Ferric iron triggers greenalite formation in simulated Archean seawater

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ABSTRACT

Sedimentary rock deposits provide the best records of (bio)geochemical cycles in the ancient ocean. Studies of these sedimentary archives show that greenalite, an Fe(II) silicate with low levels of Fe(III), was an early chemical precipitate from the Archean ocean. To better understand the formation of greenalite, we explored controls on iron silicate precipitation through experiments in simulated Archean seawater under exclusively ferrous conditions or supplemented with low Fe(III). Our results confirm a pH-driven process promoting the precipitation of iron-rich silicate phases, and they also reveal an important mechanism in which minor concentrations of Fe(III) promote the precipitation of well-ordered greenalite among other phases. This discovery of an Fe(III)-triggering iron silicate formation process suggests that Archean greenalite could represent signals of iron oxidation reactions, potentially mediated by life, in circumneutral ancient seawater.

INTRODUCTION

The early ocean shaped the evolution of microscopic life and supported the development of the earliest (bio)geochemical cycles. Chemically precipitated sediments record the (bio)geochemistry of their aqueous environments (Derry and Jacobsen, 1990), and deeper marine strata from the Archean Eon (4.0–2.5 Ga) are dominated by iron formations (silica-rich chemical sediments with >15% iron) (Simonson and Hassler, 1996). The long-term, widespread deposition of iron formations suggests anoxic conditions and high iron concentrations in seawater, yet the accumulation of iron-rich sediments was likely triggered by a chemical change or (bio)geochemical process that induced mineral precipitation (Holland, 1984; Bekker et al., 2014; Johnson and Molnar, 2019).

The identification of the original iron precipitate(s) is integral to unraveling the ancient process(es) that induced the deposition of Archean marine iron formations. Though the iron oxides prevalent in iron formations are largely accepted as primary components of these deeper marine sediments (Beukes and Gutzmer, 2008; Bekker et al., 2014; Sun et al., 2015), rigorous characterization of well-preserved clast associated with ca. 3.5 to ca. 2.4 Ga iron formations documented nanometer-scale inclusions of early iron silicates (Rasmussen et al., 2015; Muhling and Rasmussen, 2020). The best-preserved inclusions were characterized as greenalite [Fe(II),Si₅O₁₁(OH)₄], the iron end member of the two-layer serpentine group, but with ~10%–25% Fe(III) (Johnson et al., 2018). This small proportion of Fe(III) in Archean greenalite suggests that partial iron oxidation could have favored iron-silica precipitation, and indeed, metastable Fe(II,III) hydroxy salts (green rust phases) were proposed as potential precursors to iron formation silicates and oxides (Haley et al., 2017).

Understanding the formation process of iron silicates under ancient marine conditions should yield insights into Archean (bio)geochemistry. Existing iron silicate synthesis protocols have relied on oversaturated iron and silica chemical conditions set at high pH (8 to >12) (e.g., Decarreau and Bonnin, 1986; Balderrmann et al., 2014; Chemtob et al., 2015; Dzene et al., 2018). However, two independent models of early Earth marine geochemistry estimated Archean oceanic pH between ~6.5 and 7.5 (Haley and Bachan, 2017; Kriesslens-Totton et al., 2018). Geological observations suggest that dissolved silica was near or at saturation with amorphous silica (~1.9 mM) in the Archean ocean (Siever, 1992; Maliva et al., 2005; Stefrak et al., 2015).

Estimates of dissolved iron concentrations in the pre-oxygenated ocean vary between 20 μM and 2 mM Fe(II) depending on constraints set by siderite (Holland, 1984; Canfield, 2005) or ferrous greenalite (Jiang and Tosca, 2019) saturation. These geochemical differences prevent direct translations between the high-concentration, high-pH synthesis experiments and ancient processes in the Archean ocean.

A few previous studies explored iron silicate mineralization under reducing and geochemically relevant conditions plausible for the early ocean. Under reducing conditions with very low concentrations of iron and silica, Harder (1978) produced Fe[II,III]-silica coprecipitates at pH 7–9 but did not include structural data to confirm iron silicate formation. Later studies similarly showed the anoxic formation of poorly crystalline iron-silica coprecipitates but were unable to robustly characterize these phases (Farmer, 1991; Konhauser et al., 2007). Recently, Tosca et al. (2016) examined Fe(II)-silicate formation in Archean seawater-like solutions and proposed that poorly ordered experimental precipitates detected at pH ≥7.5 were precursors to greenalite. In contrast, at pH 7, Haley et al. (2017) observed that Fe[II,III] green rust formed upon partial Fe oxidation under low concentrations of silica (100–250 μM), transforming into three-layer iron silicates in solutions upon 22 °C and 50 °C aging for days to months.

While this research demonstrates that iron-silica precipitates can form in simulated ancient seawater, no study has conclusively shown greenalite formation in predicted Archean ocean chemistry. It is also unclear whether the Fe(III) in the ancient iron silicate inclusions signals a role for iron oxidation in the precipitation of these iron-silica phases. Therefore, we explored the precipitation and crystallization of iron and silica precipitates in artificial ancient seawater at the predicted Archean pH range of 6.5–7.5 under
both strictly ferrous conditions and in systems with low levels of Fe(III).

**EXPERIMENTAL METHODOLOGY**

Experiments were performed in 500 mL borosilicate glass bottles at 25 °C under anoxic conditions. Solutions were first supplemented with 1 mM sodium orthosilicate and stirred for 24 h at their respective experimental pH (6.5, 7, or 7.5), ensuring full silica depolymerization (Dietzel, 2000). We added seawater salts, then ferrous or ferrous-ferric chloride and bicarbonate buffer, and set the final pH of solutions (Table S1 in the Supplemental Material). Given our focus on iron silicate formation, we omitted calcium in the media to preclude the precipitation of calcium carbonate.

After 5 days of low-temperature (25 °C) reaction in the dark, the experiments were sub-sampled for aqueous and solid analyses and secondary hydrothermal aging. For aging, subsamples of 25 °C precipitates were sealed in a gas-tight Parr vessel (22 mL) under anoxic conditions and heated at 150 °C for 5 days to enhance crystallization, simulating ~100 m.y. of low-temperature diagenesis (Siever, 1983).

Dissolved iron, silica, and the Fe(III)/Fe(T—total) content of precipitates were measured using colorimetric assays. We used scanning electron microscopy (SEM) paired with energy dispersive X-ray spectroscopy (EDS) to image and collect micron-scale elemental maps of the experimental precipitates. Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and scanning and high-resolution TEM (STEM and HR-TEM) enabled the compilation of nanoscale structural and elemental data on the mineral phases. Additionally, we used a cobalt-sourced X-ray diffractometer (XRD) on anoxic sealed precipitate slurries to determine mineral d-spacings. A full description of the experimental and analytical methods is available in the Supplemental Material.

### pH CONTROL ON IRON-RICH SILICATE FORMATION

In measuring the mass of precipitated phases and the associated changes in solution chemistry (Table 1), we did not detect iron-silica precipitation, but observed possible colloidal silica at pH 6.5 and 7 under anoxic and ferrous conditions (see the Supplemental Material). Low quantities of visible iron-silica coprecipitate did form at the higher pH of 7.5 (Fig. S1). The mass of the observable precipitate at pH 7.5 was still not measurable, but changes in solution chemistry after 5 days at 25 °C indicated a decrease in Fe(II) from 1 mM to 0.78 mM and a decrease in Si from 1 mM to 0.73 mM (Table 1). We were unable to subsample the negligible pH 7.5 precipitate at 25 °C, so the entire pH 7.5 precipitate was aged at 150 °C and developed into a similar quantity of darker gray material (Fig. 1A).

A nanoscale examination of this 150 °C-aged ferrous pH 7.5 sample illuminated three distinct morphologies (Fig. 1). We observed aggregates of layered structures, webs of amorphous gel, and rare hexagonal platelets (Fig. 1C; Fig. S2C). The few hexagonal platelets were tentatively identified as green rust based on morphological similarities to those identified by Halevy et al. (2017). The layered structures were <10 nm thick and poorly ordered with curling features typical of frequent edge dislocations (Figs. 1D–1F). One layered structure was sufficiently crystalline for HR-TEM and had 7.3 Å basal spacing consistent with a serpentine-group clay (Fig. 1F). This lattice fringe spacing and the elemental chemistry (Fig. 1F; Fig. S3) suggest the formation of two-layer Fe-Mg silicates.

We therefore conclude that in ferrous iron solutions, higher-pH aqueous conditions promote iron-rich silicate precipitation under anoxic, environmentally relevant conditions. This pH-driven precipitation mechanism initiates at a pH of ~7.5 with amorphous material, similar to the findings of Tosca et al. (2016). These experimental results are congruous with previous studies that found high-pH aqueous conditions conducive to authigenic iron silicate clay formation (Dzene et al., 2018).

### FERRIC IRON TRIGGERS SILICATE FORMATION

Adding 5% of the total iron as Fe(III) stimulated precipitation at all tested pH levels. The quantity of solids at pH 7.5 increased approximately fivefold with Fe(III) (Table 1), producing deep-green precipitates (Fig. 2A; Fig. S1). The 25 °C bulk solid phase was XRD-amorphous (Fig. S4) and >80% Fe(II) (Table 1). SEM (Fig. S5A) and TEM (Figs. 2B–2E) imaging revealed abundant nanoscale tubular structures and poorly layered curling structures. These were morphologically similar to the ferrous layered precipitate (Figs. S3D and S3E). HR-TEM also indicated iron-oxide precipitates at 25 °C, including euhedral crystals with magenetic lattice spacing (Fig. S5D). Even after 150 °C aging, XRD of the Fe(III)/II pH 7.5 experiment did not detect ~7 Å silicates (Fig. S4), and TEM imaging showed curling layered structures instead of well-ordered stacks (Figs. 2G–2I; Figs. S6B–S6D). In HR-TEM, a lack of repeating layers precluded definitive measurements, but we estimated a basal layer spacing of ~7.9 Å (Fig. 2K). While amorphous by selected area electron diffraction (SAED) (Fig. S3), the layered phases had elemental chemistry consistent with a serpentine-group silicate similar to greenalite (Fig. S3) and lacked diagnostic green rust XRD peaks (Fig. S4). We also observed magnesite and magnetite by TEM and XRD after 150 °C aging (Fig. 2J; Figs. S4 and S7). Though the introduction of Fe(III) at pH 7.5 did not substantially alter the morphology or identity of the poorly ordered silicate-like phase, it did greatly increase the quantity of layered structures and eliminated the presence of the amorphous gel phase.

At pH lower than 7.5, precipitation occurred only upon the introduction of a mixture of ferri- and ferrous iron. Completely ferrous experiments did not yield extractable precipitates at pH 6.5 and 7 (Table 1; Fig. S1). However, with 5% of the total iron added as Fe(II) to the lower-pH experiments, orange solids formed after 5 days of 25 °C precipitation and equilibration (Fig. 3A; Fig. S1). The 25 °C precipitate largely consisted of iron-silica coprecipitates in amorphous aggregates as determined by SEM and TEM (Fig. 3B; Fig. S8A). Although the 25 °C solids were dominated by amorphous material, we detected a thin wavy structure in the pH 7 precipitate that could correspond to early silicate layers (Figs. 3E–3G; Fig. S9A). In pH 6.5 experiments, we observed two examples of iron-rich ~7 Å layered structures at 25 °C (Figs. 3B and

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**TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS**

| Experimental condition | 0% Fe(III) pH 6.5 | 0% Fe(III) pH 7.0 | 0% Fe(III) pH 7.5 | 5% Fe(III) pH 6.5 | 5% Fe(III) pH 7.0 | 5% Fe(III) pH 7.5 |
|------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Dried mass after 12 h (mg) ± 0.01 | 3.18 ± 0.01 | 4.68 ± 0.01 | 3.31 ± 0.01 | 6.54 ± 0.01 | 7.73 ± 0.01 | 15.86 ± 0.01 |
| Silica in solution after 5 days, 25 °C (mM) ± standard deviation | 0.57 ± 0.01 | 0.77 ± 0.01 | 0.73 ± 0.01 | 0.34 ± 0.01 | 0.39 ± 0.01 | 0.38 ± 0.01 |
| Fe(II) in solution after 5 days 25 °C (mM) ± standard deviation | 0.99 ± 0.01 | 0.86 ± 0.01 | 0.78 ± 0.01 | 0.58 ± 0.01 | 0.40 ± 0.01 | 0.31 ± 0.01 |
| Fe(III) in solids after 5 days, 25 °C | 0.96 ± 0.01 | 0.89 ± 0.01 | 0.18 ± 0.01 | 0.60 ± 0.01 | 0.54 ± 0.01 | 0.30 ± 0.01 |
3C; Figs. S8C–S8E). This uncommon but well-ordered stacked phase had elemental chemistry consistent with a Fe-Mg silicate (Fig. S3); thus, in tandem with its basal spacing, we interpret it to be high-Mg greenalite.

Aging of the pH 6.5 and 7 low-Fe(III) precipitates at 150 °C yielded a diversity of phases, including extensive formation of well-ordered 7 Å silicates. TEM imaging revealed considerable amorphous precipitates and minor crystalline phases identified as magnetite, hematite, and magnesite (Figs. 3H–3S; Figs. S3, S7, S10, and S11). XRD confirmed these minerals and also indicated the presence of one or more phases with ∼7 Å spacing, consistent with the presence of a serpentine-group clay and/or carbonate green rust (Fig. S4). SEM and TEM images showed a common phase with hexagonal morphology, low-Si elemental chemistry, and 3.1 Å a-axis spacing characteristic of a carbonate green rust (Fig. 3S; Figs. S3 and S10A) (Christiansen et al., 2009). We also observed substantial formation of a layered phase with 7.3–7.4 Å

![Figure 1](http://pubs.geoscienceworld.org/gsa/geology/article-pdf/doi/10.1130/G48495.1/5280063/g48495.pdf)

**Figure 1.** Transmission electron microscopy (TEM), scanning TEM (STEM), and high-resolution TEM (HR-TEM) images of experimental precipitates at pH 7.5. Minimal gray-colored precipitates formed in ferrous conditions after 150 °C aging, shown in an epitube (A), with TEM images revealing amorphous films (B), hexagonal platelets (C, enlarged in inset), and silicate-like curled clusters (B, D–E) with representative elemental chemistry of layered iron silica phases (“layered”) (D inset) and ∼7 Å lattice spacing (E,F). HAADF—High-angle annular dark-field imaging; Rel.—relative.

![Figure 2](http://pubs.geoscienceworld.org/gsa/geology/article-pdf/doi/10.1130/G48495.1/5280063/g48495.pdf)

**Figure 2.** Transmission electron microscopy (TEM), scanning TEM (STEM), and high-resolution TEM (HR-TEM) images of 5% Fe(III)/Fe (T—total) precipitates at pH 7.5, producing green precipitates at 25 °C (A) dominated by poorly ordered curling structures (B–E). The layered phase (“layered”) had iron silicate-like chemistry by energy dispersive X-ray spectroscopy (D inset). TEM imaging of this Fe[II,III] precipitate aged at 150 °C (F) shows clusters of layered structures alongside amorphous material (G–I) and nanomagnetite (J). The layered phases (“layered”) had chemistry consistent with an iron-magnesium silicate by EDS (I inset). Layered structures in H had 7.9 Å lattice spacing (K). HAADF—High-angle annular dark-field imaging; Rel.—relative.
spacing (Figs. 3 K and 3Q) and serpentine group–like elemental chemistry (Fig. S3). Additionally, SAED on multiple orientations of this phase displayed a polynanocrystalline diffraction pattern consistent with serpentine-group minerals (Fig. 3J).

**IMPLICATIONS**

Our aggregated data confirm that high-Mg greenalite was a major mineral product in the crystallized Fe[II,III] pH 6.5 and 7 experiments. However, we observe two discrepancies between this experimental assemblage and the early iron-mineral inclusions in Archean marine chert. Our experimental products contained coexisting oxidized and reduced phases in thermodynamic disequilibrium, while well-preserved Archean chert hosts primary greenalite inclusions without magnetite and hematite (Rasmussen et al.,...
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