 of the measured solution

218   value (Table 2) to limit pH-driven reactions after simulated diagenesis while removing excess

219   salts prior to analysis. The precipitate was then subsampled for future analysis and stored in

220   anoxically-sealed Mylar bags within the glovebox at 25 °C. The oven temperature was increased

221   to 150 °C for the remaining Parr vessels.

222   After 7 additional days at 150 °C, another control and bubbled Parr vessel were

223   withdrawn from the oven and taken to the glovebox (Fig. 1). The experimental solutions were

224   again cooled to 25 °C in the glovebox before the pH was measured (Table 2), and any precipitate

225   was rinsed as described above and apportioned for future analysis. After this higher temperature,

226   the control experiment appeared to contain ~0.1 gram of precipitated material while the bubbled

227   experiment had a very similar amount of material as the initial 25 °C starting amount. Finally,

228   the oven temperature for the remaining two Parr vessels was increased to 220 °C.

229   After 7 additional days at 220 °C, the last remaining control and bubbled Parr vessels

230   were transferred to the glovebox (Fig. 1). The solution pH was measured (Table 2), and the

231   precipitate was rinsed and allocated for future analysis. The control and bubbled Parr vessels that

232   remained in the glovebox for the entire 40 days at 25 °C were measured for pH (Table 2), and

233   any precipitate was rinsed and subsampled for future analysis.

234   Using the Act2 program in Geochemist's Workbench (Bethke, 2007), we additionally

235   created stability diagrams for Fe and Mg phases across pH (0-14) and redox space (redox

236   potential, or Eh) to consider the thermodynamically-predicted phases and the potential redox

237   environments that our experimental precipitates experienced during hydrothermal aging.

238

Analytical Sample Preparation and Instrument Parameters

Iron(II) and (III) Content of Solids

241   Control and bubbled experiments that produced precipitates were acidified in the

242   glovebox with anoxic 4 M HCl, vigorously shaken, and allowed to dissolve for > 12 hours,

243   following suggestions by Porsch and Kappler (2011) and Braunschweig et al. (2012) to dissolve

244   samples under anoxic conditions at low temperatures to prevent Fe(II) oxidation. However, we

245   used 4 M HCl (instead of 1 M or 6 M HCl) to maintain consistency with the ferrozine assay

246   (Viollier et al. 2000) and subsequently observed complete dissolution of our experimental solids.

247   Dissolved precipitates were analyzed by the ferrozine assay from three subsamples from each

248   experiment to determine the Fe(III)/FeT content (Stookey 1970; Viollier et al. 2000).

249   We additionally evaluated the Fe(II) content of our bubbled experiments following a

250   modified version of the Wilson vanadate method to determine the percent Fe(II) in the samples

251   using a titration-based method (Andrade et al. 2002). See the SM for more details.

252

253   **X-ray Diffraction (XRD)**

254   A precipitate slurry was pipetted as 20 µL subsamples into Cole-Parmer Kapton tubes

255   with an inner diameter of 1.46 mm and a 0.05 mm wall thickness. Kapton tubes filled with

256   experimental precipitate were allowed to partially dry for 12 hours in the glovebox before both

257   ends of the Kapton tubes were heat sealed shut. The sealed Kapton tubes were protectively

258   placed in 15 mL falcon tubes and heat sealed in mylar bags prior to shipping. Samples were sent

259   to McMaster Analytical X-Ray Diffraction Facility (MAX) for XRD analysis using a Bruker D8

260   DISCOVER cobalt source tube (Co-XRD) with a DAVINCI.DESIGN diffractometer. The

261   diffractometer was set at 35 kV and 45 mA, with a 1 mm slit and 1 mm collimator, with data

262   collected on a VÅNTEC-500 area detector with a 20 cm working distance. Each sample scan

263   included 4 frames (900 seconds per frame) at 3 separate sample areas over a 2θ range of 10-88º.

264   The 2D frames were collected with DIFFRAC.MEASUREMENT Centre Version 6.5 software

265   and patterns were integrated to 1D using DIFFRAC.EVA Version 4.2.

266

267   **Transmission Electron Microscopy (TEM)**

268   Freshly subsampled precipitates were diluted in anoxic water with a pH $\pm$ 0.1 of the

269   measured condition before pipetting 15 µL of diluted slurry onto lacey carbon coated 300-mesh

270   Cu TEM grids. We allowed residual solution to evaporate prior to analysis, drying in the

271   glovebox under anoxic conditions ($<$ 0.1 ppm O_2), before storing the grids in TEM grid holders

272   and anoxically heat sealing them in a mylar bag. The mylar bags were removed from the

273   glovebox and shipped to Colorado School of Mines, Golden, Colorado, USA for analysis.

274   Samples were examined on a Talos F200X at 200 keV for high-resolution imaging (HR-TEM)

275   up to 0.12 nm, scanning transmission electron microscopy (STEM) imaging up to 0.16 nm, and

276   Super-X window-less electron dispersive X-ray spectroscopy (EDS) analysis. Samples were

277   imaged in high-angle annular dark-field (HAADF) to discern different phases. HR-TEM imaging

278   was used to capture the crystal lattice spacing where the images were analyzed by Fast-Fourier

279   Transformation (FFT) and Inverse FFT (IFFT) using Gatan DigitalMicrograph software.

280   Additional structural data of individual phases was recorded by selected area electron diffraction

281   (SAED). Elemental data was captured by the Talos F200X Super-X EDS detector for a minimum

282   of ten minutes at each location. Bruker ESPRIT software Version 1.9 was used to analyze and

283   quantify the EDS data by the Cliff-Lorimer method with a 1x2 binning. This method converts X-

284   ray counts into raw elemental weight or atomic percent, yielding an accuracy of $\pm$1-10% of the

285   collected values. We analyzed representative areas of silicates and oxides to obtain their atomic

286   ratios of cations by first averaging the data from the most isolated particles, then recalculating

287   the oxygen atomic % using cation valence (ignoring any salt-related cations), and finally re-

288   normalizing the data to 100%. We then took the atomic ratios of (Fe+Mg)/Si and Fe/(Fe+Mg) to

289   gain insights into the silicate character. Image contrast and brightness were adjusted to optimize

290   image clarity.

291

Results

Solution and Precipitate Chemical Analysis

Over the course of this experimental set-up, we measured the pH and extent of iron

oxidation in the control and bubbled experiments. The ferrous control experiment after 19 days

at 25 °C had a measured pH of 7.14 (Table 2). This experiment had no observable precipitate but

after fully acidifying the experimental solution to dissolve any minor solids or colloids, we

determined it contained 0.07 Fe(III)/FeT in bulk (Table 3). After a total of 40 days, the 25 °C

control had a measured pH of 7.17 (Fig. 2a; Table 2). This room temperature control had no

visible color change and yielded no precipitate from which to obtain a Fe(III)/FeT precipitate

measurement.

Increased hydrothermal temperatures can mimic diagenesis by either inducing higher-

temperature reactions such as those that take place during sediment burial and/or simulating the

effects of lower diagenetic temperatures over longer geologic time periods (Siever 1986). The

control experiment that aged for an additional 7 days at 80 °C had a measured pH of 6.92 (Fig.

2a; Table 2). The 80 °C control continued not to display any color change in solution and did not

produce a precipitate for Fe(III)/FeT measurement. The control experiment subject to an

additional 7 days at 150 °C had a pH of 6.43 (Fig. 2a; Table 2). This 150 °C control did produce

a minuscule amount of dark tan-green material that had 0.27 Fe(III)/FeT (Fig. 2b; Table 4). The

control experiment aged for an additional 7 days at 220 °C was measured to have a pH of 7.65

(Fig. 2a; Table 2). This 220 °C control experiment precipitated a small amount of dark tan-green

solid material with 0.32 Fe(III)/FeT (Fig. 2b; Table 4).

313   We induced partial in situ iron(II) oxidation by bubbling trace levels of O_2 gas into

314   Archean ocean solutions for a limited amount of time, and then simulated progressive diagenesis

315   of the partially oxidized precipitates. After 19 days at 25 °C, the acidified and fully dissolved

316   replicate bubbled experiment contained 0.75 Fe(III)/FeT in bulk (dissolved precipitate plus

317   solution) (Table 3). This bubbled experimental solution had a pH of 7.33 and produced a green

318   precipitate, suggesting a Fe(II-III) phase or phases (Velde 2003) (Table 2). Indeed, our ferrozine

319   assay determined that this green precipitate contained 0.48 Fe(III)/FeT and the vanadate assay

320   indicated it was composed of 48% Fe(II) per gram (Tables 4, S2). After an additional 21 days,

321   and 40 days total, the bubbled experiment aged at 25 °C had a solution pH of 7.06 (Fig. 2a;

322   Table 2) and still contained a green precipitate. When we harvested this low-temperature bubbled

323   precipitate, it contained 0.45 Fe(III)/FeT (Fig. 2b; Table 4).

324   The bubbled experiment subject to aging at 80 °C for 7 additional days had a pH of 6.74

325   (Fig. 2a; Table 2) and continued to yield a green precipitate. This 80 °C solid was measured to

326   similarly have 0.45 Fe(III)/FeT and 55.85% Fe(II) by mass (Fig. 2b; Tables 4, S2). The bubbled

327   experiment that was further aged at 150 °C had a measured pH of 6.41 (Fig. 2a; Table 2). This

328   150 °C experiment continued to display a green precipitate and the acidified solid subsample had

329   0.51 Fe(III)/FeT (Fig. 2b; Table 4). While the ratio of Fe(III)/FeT was similar, the % Fe(II) per

330   gram dropped to 32.2% (Table S2). The bubbled experiment that was aged at 220 °C for an

331   additional 7 days had a measured pH of 5.85 (Fig. 2a; Table 2). This bubbled 220 °C experiment

332   produced a slightly darker green-black precipitate with 0.46 Fe(III)/FeT and 27.92% Fe(II)/g

333   (Fig 2b; Tables 4, S2).

334

335   **Thermodynamically Predicted Mineral Phases**

336   The stability diagrams that we constructed, paired with the measured pH values at each

337   step of the hydrothermal aging experiment (Table 2), generated a suite of predicted minerals

338   depending on the redox environment (Eh), which was not directly measured. In the case of

339   magnesium (Fig. S1), the thermodynamically stable phase at pH ~7 and 25 °C or 80 °C was

340   dissolved Mg. The solution pH after continued reaction was within the expanded magnesite

341   stability field at 150 °C, but the higher pH after 220 °C reactions (pH 7.65) shifted the predicted

342   Mg mineral product to a Mg serpentine phase like chrysotile or antigorite. For iron (Fig. S2),

343   siderite or a ferric oxide like goethite should be stable in the 25 °C experiment at pH ~7. At 80

344   °C, there is a small region of magnetite stability as well as the siderite and large goethite stability

345   fields at the experimental pH of ~6.75. With increasing experimental temperature and dropping

346   pH, the magnetite stability field grows while siderite's stable redox and pH space decreases. See

347   SM for more details.

348

349   **Bulk Mineralogy: XRD and Magnetic Response**

350   Control experiments at 150 °C and 220 °C did not produce enough precipitate for

351   analysis by XRD. XRD measurements of bubbled precipitates yielded patterns consistent with

352   several phases (Fig. 3). The bubbled experiment aged for 40 days at 25 °C produced a large and

353   diffuse diffraction peak corresponding to the Kapton tube it was measured in but no other sharp

354   diffraction peaks, suggesting an amorphous to minimally crystalline product (Fig. 3). One broad

355   peak that occurred in the 25 °C precipitate and persisted through the higher-temperature aging

356   treatments may be consistent with ferrihydrite. After 80 °C aging, the bubbled experiment

357   contained three weak diffraction peaks consistent with a serpentine group silicate such as

358   greenalite or cronstedtite and a spinel group oxide like magnetite, as well as two peaks possibly

359   indicating ferrihydrite (Fig. 3). After the 150 °C treatment, bubbled experiments displayed a

360   heightening of the peaks observed at 80 °C along with the formation of additional peaks

361   corresponding to a serpentine group silicate and spinel group oxide (Fig. 3). The bubbled

362   experiment subject to 220 °C aging showed a continued narrowing of the diffraction peaks for a

363   spinel group oxide, reflecting an increase in crystal size and/or crystallinity (Fig. 3). However,

364   the 220 °C experiment showed smaller and less sharp serpentine group peaks and only contained

365   one putative ferrihydrite peak.

366   Control and bubbled experimental precipitates across the range of temperature displayed

367   different degrees of magnetic attraction. The control 150 °C and 220 °C dark tan-green

368   precipitates were both weakly to moderately attracted to the magnet (Fig. 4a & 4b). The bubbled

369   green precipitate at 25 °C after a total of 40 days was not attracted to the magnet (Fig. 4c).

370   However, after 7 days at 80 °C, the green precipitate was weakly attracted to the magnet (Fig.

371   4d). After an additional 7 days at 150 °C, the bubbled green precipitate was strongly attracted to

372   the magnet (Fig. 4e). Seven days of aging at 220 °C produced the darkest green precipitate,

373   which was the most attracted to a magnet compared to all our experimental samples (Fig. 4f).

374

375   **Electron Microscopy Characterization**

376   **High-Temperature Control Experiments.** Unlike the 25 °C and 80 °C control experiments that

377   did not produce a precipitate for analysis, after 7 days at 150 °C, the control contained a

378   miniscule amount of tan precipitate (Fig. 5a). TEM imaging of the 150 °C control revealed

379   abundant ~500 nm clusters composed of a multi-phase mixture: poorly formed tubular spindles,

380   a faint, more amorphous globular phase, and well-ordered crystals with a rod or lath morphology

381   (Fig. 5b-l). The tubular spindles were <10 nm wide and <50 nm long (Fig. 5c-f). They were

382   mainly composed of Mg (17 at.%), Fe (variable but averaging 8.6 at.%), Si (15.5 at.%), and O

383   (58 at.%) (Fig. 5e), with an average (Fe+Mg)/Si = 1.7, reflecting a composition consistent with a

384   Mg-Fe serpentine group (Table 5). At higher resolution, we observed poorly layered particles

385   with 3-5 layers that were <5 nm wide and <50 nm long and highly susceptible to beam damage

386   (Fig. 5f). We measured the lattice spacing for one of these structures to be 6.9 Å while another

387   structure had 7.2 Å layering (Fig. 5f). Together with the lattice spacing, we tentatively identified

388   the tubular form as an iron-rich Mg-silicate in the serpentine group.

389   In other regions of the 150 °C control, we identified two types of iron oxides. We

390   observed a faint globular phase in lower magnification images (Fig. 5d, arrows) and identified

391   lattice spacings of 1.5 Å (Fig. 5f adjacent to layered phase) as well as 2.3 Å and 2.5 Å (Fig. 5f,g).

392   This poorly crystalline phase was often in an intimate mixture with a rod-like phase (Fig. 5h) but

393   elemental chemistry mapping indicated this phase was primarily iron (31%) and oxygen (54.5%)

394   (Fig. 5i,j, Table 5). These lattice spacings and elemental chemistry are similar to ferrihydrite, a

395   poorly crystalline iron oxide that often forms early after iron is oxidized in neutral waters.

396   Additionally, we imaged more crystalline blunt-edged rods, <20 nm wide and 100-150 nm long,

397   in this sample (Fig. 5h,k). These rods had a lattice spacing of 6.2 Å (Fig. 5k-l) and elemental

398   analysis indicated that they were primarily composed of Fe (28.5 at.%) and O (54.3 at.%) (Fig.

399   6i-6j; Table 5), suggesting an iron oxide mineral. This iron oxide phase also exhibited a lath

400   morphology ~20 nm wide and ~100 nm long (Fig. 6l) with a lattice spacing of 3.2 Å and 6.1 Å

401   (Fig. 5l-I and 5l-II). Neither the blunt edged rods or laths were observed to be degraded by the

402   electron beam during analysis. SAED on a region containing these blunted rods and laths

403   produced a polynanocrystalline pattern (Fig. 5m) consistent with the iron oxide lepidocrocite.

404   The control experiment further aged at 220 °C for 7 additional days also contained a

405   small amount of tan precipitate (Fig. 6a). TEM images of the 220 °C control experiment showed

406   abundant ~100-200 nm long hollow tubes with 0.6-0.8 nm inner diameters and 2-2.8 nm outer

407   diameters (Fig. 6b-d & 6f-g). The elemental chemistry of these tubular structures was primarily

408   Mg (29 at.%), Fe (5 at.%), Si (10 at.%), and O (55 at.%), suggesting they were a magnesium

409   silicate with possibly some Fe(III) substituted for Si (Fig. 6e; Table 5). Along the tube axis, we

410   were able to capture two separate instances of 7.2 Å lattice spacing and higher order lattice

411   planes of 3.6 Å (004) and 2.4 Å (006) (Fig. 6f & 6g-I.). Another tube at a different orientation

412   captured the 4.3 Å (111) lattice plane of this phase (Fig. 6g-II). SAED of the control 220 °C

413   experiment on a broad region composed mostly of tubes produced diffraction halos, suggesting a

414   poorly crystalline phase (Fig. 6j). This tubular phase had an elemental chemistry, lattice

415   spacings, and SAED pattern consistent with a precursor form of the fibrous magnesium

416   serpentine, chrysotile.

417   TEM analyses of the 220 °C control experiment also captured a ~100 nm wide globular

418   phase (Fig. 6h). The elemental data of this phase indicated that it primarily contained Fe (28

419   at.%) and O (54 at.%) (Fig. 6h-i; Table 5), suggesting an iron oxide. Additionally, the broad

420   SAED of the 220 °C control experiment had distinct diffraction planes (manifesting as dots) that

421   corresponded to the lattice spacings of 2.9 Å (220), 1.4 Å (440), and 1.0 Å (553) (Fig. 6j). These

422   lattice planes captured by SAED in tandem with an elemental chemistry rich in iron and oxygen

423   lead us to tentatively identify the globular phase as a spinel group iron oxide; notably, these

424   lattice spacings align well with maghemite. With its globular morphology rather than the platelet

425   morphology of the magnetite in the bubbled experiments (see below), it is possible that this

426   phase was not magnetite but instead was a different spinel group oxide like maghemite.

427

428   **Bubbled Experiments: Iron Oxide Phases.** We imaged the bubbled precipitates at temperatures

429   25-220 °C using TEM. All our bubbled experiments appeared to produce both a phyllosilicate

430   phase (see below) and a poorly crystalline iron oxide phase, while experiments aged at >80 °C

431   additionally contained a more crystalline iron oxide.

432   The subtle oxide phase observed in all the bubbled experiments appeared as a faint

433   globular phase in the background matrix (Fig. 7). SAED on the 25 °C assemblage produced a

434   diffuse halo pattern corresponding to 1.3 Å, 1.5 Å, and 2.6 Å lattice spacings (Fig. 8g). These

435   diffuse SAED halos reflect the formation of a poorly crystalline phase, consistent with the lack

436   of peaks by XRD (Fig. 3), but the spacings are typical of ferrihydrite. Using HR-TEM, we

437   observed that the globular phase had a recurring lattice spacing of ~2.5-2.6 Å (Fig. 7c,e,g,i). We

438   also observed a ~1.6 Å spacing (Fig. 7g). EDS spectra that included this phase suggested it was

439   rich in Fe, O, and Si (Table 5, Table S3). Together, we suggest our data points to Si-rich

440   ferrihydrite, which has major spacings at 1.5, 1.6, 2.5, and 2.6 Å in its 2-line and 6-line forms

441   (Michel et al, 2007).

442   Starting at 80 °C and increasingly at higher temperatures, we also observed a more

443   crystalline triangular or polygonal platelet phase in the bubbled experiments that we ultimately

444   identified as magnetite (Fig. 8). TEM and HR-TEM analysis of the bubbled precipitates aged at

445   80 °C, 150 °C, and 220 °C captured ~50-100 nm wide platelets with a characteristic 4.7 Å basal

446   spacing (Fig. 8c,f,h) along with additional lattice planes by FFT (Fig. 8c-I,f-I,h-I) corresponding

447   to a spinel group phase such as magnetite. For example, after 150 °C aging, FFT on an area with

448   platelets revealed lattice spacing planes of 4.8 Å (111), 2.4 Å (222), 1.6 Å (333), and 2.5 Å (311)

449   (Fig. 8f-I), very similar to the spacings expected for spinel group phases. FFT analysis on a

450 platelet-rich region after 220 °C aging (Fig. 8h-I) showed these same lattice spacings and

451 additionally a spacing at 1.7 Å (422), which is also observed in spinels. We were able to obtain a

452 SAED pattern of a platelet-rich region in this 220 °C-aged sample as well (Fig. 8i), which was

453 again consistent with a spinel group mineral like magnetite. We captured elemental data from a

454 region containing the platelet phase and observed that it was mainly composed of Fe (22 at.%), O

455 (56 at.%), and Si (11 at.%) (Fig. 8g; Table 5). We attribute the higher-than-expected

456 measurement of Si in this spinel group phase to be the result of adsorbed Si (Philippini et al.

457 2006). The lattice spacing of the platelet paired with the elemental chemistry rich in Fe and O, in

458 addition to the strong magnetic reaction of the bubbled and hydrothermally-aged precipitates

459 (Fig. 4d-f), was most consistent with identifying this platelet phase as magnetite.

460

461 **Bubbled Experiments: Silicate Phase.** Analysis of the 40-day-old 25 °C precipitate revealed

462 abundant poorly layered spindly particles that were ~2-4 nm wide and ~20 nm long (Fig. 9).

463 EDS of the layered precipitates from three separate locations yielded a compositional range of

464 17.5-21 at.% Fe, 17-19 at.% Si, 1-3 at.% Mg, 59-60 at.% O (Fig. 9e-g; Table 5). From this data,

465 we calculated an average (Fe+Mg)/Si ratio of 1.2 for these poorly layered particles (Table 5).

466 These structures were highly susceptible to beam damage, but we were able to capture four

467 representative particles, each with a maximum of 3-4 layers that had an approximate lattice

468 spacing of ~7.2-7.7 Å (Fig. 9h-I,II & 9i-I,II) measured by IFFT. The observed morphological,

469 structural, and elemental data suggested this phase was a Fe-rich incipient serpentine.

470 In the bubbled experimental precipitate aged at 80 °C for 7 additional days, TEM

471 imaging revealed layered crystals with a variable degree of ordering (Fig. 10). We observed

472 ~100 nm wide and ~300-700 nm long bladed structures and measured their lattice fringe at 7.2 Å

473   (Fig. 10b-e,h). TEM also revealed multiple instances of a triangular-trapezoidal form (Fig. 10b-

474   arrows,f-g) where the well-ordered regions had a 7.0 Å lattice fringe (Fig. 10j-I). The bladed and

475   triangular-trapezoidal structures together exhibited an average elemental chemistry with low Mg

476   (1.6 at.%) and a range of (Fe+Mg)/Si of 2.11-2.43, consistent with an iron silicate within the

477   cronstedtite-greenalite solid solution (Fig. 10d-e,g; Table 5). The large remaining portion of the

478   structure exhibited multiple crystal defects restricting the number of ordered layers (Fig. 10i-j);

479   however, we did measure a 7.2 Å lattice fringe in this region as well (Fig. 10i-I). SAED on an

480   area containing the bladed and trapezoidal structures produced recurring diffraction planes

481   congruous with a serpentine group silicate (Fig. 9k).

482   TEM analysis of the bubbled sample at 150 °C for an additional 7 days displayed well-

483   ordered layered structures ~100-200 nm long and ~10-50 nm wide (Fig. 11b-d). Using elemental

484   data from three regions containing layered structures (Fig. 11e-g), we calculated an average

485   (Fe+Mg)/Si = 1.8 with a Mg content of 4.5 at.% (Table 5). We measured 7.2-7.3 Å basal spacing

486   in two separate particles from one image (Fig. 11h, 11h-I). In another instance, a well-ordered

487   layered particle was in the proper orientation to capture both its basal lattice spacing of 7.1 Å

488   (Fig. 11i) and 24 Å superlattice (Fig. 11i-I). Collectively, the TEM data demonstrated that these

489   structures were greenalite-like minerals.

490   TEM of the bubbled experiment after 7 days at 220 °C revealed ~400 nm clusters of well-

491   ordered layered structures that were ~20-60 nm wide and ~100 nm long (Fig. 12). In general, we

492   observed fewer well-order layered structures at 220 °C compared to lower temperatures, but the

493   structures were highly crystalline. We determined that the basal lattice spacing was 7.1 Å in two

494   separate layered particles (Fig. 12c,f), with one of these particle orientations also capturing a ~21

495   Å superlattice (Fig. 12f-I). We also measured the elemental composition of these layered

496 structures in two regions (Fig. 12d,g), and observed that the particles remained Fe and Si rich but

497 the average Mg content had increased to 10% (Table 5). This data enabled us to calculate the

498 average (Fe+Mg)/Si of 1.7 (Table 5). Collectively, the TEM data demonstrated that these

499 structures were greenalite-like minerals.

500

501 **Synthesis of Experimental Results**

502 Our ferrous control experiment set at pH 7 with 1:1 Fe:Si did not produce an observable

503 precipitate from solution either at low temperature nor upon 80 °C hydrothermal aging. At 150

504 °C, we observed temperature-induced precipitation of an abundant but poorly ordered ~7 Å

505 Mg(Fe)-silicate along with ferrihydrite and lepidocrocite (Fig. 5). There may also have been a

506 magnetic mineral like magnetite in this assemblage since this assemblage showed a magnetic

507 response (Fig. 4a). Additional aging at 220 °C of the ferrous control mainly produced chrysotile

508 nanotubes and a spinel group iron-oxide that was potentially maghemite (Fig. 6). During

509 hydrothermal aging, the ferrous solution decreased in pH as temperature increased and minerals

510 precipitated. The 25 °C solution had a pH of 7.17, which decreased to pH 6.74 at 80 °C, and

511 further decreased to pH 6.43 at 150 °C (Fig. 2a; Table 2). This decrease in pH can be attributed

512 to the formation of an Fe(III) (hydr)oxide, such as the lepidocrocite and ferrihydrite that we

513 observed. Additionally, the precipitation of silicate phases will take up hydroxide ions and

514 release protons, also dropping the pH (Zolotov 2014).

515 Low O_2 bubbled experiments examined in situ Fe(II) oxidation at pH 7 in the presence of

516 silica produced a partially oxidized (~45% Fe(III)/FeT and ~48% Fe(II)/g) precipitate (Fig. 2b).

517 After 40 days at 25 °C, we characterized this low-temperature assemblage as abundant precursor

518 Fe-rich serpentine and ancillary ferrihydrite (Fig. 7a-c, Fig. 9). Aging these precipitates at 80 °C

519   produced a well-layered iron silicate and magnetite alongside ferrihydrite (Figs. 7d-e, 8a-c, 10).

520   Continued hydrothermal aging at 150 °C and 220 °C crystallized well-ordered greenalite with

521   incorporated Mg, more magnetite, and some persistent ferrihydrite (Figs. 7f-i, 8d-I, 11, 12; Table

522   5). These higher-temperature assemblages also contained lower Fe(II), ~30% by mass compared

523   to ~50% at ≤ 80 °C, although their Fe(III)/FeT ratio remained about the same (Table 4). With

524   increasing temperature, the experimental solution pH decreased from a pH of 7.33 at 25 °C down

525   to pH 5.85 at 220 °C (Fig. 2a; Table 2). The continued decrease in pH can be attributed to the

526   formation and recrystallization of the iron silicate and magnetite phases, similar to the control

527   experiments.

528

Discussion

Impacts of Temperature on Ferrous Controls at Circumneutral pH

531   Our ferrous experiments under simulated silica-rich Archean ocean conditions at pH 7

532   did not produce a precipitate at low temperature. Other studies with Archean-relevant Fe(II) and

533   Si concentrations produced iron(II) silicates at 25 °C, but only when the pH was elevated to ≥ 7.5

534   (Tosca et al. 2016; Farmer et al. 1991; Hinz et al. 2021). During the Fe(II) hydrolysis process,

535   silica inhibits Fe(II) polymerization, resulting in smaller clusters of octahedral Fe(II) and a

536   kinetic barrier to precipitation (Doelsch et al. 2002; Francisco et al. 2020). Our observations of a

537   lack of precipitation at ≤ 80 °C supports previous studies' findings that a higher pH is required to

538   induce iron(II) silicate formation under ferrous conditions at low temperature.

539   However, our ferrous experiment at 25 °C did contain a trace amount of Fe(III) (bulk

540   Fe(III)/FeT = 0.07, Table 3), which would be expected to precipitate at circumneutral pH. The

541   presence of any Fe(III) suggests there may have been slight O_2 contamination or a trace Fe(III)

542   impurity in all of our experiments. Even with this minor amount of Fe(III), the lack of precipitate

543   in this experiment is surprising since Fe(III) is highly insoluble at circumneutral pH and readily

544   precipitates as ferric oxides or Fe(II,III) phases from solution. Under these Fe, Si, and pH

545   conditions, we suspect that Fe(III) aqueous complexes, such as Fe(III)-Si, $Fe(OH)_2^+$,

546    $Fe(OH)CO_3$, and $FeCl^{2+}$ (Steffansoon 2007; Perrson 2018), hosted the measured Fe(III). Kinsela

547   et al. (2016) has shown the presence of silica—even an order of magnitude below the 1.1 mM Si

548   used in this study—hinders Fe(II) oxidation at circumneutral pH. Therefore, the absence of

549   precipitate at low temperature and 80 °C in our ferrous control experiments was likely the result

550   of the presence of high dissolved silica and insufficient Fe(III) to trigger precipitation of ferric

551   oxides or Fe(II,III) silicates as observed by Hinz et al. 2021.

552   Increased temperatures can influence chemical processes and induce mineral

553   precipitation, and our results showed precipitation in the control precipitates at 150 °C that

554   preferentially incorporated the trace dissolved Fe(III). At this elevated temperature, the control

555   precipitate contained 0.27 Fe(III)/FeT (Fig. 2b; Table 4). Indeed, we observed that Fe(III) oxides,

556   ferrihydrite and lepidocrocite, formed at 150 °C under almost entirely ferrous conditions (Fig.

557   5d,h-m). Soluble Fe(II) in the presence of poorly crystalline Fe(III) oxides like ferrihydrite is

558   capable of catalyzing the reductive dissolution and secondary mineralization of more crystalline

559   ferric oxides such as lepidocrocite or goethite (Burton et al. 2007; Cornell and Schwertmann

560   2003; Hansel et al. 2005; Nitschmann 1938; Pedersen et al. 2005). Therefore, we hypothesize

561   that the higher 150 °C temperature promoted the precipitation of ferric oxides from trace

562   dissolved Fe(III), and, in the presence of abundant Fe(II), these initial oxides partially

563   recrystallized into the lepidocrocite that we observed.

564   Our observations of the ferrous control experiment aged at 150 °C also revealed the

565   precipitation of a magnesium-rich silicate phase. While poorly ordered, the magnesium silicate

566   with ~9 at.% iron was notably the most abundant phase and manifested in distinctive tube-like

567   structures with rarely captured 6.9-7.2 Å basal spacing (Fig. 5c-f, Table 5). This spacing suggests

568   that the control liquid precipitated a poorly formed serpentine group magnesium silicate with

569   substantial incorporation of iron. Thermodynamic modeling indicates that chrysotile and

570   antigorite, two types of serpentine group Mg silicates, are only stable at pH ~7-7.5 and higher at

571   150 °C (Fig. S1c), suggesting there may be local regions of higher pH to promote precipitation

572   of this observed phase despite the bulk solution pH (6.4, Table 2) being unfavorable for this

573   silicate group.

574   After 220 °C aging, our ferrous control experiment was predominantly composed of

575   chrysotile nanotubes and a globular iron oxide (Fig. 6). The widespread fibrous chrysotile at 220

576   °C suggests the transformation of the poorly formed 150 °C Mg-silicate to the more crystalline

577   chrysotile mineral. The elemental analysis of the chrysotile nanotubes showed they included 5

578   at.% Fe (Fig. 6e; Table 5). Chrysotile has been reported to host 2-3 weight % (wt.%) Fe (Bowes

579   and Farrow 1997), where Fe(II) or Fe(III) are capable of being substituted into the octahedral site

580   but only Fe(III) can be incorporated into the tetrahedral site (Walter et al. 2019). The

581   incorporation of Fe into the chrysotile structure could have been aided by dissolution-

582   reprecipitation reactions during the crystallization of Mg silicates into chrysotile. These reactions

583   mineralizing chrysotile and releasing OH groups likely also buffered the solution to sit within the

584   chrysotile stability field, including raising the pH to the 7.65 that we measured in this experiment

585   (Table 2; Figs. 2a, S1d; Trittschack et al. 2014). There may have been substantial incorporation

586   of Fe(III) into the chrysotile structure upon 220 °C aging, similar to what occurs during

587 serpentinization (Evans 2008; Tutolo et al. 2021). Indeed, the Fe(III) content of the bulk

588 precipitate increased from 27% at 150 °C to 32% at 220 °C. Alternatively, it is possible that most

589 of the iron in chrysotile was Fe(II), and the majority of the measured 32% Fe(III) in solids was

590 associated with the iron oxide.

591

592 **In Situ Fe(II) Oxidation at Circumneutral pH and 25 °C**

593   Broadly, our trace O_2 bubbling experiments highlight that in situ Fe(II) oxidation in the

594 presence of silica produces an Fe-rich poorly ordered serpentine at pH 7 and 25 °C. The presence

595 of a small proportion of Fe(III) under silica-rich conditions has been shown to induce

596 precipitation of iron-rich solids, including silicate phases (Hinz et al. 2021). This low-Fe(III)

597 trigger provides an alternative mechanism for the formation of precursor Fe-rich serpentine at

598 low temperatures and the predicted lower pH of the Archean ocean. However, in our previous

599 study, adding Fe(III) (aq) in the presence of silica at pH 7 and 25 °C produced mainly an

600 amorphous phase with rare silicates, with a bulk iron redox state of 0.89 Fe(III)/FeT (Hinz et al.

601 2021). Yet here, in situ Fe(II) oxidation at pH 7 induced the formation of a more ferrous

602 assemblage that was 48% Fe(II)/g and contained approximately equimolar Fe(II) and Fe(III),

603 with more abundant Fe-rich precursor silicate phases alongside ferrihydrite at 25 °C (Figs. 7a-c,

604 9; Table 4).

605   Similar to the control experiments, our results from bubbled experiments suggested that

606 there was additional Fe(III) dissolved in the solution. The acidified 25 °C bubbled solution-

607 precipitate combination contained much higher Fe(III), measuring 0.75 Fe(III)/FeT, compared to

608 the 0.48 Fe(III)/FeT in solids (Tables 3,4). This higher bulk measurement possibly reflects that a

609 portion of the Fe(III) was in Fe(III) aqueous complexes, such as Fe(III)-Si, $Fe(OH)_2^+$,

610    $Fe(OH)CO_3$, and $FeCl^{2+}$, similar to what we suspect occurred with the minor amount of Fe(III)

611   in the control experiment solutions (Steffansoon 2007; Perrson 2018). The additional Fe(III)

612   measured in solution could also be attributed to colloidal Fe(II,III) phases such as silicates, green

613   rusts, or Fe(III) oxides. The Fe(III) discrepancy between the precipitate compared to bulk redox

614   state implies that we cannot discount the impact that these dissolved or colloidal Fe(III) sources

615   may have on mineral formation. However, the precipitates from bubbled experiments all

616   exhibited a consistent proportion of Fe(III) per total iron, ranging from 0.45-0.51 Fe(III)/FeT,

617   regardless of aging conditions or temperatures (Fig. 2b; Table 4). This Fe(III) stability in bubbled

618   experiments across all temperatures suggests that there was not substantial incorporation of

619   Fe(III) (aq) into the solid with increasing temperature.

620

621   **Products from Simulated Diagenesis of Partially Oxidized Iron-Silica Precipitates**

622   In tandem, the bulk redox measurements of the solids suggest that there was substantial

623   dissolution-reprecipitation during the hydrothermal aging incubations. Mineral crystallization

624   often involves a precursor metastable or amorphous phase dissolving as a more crystalline phase

625   precipitates (Ruiz-Agudo et al. 2017; DeYoreo et al. 2015, 2022). The % Fe(II)/g measurements,

626   which show a ~20% drop between 80 and 150 °C (Table 4), indicate there was dissolution of at

627   least some of the previously-precipitated Fe(II) between these temperatures. However, the

628   unchanging Fe(III)/FeT (Table 4) suggest that a similar proportion of Fe(III) also dissolved

629   during 80 °C to 150 °C recrystallization and/or transformation. While our TEM data shows that a

630   portion of the Fe(II) recrystallized in more ordered phyllosilicate and magnetite phases, some of

631   the Fe(III) appears to have remained in ferrihydrite since we observed ferrihydrite at all

632   temperatures (Fig. 7). At minimum, a fraction of the initial ferrihydrite was resistant to reactions

633 with dissolved Fe(II) and/or transformation to other iron oxides as is typically seen (Huang et al.

634 2021) and as we observed in our control experiments. Adsorbed silica may have protected some

635 ferrihydrite from further reactions even up to 220 °C, consistent with other experiments that

636 found Si-rich ferrihydrite does not transform to secondary phases until >500 °C (Rzepa et al.

637 2016; Campbell et al. 2002). Additionally, the presence of bicarbonate buffer can impede the

638 secondary transformation of ferrihydrite, potentially through bicarbonate forming aqueous

639 complexes with Fe(II) or by adsorbing to ferrihydrite (Hansel et al. 2005).

640 　　　　While iron-rich silicates were present under all hydrothermal conditions (more on their

641 transformations below), the appearance of magnetite at 80 °C and higher temperatures (Fig. 8)

642 revealed that this Fe(II,III) oxide was a secondary phase that mineralized during the simulated

643 diagenetic conditions. The increase in magnetite crystallization with higher temperatures was

644 denoted by sharpened peaks in the XRD patterns (Fig. 3), TEM observations (Fig. 8), and

645 strengthening magnetic attraction (Fig. 4d-f). Magnetite most likely formed due to reactions

646 between Fe(II) and ferrihydrite, in a known process when there is sufficient Fe(II) to adsorb to

647 the ferrihydrite and induce transformation into magnetite (Tronc et al. 1992; Hansel et al. 2003,

648 2005). Presumably a portion of the 25 °C ferrihydrite was not as protected by adsorbed silica or

649 bicarbonate and was able to adsorb and react with dissolved Fe(II). However, an alternative (or

650 additional) mechanism to form magnetite could stem from initial Fe(II,III) phyllosilicates

651 relinquishing ferric iron to form more ferrous silicates and magnetite, similar to reactions

652 described by Zolotov (2014) and potentially explaining the deterioration of greenalite-like XRD

653 peaks between 150 and 220 °C (Fig. 3).

654

655 **Effects of Simulated Diagenesis on Fe(II,III) Silicates**

656   After in situ Fe(II) oxidation at 25 °C, the initial precursor iron silicates crystallized into

657   a well-ordered iron serpentine phase upon hydrothermal aging (Fig. 13). To identify and

658   understand the identity and extent of crystallization of iron phyllosilicates, we must examine

659   their observed characteristics. The structural measurements, including the 7 Å basal spacing, of

660   the silicate products in bubbled experiments indicated they were serpentine group silicates,

661   which are composed of alternating silica tetrahedral layers and metal-bound octahedral layers.

662   The chemistry we observed in bubbled silicate products at all temperatures indicated that the

663   principal metal ion was Fe, pointing to a serpentine group iron silicate, either Fe(II) greenalite or

664   Fe(II,III) cronstedtite. One way to differentiate cronstedtite from greenalite stems from the fact

665   that the Fe(II) in greenalite has a misfit between the tetrahedral and octahedral layers, resulting in

666   a modulated structure (Guggenheim et al. 1982; Guggenheim and Eggleton 1998). This

667   superlattice structure of greenalite has a ~23 Å modulation (Guggenheim et al. 1982;

668   Guggenheim and Bailey 1989; Guggenheim and Eggleton 1998; Rasmussen et al. 2021; Johnson

669   et al. 2018), in contrast to the ~17 Å superlattice periodicity of the Mn(II) serpentine endmember

670   caryopilite and the 33-38 Å modulation of the Mg serpentine antigorite (Guggenheim et al 1982;

671   Capitani and Mellini 2004). Conversely, the Fe(III) within the cronstedtite structure has a smaller

672   ionic radius than Fe(II) or Mg. The Fe(III) substitution for silica at the tetrahedral site stabilizes

673   the layered configuration and restricts structural modulation; therefore, the ~23 Å superlattice is

674   not observed in cronstedtite (Caruso and Chernosky 1979; Wicks and O'Hanley 2018; Hybler,

675   2000). Additionally, the Fe(III) substitution at the silica tetrahedra site in cronstedtite increases

676   its ideal (Fe+Mg)/Si ratio to 4 compared to 1.5 for greenalite, providing an additional way to

677   identify the iron serpentine mineralogy.

678   We can thus place the experimental silicates at various temperatures along the greenalite-

679   cronstedtite solid solution, as well as infer their Fe(III) content, by their measured (Fe+Mg)/Si

680   ratio. To characterize the composition of the silicates and where they fall along the cronstedtite-

681   greenalite solid solution, we used the defined formulas for both endmembers, greenalite with

682   possible Mg substitution [$(Fe^{2+},Mg)_3Si_2O_5(OH)_4$] and cronstedtite with possible Mg substitution

683   [$(Fe^{2+},Fe^{3+},Mg)_3(Si,Fe^{3+})_2O_5(OH)_4$], and compared the (Fe+Mg)/Si ratio of our experimental

684   products against the idealized ratios from mineral formulas. Mg-containing greenalite

685    $(Fe^{2+},Mg)_3Si_2O_5(OH)_4$ would have a (Fe+Mg)/Si ratio of 1.5, while Mg-containing cronstedtite

686    $(Fe^{2+},Fe^{3+},Mg)_3(Si,Fe^{3+})_2O_5(OH)_4$ would have a ratio of 4. The silicate precipitated at 25 °C had

687   an (Fe+Mg)/Si of 1.2, below the theoretical (Fe+Mg)/Si ratio for greenalite of 1.5 due to its

688   elevated Si content (Table 5). This higher Si content in the initial, poorly ordered form of iron

689   silicates was similarly observed in prior studies (Tosca et al. 2016; Hinz et al. 2021).

690   At 80 °C, we observed the crystallization of a 7 Å iron silicate (Fig. 10c,e,h; Table 5)

691   with much lower relative Si, averaging a (Fe+Mg)/Si of 2.3, which falls between cronstedtite and

692   greenalite. Additionally, the 80 °C phyllosilicate displayed a pseudo-triangular morphology and

693   lacked any indication of a superlattice despite being well-crystallized (Fig. 10b-arrows,f,j),

694   consistent with observations from similar cronstedtite formation studies (Pignatelli et al. 2013

695   and Vacher et al. 2019). Based on the defined endmember formulas, the bubbled 80 °C layered

696   precipitate with (Fe+Mg)/Si of ~2.3 was characterized as a 30% cronstedtite and 70% greenalite

697   solid solution (Table 5). Assuming all the measured Fe+Mg was Fe^{2+} or Fe^{3+}, which is not too

698   inaccurate considering this sample only contained 1.6 at.% Mg on average, and assuming that

699   this Fe was equally split between the two redox states, our calculated proportion of cronstedtite

700   would suggest that this 80 °C-crystallized phyllosilicate contained approximately 15% Fe(III).

701   Therefore, there appears to be a transition from a high-Si iron silicate at low temperatures

702   to a crystalline phase within the solid solution between Fe(II) greenalite and Fe(II,III)

703   cronstedtite at 80 °C. Intriguingly, the $\Delta G_{formation}^{o}$ for cronstedtite has been found to be favorable

704   at temperatures < 120 °C, high Fe/Si ratios, and circumneutral pH, similar to our experimental

705   conditions (Zolotov 2014; Pignatelli et al. 2013, 2014; Vacher et al. 2019). The thermodynamic

706   stability field for cronstedtite under our solution conditions shrinks between 25 °C and 80 °C,

707   with the redox and pH space filled largely by magnetite (Fig. S2a-b). These stability field

708   predictions may support a transformation of initial poorly ordered Fe(II,III) silicate, i.e. a

709   precursor cronstedtite-greenalite, into magnetite. Yet the pH of our experimental solutions was

710   lower than the pH range of the stability field of cronstedtite, and our observations of

711   ferrihydrite—a precursor of goethite—would suggest that the redox environment was more

712   oxidizing than the highly reducing conditions required by cronstedtite or greenalite (Fig. S2a-b).

713   These contradictions suggest that our experimental precipitates formed in heterogeneous

714   microenvironments where pH and the redox state (commonly measured as Eh) were variable.

715   The differences between the thermodynamic predictions and our observations also suggest that

716   the kinetics of these precipitation and crystallization processes determine the solid assemblage,

717   even after 7 days of 80 °C hydrothermal aging.

718   In contrast to lower-temperature silicates, additional recrystallization and mineralization

719   at higher temperatures (150-220 °C) aging produced an iron phyllosilicate characteristic of the

720   greenalite endmember. In the abundant layered forms, we continued to observe 7 Å spacing

721   typical of a serpentine group silicate (Figs. 11h-i, 12c,f). Yet the layered phase at these

722   temperatures exhibited a 21-24 Å superlattice (Figs. 11i-I & 12f-I) and (Fe+Mg)/Si of 1.7-1.8

723   (Table 5), close to ideal greenalite and not congruent with cronstedtite. Our results thus indicate

724   that cronstedtite was not present in experiments ≥ 150 C°, supporting the thermodynamic

725   predictions (Fig S2) and hypothesis that cronstedtite does not form at higher temperatures

726   (Vacher et al. 2019). Instead, we suggest the more Fe(III)-rich cronstedtite-greenalite that

727   initially crystallized at 80 °C dissolved and partially reprecipitated into a more endmember Fe(II)

728   greenalite at ≥ 150 °C. With the narrowing stability field for greenalite, we again speculate that

729   local environments persisted—perhaps buffered by the initial silicates—where higher pH and

730   more reducing redox conditions enabled the continued presence of greenalite. However, we note

731   that the greenalite appeared less abundant in both TEM imaging at 220 °C and in the sample's

732   XRD pattern, perhaps suggesting that greenalite had indeed partially dissolved or transformed.

733   Not only did the higher-temperature aging result in greenalite mineralization, but we

734   observed an increasing incorporation of Mg in the layered silicate. While the phyllosilicate had

735   minimal magnesium at 25-80 °C (~1.5-2 at.% Mg), Mg increased to 4.5 at.% at 150 °C and 10

736   at.% at 220 °C (Fig. 13; Table 5). As there was only trace Mg in the lower temperature

737   precipitates, this incorporated magnesium almost certainly originated from the solution, which

738   contained 10 mM Mg to be analogous to Archean seawater. The large extent of Mg incorporation

739   into the silicate was comparable to the 11-15 at.% Mg in 150 °C-aged experimental iron silicates

740   either formed under ferrous conditions at pH 7.5 or triggered by a small amount of ferric iron at

741   pH 6.5-7 (Hinz et al. 2021).

742   Our simulated diagenesis experiments suggest that, similar to today (Berg et al. 2019;

743   Sun et al. 2016), a sink for magnesium in Archean time may have been in the Mg enrichment of

744   silicates during sedimentary diagenesis and burial. For example, studies of the Amazon delta

745   sediments have shown that Mg is incorporated in secondary silicate clays during simulated and

746   observed diagenesis (Michalopoulos and Aller 1995; Rude and Aller, 1989). The process of clay

747 mineralization in the sediments, also known as 'reverse weathering' or clay authigenesis, is

748 supported by the uptake of Mg in much of today's marine sediments and concomitant depletion

749 of Mg in pore waters (Sayles, 1979; Gieskes 1975; Sun et al. 2016).

750   This precipitation and/or incorporation of Mg during high temperature recrystallization is

751 also reminiscent of the behavior of Mg in hydrothermal vent systems and the flanks of mid-

752 ocean ridges, where Mg is largely removed from heated circulating seawater to form Mg-silicate

753 phases (German and Seyfried 2014; Mottl and Wheat 1994). Experiments simulating this

754 seawater-basalt interaction at 250-290 °C observed the precipitation of the Mg aluminosilicate

755 saponite (Voigt et al 2020). In our experiments, Mg likely remained dissolved until sufficiently

756 high temperatures because of the very stable Mg hydration complex (Hostetler and Christ 1968;

757 Sayles and Fyfe 1973) and then the Mg partitioned into the iron silicate as its kinetic barriers to

758 mineralization were overcome by increased temperature. Notably, our observation of increasing

759 Mg with continued aqueous alteration also follows the pattern of Mg enrichment during the

760 aqueous alteration inferred in carbonaceous CM chondrites (Suttle et al. 2021; McSween 1979;

761 Tomeoka et al. 1989; Howard et al. 2011) and increasing Mg in serpentines during

762 serpentinization alteration reactions (e.g., Evans 2008; Beard et al. 2009). Our experimental

763 results therefore support the hypothesis that Mg will exchange for Fe with progressive alteration,

764 following the chondrite alteration model of McSween (1979) and Tomeoka et al. (1989).

765

766   **Implications**

767   This study demonstrates that iron phyllosilicates will precipitate under simulated Archean

768 ocean conditions as a result of in situ Fe(II) oxidation. We showed that in situ Fe(II) oxidation in

769 the presence of silica at pH 7 can precipitate poorly ordered iron-rich phyllosilicates with a very

770   low Mg content at 25 °C. At 80 °C, these precipitates crystallized into low-Mg iron

771   phyllosilicates in the solid solution between greenalite and cronstedtite. These 80 °C iron silicate

772   nanoparticles appeared remarkably similar to inclusions in early-forming BIF chert that are

773   composed of low-Fe(III) greenalite with negligible Mg (Rasmussen et al. 2019; Johnson et al.

774   2018). With increasing temperatures simulating further diagenesis, our experimental

775   phyllosilicates transformed into a more greenalite-like mineral with less Fe(III) but considerably

776   more Mg. In contrast, the low (< 0.5 at.%) Mg content of iron phyllosilicate inclusions in BIF

777   cherts suggests that they were likely formed under low temperatures, then preserved and isolated

778   in chert, restricting further reaction with Mg-containing seawater.

779   In the context of the BIF rock record, our observations could also provide insights into

780   how diagenesis in the presence of Mg-rich fluids affects the crystallization and transformation of

781   other BIF iron silicates as well. Broader scale BIF studies of iron silicates (greenalite,

782   minnesotaite, and stilpnomelane) that are not preserved in chert can have a large range of Mg

783   content (0.6-6.7 weight % MgO) within the silicate phases (Klein 2005; Klein 1974; Floran and

784   Papike 1978). Our data would suggest the more elevated (> ~2 at.%) levels of Mg in these

785   silicates derived from continued higher-temperature alteration of the initial BIF sediments,

786   without the isolation provided by early-mineralizing chert. Consistent with this idea,

787   observations of the silicate-bearing facies collected from separate localities with different

788   degrees of BIF diagenesis were measured to have different Fe:Mg ratios (Floran and Papike

789   1978).

790   The formation of magnetite that we observed after the simulated diagenesis of iron

791   silicates at high temperatures of ≥ 150 °C illuminates how BIF sediments may be expected to

792   transform into secondary minerals. Magnetite is ubiquitous in BIF facies, but its origin is not

793   well understood (Klein 2005). Previous petrographic studies of BIFs have shown that most, if not

794   all, of the magnetite in these formations is a relatively late-formed mineral (Goodwin 1956;

795   Laberge 1964; French 1968, 1973; Han 1982; Kaufman et al. 1990; Kaufman 1996; Beukes and

796   Gutzmer 2008; Rasmussen and Muhling 2018). Magnetite in BIF deposits thus most likely

797   represents diagenetic and/or post depositional alteration, obscuring the primary mineral(s) from

798   which the magnetite derived. Intriguingly, petrographic observations support magnetite replacing

799   early iron silicate granules (French 1968; Klein 1974; Floran and Papike 1978; Rasmussen and

800   Muhling, 2018). We demonstrated that the simulated diagenesis of Fe(II,III) silicates and

801   ferrihydrite at ≥ 80 °C produces magnetite (Fig. 8). These experiments thus suggest that iron-rich

802   silicate phases are a possible precursor to diagenetic magnetite in BIFs, potentially providing

803   experimental evidence for petrographic observations of iron silicates altering to magnetite.

804   Other experimental studies have also indicated that magnetite is a secondary mineral that

805   forms during diagenesis. Magnetite can be formed as a product of microbial Fe(III) respiration

806   (Lovley et al. 1987), a process that is hypothesized to occur in BIF sediments (e.g., Walker,

807   1984; Konhauser et al. 2005; Fischer and Knoll, 2009). While few studies have simulated burial

808   diagenesis of BIFs, Posth et al. (2013) subjected ferrihydrite and glucose to 14 days of 170 °C

809   and 1200 bars to investigate the diagenetic transformation of Fe(III) oxides and microbial

810   biomass. These experiments also produced magnetite, which they linked to organic carbon-

811   induced reduction of the ferric iron, except when the ferrihydrite was silica-coated. Our results

812   suggest alternative pathways exist to form magnetite during diagenesis: hydrothermally aging

813   mixed Fe(II,III) precipitates and/or Fe(III) phases in the presence of aqueous Fe(II) additionally

814   forms magnetite in a process unrelated to organic carbon. Moreover, silica was present in our

815   solutions in the same concentration as ferrous iron; therefore, it appears that silica does not

816   always prevent the formation of magnetite during high-temperature mineralization.

817   Our simulated diagenesis experiments therefore demonstrate the effects of diagenesis on

818   iron silicates, with clear changes to the Fe(III) and Mg content, and ultimately provide support

819   for a secondary origin of magnetite and guidance on how to interpret the magnesium content in

820   iron-rich silicates in the BIF record.

821

828

829   **References**

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1186

1187   **Table and Figure Captions**

1188   Table 1. Composition of recreated Archean seawater. Iron and silica concentrations shown as

1189   measured concentrations derived from colorimetric (ferrozine and silicomolybdate) assays where

1190   * denotes the standard deviation of the measurement.

1191

1192   Table 2. pH measurements of Parr vessel precipitates and overlaying solution for control and

1193   bubbled experiments for temperatures that ranged from 25-220 °C. Note pH measurements were

1194   taken after the solution was cooled to 25 °C to minimize temperature effects and the error for

1195   each pH measurement was ± 0.02 pH units.

1196

1197   Table 3: Summary of experimental results of Fe(II) and silica in initial solutions. The measured

1198   Fe(III)/FeT content for the acidified control and bubbled experiments (solution plus precipitate)

1199   after aging in a borosilicate bottle at 25 °C for 19 days.

1200

1201   Table 4. The measured Fe(III)/FeT content by ferrozine and measured Fe(II)/g by vanadate assay

1202   of the acidified control and bubbled solid precipitate from conditions ranging 25-220 °C over 19-

1203   40 total days.

1204

1205   Table 5. Summary of the average elemental composition of the phases (in atomic % or as a ratio)

1206   at each experimental condition. Also see the raw EDS data for each experiment in Table S3.

1207

1208   Figure 1: Time-temperature scheme for hydrothermal aging of control and bubbled experiments.

1209   The reaction with O_2 and equilibrium period took place in borosilicate bottles denoted by the

1210 light gray region. Control and bubbled experiments were subsampled for pH and Fe(III)/FeT

1211 after 19 days at room temperature (star symbol). The remainder of material was portioned and

1212 transferred into anoxic Parr vessels for aging at 25, 80, 150, and 220 °C before being sampled

1213 and analyzed (filled circles).

1214

1215 Figure 2: (a) Plot of pH measurements from Parr vessel with precipitate and overlaying solution

1216 for control and bubbled experiments for temperatures that ranged from 25 - 220 °C. Note the

1217 uncertainty of the pH measurements and oven temperatures was ± 0.02 pH units and ± 0.4 °C

1218 respectively. (b) The measured Fe(III)/FeT content of the acidified control precipitates and

1219 bubbled precipitates along with the calculated standard deviation from replicate measurements.

1220

1221 Figure 3: Cobalt sourced XRD patterns from replicate bubbled experimental precipitates subject

1222 to simulated diagenesis at 25 °C (Blue), 80 °C (Green), 150 °C (Black), and 220 °C (Red).

1223 Plotted for comparison: blank kapton tube (K); 1:1 iron-silicates greenalite (G),

1224 $[Fe^{2+}_3Si_2O_5(OH)_4]$ (from Guggenheim et al. 1982) and cronstedtite (C),

1225 $[(Fe^{2+},Fe^{3+})_3(Si,Fe^{3+})_2O_5(OH)_4]$ (Lab Standard, Caltech Mineralogical Collection); a spinel group

1226 iron-oxide, magnetite (M), $[Fe^{2+}Fe^{3+}_2O_4]$ (from Haavik et al. 2000); and 6-line ferrihydrite (F)

1227 $[Fe^{3+}_{10}O_{14}(OH)_2$ (from Michel et al. 2007). Both the copper and cobalt two theta axes are plotted

1228 for comparison. The experimental and standard diffraction patterns were vertically offset for

1229 clarity.

1230

1231 Figure 4: The precipitate from the 150 °C control experiment had a tan color (**a**-left) and was

1232 moderately attracted to the magnet (**a**-right). The precipitate from the 220 °C control experiment

1233   continued to have a tan color (**b**-left) but only some particles appeared to be attracted to the

1234   magnet (**b**-right). The precipitate from the bubbled experiment after aging at 25 °C had a green

1235   color (**c**-top) and was not attracted to the magnet (**c**-bottom). The bubbled experiment harvested

1236   after aging at 80 °C was green (**d**-top) and was moderately attracted to the magnet (**d**-bottom).

1237   The bubbled 150 °C precipitate was dark green (**e**-top) and continued to be moderately attracted

1238   to the magnet (**e**-bottom). The bubbled 220 °C precipitate was darker green (**f**-top) and was

1239   highly attracted to the magnet (**f**-bottom).

1240

1241   Figure 5: Tan precipitate harvested from control experiment after 7 days at 150 °C (**a**). Clumps

1242   of heterogeneous particles (**b-c**) included poorly formed tubular spindles (**c-d**) and faint poorly

1243   crystalline globular masses (**d-arrows**). Some of these particles were primarily composed of Mg-

1244   Si-Fe (**e,** Tables 5 and S3) and appeared to be layered structures with frayed edges with two

1245   particles showing 6.9 Å and 7.2 Å lattice spacings (**f**). Other globular particles did not show

1246   layering but had lattice spacings including 1.5 Å (**f**), 2.3 Å (**g**), and 2.5 Å (**g-I**). In other regions,

1247   we observed blunt-edged rods intermixed with masses of minute globules (**h**) with both

1248   containing Fe- and O-rich measured elemental chemistry (**i-j**; Table 5). Basal spacing of the

1249   blunt-edge rods was measured to be 6.2 Å (**k**), similar to another phase with a lathe-like

1250   morphology (**l**) with 3.2 Å and 6.1 Å lattice spacing (**l-I & l-II**). The polynanocrystalline SAED

1251   pattern from a region containing blunt-edged rods and lathes was most consistent with

1252   lepidocrocite (**m**).

1253

1254   Figure 6: Tan precipitate harvested from control experiment after aging for 7 days at 220 °C (**a**).

1255   Homogenous clumps composed of hollow tubes (**b-d**) and measured elemental chemistry (**e**).

1256 Viewing down the tube axis and along the profile of the tube we measured the lattice spacing to

1257 be 7.2 Å in both instances (**f & g-I**) and measured 4.3 Å at a different orientation (**g-II.**). A

1258 globular phase was observed (**h**) with elemental chemistry rich in Fe and O (**i**). SAED of a region

1259 containing both the tubular and globular phase respectively produced a polynanocrystalline

1260 pattern consistent with a magnesium-silicate and planes for a spinel group phase (**j**).

1261

1262 Figure 7: Subtle globular phase observed in all bubbled experiments and tentatively identified as

1263 ferrihydrite. At 25 °C, TEM imaging captured a faint background, webbing-like phase (**a-**

1264 **arrows**) and SAED of the region showed diffuse halos corresponding to 1.3 Å, 1.5 Å, and 2.6 Å

1265 lattice spacings (**b**). HR-TEM and IFFT analysis of this phase identified a lattice spacing of 2.6

1266 Å (**c, c-I, c-II**). Similarly, we observed a globular phase at 80 °C (d-e) with a major spacing at

1267 2.5 Å and 2.6 Å (**e-I, e-II**). An image of the bubbled precipitate at 150 °C showed an aggregate

1268 of small globules (**e-f**) and analysis of this 'background' phase showed 1.6 and 2.6 Å spacing (**g-**

1269 **I, g-II**). After 220 °C aging, TEM imaging continued to show faint round morphologies (**h-i**)

1270 with 2.6 Å lattice spacing (**i-II**).

1271

1272 Figure 8: After hydrothermal aging, we observed a plate-like phase that often had a triangular or

1273 polygonal shape, ultimately identified as magnetite. One TEM image of the 80 °C sample

1274 showed all three phases that we observed, including triangular platelets (**a-arrows**). This phase

1275 was also identified intermixed with layered structures (**b**) where we measured a 4.7 Å lattice

1276 fringe (**c**) and multiple FFT lattice spacings corresponding to a spinel group phase such as

1277 magnetite (**c-I**). We also observed a platelet phase after the 150 °C hydrothermal treatment (**d-**

1278 **arrows, e**) with 4.7 Å lattice spacing (**f**) where FFT confirmed the presence of lattice planes

1279 consistent with a spinel group mineral (**f-I**). Additionally, we obtained iron- and oxygen-rich

1280 elemental chemistry on a platelet phase after 220 °C aging (**g**) and measured 4.7 Å lattice

1281 spacing (**h**) and FFT lattice planes consistent with a spinel group identification (**h-I**). SAED of

1282 an area containing the platelets displayed polynanocrystalline halos at the lattice planes of a

1283 spinel group mineral (**i**).

1284

1285 Figure 9: TEM-based observations of poorly layered structures from green precipitate (**a**)

1286 harvested from the bubbled experiment held at 25 °C for 40 days. We saw abundant particles

1287 with a spindly morphology in clusters (**b-d**) where we mapped and analyzed their elemental

1288 chemistry (**e-g**), finding the major elements were Fe, Si, and O with minor Mg. Note that the

1289 average compositions shown in (**f**) and (**g**) are from hand-drawn regions to pick out the layered

1290 particles, and the chemistry in (**g**) derives from the interior silicate-rich portion of the aggregate.

1291 The best captured particles exhibited a maximum of 3-4 layers (**h-i**) with an approximate basal

1292 spacing of ~7.2-7.7 Å determined by IFFT (**h-I, h-II, i-I, & i-II**).

1293

1294 Figure 10: TEM analyses of green precipitate (**a**) harvested from the bubbled experiment after 7

1295 days at 80 °C, focusing on the layered structures. We observed a heterogeneous mixture of

1296 morphologies, including well-ordered blades (**b-e**) with the elemental chemistry maps shown for

1297 Fe, Si, Mg, and O (**d**) and average chemistry shown in (**e**). There were also trapezoidal structures

1298 (**b-arrows, f-g, i-j**) with similar chemistry rich in Fe, Si, and O (chemistry shown from "caps" of

1299 structures). The blades showed a 7.2 Å lattice fringe (**h**), while the trapezoidal structure's "body"

1300 (**i**) had frequent crystal defects (**i-arrows**) but still contained 7.2 Å lattice spacing (**i-I**). The well-

1301 crystallized "caps" of the trapezoidal structure (**j**) had 7.0 Å and 2.1 Å lattice spacing (**j-I & j-II**)

1302 while SAED of a heterogeneous area similar to panel b produced recurring lattice planes

1303 consistent with a serpentine group phase (**k**).

1304

1305 Figure 11: Layered phase observations from the dark green precipitate (**a**) harvested from the

1306 bubbled experiment after 7 days at 150 °C. TEM revealed a heterogeneous mixture of phases (**b**)

1307 including well-ordered blades (**c-f**) where the elemental chemistry of the layered blades indicated

1308 a phase rich in Fe and Si with around 5% Mg (**e-g**; Table 5). Lattice spacings of this layered

1309 phase were measured to be 7.2 Å (**h**) and 7.3 Å (**h-I**), with some particles showing not only the

1310 basal lattice spacing (001) 7.1 Å (**i**) but also a 24 Å superlattice modulation (**i-I**).

1311

1312 Figure 12: Layered structures in the bubbled experiment after 7 days at 220 °C, which yielded

1313 the darkest green-black precipitate (**a**). TEM revealed the heterogeneous phases (**b**) within this

1314 experiment that included well-ordered blades with a 7.1 Å lattice spacing (**c**) along with

1315 elemental chemistry rich in Fe, Si, and Mg (**d**). An additional example of this layered, bladed

1316 phase (**e**) showed a 7.1 Å d-spacing (001) with superlattice modulation of 21 Å (**f & f-I**), and

1317 similar elemental chemistry (**g**).

1318

1319 Figure 13: Compilation of the layered phase observed in bubbled experiments at temperatures

1320 25, 80, 150 and 220 °C. At 25 °C, we observed spindly particles (**a**) with a maximum of 4 layers

1321 (**a-I**) measured as having an approximate lattice spacing of 7.7 Å by IFFT (**a-II**) with FFT only

1322 showing the basal d-spacing (001) (**a-III**). Cluster of poorly layered particles in HAADF (**a-IV**)

1323 shows Mg distribution and content on average (**a-V**). At 80 °C, we observed well-ordered

1324 particles (**b**) with extensive layering (**b-I**) with a lattice fringe of 7.2 Å as measured by IFFT (**b-**

1325   **II**) and showing multiple lattice planes by FFT (**b-III**). Region with well-ordered layered blades

1326   in HAADF (**b-IV**) and Mg distribution and average content (**b-V**). We observed similar well-

1327   ordered particles at 150 °C (**c**) with extensive layering (**c-I**) where the lattice fringe was 7.1 Å by

1328   IFFT (**c-II**) and displayed recurring lattice planes by FFT (**c-III**). Collection of well-ordered

1329   particles in HAADF (**c-IV**) alongside Mg distribution and content (**c-V**). At 220 °C, we

1330   continued to observe a well-ordered layered phase (**d & d-I**) with a measured lattice fringe of 7.1

1331   Å by IFFT (**d-II**) and recurring lattice planes by FFT (**d-III**). Collection of well-ordered particles

1332   in HAADF (**d-IV**) and Mg distribution and content (**d-V**).

1333

1334 **Main Text Tables**

1335 **Table 1**

Chemical Component, Chemical Formula	Concentration [mM]
Sodium chloride, NaCl	400
Sodium bicarbonate, $NaHCO_3$	30
Magnesium chloride hexahydrate, $MgCl_2 * 6H_2O$	10
Ammonium chloride, NH_4Cl	10
Potassium chloride, KCl	7
Sodium orthosilicate, Na_4SiO_4	1.1 ± 0.08*
Ferrous chloride tetrahydrate, $FeCl_2 * 4H_2O$	1.1 ± 0.09*
Total cation equivalents from salts (est. from acid/base)	473.6 (500)
Total anion equivalents from salts (est. from acid/base)	473.6 (480-490)

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Table 2

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Temperature (°C)	Time (Days)	Bubbled (pH)	Control (pH)
25	19	7.33	7.14
25	40	7.06	7.17
80	7 (26)	6.74	6.92
150	7 (33)	6.41	6.43
220	7 (40)	5.85	7.65

1345

Table 3

1346

Condition	Measurement ± Standard Deviation
Silica in initial solution [mM]	1.1 ± 0.08
Fe(II) in initial solution [mM]	1.1 ± 0.03
Fe[III] (bulk) of acidified control after 19 days 25 °C FeT	0.07 ± 0.02
Fe[III] (bulk) in acidified bubbled exp after 19 days 25 °C FeT	0.75 ± 0.05

1347

1348

1349 **Table 4**

Condition	$\dfrac{Fe[III]}{FeT}$ (Ferrozine)	% Fe(II)/g (vanadate)
Control solids after 7 days 150 °C (33 days total)	0.27 ± 0.9	
Control solids after 7 days 220 °C (40 days total)	0.32 ± 2	
Bubbled solids after 19-21 days 25 °C	0.48 ± 0.06	48.14
Bubbled solids after 40 days 25 °C	0.45 ± 1.8	
Bubbled solids after 7 days 80 °C (26 days total)	0.45 ± 2.5	55.85
Bubbled solids after 7 days 150 °C (33 days total)	0.51 ± 0.06	32.22
Bubbled solids after 7 days 220 °C (40 days total)	0.46 ± 2.4	27.92

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Table 5

Experimental Condition	Average Atomic %					Elemental Ratios		
	Fe	Mg	Si	Al	O	avg Fe/(Fe+Mg)	avg (Fe+Mg)/Si	range (Fe+Mg)/Si
Bubbled 25C Poorly Layered	19.94	2.00	17.91	0.96	59.19	0.91	1.23	1.06-1.34
Bubbled 25C Mixed poorly crystalline oxides, layered, salts	18.96	1.83	18.04	1.73	59.45	0.91	n.a.	n.a.
Bubbled 80C Well Ordered Layered	27.70	1.61	12.94	1.03	56.73	0.95	2.27	2.11-2.43
Bubbled 150C Well Ordered Layered	22.13	4.54	14.91	0.77	57.65	0.83	1.79	1.59-2.14
Bubbled 220C Well Ordered Layered	16.22	10.02	15.23	0.87	58.01	0.62	1.72	1.6-1.85
Bubbled 220C Spinel Group Oxide	22.44	9.17	10.68	1.59	56.13	0.71	n.a.	n.a.
Control 150C Poorly Layered	8.58	17.35	15.50	0.65	57.91	0.33	1.67	1.45-1.67
Control 150C Iron Oxide Mass	31.08	4.17	7.89	2.33	54.53	0.88	n.a.	n.a.
Control 150C Iron Oxide Rods	28.54	7.13	7.39	2.59	54.34	0.80	n.a.	n.a.
Control 220C Well Ordered Layered	4.78	28.84	10.21	0.85	55.32	0.14	3.29	3.29
Control 220C Spinel Group Oxide	27.81	9.24	7.40	1.48	54.07	0.75	n.a.	n.a.

Figure 1
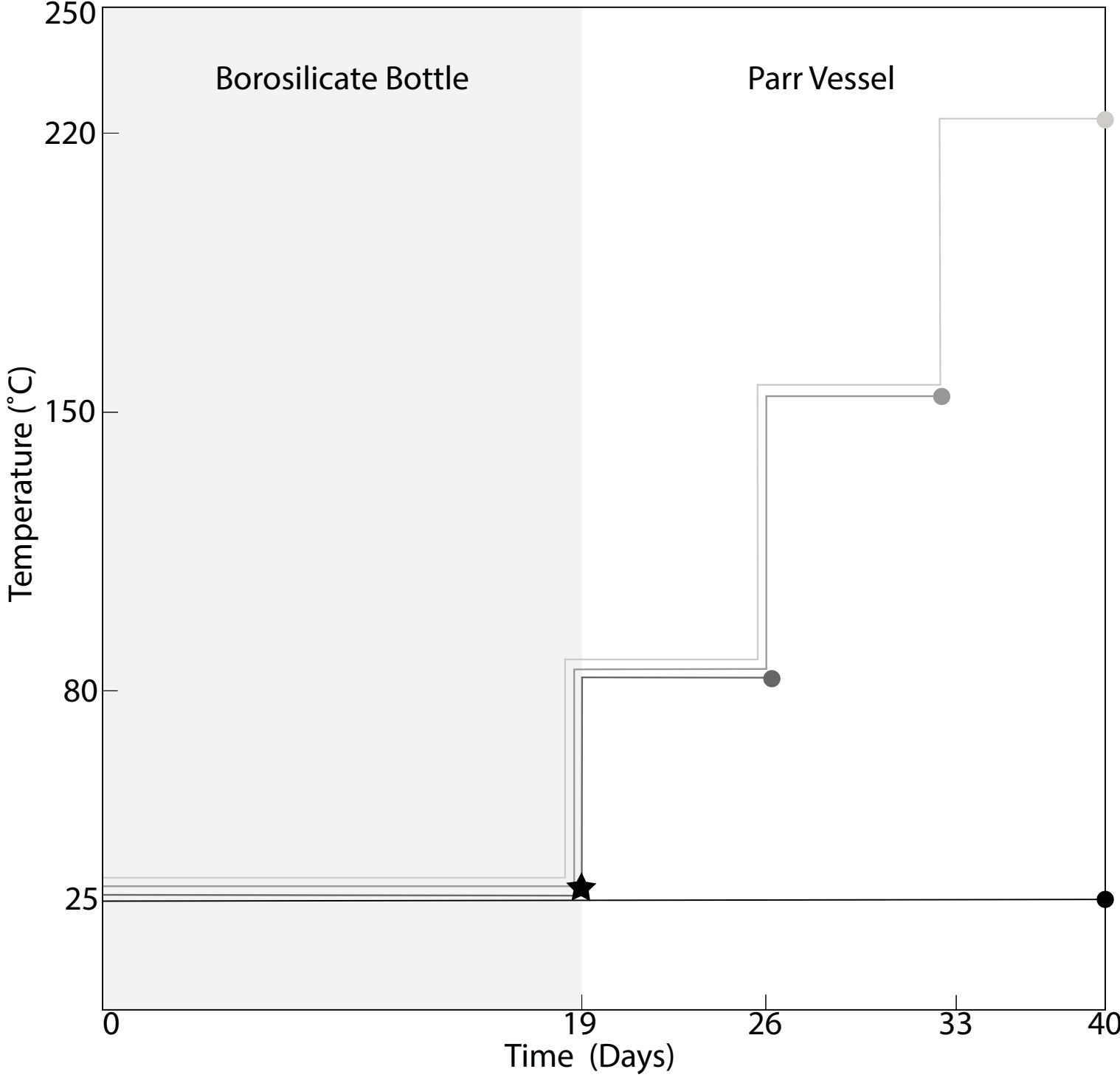
Figure 2
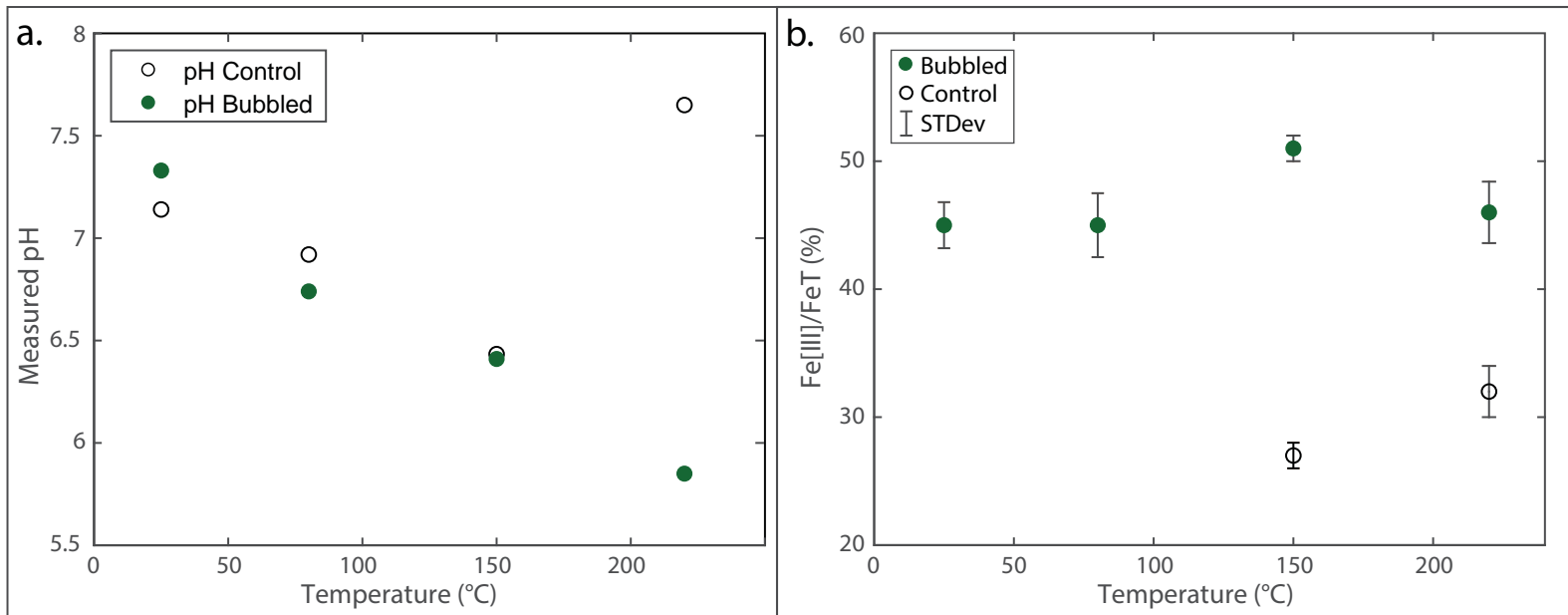
Figure 3

Figure 4

Figure 5

a.

b.

c. 500 nm

50 nm

d. 100 nm

e. Mg-rich Regions
Atomic %
Mg: 16
Fe: 12
Si: 13
O: 57
Al: 1.54
50 nm

f. 7.2 Å
6.9 Å
3.4 Å
1.5 Å
10 nm

g. 2.3 Å
I
2.5 Å
5 nm
10 nm

h. k.
100 nm

i. Interior Mass
Atomic %
Fe: 31
Si: 8
Mg: 4
O: 55
Al: 2

Rod
Atomic %
Fe: 34
Si: 5.4
Mg: 5
O: 53
Al: 2.6
50 nm

j. Fe O
50 nm
Si Mg

k. 6.2 Å
10 nm

l. I II
I 3.2 Å II 6.1 Å
2 nm 10 nm 2 nm 10 nm

m. [321]
[511]
[220]
[301]
[210]
10 nm⁻¹

Figure 6

a.

b.
200 nm

c.
50 nm

d.
100 nm

e.
Atomic %
Mg: 29
Fe: 5
Si: 10
Al: 1
O: 55
100 nm

f.
7.2 Å
10 nm

g.
I.
II.
7.2 Å
2 nm
4.3Å
2 nm
10 nm

h.
i.
Box Area
Atomic %
Fe: 28
Si: 7
Mg: 9
O: 54
Al: 1.5
50 nm

i.
Fe
O
50 nm
Si
Mg

j.
[2010]
[208]
[202]
[004]
[020]
[002]
[220]
[440]
[553]
5 nm⁻¹

Figure 7

| Bubbled, 25 °C | Bubbled, 80 °C | Bubbled, 150 °C | Bubbled, 220 °C |

a.

b.
1.3 Å
1.5 Å
2.6 Å
5 nm⁻¹   200 nm

d.
200 nm

f.
100 nm

h.
50 nm

c.
50 nm

e.
500 nm

g.
40 nm

i.
200 nm

I.   II.
2.6 Å
10 nm   2 nm

I.   II.
2.6 Å
2.5 Å
10 nm   2 nm

I. 1.6 Å   II.
2.6 Å
10 nm   2 nm

I.   II.
2.6 Å
10 nm   2 nm

Figure 8

Bubbled, 80 °C

a. 200 nm

b. 250 nm

c. 4.7 Å — 10 nm — I. — .400 — 311 — 111 — 222 — 10 nm⁻¹

Bubbled, 150 °C

d. 250 nm

e. 20 nm — f.

f. 4.7 Å — I. — 10 nm — 111 — 222 — 311 — 333 — 10 nm⁻¹

Bubbled, 220 °C

g. **Atomic %** Fe:22 Si:11 Mg:9 O:56 — 20 nm

h. 4.7 Å — I. — 10 nm — I. — 111 — 222 — 333 — 311 — 422 — 20 nm⁻¹

i. [440] [400] [222] [220] [111] — 10 nm⁻¹

Figure 9

a.

b.
500 nm

c.
h.
50 nm

d.
i.
100 nm

e.
HAADF   50 nm   Fe
Si   Mg

f.   HAADF
Atomic %
Fe:21
Si:17
Mg:2
O:59
Al: 1
50nm

g.   HAADF
Atomic %
Fe:21
Si:17.5
Mg:1
O:59
Al: 1
50nm

h.
I.   ~7.7 Å   2 nm
II.   ~7.6 Å   2 nm
I.
II.
20 nm

i.
I.
II.
I.   ~7.3 Å   2 nm
II.   ~7.2 Å   2 nm
20 nm

Figure 10

a.

b.

500 nm

c.

h.

100 nm

d.

Fe   Si

Mg   O

100 nm

e.

HAADF

Atomic %
Fe: 27
Si: 13
Mg: 1.6
O: 57
Al: 1

100 nm

f.

i.

100 nm

g.

Atomic %
Fe: 29
Si: 13
Mg: 1.6
O: 56
Al: 1

HAADF

100 nm

h.

7.2 Å

10 nm

i.

I.

I.

7.2 Å

1 nm

50 nm

j.

I.

II.

I.

7.0 Å

2 nm

II.

2.1 Å

1 nm

10 nm

k.

[004]

[003]

[002]

[001] [100]

[111]

[202]

[212]

10 nm⁻¹

Figure 11

Figure 12

Figure 13

Bubbled, 25 °C	Bubbled, 80 °C	Bubbled, 150 °C	Bubbled, 220 °C

a. 20 nm

b. 10 nm

c. 20 nm

d. 10 nm

I. 2 nm II. ~7.7 Å 2 nm III. 001 20 nm⁻¹

I. 2 nm II. 7.2 Å 1 nm III. 003 002 001 10 nm⁻¹

I. 10 nm II. 7.1 Å 4 nm III. 004 003 002 001 110 210 20 nm⁻¹

I. 5 nm II. 7.1 Å 2 nm III. 001 002 003 004 20 nm⁻¹

IV. 50 nm

V. Mg at.% 2.0 Mg/Fe+Mg 0.09

V. Mg at.% 1.6 Mg/Fe+Mg 0.05

V. Mg at.% 4.5 Mg/Fe+Mg 0.17

V. Mg at.% 10 Mg/Fe+Mg 0.38