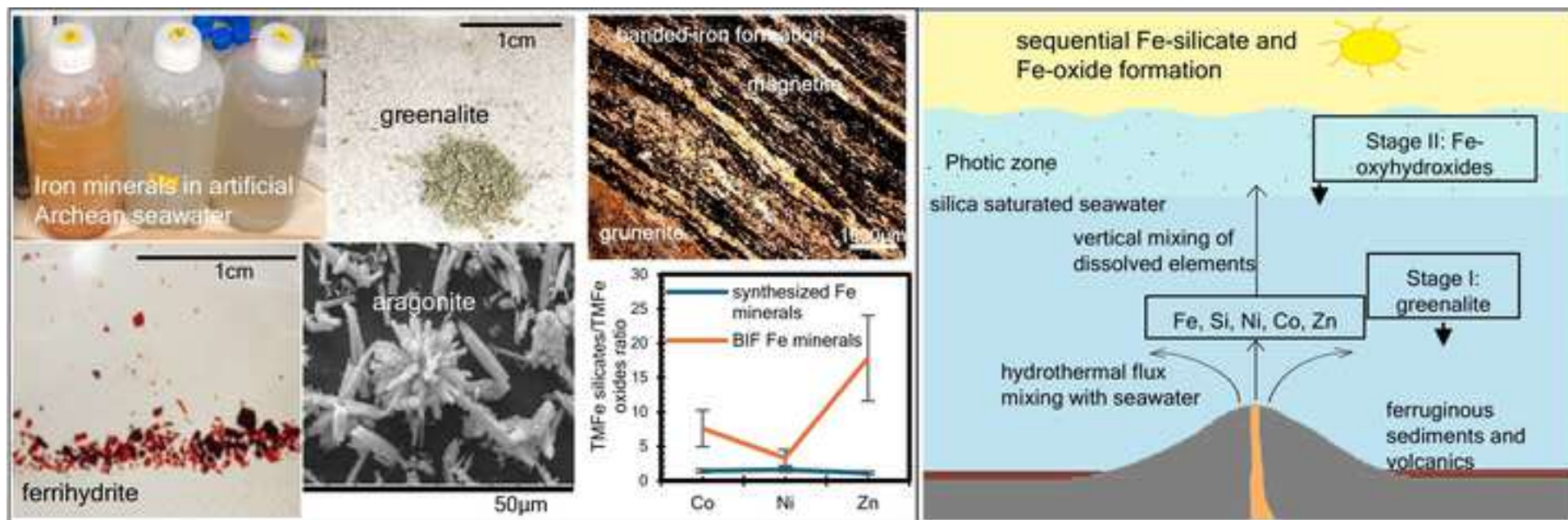




Highlights (85 characters each)

- Ni, Co and Zn distribution coefficients for primary BIF minerals
- Contrasting trace element chemistry of BIF Fe -silicates and -oxides
- Fluctuating Ni, Co and Zn concentrations in the 4.2 and 3.2 Ga seawater
- Greenalite and Fe-oxyhydroxides as double mineral sinks in the early ocean
- Double mineral sinks depleted Zn while Ni and Co remained bioavailable

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Title: Fluctuating nickel, cobalt, and zinc concentrations in the Hadean to early Archean (>3 Ga) ocean

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Abstract

Chemical evolution of seawater composition is thought to have exerted considerable influence on biological evolution throughout Earth's history. However, the chemical structure and dynamics of the early ocean (>3.0 Ga) are poorly understood. Here, we experimentally studied trace metal (TM) scavenging by greenalite and Fe-(oxy)hydroxide minerals precipitated under simulated early Precambrian conditions, alongside *in-situ* TM compositions of magnetite and grunerite in 4.2 and 3.2 Ga banded iron formations (BIFs). Our geochemical experiments mimicking early Precambrian seawater conditions show that both primary greenalite and Fe-(oxy)hydroxide TM sinks influenced the overall concentrations of dissolved Ni, Co, and Zn in the early seawater column. Reconstructed TM values from BIF minerals using experimentally determined distribution coefficients indicate fluctuating Ni, Co and Zn levels in the ambient seawater. Our results suggest that processes like deep-water hydrothermalism, sequential greenalite and Fe-(oxy)hydroxides formation due to a vertical transportation delay of hydrothermal components to surface water, dilution of hydrothermal components, and a microbial physiological resuscitation lag likely regulated the abundance and distribution of TMs in the Hadean to early Archean seawater. Using the ratios of Ni/Zn or Co/Zn bound to greenalite and Fe-(oxy)hydroxides as a model, our data indicate quantitative removal of Zn—

first by greenalite, followed by Fe-(oxy)hydroxide sinks. The resultant high Ni/Zn ratios in the Hadean to early Archean seawater column after each periodic Fe mineral formation cohere with the dependence of early marine biogenic methanogenesis on Ni enzymes and a low requirement for Zn enzymes by primordial life.

1. Introduction

The dynamic distribution and concentration of bioessential trace metals (TMs) in seawater column throughout Earth's history are thought to have influenced the trajectory of biological evolution and the pattern and timing of the incorporation and use of TMs in metalloenzymes throughout Earth's history (Moore et al., 2017; Saito et al., 2003). Consequently, preferential TM utilization by biological species with different evolutionary histories has resulted in the development of various models linking TM bioavailability to temporal and spatial biodiversification on the Tree of Life (Saito et al., 2003). For example, high dissolved seawater nickel (Ni) has been linked with the rise and predominance of methanogenic Archaea in the Archean ocean (Konhauser et al., 2009), whereas a low concentration of zinc (Zn) in Archean seawater is correlated with the lack of Zn-dependent metabolism in early life (Saito et al., 2003; Tostevin and Ahmed, 2023). Alternatively, a few geochemical studies have proposed invariant nature of dissolved marine Zn concentrations throughout most of Earth's history, leading to little or no pressure on the pattern of biological Zn utilization (Robbins et al., 2013; Scott et al., 2013). A recent phylogenetic study by Bodden et al. (2021) also highlighted that ancestral cyanobacteria possibly used Cu- and Zn-dependent superoxide dismutase enzymes during the Archean Eon.

Widespread ocean anoxia, coupled with elevated and episodic submarine hydrothermal activity (Brenner et al., 2024), contributed high dissolved ferrous iron (Fe(II)) content to the early seawater (ferruginous conditions), while the absence of biological sinks promoted aqueous silica saturation (Poulton and Canfield, 2011; Siever, 1992). These conditions are thought to have triggered pervasive precipitation of primary hydrous Fe(II) silicates like greenalite (Hinz et al., 2021; Rasmussen et al., 2019, 2017, 2015b, 2015a; Tosca et al., 2016) and hydrous ferric Fe(III) and Fe(II) (oxy)hydroxide minerals such as ferrihydrite (Bekker et al., 2010; Kappler et al., 2005) and green rust (Halevy et al., 2017; Zegeye et al., 2012), respectively, with a high amount of silica adsorbed on them (Fischer and Knoll, 2006). For instance, the worldwide prevalence of primary greenalite, low-grade metamorphic minnesotaite, and medium-to-high-grade metamorphic grunerite (Mel'nik, 1982) (Section S1, supplementary data 1), together with magnetite and hematite in Hadean and Archean banded iron formations (BIFs) and associated chert (Dymek and Klein, 1988; Ghosh, 2020; Katsuta et al., 2012; Klein, 2005; Mloszewska et al., 2012; Muhling and Rasmussen, 2020; Pecoits et al., 2009; Pitarello et al.,

2019; Rasmussen et al., 2019, 2017, 2015a; Rasmussen and Muhling, 2018; Wang et al., 2014),
testifies to this global ferruginous/silica-rich, anoxic Archean seawater state.

According to the geological rock record (Ghosh, 2020; Konhauser et al., 2009) and
experimental modeling (Robbins et al., 2019), Fe-oxyhydroxides were dominant Fe-mineral
phases in Precambrian surface seawaters. The oxidation of dissolved Fe(II) to Fe(III) minerals
likely occurred via various abiotic/biotic pathways, including anoxygenic photosynthetic
microbial activity (photoferrotrophy), limited oxygenation by cyanobacteria in oxygen oases
and/or UV-photooxidation (Konhauser et al., 2018; Swanner et al., 2015; Tabata et al., 2021;
Thompson et al., 2019). Besides, in the absence of significant iron oxidation, pervasive abiotic
precipitation of primary greenalite could occur throughout the anoxic water column (Muhling
et al., 2023; Nke et al., 2024). Thus, for a more holistic reconstruction of dissolved seawater
nutrient levels using Fe minerals as proxies, comparative co-precipitation and adsorption
models of the associated Fe-(oxy)hydroxide and greenalite mineral sinks (Ghosh, 2020; Pecoits
et al., 2009; Rasmussen et al., 2015b) are needed. This approach is particularly vital because
the efficient removal of trace nutrients from seawater by authigenic seawater Fe minerals
should reflect the sum of their distinct binding affinities. For instance, a recent study showed
that greenalite can incorporate significant amounts of Zn, vanadium (V) and copper (Cu) from
early marine water, and therefore is a potential sink for dissolved trace nutrients (Tostevin and
Ahmed, 2023). However, accurately evaluating the impact of BIF minerals as early ocean TM
sinks requires assessing the combined and comparative binding affinities of Fe-oxyhydroxides
and greenalite during formation, alongside correlating these findings with TM concentrations
preserved in BIFs.

The dual precipitation of Fe-(oxy)hydroxides and greenalite together likely heavily influenced
the spatiotemporal TM distribution in the early ocean. To better constrain early seawater Ni,
Co, and Zn variations, we studied TM distribution kinetics during Fe-(oxy)hydroxides and
greenalite formation under simulated early Precambrian seawater conditions. The experimental
data were then correlated with the Ni, Co, and Zn compositions of alternating magnetite and
grunerite mineral bands preserved in 4.2-3.2 Ga Algoma-type BIFs, deposited in volcanically
active, deep-water basinal settings prior to the widespread development of stable Superior-type
continental shelves (discussed below). Our results demonstrate that sequential greenalite and
Fe-(oxy)hydroxide formation regulated oceanic Ni, Co, and Zn distributions, ultimately driving
a coupled depletion of Zn in the early water column.

2. Material and methods

2.1. Geology of the studied BIFs

The reference BIFs of this study are of the Algoma-type and belong to the ~3.2 Ga Badampahar (Ghosh et al., 2019; Ghosh and Baidya, 2017a, 2017b) and ~4.2 Ga Nuvvuagittuq (Mloszewska et al., 2013, 2012; Sole et al., 2025) greenstone belts. A detailed geological description of the Badampahar rocks can be found in earlier studies (Ghosh et al., 2019; Ghosh and Baidya, 2017a). In brief, the Badampahar rock sequence contains BIFs, bedded cherts, mafic-ultramafic volcanic rocks, phyllites and minor siliciclastic rocks, and it occurs as an enclave within the Mayurbhanj Granite at the eastern peripheral part of the Singhbhum Craton, India (Fig. S1, Supplementary Data 1). The Badampahar greenstone rocks are variably metamorphosed between the greenschist and lower amphibolite facies (Ghosh and Baidya, 2017a). The BIFs with patches of iron ores occur intercalated with cherts, komatiites, and basalts in the lower and middle parts of the stratigraphic sequence, whereas basalts, phyllites, and bedded cherts dominate the upper part of the sequence. The BIFs (Figs. 1-3) generally contain magnetite, grunerite ($\pm$ ferroactinolite) and quartz as alternating pure and mixed mineral bands (Ghosh, 2020; Ghosh and Baidya, 2017b).

A detailed description of the Nuvvuagittuq rocks (c. 4.2 Ga) and the BIFs of the used dataset can be found in earlier studies (Mloszewska et al., 2013, 2012; Sole et al., 2025). Briefly, the Nuvvuagittuq rocks are dominated by Ca-depleted amphibolites (volcanics), BIFs, and mafic-ultramafic intrusives that occur as enclaves within gneisses of the Northeast Superior Province, which is a part of the larger Superior Craton in northern Québec, Canada. The BIFs of Nuvvuagittuq are very similar to the Badampahar BIFs in terms of texture, mineralogy, and chemistry. The iron minerals are magnetite and grunerite ($\pm$ ferroactinolite $\pm$ augite) and exhibit marine chemical sediment-like chemical patterns (Figs. 4b-c). Mloszewska et al. (2012) categorized the BIF samples as “banded iron formations” (with up to 40 modal % magnetite) and “banded silicate formations” (with up to 10 modal% magnetite).

Collectively, this study focuses on 4.2 and 3.2 Ga BIFs of Algoma-type setting, which is representative of the Hadean to early Archean (>3 Ga) time when major continental shelves (Superior-type settings) had not yet widely developed due to the lack of large, stable landmasses (Chowdhury et al., 2025). The studied Nuvvuagittuq and Badampahar BIFs occur intercalated with volcanic sequences and generally lack major clastic sediment inputs (Ghosh et al., 2019; O’Neil et al., 2011). This context strongly points to a depositional basin dominated

by submarine volcanism, hydrothermal activity, metal fluxes, and subsequent Fe mineral formation.

In this paper, we used *in-situ* magnetite and grunerite mineral chemistry data of Nuvvuagittuq and Badampahar BIF analyzed by Mloszewska et al. (2012) and Ghosh (2020), respectively, together with new *in-situ* trace element analysis of magnetite and grunerite present in the Fe-mineral- and quartz-rich bands of six BIFs from Badampahar.

2.2. Geochemical experiments

A synthetic Archean seawater stock solution was prepared by adding relevant sea salts, such as 400 mM sodium chloride, 7 mM potassium chloride, 5 mM ammonium chloride, 1.2 mM sodium orthosilicate, 20 mM calcium chloride, and 20 mM magnesium chloride in milliQ water, according to Precambrian estimates (Hinz et al., 2021). This was followed by the addition of 1 mM Fe, 0-10 mM HCO_3^- and 1 μM of each TM (Ni, Co, and Zn) to the deoxygenated solution inside an anaerobic chamber. Thermodynamic calculations using the VISUAL MINTEQ software (Gustafsson, 2013) show that a TM concentration of 1 μM each is much below the limit required to produce individual solid phases (Table S1, supplementary data 1). Five sets of TM co-precipitation-adsorption experiments (Table 1) were performed with pure ferric, pure ferrous, and mixed-valent ferric/ferrous ratios of 1:2 and 2:1 in the starting solution to produce greenalite (ferrous), ferrihydrite (ferric), and mixed-valent ferric/ferrous Fe minerals. All experiments were conducted in 1 L Teflon vials at 25 °C and a pH of 7.5-7.8 (Guo and Korenaga, 2025; Tosca et al., 2016) inside an inert anaerobic chamber atmosphere of <1 ppm O_2 . Another set of ferrihydrite synthesis experiments was performed in open-air conditions. In addition, a sodium bicarbonate control at different concentrations (2, 5 and 10 mM) was used in replicate greenalite and anoxic ferrihydrite experiments. The experiments lasted for 10 days, with solution sub-samples collected at specific time intervals. The 10-day experimental duration precipitated a harvestable amount of greenalite and brought solution Fe concentrations close to ~0.5 mM, which thermodynamically inhibits any significant further greenalite formation in the chosen 7.5-7.8 pH range (Tosca et al., 2016). Two additional TM adsorption experiments with freshly formed ferrihydrite in a similar seawater medium were conducted to obtain TM adsorption kinetics. On day ten, samples were filtered, and the solid-phase residues were characterized mineralogically by the next day. Some solid samples were further treated at a diagenetic temperature of 125 °C for five days, followed by chemical analysis.

2.3. Chemical and mineralogical analysis

All analytical work was conducted using the in-house facilities of the University of Tokyo, Japan. A scanning electron microscope equipped with an energy-dispersive spectrometer was used to examine the experimental solids at the micrometer scale and to approximate their major elemental compositions. The experimental solution and solid samples were analyzed for major and trace elements (supplementary dataset) using a quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS). Solution samples were diluted 250-fold in 2% HNO₃ and measured with matrix-matching calibration standards, internal standards (Sc and In), duplicates, and blanks. Analytical uncertainty measured by repeated standard and sample analyses was <6%. Experimental solid samples were weighed in 50 mL Teflon vials and dissolved using a sequence of concentrated HF + HClO₄, HNO₃ and HCl digestions on a hotplate at 120-180 °C. Samples were diluted 10⁵-fold in 2% HNO₃ and analyzed with matrix-matching calibration standards and internal standards (Sc and In) using the aforementioned Q-ICP-MS. The analytical uncertainty of repeated standard analyses was <5% (supplementary dataset).

The six 3.2 Ga Badampahar BIF samples used in this study were pre-screened for weathering, hydrothermal alteration, or the presence of any unwanted Fe-minerals through petrography and SEM analysis. The BIF samples are devoid of any visible alteration or hydrothermal texture; magnetite and grunerite (±ferroactinolite) are the only Fe-minerals present. The sample thin sections were ablated in a He atmosphere, and the sample carrier gas (flow rate 0.9586 L/min), He, was mixed with Ar using a Y-junction. Depending on the grain size, beam diameter varied between 40 µm and 50 µm, and the frequency was kept at 5 Hz. All grains were analyzed with a laser energy of 4.4 J/cm². The following isotopes were analyzed: ²⁴Mg, ²⁷Al, ²⁹Si, ³⁹K, ⁴⁴Ca, ⁵¹V, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn, ⁷¹Ga, ⁸⁹Y, ⁹⁰Zr, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ²³²Th, and ²³⁸U. Analyses were performed in peak-hopping mode, with each analysis consisting of a 20 s background measurement with the laser turned off and a 40 s peak signal measurement with the laser turned on. *In-situ* high-resolution mineral chemistry data were produced via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of the trace elements associated with the grunerite and magnetite minerals. Calibration was performed using NIST610, NIST612, BCR-2g glass standards, and data were reduced using Fe and Si as internal standards. Concentrations of Fe and Si measured with electron probe microanalysis (EPMA) were used to normalize

signal intensities. The Analytical uncertainties of the LA-ICP-MS analysis, determined by repeated standard measurements, were <6% for all elements.

X-Ray diffraction (XRD) samples were air-dried inside an anaerobic chamber and analyzed on a zero-background quartz sample holder within 15 minutes of air exposure. The analytical settings of the Rigaku RINT-2100 X-ray diffractometer (Cu-source tube) used for XRD mineralogical analysis were as follows: less-fluorescence mode, a 5°/minute scan speed (2 θ range ~ 5-70°), 40 kV, 30 mA, a 5 mm slit, a 0.8 mm collimator and a Dtex-Ultra detector. The XRD patterns were baseline-corrected and smoothened for improved visualization and matched with standard mineral XRD patterns. We further studied the synthesized samples with X-ray absorption spectroscopy (XAS) at the BL-9A beamline of the Photon Factory (Tsukuba, Japan) to improve mineralogical characterization. We measured Fe K-edge X-ray absorption near edge structure (XANES) spectra of the synthesized minerals at ambient pressure and temperature using a Si (111) double-crystal monochromator in transmission mode. After energy calibration and normalization, we used the linear combination fitting tool of the LARCH software (Newville, 2013) to fit the spectral XANES features of the synthesized minerals with a combination of the spectra of reference minerals, including hematite, goethite, ferrihydrite, magnetite, green rusts, greenalite, cronstedtite and siderite. We also analyzed the pre-edge peaks (Wilke et al., 2001) by extracting pre-edge jump with a spline function and fitting it with three Gaussian functions. An Fe redox calibration curve for the pre-edge centroid positions, constructed using standard minerals (e.g., fayalite, magnetite, and hematite) of varying Fe redox states, allowed us to calculate the redox states of Fe in the mixed-valent experimental samples.

3. Results

3.1. Texture and mineralogy of the reference BIFs

Our investigated reference BIFs from the ~3.2 Ga Badampahar (Figs. 1–3) and ~4.2 Ga Nuvvuagittuq formations consist primarily of alternating magnetite-, grunerite-, and quartz-rich bands. Detailed descriptions of the petrography and mineral paragenesis of these reference BIFs are available in earlier studies (Ghosh, 2020; Mloszewska et al., 2012). In brief, the Badampahar BIF samples are finely banded at a sub-millimeter scale and consist mostly of alternating bands of magnetite, quartz, and grunerite ($\pm$ ferroactinolite) (Figs. 1a–c). The bands exhibit variable thicknesses (0.05–1 mm) and mineral proportions, specifically comprising

magnetite-rich, grunerite-rich, quartz-rich, grunerite+quartz-rich, and magnetite+quartz-rich assemblages. A metamorphic coarse granoblastic texture is prominent within the bands, and the minerals often include one another and exhibit sharp contacts (Figs. 1e–f, 2, 3). Many previous petrographic studies (Rasmussen et al., 2017; Rasmussen and Muhling, 2018) have suggested a common greenalite precursor for all BIF Fe-minerals, and propose that Fe-oxides in BIFs likely originated from precursor Fe-silicates. However, (i) the presence of distinct, alternating bands composed of magnetite-, grunerite-, and quartz- dominant mineralogy, (ii) the absence of reaction textures among the minerals (e.g., the absence of a grunerite rim between magnetite and quartz), (iii) absence of Fe-oxides in some grunerite-bearing cherts (Fig. 3) and (iv) the distinct chemical composition of grunerite compared to magnetite (Figs. 2–4) collectively do not support the origin of Fe-oxides as a post-depositional oxidative or metamorphic products of Fe silicates and *vice versa*. Instead, these features indicate different precursor minerals for magnetite, grunerite, and quartz. Similar textural and compositional features have also been reported for the Nuvvuagittuq (Mloszewska et al., 2012) and Isua (Dymek and Klein, 1988) BIFs.

To further evaluate this, we compared the textural and chemical characteristics of grunerite from two different associations: (i) grunerite occurring in contact with magnetite—in Fe-oxide-rich BIF samples (Fig. 2), and (ii) grunerite surrounded by quartz in the Fe-oxide-absent cherts of the Badampahar belt (Fig. 3). These comparison is grounded in the fact that both sample types experienced the same metamorphic grade (i.e., greenschist-to-lower-amphibolite facies). Therefore, they would be expected to comprise similar endmember minerals if precursor composition was mainly controlled by a single mineral phase, for example, Fe-silicates, Fe-oxides, or a mixture of both. If Fe-oxides were the product of Fe-silicate metamorphism, they should consistently occur in association with metamorphic grunerite; however, this is not the case (Fig. 3). Moreover, the occurrence of these distinct mineralogical associations implies that differing ambient water conditions must have prevailed to enable the precipitation of these distinct precursor mineral phases.

3.2. Comparative chemistry of individual Hadean to early Archean BIF grunerite and magnetite

Overall, the reference BIFs are characterized by grunerite with significantly higher Mg, Mn, Ni, Co, and Zn concentrations and lower Ba, V, and P concentrations, compared to the

associated magnetite (Fig. 4a; Table 2). A low concentration of poorly mobile heavy metals, like Zr (<2 ppm), points to negligible detrital contamination (Table 2). In contrast, the distinct chemical patterns recorded for Ni, Co, and Zn abundances in magnetite and grunerite are likely primary. Such patterns are consistent across global BIF magnetite and Fe-silicate minerals present in BIFs and cherts (discussed in sections 4.1 and 4.2). This proposition is corroborated by a similar rare earth element (REE) distribution pattern, marked by light-REE depletion and mid-/heavy-REE enrichment within the distinct magnetite and Fe-silicate layers, regardless of metamorphic grade and age (Figs. 4b, c). Therefore, the precursors to the magnetite and grunerite bands (Figs. 1, 2) in the reference BIFs likely formed via independent seawater processes (Ghosh, 2020). Greenalite, the precursor of grunerite, likely formed by an abiotic reaction between seawater Fe(II) and silica in the deep, dark, and anoxic seawater column. Conversely, Fe-(oxy)hydroxides, the precursors of magnetite, formed via abiotic/biotic Fe(II) oxidation processes within the oceanic photic zone (discussed further in Section 4.1).

3.3.Characterization of synthetic minerals

We analyzed the XRD patterns and Fe K-edge XANES spectra (7111 eV) of experimental samples and standards to identify synthetic mineral phases (Fig. 5). All greenalite synthesis experiments produced dark green, poorly crystalline greenalite. These samples generated XRD patterns with two broad peaks centered around 2.57 and 1.59 Å d-space (Fig. 5e); however, the characteristic greenalite XRD peak around 7.1 Å was not prominent. This result indicates the poorly ordered nature of the synthesized greenalite, which retains regions of short-range crystalline order, and aligns with the XRD profiles reported for greenalite synthesized by Tosca et al. (2016). Therefore, to confirm the mineralogy of greenalite, we conducted synchrotron Fe K-edge XANES analysis (Fig. 5i). The XANES spectra of the synthesized greenalite match well with BIF greenalite. Linear combination fitting (LCF) results of XANES spectra confirmed a satisfactory fit between the synthesized greenalite phase and the reference natural BIF greenalite (Table 3).

Ferrihydrite synthesis experiments yielded reddish-brown 2-line ferrihydrite, which generated typical XRD patterns of ferrihydrite with two broad peaks centered around 2.50 and 1.51 Å d-space (Fig. 5f). LCF results (Table 3) show that the synthesized ferrihydrite best fits a combination of 66% hematite, 16% goethite, and 17% ferrihydrite. This suggests partial transformation of the metastable ferrihydrite into more crystalline phases (Cudennec and Lecerf, 2006). Mixed-valent synthesized samples were dark brown. Precipitates from the ferric

iron-dominant solution (33.3% Fe(II)) produced XRD patterns like 2-line ferrihydrite, whereas precipitates from the ferrous iron-dominant solution (33.3% Fe(III)) could not be identified with XRD (Fig. 5g, h). The precipitates of Fe(III)-dominant mixed-valent solution were successfully fit with 25.6% hematite, 43.9% goethite, and 33.4% ferrihydrite (Table 3), and its pre-edge peak centroid plotted close to magnetite on the pre-edge calibration curve (Figs. 5k, S4, supplementary data 1). Consequently, we interpret this phase as an amorphous mixture of Fe-oxyhydroxides rich in ferrous iron (HFO*). The precipitate from the Fe(II)-dominant solution was fit with 57.7% HFO*, 13.8% ferrihydrite, and 20.5% greenalite (Table 3), with its pre-edge peak centroid occurring at a slightly lower energy position than magnetite (Fig. 5k, S4, Supplementary data 1). It is inferred to be a mixture of greenalite and HFO*. The co-precipitation of aragonite along with greenalite and ferrihydrite was verified by chemical composition and radiating starburst-like crystals under SEM (Fig. 5d), as well as sharp XRD peaks at 3.40, 3.27, and 1.98 Å d-space (Fig. 5j).

3.4. Trace metal distribution during experimental Fe-(oxy)hydroxides and greenalite formation

To resolve the question of whether greenalite exhibits a higher Ni, Co, and Zn incorporation capacity than Fe-(oxy)hydroxides, we conducted co-precipitation-adsorption kinetic studies to evaluate the distribution of Ni, Co, and Zn into these phases under simulated Archean seawater conditions (Fig. 5). The experimental results were then compared with the Ni, Co, and Zn compositions of reference BIF grunerite and magnetite (Fig. 6). To achieve this objective, we synthesized greenalite and Fe-(oxy)hydroxides across a range of initial solution Fe(II)/Fe(III) ratios (i.e., 1:0, 1:2, 2:1 and 0:1; total Fe = 1 mM) in an analogous early Precambrian seawater with 1.2 mM silica and 1 µM/L each of Ni, Co, and Zn (see Methods). The independent Fe(II) and Fe(III) experiments resulted in the formation of greenalite and Si-rich ferrihydrite, respectively. Meanwhile, the mixed-valent Fe(III)-rich and Fe(II)-rich experiments produced mixed-valent Si-rich Fe-(oxy)hydroxides (HFO*) with an average Fe redox state close to magnetite, and a mixture of HFO*+greenalite minerals, respectively. Combined XRD and XANES analyses successfully identified these mineral phases (Fig. 5i; Table 3). The presence of ≥ 5 mM/L HCO_3^- in solution precipitated aragonite along with ferrihydrite or greenalite. However, quantifying the Ni, Co and Zn distribution coefficients for the Fe-minerals was not possible at these varied HCO_3^- concentrations due to excessive aragonite formation driven by

the reaction between Ca^{2+} and HCO_3^- . Therefore, carbonate experiments were not further replicated.

All synthesized Fe minerals incorporated Zn within minutes to hours; however, Ni and Co incorporation mostly mirrored the Fe distribution trend (Fig. 6). Trace metal distribution coefficients (K_D) were calculated using the following equation:

$${}^{\text{TM}}K_D = [(M_{\text{TM}})/[SW_{\text{TM}}]] \quad (\text{equation 1})$$

where M_{TM} is the molar trace metal/Fe ratios in the mineral and SW_{TM} is the molar trace metal/Fe ratios in the seawater.

Accordingly, the Co and Ni K_D values calculated from the analytical data of solids and concentrations remaining in solution (Fig. 6d; Table 1) were observed to be slightly higher for greenalite (0.736 and 0.506) relative to the ferrihydrite and the HFO* precipitates (0.334-0.474 and 0.276-0.359), respectively. On average, the conversion ~8 and ~22% dissolved Fe(II) to greenalite incorporated ~69 and ~99% Zn into the greenalite lattice within 2 and 48 hours, respectively (Supplementary data 2). This rapid incorporation resulted in calculated Zn K_D ~8.5 and 4.5, according to the first 2 hours and 48 hours data points, respectively. True Zn K_D for ferrihydrite could not be initially determined as both oxic and anoxic conditions precipitated ferrihydrite within minutes of synthesis. To resolve this issue, we performed another set of oxic ferrihydrite synthesis experiments using a similar Fe concentration of 0.08 mM consumed by greenalite formation in the first two hours (Fig. 6a, Supplementary Data 2), leaving the remaining parameters unchanged. Results show that conversion of a much lower concentration of Fe to ferrihydrite (assuming partial oxidation) exhausted ~0.85 μM Zn from the solution within two hours. The 10.5 Zn K_D for ferrihydrite calculated in this way is comparable to the 8.5 Zn K_D value estimated for greenalite (Fig. 6d). The extremely high Zn K_D for both minerals indicates stronger, rapid and dominant structural drawdown of Zn, contrasting sharply with the significantly slower Ni and Co co-precipitation and adsorption rates.

While several foundational studies have advanced our understanding of TM dynamics in BIFs, empirical datasets evaluating the co-precipitation and adsorption of Ni, Co, and Zn on primary BIF minerals under Precambrian seawater conditions remain remarkably limited. Tostevin and Ahmed (2023) previously evaluated the K_D of multiple TMs (including Ni, Co, Zn, V, Mn, and Mo) for greenalite precipitated under anoxic Archean seawater conditions. Utilizing elevated TM concentrations (~18 μM) and a higher pH ~8-8.5, they reported a markedly high K_D for Zn (5379) relative to Ni (0.33) and Co (0.74). However, as Zn was rapidly sequestered into the

greenalite matrix within minutes to hours, true thermodynamic equilibrium partition coefficients could not be resolved; their reported Zn K_D remains an approximation derived from the initial data point of a time-resolved sampling series. In contrast, our experiments employed more environmentally realistic, lower TM concentrations ($\sim 1 \mu\text{M}$) to circumvent these rapid, non-equilibrium kinetics. Our data yield a comparable overall trend—characterized by preferential Zn uptake over Ni and Co—but refine these values to a significantly lower Zn K_D of ~ 8.5 , alongside consistent, low K_D values for Ni (0.506) and Co (0.736).

Robbins et al. (2013) reconstructed early ocean Zn levels based on ferrihydrite surface adsorption thermodynamic modeling using Visual MINTEQ. However, structural work by Waychunas et al. (2002) demonstrated that co-precipitation incorporates metals via complex polydentate, inner-sphere geometries sharing apices with multiple adjacent ferrihydrite polyhedra, which behaves distinctly from simple surface adsorption. Our empirical co-precipitation experiments directly capture this higher-efficiency incorporation mechanism, providing a more accurate empirical Zn K_D for BIF paleomarine reconstructions.

Similarly, Konhauser et al. (2009) performed Ni-ferrihydrite co-precipitation and adsorption experiments to reconstruct early seawater Ni concentrations from BIFs. They determined Ni K_D for ferrihydrite of 0.00396 and 0.00123 μM^{-1} for 0.67 and 2.2 mM dissolved silica concentrations, respectively, in seawater with a low dissolved Fe concentration of 0.179 mM. If we recalculate these Ni K_D s values using the standard K_D equation (Equation 1), they become 0.708 and 0.220 for 0.67 and 2.2 mM dissolved silica, respectively. These recalculated values match closely with our calculated Ni K_D of 0.359 for Fe-oxyhydroxides at 1.2 mM silica.

A subsequent study by Eickhoff et al (2014) also calculated Ni distribution for biogenic and abiogenic ferrihydrite and showed lower co-precipitation and adsorption of Ni to ferrihydrite in presence of microbial cells. Sugiyama and Halevy (2026) investigated the co-precipitation of transition metals—including Ni, Co, and Zn at variable initial concentrations (0.1–300 μM)—with carbonate-green rust synthesized under low-silica (0.1 mM) and Ca-depleted Archean seawater conditions. They reported approximately 95% Zn, 84% Co, and 68% Ni incorporation into the green rust matrix at an initial TM concentration of 1 μM . This

comparative affinity sequence of transition TMs, $\text{Zn} > \text{Co} > \text{Ni}$, in iron minerals aligns well with our experimental observations.

However, when normalized to Fe content, grunerite in Archean BIFs is significantly enriched in Ni, Co, and Zn by 3.3-, 7.6- and 17.8-folds, respectively, relative to magnetite (Fig. 6e). In contrast, our experimental data show that the grunerite precursor greenalite only enriches Ni, Co, and Zn by 1.6-, 1.43- and 1.13-fold, respectively, relative to the magnetite precursors synthesized under our early Precambrian seawater analogue conditions (Fig. 6e). This near equal experimental incorporation of TMs by greenalite and Fe-(oxy)hydroxides cannot therefore explain the highly contrasting TM inventories of natural BIF grunerite and magnetite—assuming their precursor minerals formed together with equal access to seawater TMs. Consequently, these discrepancies suggest that additional pathways must be involved in the differential incorporation of TMs from ancient seawater, as explored below.

3.3. Aging at diagenetic temperature

BIFs underwent burial diagenesis over timescales spanning millions of years, a process that is impossible to truly replicate under laboratory-scale conditions. To assess the potential impact of diagenetic temperature on mineral composition, we subjected the experimental mineral phases (i.e. greenalite and Fe-(oxy)hydroxides) to thermal aging in sealed autoclave vials at 125 °C for 5 days. The minerals were suspended in an artificial seawater solution (1:20 volumetric ratio) of pH~7.7. We also used distilled water instead of seawater solution as a secondary control in replication experiments to assess the extent of trace element leaching. Notably, this thermal treatment used in this study isolates only the temperature component of natural diagenesis. In geological systems, diagenesis is a synergistic process driven by both temperature and pressure, the latter of which was not replicated in our experimental setup. Furthermore, this abiotic heating approach does not account for early diagenetic transformations driven by chemoheterotrophic microbial processes, which actively alter organic matter and mineral assemblages in natural sedimentary environments.

At the end of each experiment, we collected the aged mineral samples by centrifugation and analyzed them to track chemical alterations. Analytical results of the aged samples show overall insignificant changes ($< \pm 20\%$) in the Ni/Fe, Co/Fe and Zn/Fe ratios relative to the untreated starting samples (Fig. S5; Supplementary Data 1). These observations correspond well with the limited Ni, Co, and Zn mobility results of similar diagenetic experiments

performed by Tostevin and Ahmed (2023) on greenalite (100 °C, 21 days) and Robbins et al. (2015) on ferrihydrite (170 °C, 14 days). Aged greenalite samples in the seawater medium show average enrichments of 15-, 13-, and 6 % for Co, Ni, and Zn. By comparison, grunerite in the reference BIFs is significantly enriched in Ni, Co, and Zn by 3.3-, 7.6- and 17.8-fold compared to magnetite. When grunerite trace element values are normalized using our experimental diagenetic trace element enrichment factors, the resulting Ni, Co, and Zn in BIF grunerite relative to magnetite remain high at 2.9-, 6.6- and 16.8-fold, respectively.

4. Discussion

4.1. Origin of the reference BIF magnetite and grunerite

Iron-silicate-rich, Algoma-type BIFs deposited globally throughout the predominantly anoxic Hadean to early Archean eons (>3 Ga). Key examples include the ~4.2 Ga Nuvvuagittuq greenstone belt in Canada (Mloszewska et al., 2012), the ~3.8 Ga Isua greenstone belt in Greenland (Dymek and Klein, 1988), the ~3.2 Ga Cardinal and Kangaroo Cave formations in Australia (Muhling et al., 2023), and the ~3.2 Ga Badampahar greenstone belt in India (Ghosh, 2020). These BIFs typically consist of magnetite as the Fe-oxide phase and greenalite/minnesotaite/grunerite(±ferroactinolite) as the Fe-silicate phases, along with quartz, mainly arranged as alternating mineral bands (e.g., Figs. 1-2). Notably, these BIFs exhibit remarkably uniform mineralogical and banding patterns, regardless of where they occur, composed mostly of Fe-oxide and -silicate-rich lithologies. Of all the BIFs studied worldwide, it is generally accepted that they collectively represent a global record of the Hadean to early Archean seawater from which they precipitated. While evaluating all these BIFs is beyond the scope of this work, the reference samples from the 4.2 Ga Nuvvuagittuq and 3.2 Ga Badampahar successions, broadly, are mineralogically and texturally representative of the Hadean to early Archean BIF lithologies.

Mloszewska et al. (2012) highlighted minnesotaite (Fe-silicate) or siderite (Fe-carbonate) as possible precursors to grunerite, and hematite and siderite as precursors to magnetite. Notably, iron-bearing carbonate minerals are usually considered diagenetic and are excluded as primary BIF minerals, as their nucleation requires high saturation of Fe(II) and carbonate ions together with low dissolved silica — conditions that were unlikely to form in the silica-rich Archean seawater conditions (Jiang and Tosca, 2019). Conversely, Mel'nik (1982) and Klein (2005) suggested a prograde metamorphic pathway for grunerite formation from greenalite via minnesotaite. Based on petrographic and mineral chemistry studies of these BIFs, Ghosh

(2020) suggested two dominant initial Fe-minerals in the reference BIFs: greenalite (the precursor to grunerite) and Fe-(oxy)hydroxides (precursors to magnetite), which precipitated sequentially in the Hadean to early Archean oceans, whereas quartz-rich bands reflect non-depositional periods of Fe-minerals.

In BIFs, magnetite is commonly considered to have originated from the transformation of authigenic ferrihydrite or green rust precursor minerals via various biotic and abiotic processes (Halama et al., 2016; Halevy et al., 2017; Han et al., 2020; Konhauser et al., 2005), while grunerite is thought to form from authigenic greenalite precursors associated with prograde greenschist facies metamorphism (Klein, 2005; Mel'nik, 1982). Studies such as Rasmussen et al. (2017), Rasmussen and Muhling (2018) and Tosca et al. (2025) highlighted greenalite as the primary precursor of all BIF Fe minerals. However, this single-precursor hypothesis lacks direct experimental evidence, whereas hydrogeological modelling studies (Robbins et al., 2019) and isotopic studies (Planavsky et al., 2012) suggested multiple precursor phases, specifically identifying Fe-(oxy)hydroxides as precursors of BIF magnetite. Rasmussen and Muhling (2018) suggested that pore-water siderite in greenalite-rich BIF bands could later transform to magnetite. While minor magnetite occurs disseminated within BIF grunerite and quartz bands, the presence of distinct, thick (up to 1 mm) magnetite bands consisting of >90 modal% magnetite (Fig. 1) is inconsistent with an origin via the thermal decomposition of localized pore-water siderite. Alternatively, Nims and Johnson (2022) demonstrated that Fe(III)-reducing bacteria could generate secondary Fe-silicate phases from ferrihydrite in a Si-rich environment. However, Fe-silicates and -oxides occur in distinct bands in our BIFs, and their chemical compositions are distinctly different (Fig. 4a). This divergence suggests that ferrihydrite was not a common precursor for both magnetite and grunerite; otherwise, the two minerals would exhibit similar chemical compositions. In addition, the BIF grunerite data from the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq successions can be compared to primary BIF greenalite data from the 3.2 Ga, lower-metamorphic-grade Kangaroo-Cardinal formations. All of them show similarly high enrichment in Mg, Mn, Ni, Co, and Zn, supporting the origin of grunerite from greenalite (Table 2).

Collectively, primary authigenic Fe-(oxy)hydroxides and greenalite are the most plausible precursors of magnetite and grunerite, respectively, in the reference Nuvvuagittuq and Badampahar BIFs.

4.2. Postdepositional influence on BIF mineral chemistry

Previous studies (Robbins et al., 2015; Tostevin and Ahmed, 2023), as well as the aging experiments presented herein (section 3.3), show that Fe-(oxy)hydroxides and greenalite strongly bind Ni, Co, and Zn, resisting diagenesis or hydrothermal leaching. Isochemical metamorphism is common for Archean BIFs, where, for example, low- to high-grade regional metamorphism is known to result in the loss of water and carbon dioxide while preserving the elemental composition of primary minerals (Klein, 2005, 1983). The preservation of heterogeneous Fe isotopic patterns across the Fe-mineral bands of Archean BIFs testifies to minimal post-depositional influence on BIF chemical compositions (Frost et al., 2007).

We compared the Badampahar and Nuvvuagittuq BIF grunerite data to available low- metamorphic-grade BIF greenalite data. Primary greenalite preserved in the 3.2 Ga Cardinal-Kangaroo formations, Australia (Muhling et al., 2023) shows a remarkable geochemical similarity to our studied BIF grunerite, regardless of metamorphic grade (Table 2). We also compared our magnetite data to other BIF magnetite data, which show that an equivalent low abundance of Ni, Co, and Zn in BIF magnetite compared to average Fe-silicates is common across worldwide BIF deposits (Fig. S3, Supplementary Data 1).

Furthermore, post-depositional microscale chemical exchange between the magnetite and grunerite precursors cannot explain their TM content. As stated above, we compared the TM compositions of grunerite bands in contact with the BIF magnetite bands (55, 20 and 216 ppm; Fig. 2) with grunerite surrounded by quartz in Fe-oxide-absent chert (151, 21, and 305 ppm; Fig. 3), finding a similarly high abundance of Ni, Co and Zn in both types of grunerite (Table 2). These observations, coupled with the high structural capacity of magnetite to accommodate large amounts of Ni, Co, and Zn (>990 ppm; Nadoll et al., 2014), suggest an originally depleted Fe-(oxy)hydroxides precursor phase for magnetite formation. We therefore conclude that the chemical content of the grunerite and magnetite conserved in the studied BIFs is representative of spatiotemporal differentiation during authigenic primary mineral precipitation from early Archean seawater rather than post-depositional influences.

4.3. Seawater chemical variability

The dissolved seawater Ni, Co, and Zn compositions were calculated using our estimated K_D values according to Equation 1 ($SW_{TM} = M_{TM} / {}^{TM}K_D$), assuming a ~1 mM dissolved seawater Fe concentration for the model baseline (Jiang and Tosca, 2019). The results indicate that the ambient water present during BIF Fe-(oxy)hydroxides formation was highly depleted in Ni,

Co, and Zn relative to that of greenalite (Table 4). For example, magnetite-reconstructed mean seawater Ni, Co, and Zn concentrations at 4.2 Ga and 3.2 Ga are 287, 19.5, and 5.26 nM, and 119, 29.7, and 2.58 nM, respectively. In contrast, grunerite-reconstructed mean seawater Ni, Co, and Zn concentrations at 4.2 Ga and 3.2 Ga are 513, 133, and 82.1 nM, and 376, 94.2, and 78.9 nM, respectively. Interestingly, the reconstructed seawater compositions from the 3.2 Ga Cardinal-Kangaroo greenalite and the 3.2 Ga Badampahar grunerite are broadly comparable due to their high Ni, Co, and Zn contents (Table 4). We also note that reconstruction of these TM concentrations strongly depends on the assumed seawater Fe concentration in Equation 1. Any deviation in the assumed early seawater Fe concentration would stoichiometrically alter the reconstructed TM concentrations. Consequently, the objective of this study is not to reconstruct the absolute Ni, Co, and Zn concentrations of early seawater; rather, we assess comparative TM concentrations of ambient seawaters that precipitated BIF greenalite and Fe-oxyhydroxides.

Volcanogenic hydrothermal fluids usually contain higher concentrations of Ni, Co, and Zn than modern seawater (Douville et al., 2002). A high degree of submarine volcanism and hydrothermal activity in the early Precambrian ocean (Lowell and Keller, 2003) would have intensified hydrothermal Ni, Co, and Zn fluxes to the seawater. This association raises the question of the extent to which greenalite chemistry reflects a pristine hydrothermal input versus a highly diluted, seawater-dominated fluid mixture. Both BIF Fe-silicates and Fe-oxides show typical seawater-like shale-normalized heavy-REE enrichment patterns with superchondritic Y/Ho ratios (Figs. 4b-c). Such fractionated REE patterns with minor Eu enrichment could only be achieved by the mixing of seawater with volcanogenic hydrothermal fluids at a ratio of >1000:1 (Fig. 4c). Studies such as Nke et al. (2024) and Muhling et al. (2023) also suggested a seawater origin for Archean to Paleoproterozoic BIF greenalite. Overall, our REE data discard greenalite or Fe-(oxy)hydroxides formation directly from high-temperature hydrothermal fluids, confirming a significant (>1000-fold) dilution of the hydrothermal components prior to precursor mineral precipitation.

The alternating Fe-(oxy)hydroxides and greenalite-rich precursor bands in BIFs, together with the contrasting ambient seawater compositions during their respective formation, indicate periodic fluctuations of dissolved Ni, Co, and Zn in Hadean to early Archean seawater. We discuss three main possibilities for the development of these contrasting compositions in the reconstructed 4.2-3.2 Ga seawater from magnetite and grunerite, as follows: (i) Fe-

(oxy)hydroxides and greenalite formation at different depths in the seawater column; (ii) faster abiotic greenalite formation compared to biogenic Fe-(oxy)hydroxides formation; and (iii) the biological retention of TMs during Fe-(oxy)hydroxides formation.

4.3.1. Fe-(oxy)hydroxides and greenalite formation at different depths

Greenalite and Fe-(oxy)hydroxides likely formed sequentially at different depths of the water column within the Hadean to early Archean ocean. This spatial separation occurred because Fe-(oxy)hydroxides formation, via either abiotic or biotic pathways, required a shallow photic zone setting (Konhauser et al., 2018; Swanner et al., 2015; Tabata et al., 2021), whereas greenalite could form in deep, dark, anoxic bottom waters soon after seafloor hydrothermal events (Tosca et al., 2016). In this model, episodic hydrothermal fluids advected from seafloor vents and mixed rapidly with deep Archean seawater (Germanovich et al., 2015), where greenalite first precipitated in the absence of major primary Fe-(oxy)hydroxides formation. In this sulfur-cycle-deficient Archean seawater (Canfield et al., 2000), greenalite thus had early access to the deep seawater TM pool. Upwelling delay and the dilution of deep-sea hydrothermal components towards the photic zone resulted in the rapid uptake of Fe and TMs into greenalite—particularly Zn, given its exceptionally high K_D and fast uptake kinetics (Fig. 6d). This preferential uptake generated a moderate depletion of Ni and Co, and a severe depletion of Zn, in the residual deep seawater upwelling toward the surface. Concurrently, any fraction of the Fe and TM pool that escaped sequestration by deep-water greenalite was further diluted during transport, subsequently co-precipitating with or adsorbing onto primary Fe-(oxy)hydroxides and minor greenalite phases at the ocean surface.

Notably, greenalite formation required high dissolved Fe(II) saturation (>0.5 mM at 25°C and pH 7.5; Tosca et al., 2016), whereas biological Fe-(oxy)hydroxides formation could happen even at micromolar dissolved Fe concentration (Konhauser et al., 2007). Once deep-water abiotic greenalite formation consumed enough iron to drop below this 0.5 mM threshold, further greenalite precipitation ceased. The residual, lower Fe(II) fluid was then free to upwell into the surface ocean, precipitating TM-depleted Fe-oxyhydroxides without competing with greenalite formation. This mechanism explains the deposition of Fe-(oxy)hydroxide-rich, greenalite-depleted bands directly following greenalite-rich bands. As the surface-formed Fe-(oxy)hydroxides settled through the water column to form seafloor BIF sediments, they passed through deep waters that had already been stripped of TMs by earlier greenalite precipitation and further diluted by diffusion. Consequently, these settling Fe-(oxy)hydroxides could only

adsorb minor amounts of residual TMs from the deep water column. Collectively, this depth-dependent spatial segregation produced the contrasting Ni, Co, and Zn signatures preserved in BIF Fe-oxides and Fe-silicates.

Modern oceanographic observations and ancient deep-sea models show that hydrothermal plumes laterally travel tens to hundreds of kilometres away from vent fields by ocean currents while staying trapped at depth, thereby maintaining their primary chemical integrity. Driven by background deep-ocean current velocities, a plume is envisaged to travel ~1 to 9 km/day after eruption (Tagliabue et al., 2022), reasonably explaining the kilometer-scale lateral stretch of the reference BIF bands and their deposition not always near localized vent sites. Once a plume stalls at its level of neutral buoyancy (after a few hundred meters of rapid uprise), vertical transport up to the surface photic zone is no longer driven by local plume buoyancy. Instead, it relies on basin-scale upwelling (e.g., wind-driven or convective basin overturning), which operates at a much slower vertical velocity of ~1 m/day (Liang et al., 2017; Tagliabue et al., 2022). Because this vertical transit is so slow, it could provide a massive temporal window for settling greenalite to systematically strip the fluid of its TMs. When this heavily evolved fluid finally reached the surface, its remaining Fe(II) (<0.5 mM) precipitated as trace-metal-depleted ferrihydrite. This framework fits within the spatial and hydrodynamic constraints of a single Algoma-type basin.

4.3.2. Faster abiotic greenalite formation compared to biogenic Fe-(oxy)hydroxides formation

Alternatively, the sequential greenalite and Fe-(oxy)hydroxides formation within a shallow seawater setting could be driven by early, rapid abiotic greenalite-rich precipitation followed by slower biogenic Fe-(oxy)hydroxides formation. This sequence is mediated by a physiological resuscitation lag within a marine microbial seed bank responding to episodic hydrothermal forcing.

In natural environments, up to 90% of the ambient bacterial population often exists in a metabolically inactive, dormant, or "viable but non-culturable" state as an evolutionary adaptation to prolonged nutrient limitation (Jones and Lennon, 2010). These dormant cells act as a dynamic "seed bank" distributed throughout the water column. When an environment experiences a sudden pulse of a limiting substrate or electron donor—such as an injection of hydrothermal Fe(II) into an anoxic Archean basin—dormant marine bacteria do not resume maximum metabolic activity instantly. They undergo a well-characterized metabolic transition

period (the environmental "lag phase") required to upregulate specific functional genes, synthesize respiratory enzymes, and repair cellular structures before entering an active growth phase (Blagodatskaya and Kuzyakov, 2013). Culture experiments with modern ocean Fe(II)-oxidizing microbes show a microbial growth lag phase lasting 2-10 days (Wu et al., 2014).

Similarly, during periods of hydrothermal quiescence or adverse seasonal shifts in the Hadean to early Archean ocean—e.g., during the deposition of alternating chert bands (Posth et al., 2008; Pirajno and Wu, 2021)—the local Fe(II)-oxidizing bacterial population could experience severe substrate starvation and collapse into dormancy or localized, low-abundance niches. In a shallow-depth seawater setting (e.g., <500 m), a fresh buoyant hydrothermal pulse, together with its rapid upwelling into the surface waters, would trigger immediate, rapid abiotic greenalite precipitation throughout the water column. The hydrothermal Fe(II) would simultaneously initiate the metabolic resuscitation of the photic-zone microbial seed bank. Because this biological awakening requires a discrete physiological timeframe, microbial Fe(II) oxidation would not begin immediately, temporarily allowing some greenalite to form unhindered within the shallow water and sink below the photic zone to form discrete Fe-silicate bands. However, the ultimate preservation of this shallow-water greenalite was dictated strictly by its residence time in the photic zone. Once the microbial community fully resuscitated and initiated active Fe(II) oxidation, any remaining shallow-water greenalite would undergo dissolution and oxidation to Fe-(oxy)hydroxides, thus cleanly recording the stratigraphically discrete, alternating mineral layers.

Thus, a few days of microbial growth delay would allow moderate Ni and Co and high Zn depletion in the seawater by early formed greenalite, as found in our experiments (Fig. 6a). Consequently, Fe-(oxy)hydroxides would precipitate from relatively Fe and TM depleted seawater following greenalite rich precipitation, thereby producing the observed contrasting compositions of the Fe -oxide and Fe-silicate phases in BIFs. However, this “microbial growth-lag” model does not apply to BIFs deposited in deeper ocean settings, because a deeper seawater column likely allowed early greenalite formation in deeper waters—depleting the slowly upwelling water of Fe(II) and preventing further greenalite formation in surface waters.

Although the majority of BIFs show the presence of Fe-oxides and Fe-silicates in alternating bands (Ghosh, 2020; Mloszewska et al., 2012), BIFs with the total absence of Fe-oxides or Fe-silicates have also been reported. The absence of Fe-silicates in BIFs can be explained by BIF deposition in early shallow ocean settings with high microbial activity, which limited greenalite

formation or oxidized early-formed greenalite. On the other hand, BIF sequences lacking significant Fe-oxides may reflect deposition during transient periods of adverse environmental conditions (e.g., seasonal temperature or chemical fluctuations; Posth et al., 2008) that suppressed local microbial activity, thereby temporarily permitting only abiotic, greenalite-rich precipitation. BIFs with mixed mineral bands containing both Fe-silicates and Fe-oxides can be explained by co-precipitation of greenalite and Fe-(oxy)hydroxides from TM-rich deeper seawater and TM-depleted surface seawaters, along with frequent cycles of hydrothermal and microbial activities and sediment mixing by ocean currents and turbulence.

4.3.3. Microbial retention of trace elements

Eickhoff et al. (2014) demonstrated that Ni incorporation into Fe-(oxy)hydroxides is 2-3 times reduced by the presence of microbial cells. Therefore, if we consider 2.5 times lower incorporation of Ni, Co and Zn for Fe-(oxy)hydroxides particles in the early ocean, Fe-oxide-reconstructed seawater Ni, Co and Zn concentrations could be 717, 48 and 13 nM for the 3.8 Ga ocean and 297, 74.2 and 6.45 nM for the 3.2 Ga ocean, respectively. This suggests comparable Ni and Co concentrations for the Fe-(oxy)hydroxides and greenalite reconstructed early Archean seawater. However, the highly contrasting Zn composition is not explainable by this mechanism alone, thereby supporting a sequential mineral formation process discussed earlier.

From another perspective, active Fe-oxidizing microbes could retain only minor TMs in seawater. We adapted the photoferrotrophic TM retention model of Konhauser et al. (2018), considering a 5×10^7 cells/L cell density of photoferrotrophs for the maximum annual Fe deposition as Fe-(oxy)hydroxides of BIFs. The model relies on the TM retention capacity of photoferrotrophic cells grown in simulated Paleoproterozoic seawater containing 400 nM Ni, 10 nM Co and 10 nM Zn. The 5×10^7 photoferrotrophic cells/L with an average TM retention capacity of 9.33×10^{-10} nM Ni, 7.84×10^{-10} nM Co and 8.09×10^{-9} Zn per cell could retain a maximum of 0.05 nM Ni, 0.04 nM Co and 0.4 nM Zn in 1L early Precambrian surface seawater that is negligible compared to the estimated seawater compositions (Table 4).

In addition, the Fe(II)-oxidizing microbial biomass deposited with Fe-(oxy)hydroxides were mostly degraded and recycled in the deep early ocean, with an estimated 3-5% potentially contributing to dissimilatory Fe-reduction (Konhauser et al., 2005). Biomass participation in dissimilatory Fe-reduction may have contributed TMs to the forming magnetite. According to

a 1C:4Fe utilization ratio for Fe-reduction (Konhauser et al., 2005), we calculated that the complete consumption of 25.8 g of biomass (considering 50 wt.% C in a bacterial cell with unit cell mass 1.3×10^{-9} mg²³; Hallbeck and Pedersen, 1991) would produce 1 kg of magnetite from ferrihydrite. The 25.8 g biomass could thus have contributed a maximum of 0.018 μ M of Ni, 0.016 μ M of Co, and 0.160 μ M of Zn to magnetite, whereas average magnetite in the studied BIFs contains 942 μ M/Kg of Ni, 140 μ M/Kg of Co, and 510 μ M/Kg of Zn, suggesting biomass contributed an insignificant portion of Ni, Co and Zn, respectively, to magnetite.

These findings indicate that TMs are more closely associated with Fe-(oxy)hydroxides than with microbial cells or extracellular organic substances under early seawater conditions. This suggests a strong link between seawater TM content and primary Fe-(oxy)hydroxides formation, regardless of whether the process was biological or abiotic. Thus, the TM composition of primary Fe-(oxy)hydroxides, which we use to infer BIF composition, approximates the likely original seawater composition with insignificant influence due to partitioning on buried organic matter.

4.4. Trace-metal mass-balance framework for the sequential Fe-mineral formation

While absolute Archean metal concentrations are difficult to constrain from modern marine settings, the partitioning of Ni, Co, and Zn into Fe-minerals was likely governed by local chemical kinetics where mineral precipitation rates outpaced physical basinal mixing. By viewing the early seawater column as a dynamic, sequentially precipitating system rather than a static one, our model achieves internal mass-balance consistency. Because greenalite has an exceptionally high partition coefficient for Zn, its rapid crystallization acted as an immediate elemental sink, systematically depleting the local fluid via Rayleigh-style distillation.

We tested this using an initial baseline composition of ~1 mM Fe (Tosca et al., 2016), ~79 nM Zn, ~94.3 nM Co, and ~376 nM Ni (reconstructed from the 3.2 Ga Badampahar grunerite; Table 4) in the primary seawater and hydrothermal fluid mixture. Our experimental data (Fig. 6a, Supplementary Data 2) track this chemical evolution as follows:

- An 8% Fe consumption by greenalite removes 69% Zn, 1% Co, and 4% Ni. Residual fluid: 0.92 mM Fe, 24.5 nM Zn, 93 nM Co, 360 nM Ni; **Ni/Zn = 14.7; Co/Zn = 3.79.**
- A 14% Fe conversion removes 89% Zn, 7% Co, and 8% Ni. Residual fluid: 0.86 mM Fe, 9 nM Zn, 88 nM Co, 346 nM Ni; **Ni/Zn = 38.4; Co/Zn = 9.78.**

- A 22% Fe conversion removes 99% Zn, 13% Co, and 10% Ni. Residual fluid: 0.78 mM Fe, 1 nM Zn, 82 nM Co, 338 nM Ni; **Ni/Zn = 338; Co/Zn = 82**.

Crucially, our independent, back-calculated seawater compositions reconstructed from the 3.2 Ga Badampahar magnetite bands (Table 4) yield **Ni/Zn = 46.1 and Co/Zn = 11.5** (2.58 nM Zn, 29.7 nM Co, and 119 nM Ni). These values show an excellent alignment with our experimental mass-balance estimates between the 14-22% Fe consumption by greenalite formation marks. This strongly confirms that Fe-oxyhydroxides (the precursors to magnetite) precipitated from a pre-depleted, evolved fluid reservoir left behind by rapid greenalite formation. Notably, considering a lower dissolved seawater Fe concentration, e.g. 0.5 mM instead of ~1 mM, during Fe-oxyhydroxides formation results in lower values of 1.29 nM Zn, 14.8 nM Co, and 59.5 nM Ni (a stoichiometric half) in the magnetite-reconstructed surface seawater; however, the ratios of Ni/Zn and Co/Zn remain unchanged.

4.5. The impact of Fe mineralization on the early seawater Ni, Co, and Zn

Our geochemical experiments mimicking early Precambrian seawater conditions show that the dual primary mineral sinks — greenalite and Fe-(oxy)hydroxides — could influence overall dissolved Archean seawater column Ni, Co, and Zn concentrations, and probably many other TMs that remain to be investigated. The most profound effect was exerted on dissolved Zn concentrations because of its extremely high affinity for primary greenalite and Fe-(oxy)hydroxides minerals compared to Ni and Co, which likely exhausted Zn from early seawater after each cycle of Fe mineral deposition. This observation implies that Ni and Co were more available to early life for metabolic processes than Zn. Moreover, the predominance of unfractionated Zn isotopes in the early Archean BIFs (Pons et al., 2013) can be explained by our quantitative seawater Zn-exhaustion model, where the surge of hydrothermal fluids and plumes into Archean seawater was accompanied by two-step greenalite and Fe-(oxy)hydroxides incorporation of Zn. Our model further points to the absence of a modern conventional Zn cycle associated with sulfidation and viable eukaryotic/complex metabolisms (Butterfield, 2015; Canfield et al., 2000; Vance et al., 2016) associated with strong fractionation of Zn towards more negative isotopic values presently traced back to the Paleoproterozoic ocean (El Albani et al., 2023; Ossa Ossa et al., 2023).

5. Conclusions

Collectively, the alternating magnetite and grunerite-rich bands in the reference Algoma-type BIFs of the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq successions, together with their contrasting compositions, indicate consecutive greenalite and Fe-(oxy)hydroxides formation

events in the early ocean. Specifically, the near-equal trace elemental incorporation capacity of Fe-(oxy)hydroxides and greenalite, contrasted yet with their distinct chemistry in the BIFs, points to a periodic fluctuation in Ni, Co, and Zn levels in the early seawater. Such chemical variability could be driven by a combination of complex marine processes, including deep-sea episodic hydrothermalism (Brenner et al., 2024), diffusion and dilution of hydrothermal components, and sequential Fe mineral formation governed by the transportation lag of hydrothermal components reaching surface waters, and a microbial physiological resuscitation lag. Our geochemical experiments under simulated early seawater conditions show that both primary greenalite and Fe-(oxy)hydroxides could influence overall dissolved early seawater TM concentrations—especially that of Zn. The experimental data, together with the geochemistry of the BIF Fe-silicates and Fe-oxides and Precambrian Zn isotopic record, support a complete Zn-exhaustion model with each episode of Fe-mineralization in the early ocean.

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Figure captions

Fig. 1. (a) Field exposure of a reference BIF sequence with an inset image the Fe silicate-rich BIF sample (E28) in the Badampahar greenstone belt, Singhbhum craton, India. **(b-d)** Plane polarized light photomicrographs of reference BIF and chert samples (D73, E28 and E5). BIF samples show alternating bands consisting grunerite (Grt), magnetite (Mt) and quartz (Qz) as pure and mixed mineral bands. **(e-f)** Back scattered electron (BSE) photomicrographs exhibit sharp contact among minerals with the apparent absence of any reaction texture.

Fig. 2. Scanning electron photomicrographs combined with elemental mapping of a BIF sample (E28) containing grunerite (Grt) and magnetite (Mt).

Fig. 3. Scanning electron photomicrographs combined with elemental mapping of a chert (E5) containing grunerite (Grt) and quartz (qz).

Fig. 4. (a) Key elemental abundance patterns in magnetite and grunerite in BIFs from the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq belts. Error bars indicate percentage standard deviation from the mean. **(b)** Post Archean Australian shale (PAAS; Taylor and McLennan, 1985) normalized seawater-like rare earth element (REE) patterns of magnetite and grunerite in reference Badampahar and Nuvvuagittuq BIFs. **(c)** Y/Ho vs. Eu/Sm binary diagram to visualize hydrothermal vs. seawater contribution for BIF Fe mineral formation. (Data source: Mloszewska et al., 2012; Alibert, 2016; Muhling et al., 2023)

Figure 5 (a) Experimental solution with synthesized minerals in Teflon bottles. **(b-d)** synthesized greenalite, ferrihydrite and aragonite. **(e-h)** Characteristic XRD patterns of synthesized greenalite, ferrihydrite and mixed-valent minerals. **(i)** Fe K-edge XANES spectra of synthesized minerals along with standards and relevant published mineral data; # = data from Johnson et al. (2018). **(j)** XRD patterns of synthesized aragonite. **(k)** XANES pre-edge calibration curve of reference minerals in red circle with synthesized minerals in black square. HFO*=mixed valent Fe-(oxy)hydroxides.

Fig. 6. Time-resolved elemental distribution profile **(a-c)** of coprecipitation experiments. **(d)** Box and whisker plot displaying the distribution coefficients of Co, Ni and Zn for the synthesized greenalite, ferrihydrite and HFO*. **(e)** Enrichment of Co, Ni, and Zn in Fe silicates relative to Fe oxides in BIFs (orange line) and in experimental samples (blue line).

Co, Ni, and Zn data are normalized to Fe content of relevant minerals to account for variability associated precipitated Fe mineral concentration. Error bars indicate the percentage standard deviation from the mean.

Fig. 7. Schematic model of sequential greenalite and Fe-oxyhydroxides formation in the early ocean. Greenalite forms at stage I soon after hydrothermal pulsation, whereas Fe-oxyhydroxides forms later in stage II after most of the greenalite has already formed.

Table Captions

Table 1. Summary of experiments, compositions of solid phases and distribution coefficients (K_D).

Table 2. Elemental compositions of average Fe minerals in different BIFs and chert.

Table 3. Fe k-edge XANES spectra linear combination best fit results of experimental samples.

Table 4. Composition of ambient seawater calculated from average Archean BIF magnetite and Fe silicates. Full composition ranges are in bracket.

Supplementary Data

Supplementary data 1: Contains supplementary text S1, Figures S1-S5 and Table S1.

Supplementary data 2: Contains supplementary dataset as Tables 1-3.

Title: Fluctuating nickel, cobalt, and zinc concentrations in the Hadean to early Archean (>3 Ga) ocean

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Abstract

Chemical evolution of seawater composition is thought to have exerted considerable influence on biological evolution throughout Earth's history. However, the chemical structure and dynamics of the early ocean (>3.0 Ga) are poorly understood. Here, we experimentally studied trace metal (TM) scavenging by greenalite and Fe-(oxy)hydroxide minerals precipitated under simulated early Precambrian conditions, alongside *in-situ* TM compositions of magnetite and grunerite in 4.2 and 3.2 Ga banded iron formations (BIFs). Our geochemical experiments mimicking early Precambrian seawater conditions show that both primary greenalite and Fe-(oxy)hydroxide TM sinks influenced the overall concentrations of dissolved Ni, Co, and Zn in the early seawater column. Reconstructed TM values from BIF minerals using experimentally determined distribution coefficients indicate fluctuating Ni, Co and Zn levels in the ambient seawater. Our results suggest that processes like deep-water hydrothermalism, sequential greenalite and Fe-(oxy)hydroxides formation due to a vertical transportation delay of hydrothermal components to surface water, dilution of hydrothermal components, and a microbial physiological resuscitation lag likely regulated the abundance and distribution of TMs in the Hadean to early Archean seawater. Using the ratios of Ni/Zn or Co/Zn bound to greenalite and Fe-(oxy)hydroxides as a model, our data indicate quantitative removal of Zn—

first by greenalite, followed by Fe-(oxy)hydroxide sinks. The resultant high Ni/Zn ratios in the Hadean to early Archean seawater column after each periodic Fe mineral formation cohere with the dependence of early marine biogenic methanogenesis on Ni enzymes and a low requirement for Zn enzymes by primordial life.

1. Introduction

The dynamic distribution and concentration of bioessential trace metals (TMs) in seawater column throughout Earth's history are thought to have influenced the trajectory of biological evolution and the pattern and timing of the incorporation and use of TMs in metalloenzymes throughout Earth's history (Moore et al., 2017; Saito et al., 2003). Consequently, preferential TM utilization by biological species with different evolutionary histories has resulted in the development of various models linking TM bioavailability to temporal and spatial biodiversification on the Tree of Life (Saito et al., 2003). For example, high dissolved seawater nickel (Ni) has been linked with the rise and predominance of methanogenic Archaea in the Archean ocean (Konhauser et al., 2009), whereas a low concentration of zinc (Zn) in Archean seawater is correlated with the lack of Zn-dependent metabolism in early life (Saito et al., 2003; Tostevin and Ahmed, 2023). Alternatively, a few geochemical studies have proposed invariant nature of dissolved marine Zn concentrations throughout most of Earth's history, leading to little or no pressure on the pattern of biological Zn utilization (Robbins et al., 2013; Scott et al., 2013). A recent phylogenetic study by Bodden et al. (2021) also highlighted that ancestral cyanobacteria possibly used Cu- and Zn-dependent superoxide dismutase enzymes during the Archean Eon.

Widespread ocean anoxia, coupled with elevated and episodic submarine hydrothermal activity (Brenner et al., 2024), contributed high dissolved ferrous iron (Fe(II)) content to the early seawater (ferruginous conditions), while the absence of biological sinks promoted aqueous silica saturation (Poulton and Canfield, 2011; Siever, 1992). These conditions are thought to have triggered pervasive precipitation of primary hydrous Fe(II) silicates like greenalite (Hinz et al., 2021; Rasmussen et al., 2019, 2017, 2015b, 2015a; Tosca et al., 2016) and hydrous ferric Fe(III) and Fe(II) (oxy)hydroxide minerals such as ferrihydrite (Bekker et al., 2010; Kappler et al., 2005) and green rust (Halevy et al., 2017; Zegeye et al., 2012), respectively, with a high amount of silica adsorbed on them (Fischer and Knoll, 2006). For instance, the worldwide prevalence of primary greenalite, low-grade metamorphic minnesotaite, and medium-to-high-grade metamorphic grunerite (Mel'nik, 1982) (Section S1, supplementary data 1), together with magnetite and hematite in Hadean and Archean banded iron formations (BIFs) and associated chert (Dymek and Klein, 1988; Ghosh, 2020; Katsuta et al., 2012; Klein, 2005; Mloszewska et al., 2012; Muhling and Rasmussen, 2020; Pecoits et al., 2009; Pitarello et al.,

2019; Rasmussen et al., 2019, 2017, 2015a; Rasmussen and Muhling, 2018; Wang et al., 2014),
testifies to this global ferruginous/silica-rich, anoxic Archean seawater state.

According to the geological rock record (Ghosh, 2020; Konhauser et al., 2009) and
experimental modeling (Robbins et al., 2019), Fe-oxyhydroxides were dominant Fe-mineral
phases in Precambrian surface seawaters. The oxidation of dissolved Fe(II) to Fe(III) minerals
likely occurred via various abiotic/biotic pathways, including anoxygenic photosynthetic
microbial activity (photoferrotrophy), limited oxygenation by cyanobacteria in oxygen oases
and/or UV-photooxidation (Konhauser et al., 2018; Swanner et al., 2015; Tabata et al., 2021;
Thompson et al., 2019). Besides, in the absence of significant iron oxidation, pervasive abiotic
precipitation of primary greenalite could occur throughout the anoxic water column (Muhling
et al., 2023; Nke et al., 2024). Thus, for a more holistic reconstruction of dissolved seawater
nutrient levels using Fe minerals as proxies, comparative co-precipitation and adsorption
models of the associated Fe-(oxy)hydroxide and greenalite mineral sinks (Ghosh, 2020; Pecoits
et al., 2009; Rasmussen et al., 2015b) are needed. This approach is particularly vital because
the efficient removal of trace nutrients from seawater by authigenic seawater Fe minerals
should reflect the sum of their distinct binding affinities. For instance, a recent study showed
that greenalite can incorporate significant amounts of Zn, vanadium (V) and copper (Cu) from
early marine water, and therefore is a potential sink for dissolved trace nutrients (Tostevin and
Ahmed, 2023). However, accurately evaluating the impact of BIF minerals as early ocean TM
sinks requires assessing the combined and comparative binding affinities of Fe-oxyhydroxides
and greenalite during formation, alongside correlating these findings with TM concentrations
preserved in BIFs.

The dual precipitation of Fe-(oxy)hydroxides and greenalite together likely heavily influenced
the spatiotemporal TM distribution in the early ocean. To better constrain early seawater Ni,
Co, and Zn variations, we studied TM distribution kinetics during Fe-(oxy)hydroxides and
greenalite formation under simulated early Precambrian seawater conditions. The experimental
data were then correlated with the Ni, Co, and Zn compositions of alternating magnetite and
grunerite mineral bands preserved in 4.2-3.2 Ga Algoma-type BIFs, deposited in volcanically
active, deep-water basinal settings prior to the widespread development of stable Superior-type
continental shelves (discussed below). Our results demonstrate that sequential greenalite and
Fe-(oxy)hydroxide formation regulated oceanic Ni, Co, and Zn distributions, ultimately driving
a coupled depletion of Zn in the early water column.

2. Material and methods

2.1. Geology of the studied BIFs

The reference BIFs of this study are of the Algoma-type and belong to the ~3.2 Ga Badampahar (Ghosh et al., 2019; Ghosh and Baidya, 2017a, 2017b) and ~4.2 Ga Nuvvuagittuq (Mloszewska et al., 2013, 2012; Sole et al., 2025) greenstone belts. A detailed geological description of the Badampahar rocks can be found in earlier studies (Ghosh et al., 2019; Ghosh and Baidya, 2017a). In brief, the Badampahar rock sequence contains BIFs, bedded cherts, mafic-ultramafic volcanic rocks, phyllites and minor siliciclastic rocks, and it occurs as an enclave within the Mayurbhanj Granite at the eastern peripheral part of the Singhbhum Craton, India (Fig. S1, Supplementary Data 1). The Badampahar greenstone rocks are variably metamorphosed between the greenschist and lower amphibolite facies (Ghosh and Baidya, 2017a). The BIFs with patches of iron ores occur intercalated with cherts, komatiites, and basalts in the lower and middle parts of the stratigraphic sequence, whereas basalts, phyllites, and bedded cherts dominate the upper part of the sequence. The BIFs (Figs. 1-3) generally contain magnetite, grunerite ($\pm$ ferroactinolite) and quartz as alternating pure and mixed mineral bands (Ghosh, 2020; Ghosh and Baidya, 2017b).

A detailed description of the Nuvvuagittuq rocks (c. 4.2 Ga) and the BIFs of the used dataset can be found in earlier studies (Mloszewska et al., 2013, 2012; Sole et al., 2025). Briefly, the Nuvvuagittuq rocks are dominated by Ca-depleted amphibolites (volcanics), BIFs, and mafic-ultramafic intrusives that occur as enclaves within gneisses of the Northeast Superior Province, which is a part of the larger Superior Craton in northern Québec, Canada. The BIFs of Nuvvuagittuq are very similar to the Badampahar BIFs in terms of texture, mineralogy, and chemistry. The iron minerals are magnetite and grunerite ($\pm$ ferroactinolite $\pm$ augite) and exhibit marine chemical sediment-like chemical patterns (Figs. 4b-c). Mloszewska et al. (2012) categorized the BIF samples as “banded iron formations” (with up to 40 modal % magnetite) and “banded silicate formations” (with up to 10 modal% magnetite).

Collectively, this study focuses on 4.2 and 3.2 Ga BIFs of Algoma-type setting, which is representative of the Hadean to early Archean (>3 Ga) time when major continental shelves (Superior-type settings) had not yet widely developed due to the lack of large, stable landmasses (Chowdhury et al., 2025). The studied Nuvvuagittuq and Badampahar BIFs occur intercalated with volcanic sequences and generally lack major clastic sediment inputs (Ghosh et al., 2019; O’Neil et al., 2011). This context strongly points to a depositional basin dominated

by submarine volcanism, hydrothermal activity, metal fluxes, and subsequent Fe mineral formation.

In this paper, we used *in-situ* magnetite and grunerite mineral chemistry data of Nuvvuagittuq and Badampahar BIF analyzed by Mloszewska et al. (2012) and Ghosh (2020), respectively, together with new *in-situ* trace element analysis of magnetite and grunerite present in *the* Fe-mineral- and quartz-rich bands of six BIFs from Badampahar.

2.2. Geochemical experiments

A synthetic Archean seawater stock solution was prepared by adding relevant sea salts, such as 400 mM sodium chloride, 7 mM potassium chloride, 5 mM ammonium chloride, 1.2 mM sodium orthosilicate, 20 mM calcium chloride, and 20 mM magnesium chloride in milliQ water, according to Precambrian estimates (Hinz et al., 2021). This was followed by the addition of 1 mM Fe, 0-10 mM HCO_3^- and 1 μM of each TM (Ni, Co, and Zn) to the deoxygenated solution inside an anaerobic chamber. Thermodynamic calculations using the VISUAL MINTEQ software (Gustafsson, 2013) show that a TM concentration of 1 μM each is much below the limit required to produce individual solid phases (Table S1, supplementary data 1). Five sets of TM co-precipitation-adsorption experiments (Table 1) were performed with pure ferric, pure ferrous, and mixed-valent ferric/ferrous ratios of 1:2 and 2:1 in the starting solution to produce greenalite (ferrous), ferrihydrite (ferric), and mixed-valent ferric/ferrous Fe minerals. All experiments were conducted in 1 L Teflon vials at 25 °C and a pH of 7.5-7.8 (Guo and Korenaga, 2025; Tosca et al., 2016) inside an inert anaerobic chamber atmosphere of <1 ppm O_2 . Another set of ferrihydrite synthesis experiments was performed in open-air conditions. In addition, a sodium bicarbonate control at different concentrations (2, 5 and 10 mM) was used in replicate greenalite and anoxic ferrihydrite experiments. The experiments lasted for 10 days, with solution sub-samples collected at specific time intervals. The 10-day experimental duration precipitated a harvestable amount of greenalite and brought solution Fe concentrations close to ~0.5 mM, which thermodynamically inhibits any significant further greenalite formation in the chosen 7.5-7.8 pH range (Tosca et al., 2016). Two additional TM adsorption experiments with freshly formed ferrihydrite in a similar seawater medium were conducted to obtain TM adsorption kinetics. On day ten, samples were filtered, and the solid-phase residues were characterized mineralogically by the next day. Some solid samples were further treated at a diagenetic temperature of 125 °C for five days, followed by chemical analysis.

2.3. Chemical and mineralogical analysis

All analytical work was conducted using the in-house facilities of the University of Tokyo, Japan. A scanning electron microscope equipped with an energy-dispersive spectrometer was used to examine the experimental solids at the micrometer scale and to approximate their major elemental compositions. The experimental solution and solid samples were analyzed for major and trace elements (supplementary dataset) using a quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS). Solution samples were diluted 250-fold in 2% HNO₃ and measured with matrix-matching calibration standards, internal standards (Sc and In), duplicates, and blanks. Analytical uncertainty measured by repeated standard and sample analyses was <6%. Experimental solid samples were weighed in 50 mL Teflon vials and dissolved using a sequence of concentrated HF + HClO₄, HNO₃ and HCl digestions on a hotplate at 120-180 °C. Samples were diluted 10⁵-fold in 2% HNO₃ and analyzed with matrix-matching calibration standards and internal standards (Sc and In) using the aforementioned Q-ICP-MS. The analytical uncertainty of repeated standard analyses was <5% (supplementary dataset).

The six 3.2 Ga Badampahar BIF samples used in this study were pre-screened for weathering, hydrothermal alteration, or the presence of any unwanted Fe-minerals through petrography and SEM analysis. The BIF samples are devoid of any visible alteration or hydrothermal texture; magnetite and grunerite (±ferroactinolite) are the only Fe-minerals present. The sample thin sections were ablated in a He atmosphere, and the sample carrier gas (flow rate 0.9586 L/min). He, was mixed with Ar using a Y-junction. Depending on the grain size, beam diameter varied between 40 µm and 50 µm, and the frequency was kept at 5 Hz. All grains were analyzed with a laser energy of 4.4 J/cm². The following isotopes were analyzed: ²⁴Mg, ²⁷Al, ²⁹Si, ³⁹K, ⁴⁴Ca, ⁵¹V, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn, ⁷¹Ga, ⁸⁹Y, ⁹⁰Zr, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ²³²Th, and ²³⁸U. Analyses were performed in peak-hopping mode, with each analysis consisting of a 20 s background measurement with the laser turned off and a 40 s peak signal measurement with the laser turned on. *In-situ* high-resolution mineral chemistry data were produced via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of the trace elements associated with the grunerite and magnetite minerals. Calibration was performed using NIST610, NIST612, BCR-2g glass standards, and data were reduced using Fe and Si as internal standards. Concentrations of Fe and Si measured with electron probe microanalysis (EPMA) were used to normalize

signal intensities. The Analytical uncertainties of the LA-ICP-MS analysis, determined by repeated standard measurements, were <6% for all elements.

X-Ray diffraction (XRD) samples were air-dried inside an anaerobic chamber and analyzed on a zero-background quartz sample holder within 15 minutes of air exposure. The analytical settings of the Rigaku RINT-2100 X-ray diffractometer (Cu-source tube) used for XRD mineralogical analysis were as follows: less-fluorescence mode, a 5°/minute scan speed (2 θ range ~ 5-70°), 40 kV, 30 mA, a 5 mm slit, a 0.8 mm collimator and a Dtex-Ultra detector. The XRD patterns were baseline-corrected and smoothened for improved visualization and matched with standard mineral XRD patterns. We further studied the synthesized samples with X-ray absorption spectroscopy (XAS) at the BL-9A beamline of the Photon Factory (Tsukuba, Japan) to improve mineralogical characterization. We measured Fe K-edge X-ray absorption near edge structure (XANES) spectra of the synthesized minerals at ambient pressure and temperature using a Si (111) double-crystal monochromator in transmission mode. After energy calibration and normalization, we used the linear combination fitting tool of the LARCH software (Newville, 2013) to fit the spectral XANES features of the synthesized minerals with a combination of the spectra of reference minerals, including hematite, goethite, ferrihydrite, magnetite, green rusts, greenalite, cronstedtite and siderite. We also analyzed the pre-edge peaks (Wilke et al., 2001) by extracting pre-edge jump with a spline function and fitting it with three Gaussian functions. An Fe redox calibration curve for the pre-edge centroid positions, constructed using standard minerals (e.g., fayalite, magnetite, and hematite) of varying Fe redox states, allowed us to calculate the redox states of Fe in the mixed-valent experimental samples.

3. Results

3.1. Texture and mineralogy of the reference BIFs

Our investigated reference BIFs from the ~3.2 Ga Badampahar (Figs. 1–3) and ~4.2 Ga Nuvvuagittuq formations consist primarily of alternating magnetite-, grunerite-, and quartz-rich bands. Detailed descriptions of the petrography and mineral paragenesis of these reference BIFs are available in earlier studies (Ghosh, 2020; Mloszewska et al., 2012). In brief, the Badampahar BIF samples are finely banded at a sub-millimeter scale and consist mostly of alternating bands of magnetite, quartz, and grunerite ($\pm$ ferroactinolite) (Figs. 1a–c). The bands exhibit variable thicknesses (0.05–1 mm) and mineral proportions, specifically comprising

magnetite-rich, grunerite-rich, quartz-rich, grunerite+quartz-rich, and magnetite+quartz-rich assemblages. A metamorphic coarse granoblastic texture is prominent within the bands, and the minerals often include one another and exhibit sharp contacts (Figs. 1e–f, 2, 3). Many previous petrographic studies (Rasmussen et al., 2017; Rasmussen and Muhling, 2018) have suggested a common greenalite precursor for all BIF Fe-minerals, and propose that Fe-oxides in BIFs likely originated from precursor Fe-silicates. However, (i) the presence of distinct, alternating bands composed of magnetite-, grunerite-, and quartz- dominant mineralogy, (ii) the absence of reaction textures among the minerals (e.g., the absence of a grunerite rim between magnetite and quartz), (iii) absence of Fe-oxides in some grunerite-bearing cherts (Fig. 3) and (iv) the distinct chemical composition of grunerite compared to magnetite (Figs. 2–4) collectively do not support the origin of Fe-oxides as a post-depositional oxidative or metamorphic products of Fe silicates and *vice versa*. Instead, these features indicate different precursor minerals for magnetite, grunerite, and quartz. Similar textural and compositional features have also been reported for the Nuvvuagittuq (Mloszewska et al., 2012) and Isua (Dymek and Klein, 1988) BIFs.

To further evaluate this, we compared the textural and chemical characteristics of grunerite from two different associations: (i) grunerite occurring in contact with magnetite—in Fe-oxide-rich BIF samples (Fig. 2), and (ii) grunerite surrounded by quartz in the Fe-oxide-absent cherts of the Badampahar belt (Fig. 3). These comparison is grounded in the fact that both sample types experienced the same metamorphic grade (i.e., greenschist-to-lower-amphibolite facies). Therefore, they would be expected to comprise similar endmember minerals if precursor composition was mainly controlled by a single mineral phase, for example, Fe-silicates, Fe-oxides, or a mixture of both. If Fe-oxides were the product of Fe-silicate metamorphism, they should consistently occur in association with metamorphic grunerite; however, this is not the case (Fig. 3). Moreover, the occurrence of these distinct mineralogical associations implies that differing ambient water conditions must have prevailed to enable the precipitation of these distinct precursor mineral phases.

3.2.Comparative chemistry of individual Hadean to early Archean BIF grunerite and magnetite

Overall, the reference BIFs are characterized by grunerite with significantly higher Mg, Mn, Ni, Co, and Zn concentrations and lower Ba, V, and P concentrations, compared to the

associated magnetite (Fig. 4a; Table 2). A low concentration of poorly mobile heavy metals, like Zr (<2 ppm), points to negligible detrital contamination (Table 2). In contrast, the distinct chemical patterns recorded for Ni, Co, and Zn abundances in magnetite and grunerite are likely primary. Such patterns are consistent across global BIF magnetite and Fe-silicate minerals present in BIFs and cherts (discussed in sections 4.1 and 4.2). This proposition is corroborated by a similar rare earth element (REE) distribution pattern, marked by light-REE depletion and mid-/heavy-REE enrichment within the distinct magnetite and Fe-silicate layers, regardless of metamorphic grade and age (Figs. 4b, c). Therefore, the precursors to the magnetite and grunerite bands (Figs. 1, 2) in the reference BIFs likely formed via independent seawater processes (Ghosh, 2020). Greenalite, the precursor of grunerite, likely formed by an abiotic reaction between seawater Fe(II) and silica in the deep, dark, and anoxic seawater column. Conversely, Fe-(oxy)hydroxides, the precursors of magnetite, formed via abiotic/biotic Fe(II) oxidation processes within the oceanic photic zone (discussed further in Section 4.1).

3.3.Characterization of synthetic minerals

We analyzed the XRD patterns and Fe K-edge XANES spectra (7111 eV) of experimental samples and standards to identify synthetic mineral phases (Fig. 5). All greenalite synthesis experiments produced dark green, poorly crystalline greenalite. These samples generated XRD patterns with two broad peaks centered around 2.57 and 1.59 Å d-space (Fig. 5e); however, the characteristic greenalite XRD peak around 7.1 Å was not prominent. This result indicates the poorly ordered nature of the synthesized greenalite, which retains regions of short-range crystalline order, and aligns with the XRD profiles reported for greenalite synthesized by Tosca et al. (2016). Therefore, to confirm the mineralogy of greenalite, we conducted synchrotron Fe K-edge XANES analysis (Fig. 5i). The XANES spectra of the synthesized greenalite match well with BIF greenalite. Linear combination fitting (LCF) results of XANES spectra confirmed a satisfactory fit between the synthesized greenalite phase and the reference natural BIF greenalite (Table 3).

Ferrihydrite synthesis experiments yielded reddish-brown 2-line ferrihydrite, which generated typical XRD patterns of ferrihydrite with two broad peaks centered around 2.50 and 1.51 Å d-space (Fig. 5f). LCF results (Table 3) show that the synthesized ferrihydrite best fits a combination of 66% hematite, 16% goethite, and 17% ferrihydrite. This suggests partial transformation of the metastable ferrihydrite into more crystalline phases (Cudennec and Lecerf, 2006). Mixed-valent synthesized samples were dark brown. Precipitates from the ferric

iron-dominant solution (33.3% Fe(II)) produced XRD patterns like 2-line ferrihydrite, whereas precipitates from the ferrous iron-dominant solution (33.3% Fe(III)) could not be identified with XRD (Fig. 5g, h). The precipitates of Fe(III)-dominant mixed-valent solution were successfully fit with 25.6% hematite, 43.9% goethite, and 33.4% ferrihydrite (Table 3), and its pre-edge peak centroid plotted close to magnetite on the pre-edge calibration curve (Figs. 5k, S4, supplementary data 1). Consequently, we interpret this phase as an amorphous mixture of Fe-oxyhydroxides rich in ferrous iron (HFO*). The precipitate from the Fe(II)-dominant solution was fit with 57.7% HFO*, 13.8% ferrihydrite, and 20.5% greenalite (Table 3), with its pre-edge peak centroid occurring at a slightly lower energy position than magnetite (Fig. 5k, S4, Supplementary data 1). It is inferred to be a mixture of greenalite and HFO*. The co-precipitation of aragonite along with greenalite and ferrihydrite was verified by chemical composition and radiating starburst-like crystals under SEM (Fig. 5d), as well as sharp XRD peaks at 3.40, 3.27, and 1.98 Å d-space (Fig. 5j).

3.4. Trace metal distribution during experimental Fe-(oxy)hydroxides and greenalite formation

To resolve the question of whether greenalite exhibits a higher Ni, Co, and Zn incorporation capacity than Fe-(oxy)hydroxides, we conducted co-precipitation-adsorption kinetic studies to evaluate the distribution of Ni, Co, and Zn into these phases under simulated Archean seawater conditions (Fig. 5). The experimental results were then compared with the Ni, Co, and Zn compositions of reference BIF grunerite and magnetite (Fig. 6). To achieve this objective, we synthesized greenalite and Fe-(oxy)hydroxides across a range of initial solution Fe(II)/Fe(III) ratios (i.e., 1:0, 1:2, 2:1 and 0:1; total Fe = 1 mM) in an analogous early Precambrian seawater with 1.2 mM silica and 1 µM/L each of Ni, Co, and Zn (see Methods). The independent Fe(II) and Fe(III) experiments resulted in the formation of greenalite and Si-rich ferrihydrite, respectively. Meanwhile, the mixed-valent Fe(III)-rich and Fe(II)-rich experiments produced mixed-valent Si-rich Fe-(oxy)hydroxides (HFO*) with an average Fe redox state close to magnetite, and a mixture of HFO*+greenalite minerals, respectively. Combined XRD and XANES analyses successfully identified these mineral phases (Fig. 5i; Table 3). The presence of ≥ 5 mM/L HCO_3^- in solution precipitated aragonite along with ferrihydrite or greenalite. However, quantifying the Ni, Co and Zn distribution coefficients for the Fe-minerals was not possible at these varied HCO_3^- concentrations due to excessive aragonite formation driven by

the reaction between Ca^{2+} and HCO_3^- . Therefore, carbonate experiments were not further replicated.

All synthesized Fe minerals incorporated Zn within minutes to hours; however, Ni and Co incorporation mostly mirrored the Fe distribution trend (Fig. 6). Trace metal distribution coefficients (K_D) were calculated using the following equation:

$${}^{\text{TM}}K_D = [(M_{\text{TM}})/[SW_{\text{TM}}]] \quad (\text{equation 1})$$

where M_{TM} is the molar trace metal/Fe ratios in the mineral and SW_{TM} is the molar trace metal/Fe ratios in the seawater.

Accordingly, the Co and Ni K_D values calculated from the analytical data of solids and concentrations remaining in solution (Fig. 6d; Table 1) were observed to be slightly higher for greenalite (0.736 and 0.506) relative to the ferrihydrite and the HFO* precipitates (0.334-0.474 and 0.276-0.359), respectively. On average, the conversion ~8 and ~22% dissolved Fe(II) to greenalite incorporated ~69 and ~99% Zn into the greenalite lattice within 2 and 48 hours, respectively (Supplementary data 2). This rapid incorporation resulted in calculated Zn K_D ~8.5 and 4.5, according to the first 2 hours and 48 hours data points, respectively. True Zn K_D for ferrihydrite could not be initially determined as both oxic and anoxic conditions precipitated ferrihydrite within minutes of synthesis. To resolve this issue, we performed another set of oxic ferrihydrite synthesis experiments using a similar Fe concentration of 0.08 mM consumed by greenalite formation in the first two hours (Fig. 6a, Supplementary Data 2), leaving the remaining parameters unchanged. Results show that conversion of a much lower concentration of Fe to ferrihydrite (assuming partial oxidation) exhausted ~0.85 μM Zn from the solution within two hours. The 10.5 Zn K_D for ferrihydrite calculated in this way is comparable to the 8.5 Zn K_D value estimated for greenalite (Fig. 6d). The extremely high Zn K_D for both minerals indicates stronger, rapid and dominant structural drawdown of Zn, contrasting sharply with the significantly slower Ni and Co co-precipitation and adsorption rates.

While several foundational studies have advanced our understanding of TM dynamics in BIFs, empirical datasets evaluating the co-precipitation and adsorption of Ni, Co, and Zn on primary BIF minerals under Precambrian seawater conditions remain remarkably limited. Tostevin and Ahmed (2023) previously evaluated the K_D of multiple TMs (including Ni, Co, Zn, V, Mn, and Mo) for greenalite precipitated under anoxic Archean seawater conditions. Utilizing elevated TM concentrations (~18 μM) and a higher pH~ 8-8.5, they reported a markedly high K_D for Zn (5379) relative to Ni (0.33) and Co (0.74). However, as Zn was rapidly sequestered into the

greenalite matrix within minutes to hours, true thermodynamic equilibrium partition coefficients could not be resolved; their reported Zn K_D remains an approximation derived from the initial data point of a time-resolved sampling series. In contrast, our experiments employed more environmentally realistic, lower TM concentrations ($\sim 1 \mu\text{M}$) to circumvent these rapid, non-equilibrium kinetics. Our data yield a comparable overall trend—characterized by preferential Zn uptake over Ni and Co—but refine these values to a significantly lower Zn K_D of ~ 8.5 , alongside consistent, low K_D values for Ni (0.506) and Co (0.736).

Robbins et al. (2013) reconstructed early ocean Zn levels based on ferrihydrite surface adsorption thermodynamic modeling using Visual MINTEQ. However, structural work by Waychunas et al. (2002) demonstrated that co-precipitation incorporates metals via complex polydentate, inner-sphere geometries sharing apices with multiple adjacent ferrihydrite polyhedra, which behaves distinctly from simple surface adsorption. Our empirical co-precipitation experiments directly capture this higher-efficiency incorporation mechanism, providing a more accurate empirical Zn K_D for BIF paleomarine reconstructions.

Similarly, Konhauser et al. (2009) performed Ni-ferrihydrite co-precipitation and adsorption experiments to reconstruct early seawater Ni concentrations from BIFs. They determined Ni K_D for ferrihydrite of 0.00396 and 0.00123 μM^{-1} for 0.67 and 2.2 mM dissolved silica concentrations, respectively, in seawater with a low dissolved Fe concentration of 0.179 mM. If we recalculate these Ni K_D s values using the standard K_D equation (Equation 1), they become 0.708 and 0.220 for 0.67 and 2.2 mM dissolved silica, respectively. These recalculated values match closely with our calculated Ni K_D of 0.359 for Fe-oxyhydroxides at 1.2 mM silica.

A subsequent study by Eickhoff et al (2014) also calculated Ni distribution for biogenic and abiogenic ferrihydrite and showed lower co-precipitation and adsorption of Ni to ferrihydrite in presence of microbial cells. Sugiyama and Halevy (2026) investigated the co-precipitation of transition metals—including Ni, Co, and Zn at variable initial concentrations (0.1–300 μM)—with carbonate-green rust synthesized under low-silica (0.1 mM) and Ca-depleted Archean seawater conditions. They reported approximately 95% Zn, 84% Co, and 68% Ni incorporation into the green rust matrix at an initial TM concentration of 1 μM . This

comparative affinity sequence of transition TMs, $\text{Zn} > \text{Co} > \text{Ni}$, in iron minerals aligns well with our experimental observations.

However, when normalized to Fe content, grunerite in Archean BIFs is significantly enriched in Ni, Co, and Zn by 3.3-, 7.6- and 17.8-folds, respectively, relative to magnetite (Fig. 6e). In contrast, our experimental data show that the grunerite precursor greenalite only enriches Ni, Co, and Zn by 1.6-, 1.43- and 1.13-fold, respectively, relative to the magnetite precursors synthesized under our early Precambrian seawater analogue conditions (Fig. 6e). This near equal experimental incorporation of TMs by greenalite and Fe-(oxy)hydroxides cannot therefore explain the highly contrasting TM inventories of natural BIF grunerite and magnetite—assuming their precursor minerals formed together with equal access to seawater TMs. Consequently, these discrepancies suggest that additional pathways must be involved in the differential incorporation of TMs from ancient seawater, as explored below.

3.3. Aging at diagenetic temperature

BIFs underwent burial diagenesis over timescales spanning millions of years, a process that is impossible to truly replicate under laboratory-scale conditions. To assess the potential impact of diagenetic temperature on mineral composition, we subjected the experimental mineral phases (i.e. greenalite and Fe-(oxy)hydroxides) to thermal aging in sealed autoclave vials at 125 °C for 5 days. The minerals were suspended in an artificial seawater solution (1:20 volumetric ratio) of pH~7.7. We also used distilled water instead of seawater solution as a secondary control in replication experiments to assess the extent of trace element leaching. Notably, this thermal treatment used in this study isolates only the temperature component of natural diagenesis. In geological systems, diagenesis is a synergistic process driven by both temperature and pressure, the latter of which was not replicated in our experimental setup. Furthermore, this abiotic heating approach does not account for early diagenetic transformations driven by chemoheterotrophic microbial processes, which actively alter organic matter and mineral assemblages in natural sedimentary environments.

At the end of each experiment, we collected the aged mineral samples by centrifugation and analyzed them to track chemical alterations. Analytical results of the aged samples show overall insignificant changes ($< \pm 20\%$) in the Ni/Fe, Co/Fe and Zn/Fe ratios relative to the untreated starting samples (Fig. S5; Supplementary Data 1). These observations correspond well with the limited Ni, Co, and Zn mobility results of similar diagenetic experiments

performed by Tostevin and Ahmed (2023) on greenalite (100 °C, 21 days) and Robbins et al. (2015) on ferrihydrite (170 °C, 14 days). Aged greenalite samples in the seawater medium show average enrichments of 15-, 13-, and 6 % for Co, Ni, and Zn. By comparison, grunerite in the reference BIFs is significantly enriched in Ni, Co, and Zn by 3.3-, 7.6- and 17.8-fold compared to magnetite. When grunerite trace element values are normalized using our experimental diagenetic trace element enrichment factors, the resulting Ni, Co, and Zn in BIF grunerite relative to magnetite remain high at 2.9-, 6.6- and 16.8-fold, respectively.

4. Discussion

4.1. Origin of the reference BIF magnetite and grunerite

Iron-silicate-rich, Algoma-type BIFs deposited globally throughout the predominantly anoxic Hadean to early Archean eons (>3 Ga). Key examples include the ~4.2 Ga Nuvvuagittuq greenstone belt in Canada (Mloszewska et al., 2012), the ~3.8 Ga Isua greenstone belt in Greenland (Dymek and Klein, 1988), the ~3.2 Ga Cardinal and Kangaroo Cave formations in Australia (Muhling et al., 2023), and the ~3.2 Ga Badampahar greenstone belt in India (Ghosh, 2020). These BIFs typically consist of magnetite as the Fe-oxide phase and greenalite/minnesotaite/grunerite(±ferroactinolite) as the Fe-silicate phases, along with quartz, mainly arranged as alternating mineral bands (e.g., Figs. 1-2). Notably, these BIFs exhibit remarkably uniform mineralogical and banding patterns, regardless of where they occur, composed mostly of Fe-oxide and -silicate-rich lithologies. Of all the BIFs studied worldwide, it is generally accepted that they collectively represent a global record of the Hadean to early Archean seawater from which they precipitated. While evaluating all these BIFs is beyond the scope of this work, the reference samples from the 4.2 Ga Nuvvuagittuq and 3.2 Ga Badampahar successions, broadly, are mineralogically and texturally representative of the Hadean to early Archean BIF lithologies.

Mloszewska et al. (2012) highlighted minnesotaite (Fe-silicate) or siderite (Fe-carbonate) as possible precursors to grunerite, and hematite and siderite as precursors to magnetite. Notably, iron-bearing carbonate minerals are usually considered diagenetic and are excluded as primary BIF minerals, as their nucleation requires high saturation of Fe(II) and carbonate ions together with low dissolved silica — conditions that were unlikely to form in the silica-rich Archean seawater conditions (Jiang and Tosca, 2019). Conversely, Mel'nik (1982) and Klein (2005) suggested a prograde metamorphic pathway for grunerite formation from greenalite via minnesotaite. Based on petrographic and mineral chemistry studies of these BIFs, Ghosh

(2020) suggested two dominant initial Fe-minerals in the reference BIFs: greenalite (the precursor to grunerite) and Fe-(oxy)hydroxides (precursors to magnetite), which precipitated sequentially in the Hadean to early Archean oceans, whereas quartz-rich bands reflect non-depositional periods of Fe-minerals.

In BIFs, magnetite is commonly considered to have originated from the transformation of authigenic ferrihydrite or green rust precursor minerals via various biotic and abiotic processes (Halama et al., 2016; Halevy et al., 2017; Han et al., 2020; Konhauser et al., 2005), while grunerite is thought to form from authigenic greenalite precursors associated with prograde greenschist facies metamorphism (Klein, 2005; Mel'nik, 1982). Studies such as Rasmussen et al. (2017), Rasmussen and Muhling (2018) and Tosca et al. (2025) highlighted greenalite as the primary precursor of all BIF Fe minerals. However, this single-precursor hypothesis lacks direct experimental evidence, whereas hydrogeological modelling studies (Robbins et al., 2019) and isotopic studies (Planavsky et al., 2012) suggested multiple precursor phases, specifically identifying Fe-(oxy)hydroxides as precursors of BIF magnetite. Rasmussen and Muhling (2018) suggested that pore-water siderite in greenalite-rich BIF bands could later transform to magnetite. While minor magnetite occurs disseminated within BIF grunerite and quartz bands, the presence of distinct, thick (up to 1 mm) magnetite bands consisting of >90 modal% magnetite (Fig. 1) is inconsistent with an origin via the thermal decomposition of localized pore-water siderite. Alternatively, Nims and Johnson (2022) demonstrated that Fe(III)-reducing bacteria could generate secondary Fe-silicate phases from ferrihydrite in a Si-rich environment. However, Fe -silicates and -oxides occur in distinct bands in our BIFs, and their chemical compositions are distinctly different (Fig. 4a). This divergence suggests that ferrihydrite was not a common precursor for both magnetite and grunerite; otherwise, the two minerals would exhibit similar chemical compositions. In addition, the BIF grunerite data from the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq successions can be compared to primary BIF greenalite data from the 3.2 Ga, lower-metamorphic-grade Kangaroo-Cardinal formations. All of them show similarly high enrichment in Mg, Mn, Ni, Co, and Zn, supporting the origin of grunerite from greenalite (Table 2).

Collectively, primary authigenic Fe-(oxy)hydroxides and greenalite are the most plausible precursors of magnetite and grunerite, respectively, in the reference Nuvvuagittuq and Badampahar BIFs.

4.2. Postdepositional influence on BIF mineral chemistry

Previous studies (Robbins et al., 2015; Tostevin and Ahmed, 2023), as well as the aging experiments presented herein (section 3.3), show that Fe-(oxy)hydroxides and greenalite strongly bind Ni, Co, and Zn, resisting diagenesis or hydrothermal leaching. Isochemical metamorphism is common for Archean BIFs, where, for example, low- to high-grade regional metamorphism is known to result in the loss of water and carbon dioxide while preserving the elemental composition of primary minerals (Klein, 2005, 1983). The preservation of heterogeneous Fe isotopic patterns across the Fe-mineral bands of Archean BIFs testifies to minimal post-depositional influence on BIF chemical compositions (Frost et al., 2007).

We compared the Badampahar and Nuvvuagittuq BIF grunerite data to available low-metamorphic-grade BIF greenalite data. Primary greenalite preserved in the 3.2 Ga Cardinal-Kangaroo formations, Australia (Muhling et al., 2023) shows a remarkable geochemical similarity to our studied BIF grunerite, regardless of metamorphic grade (Table 2). We also compared our magnetite data to other BIF magnetite data, which show that an equivalent low abundance of Ni, Co, and Zn in BIF magnetite compared to average Fe-silicates is common across worldwide BIF deposits (Fig. S3, Supplementary Data 1).

Furthermore, post-depositional microscale chemical exchange between the magnetite and grunerite precursors cannot explain their TM content. As stated above, we compared the TM compositions of grunerite bands in contact with the BIF magnetite bands (55, 20 and 216 ppm; Fig. 2) with grunerite surrounded by quartz in Fe-oxide-absent chert (151, 21, and 305 ppm; Fig. 3), finding a similarly high abundance of Ni, Co and Zn in both types of grunerite (Table 2). These observations, coupled with the high structural capacity of magnetite to accommodate large amounts of Ni, Co, and Zn (>990 ppm; Nadoll et al., 2014), suggest an originally depleted Fe-(oxy)hydroxides precursor phase for magnetite formation. We therefore conclude that the chemical content of the grunerite and magnetite conserved in the studied BIFs is representative of spatiotemporal differentiation during authigenic primary mineral precipitation from early Archean seawater rather than post-depositional influences.

4.3. Seawater chemical variability

The dissolved seawater Ni, Co, and Zn compositions were calculated using our estimated K_D values according to Equation 1 ($SW_{TM} = M_{TM} / {}^{TM}K_D$), assuming a ~1 mM dissolved seawater Fe concentration for the model baseline (Jiang and Tosca, 2019). The results indicate that the ambient water present during BIF Fe-(oxy)hydroxides formation was highly depleted in Ni,

Co, and Zn relative to that of greenalite (Table 4). For example, magnetite-reconstructed mean seawater Ni, Co, and Zn concentrations at 4.2 Ga and 3.2 Ga are 287, 19.5, and 5.26 nM, and 119, 29.7, and 2.58 nM, respectively. In contrast, grunerite-reconstructed mean seawater Ni, Co, and Zn concentrations at 4.2 Ga and 3.2 Ga are 513, 133, and 82.1 nM, and 376, 94.2, and 78.9 nM, respectively. Interestingly, the reconstructed seawater compositions from the 3.2 Ga Cardinal-Kangaroo greenalite and the 3.2 Ga Badampahar grunerite are broadly comparable due to their high Ni, Co, and Zn contents (Table 4). We also note that reconstruction of these TM concentrations strongly depends on the assumed seawater Fe concentration in Equation 1. Any deviation in the assumed early seawater Fe concentration would stoichiometrically alter the reconstructed TM concentrations. Consequently, the objective of this study is not to reconstruct the absolute Ni, Co, and Zn concentrations of early seawater; rather, we assess comparative TM concentrations of ambient seawaters that precipitated BIF greenalite and Fe-oxyhydroxides.

Volcanogenic hydrothermal fluids usually contain higher concentrations of Ni, Co, and Zn than modern seawater (Douville et al., 2002). A high degree of submarine volcanism and hydrothermal activity in the early Precambrian ocean (Lowell and Keller, 2003) would have intensified hydrothermal Ni, Co, and Zn fluxes to the seawater. This association raises the question of the extent to which greenalite chemistry reflects a pristine hydrothermal input versus a highly diluted, seawater-dominated fluid mixture. Both BIF Fe-silicates and Fe-oxides show typical seawater-like shale-normalized heavy-REE enrichment patterns with superchondritic Y/Ho ratios (Figs. 4b-c). Such fractionated REE patterns with minor Eu enrichment could only be achieved by the mixing of seawater with volcanogenic hydrothermal fluids at a ratio of >1000:1 (Fig. 4c). Studies such as Nke et al. (2024) and Muhling et al. (2023) also suggested a seawater origin for Archean to Paleoproterozoic BIF greenalite. Overall, our REE data discard greenalite or Fe-(oxy)hydroxides formation directly from high-temperature hydrothermal fluids, confirming a significant (>1000-fold) dilution of the hydrothermal components prior to precursor mineral precipitation.

The alternating Fe-(oxy)hydroxides- and greenalite-rich precursor bands in BIFs, together with the contrasting ambient seawater compositions during their respective formation, indicate periodic fluctuations of dissolved Ni, Co, and Zn in Hadean to early Archean seawater. We discuss three main possibilities for the development of these contrasting compositions in the reconstructed 4.2-3.2 Ga seawater from magnetite and grunerite, as follows: (i) Fe-

(oxy)hydroxides and greenalite formation at different depths in the seawater column; (ii) faster abiotic greenalite formation compared to biogenic Fe-(oxy)hydroxides formation; and (iii) the biological retention of TMs during Fe-(oxy)hydroxides formation.

4.3.1. Fe-(oxy)hydroxides and greenalite formation at different depths

Greenalite and Fe-(oxy)hydroxides likely formed sequentially at different depths of the water column within the Hadean to early Archean ocean. This spatial separation occurred because Fe-(oxy)hydroxides formation, via either abiotic or biotic pathways, required a shallow photic zone setting (Konhauser et al., 2018; Swanner et al., 2015; Tabata et al., 2021), whereas greenalite could form in deep, dark, anoxic bottom waters soon after seafloor hydrothermal events (Tosca et al., 2016). In this model, episodic hydrothermal fluids advected from seafloor vents and mixed rapidly with deep Archean seawater (Germanovich et al., 2015), where greenalite first precipitated in the absence of major primary Fe-(oxy)hydroxides formation. In this sulfur-cycle-deficient Archean seawater (Canfield et al., 2000), greenalite thus had early access to the deep seawater TM pool. Upwelling delay and the dilution of deep-sea hydrothermal components towards the photic zone resulted in the rapid uptake of Fe and TMs into greenalite—particularly Zn, given its exceptionally high K_D and fast uptake kinetics (Fig. 6d). This preferential uptake generated a moderate depletion of Ni and Co, and a severe depletion of Zn, in the residual deep seawater upwelling toward the surface. Concurrently, any fraction of the Fe and TM pool that escaped sequestration by deep-water greenalite was further diluted during transport, subsequently co-precipitating with or adsorbing onto primary Fe-(oxy)hydroxides and minor greenalite phases at the ocean surface.

Notably, greenalite formation required high dissolved Fe(II) saturation (>0.5 mM at 25°C and pH 7.5; Tosca et al., 2016), whereas biological Fe-(oxy)hydroxides formation could happen even at micromolar dissolved Fe concentration (Konhauser et al., 2007). Once deep-water abiotic greenalite formation consumed enough iron to drop below this 0.5 mM threshold, further greenalite precipitation ceased. The residual, lower Fe(II) fluid was then free to upwell into the surface ocean, precipitating TM-depleted Fe-oxyhydroxides without competing with greenalite formation. This mechanism explains the deposition of Fe-(oxy)hydroxide-rich, greenalite-depleted bands directly following greenalite-rich bands. As the surface-formed Fe-(oxy)hydroxides settled through the water column to form seafloor BIF sediments, they passed through deep waters that had already been stripped of TMs by earlier greenalite precipitation and further diluted by diffusion. Consequently, these settling Fe-(oxy)hydroxides could only

adsorb minor amounts of residual TMs from the deep water column. Collectively, this depth-dependent spatial segregation produced the contrasting Ni, Co, and Zn signatures preserved in BIF Fe-oxides and Fe-silicates.

Modern oceanographic observations and ancient deep-sea models show that hydrothermal plumes laterally travel tens to hundreds of kilometres away from vent fields by ocean currents while staying trapped at depth, thereby maintaining their primary chemical integrity. Driven by background deep-ocean current velocities, a plume is envisaged to travel ~1 to 9 km/day after eruption (Tagliabue et al., 2022), reasonably explaining the kilometer-scale lateral stretch of the reference BIF bands and their deposition not always near localized vent sites. Once a plume stalls at its level of neutral buoyancy (after a few hundred meters of rapid uprise), vertical transport up to the surface photic zone is no longer driven by local plume buoyancy. Instead, it relies on basin-scale upwelling (e.g., wind-driven or convective basin overturning), which operates at a much slower vertical velocity of ~1 m/day (Liang et al., 2017; Tagliabue et al., 2022). Because this vertical transit is so slow, it could provide a massive temporal window for settling greenalite to systematically strip the fluid of its TMs. When this heavily evolved fluid finally reached the surface, its remaining Fe(II) (<0.5 mM) precipitated as trace-metal-depleted ferrihydrite. This framework fits within the spatial and hydrodynamic constraints of a single Algoma-type basin.

4.3.2. **Faster abiotic greenalite formation compared to biogenic Fe-(oxy)hydroxides formation**

Alternatively, the sequential greenalite and Fe-(oxy)hydroxides formation within a shallow seawater setting could be driven by early, rapid abiotic greenalite-rich precipitation followed by slower biogenic Fe-(oxy)hydroxides formation. This sequence is mediated by a physiological resuscitation lag within a marine microbial seed bank responding to episodic hydrothermal forcing.

In natural environments, up to 90% of the ambient bacterial population often exists in a metabolically inactive, dormant, or "viable but non-culturable" state as an evolutionary adaptation to prolonged nutrient limitation (Jones and Lennon, 2010). These dormant cells act as a dynamic "seed bank" distributed throughout the water column. When an environment experiences a sudden pulse of a limiting substrate or electron donor—such as an injection of hydrothermal Fe(II) into an anoxic Archean basin—dormant marine bacteria do not resume maximum metabolic activity instantly. They undergo a well-characterized metabolic transition

period (the environmental "lag phase") required to upregulate specific functional genes, synthesize respiratory enzymes, and repair cellular structures before entering an active growth phase (Blagodatskaya and Kuzyakov, 2013). Culture experiments with modern ocean Fe(II)-oxidizing microbes show a microbial growth lag phase lasting 2-10 days (Wu et al., 2014).

Similarly, during periods of hydrothermal quiescence or adverse seasonal shifts in the Hadean to early Archean ocean—e.g., during the deposition of alternating chert bands (Posth et al., 2008; Pirajno and Wu, 2021)—the local Fe(II)-oxidizing bacterial population could experience severe substrate starvation and collapse into dormancy or localized, low-abundance niches. In a shallow-depth seawater setting (e.g., <500 m), a fresh buoyant hydrothermal pulse, together with its rapid upwelling into the surface waters, would trigger immediate, rapid abiotic greenalite precipitation throughout the water column. The hydrothermal Fe(II) would simultaneously initiate the metabolic resuscitation of the photic-zone microbial seed bank. Because this biological awakening requires a discrete physiological timeframe, microbial Fe(II) oxidation would not begin immediately, temporarily allowing some greenalite to form unhindered within the shallow water and sink below the photic zone to form discrete Fe-silicate bands. However, the ultimate preservation of this shallow-water greenalite was dictated strictly by its residence time in the photic zone. Once the microbial community fully resuscitated and initiated active Fe(II) oxidation, any remaining shallow-water greenalite would undergo dissolution and oxidation to Fe-(oxy)hydroxides, thus cleanly recording the stratigraphically discrete, alternating mineral layers.

Thus, a few days of microbial growth delay would allow moderate Ni and Co and high Zn depletion in the seawater by early formed greenalite, as found in our experiments (Fig. 6a). Consequently, Fe-(oxy)hydroxides would precipitate from relatively Fe and TM depleted seawater following greenalite rich precipitation, thereby producing the observed contrasting compositions of the Fe -oxide and Fe-silicate phases in BIFs. However, this “microbial growth-lag” model does not apply to BIFs deposited in deeper ocean settings, because a deeper seawater column likely allowed early greenalite formation in deeper waters—depleting the slowly upwelling water of Fe(II) and preventing further greenalite formation in surface waters.

Although the majority of BIFs show the presence of Fe-oxides and Fe-silicates in alternating bands (Ghosh, 2020; Mloszewska et al., 2012), BIFs with the total absence of Fe-oxides or Fe-silicates have also been reported. The absence of Fe-silicates in BIFs can be explained by BIF deposition in early shallow ocean settings with high microbial activity, which limited greenalite

formation or oxidized early-formed greenalite. On the other hand, BIF sequences lacking significant Fe-oxides may reflect deposition during transient periods of adverse environmental conditions (e.g., seasonal temperature or chemical fluctuations; Posth et al., 2008) that suppressed local microbial activity, thereby temporarily permitting only abiotic, greenalite-rich precipitation. BIFs with mixed mineral bands containing both Fe-silicates and Fe-oxides can be explained by co-precipitation of greenalite and Fe-(oxy)hydroxides from TM-rich deeper seawater and TM-depleted surface seawaters, along with frequent cycles of hydrothermal and microbial activities and sediment mixing by ocean currents and turbulence.

4.3.3. Microbial retention of trace elements

Eickhoff et al. (2014) demonstrated that Ni incorporation into Fe-(oxy)hydroxides is 2-3 times reduced by the presence of microbial cells. Therefore, if we consider 2.5 times lower incorporation of Ni, Co and Zn for Fe-(oxy)hydroxides particles in the early ocean, Fe-oxide-reconstructed seawater Ni, Co and Zn concentrations could be 717, 48 and 13 nM for the 3.8 Ga ocean and 297, 74.2 and 6.45 nM for the 3.2 Ga ocean, respectively. This suggests comparable Ni and Co concentrations for the Fe-(oxy)hydroxides and greenalite reconstructed early Archean seawater. However, the highly contrasting Zn composition is not explainable by this mechanism alone, thereby supporting a sequential mineral formation process discussed earlier.

From another perspective, active Fe-oxidizing microbes could retain only minor TMs in seawater. We adapted the photoferrotrophic TM retention model of Konhauser et al. (2018), considering a 5×10^7 cells/L cell density of photoferrotrophs for the maximum annual Fe deposition as Fe-(oxy)hydroxides of BIFs. The model relies on the TM retention capacity of photoferrotrophic cells grown in simulated Paleoproterozoic seawater containing 400 nM Ni, 10 nM Co and 10 nM Zn. The 5×10^7 photoferrotrophic cells/L with an average TM retention capacity of 9.33×10^{-10} nM Ni, 7.84×10^{-10} nM Co and 8.09×10^{-9} Zn per cell could retain a maximum of 0.05 nM Ni, 0.04 nM Co and 0.4 nM Zn in 1L early Precambrian surface seawater that is negligible compared to the estimated seawater compositions (Table 4).

In addition, the Fe(II)-oxidizing microbial biomass deposited with Fe-(oxy)hydroxides were mostly degraded and recycled in the deep early ocean, with an estimated 3-5% potentially contributing to dissimilatory Fe-reduction (Konhauser et al., 2005). Biomass participation in dissimilatory Fe-reduction may have contributed TMs to the forming magnetite. According to

a 1C:4Fe utilization ratio for Fe-reduction (Konhauser et al., 2005), we calculated that the complete consumption of 25.8 g of biomass (considering 50 wt.% C in a bacterial cell with unit cell mass 1.3×10^{-9} mg²³; Hallbeck and Pedersen, 1991) would produce 1 kg of magnetite from ferrihydrite. The 25.8 g biomass could thus have contributed a maximum of 0.018 μ M of Ni, 0.016 μ M of Co, and 0.160 μ M of Zn to magnetite, whereas average magnetite in the studied BIFs contains 942 μ M/Kg of Ni, 140 μ M/Kg of Co, and 510 μ M/Kg of Zn, suggesting biomass contributed an insignificant portion of Ni, Co and Zn, respectively, to magnetite.

These findings indicate that TMs are more closely associated with Fe-(oxy)hydroxides than with microbial cells or extracellular organic substances under early seawater conditions. This suggests a strong link between seawater TM content and primary Fe-(oxy)hydroxides formation, regardless of whether the process was biological or abiotic. Thus, the TM composition of primary Fe-(oxy)hydroxides, which we use to infer BIF composition, approximates the likely original seawater composition with insignificant influence due to partitioning on buried organic matter.

4.4. Trace-metal mass-balance framework for the sequential Fe-mineral formation

While absolute Archean metal concentrations are difficult to constrain from modern marine settings, the partitioning of Ni, Co, and Zn into Fe-minerals was likely governed by local chemical kinetics where mineral precipitation rates outpaced physical basinal mixing. By viewing the early seawater column as a dynamic, sequentially precipitating system rather than a static one, our model achieves internal mass-balance consistency. Because greenalite has an exceptionally high partition coefficient for Zn, its rapid crystallization acted as an immediate elemental sink, systematically depleting the local fluid via Rayleigh-style distillation.

We tested this using an initial baseline composition of ~1 mM Fe (Tosca et al., 2016), ~79 nM Zn, ~94.3 nM Co, and ~376 nM Ni (reconstructed from the 3.2 Ga Badampahar grunerite; Table 4) in the primary seawater and hydrothermal fluid mixture. Our experimental data (Fig. 6a, Supplementary Data 2) track this chemical evolution as follows:

- An 8% Fe consumption by greenalite removes 69% Zn, 1% Co, and 4% Ni. Residual fluid: 0.92 mM Fe, 24.5 nM Zn, 93 nM Co, 360 nM Ni; **Ni/Zn = 14.7; Co/Zn = 3.79.**
- A 14% Fe conversion removes 89% Zn, 7% Co, and 8% Ni. Residual fluid: 0.86 mM Fe, 9 nM Zn, 88 nM Co, 346 nM Ni; **Ni/Zn = 38.4; Co/Zn = 9.78.**

- A 22% Fe conversion removes 99% Zn, 13% Co, and 10% Ni. Residual fluid: 0.78 mM Fe, 1 nM Zn, 82 nM Co, 338 nM Ni; **Ni/Zn = 338; Co/Zn = 82**.

Crucially, our independent, back-calculated seawater compositions reconstructed from the 3.2 Ga Badampahar magnetite bands (Table 4) yield **Ni/Zn = 46.1 and Co/Zn = 11.5** (2.58 nM Zn, 29.7 nM Co, and 119 nM Ni). These values show an excellent alignment with our experimental mass-balance estimates between the 14-22% Fe consumption by greenalite formation marks. This strongly confirms that Fe-oxyhydroxides (the precursors to magnetite) precipitated from a pre-depleted, evolved fluid reservoir left behind by rapid greenalite formation. Notably, considering a lower dissolved seawater Fe concentration, e.g. 0.5 mM instead of ~1 mM, during Fe-oxyhydroxides formation results in lower values of 1.29 nM Zn, 14.8 nM Co, and 59.5 nM Ni (a stoichiometric half) in the magnetite-reconstructed surface seawater; however, the ratios of Ni/Zn and Co/Zn remain unchanged.

4.5. The impact of Fe mineralization on the early seawater Ni, Co, and Zn

Our geochemical experiments mimicking early Precambrian seawater conditions show that the dual primary mineral sinks — greenalite and Fe-(oxy)hydroxides — could influence overall dissolved Archean seawater column Ni, Co, and Zn concentrations, and probably many other TMs that remain to be investigated. The most profound effect was exerted on dissolved Zn concentrations because of its extremely high affinity for primary greenalite and Fe-(oxy)hydroxides minerals compared to Ni and Co, which likely exhausted Zn from early seawater after each cycle of Fe mineral deposition. This observation implies that Ni and Co were more available to early life for metabolic processes than Zn. Moreover, the predominance of unfractionated Zn isotopes in the early Archean BIFs (Pons et al., 2013) can be explained by our quantitative seawater Zn-exhaustion model, where the surge of hydrothermal fluids and plumes into Archean seawater was accompanied by two-step greenalite and Fe-(oxy)hydroxides incorporation of Zn. Our model further points to the absence of a modern conventional Zn cycle associated with sulfidation and viable eukaryotic/complex metabolisms (Butterfield, 2015; Canfield et al., 2000; Vance et al., 2016) associated with strong fractionation of Zn towards more negative isotopic values presently traced back to the Paleoproterozoic ocean (El Albani et al., 2023; Ossa Ossa et al., 2023).

5. Conclusions

Collectively, the alternating magnetite and grunerite-rich bands in the reference Algoma-type BIFs of the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq successions, together with their contrasting compositions, indicate consecutive greenalite and Fe-(oxy)hydroxides formation

events in the early ocean. Specifically, the near-equal trace elemental incorporation capacity of Fe-(oxy)hydroxides and greenalite, contrasted yet with their distinct chemistry in the BIFs, points to a periodic fluctuation in Ni, Co, and Zn levels in the early seawater. Such chemical variability could be driven by a combination of complex marine processes, including deep-sea episodic hydrothermalism (Brenner et al., 2024), diffusion and dilution of hydrothermal components, and sequential Fe mineral formation governed by the transportation lag of hydrothermal components reaching surface waters, and a microbial physiological resuscitation lag. Our geochemical experiments under simulated early seawater conditions show that both primary greenalite and Fe-(oxy)hydroxides could influence overall dissolved early seawater TM concentrations—especially that of Zn. The experimental data, together with the geochemistry of the BIF Fe-silicates and Fe-oxides and Precambrian Zn isotopic record, support a complete Zn-exhaustion model with each episode of Fe-mineralization in the early ocean.

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Figure captions

Fig. 1. (a) Field exposure of a reference BIF sequence with an inset image the Fe silicate-rich BIF sample (E28) in the Badampahar greenstone belt, Singhbhum craton, India. **(b-d)** Plane polarized light photomicrographs of reference BIF and chert samples (D73, E28 and E5). BIF samples show alternating bands consisting grunerite (Grt), magnetite (Mt) and quartz (Qz) as pure and mixed mineral bands. **(e-f)** Back scattered electron (BSE) photomicrographs exhibit sharp contact among minerals with the apparent absence of any reaction texture.

Fig. 2. Scanning electron photomicrographs combined with elemental mapping of a BIF sample (E28) containing grunerite (Grt) and magnetite (Mt).

Fig. 3. Scanning electron photomicrographs combined with elemental mapping of a chert (E5) containing grunerite (Grt) and quartz (qz).

Fig. 4. (a) Key elemental abundance patterns in magnetite and grunerite in BIFs from the 3.2 Ga Badampahar and 4.2 Ga Nuvvuagittuq belts. Error bars indicate percentage standard deviation from the mean. **(b)** Post Archean Australian shale (PAAS; Taylor and McLennan, 1985) normalized seawater-like rare earth element (REE) patterns of magnetite and grunerite in reference Badampahar and Nuvvuagittuq BIFs. **(c)** Y/Ho vs. Eu/Sm binary diagram to visualize hydrothermal vs. seawater contribution for BIF Fe mineral formation. (Data source: Mloszewska et al., 2012; Alibert, 2016; Muhling et al., 2023)

Figure 5 (a) Experimental solution with synthesized minerals in Teflon bottles. **(b-d)** synthesized greenalite, ferrihydrite and aragonite. **(e-h)** Characteristic XRD patterns of synthesized greenalite, ferrihydrite and mixed-valent minerals. **(i)** Fe K-edge XANES spectra of synthesized minerals along with standards and relevant published mineral data; # = data from Johnson et al. (2018). **(j)** XRD patterns of synthesized aragonite. **(k)** XANES pre-edge calibration curve of reference minerals in red circle with synthesized minerals in black square. HFO*=mixed valent Fe-(oxy)hydroxides.

Fig. 6. Time-resolved elemental distribution profile **(a-c)** of coprecipitation experiments. **(d)** Box and whisker plot displaying the distribution coefficients of Co, Ni and Zn for the synthesized greenalite, ferrihydrite and HFO*. **(e)** Enrichment of Co, Ni, and Zn in Fe silicates relative to Fe oxides in BIFs (orange line) and in experimental samples (blue line).

Co, Ni, and Zn data are normalized to Fe content of relevant minerals to account for variability associated precipitated Fe mineral concentration. Error bars indicate the percentage standard deviation from the mean.

Fig. 7. Schematic model of sequential greenalite and Fe-oxyhydroxides formation in the early ocean. Greenalite forms at stage I soon after hydrothermal pulsation, whereas Fe-oxyhydroxides forms later in stage II after most of the greenalite has already formed.

Table Captions

Table 1. Summary of experiments, compositions of solid phases and distribution coefficients (K_D).

Table 2. Elemental compositions of average Fe minerals in different BIFs and chert.

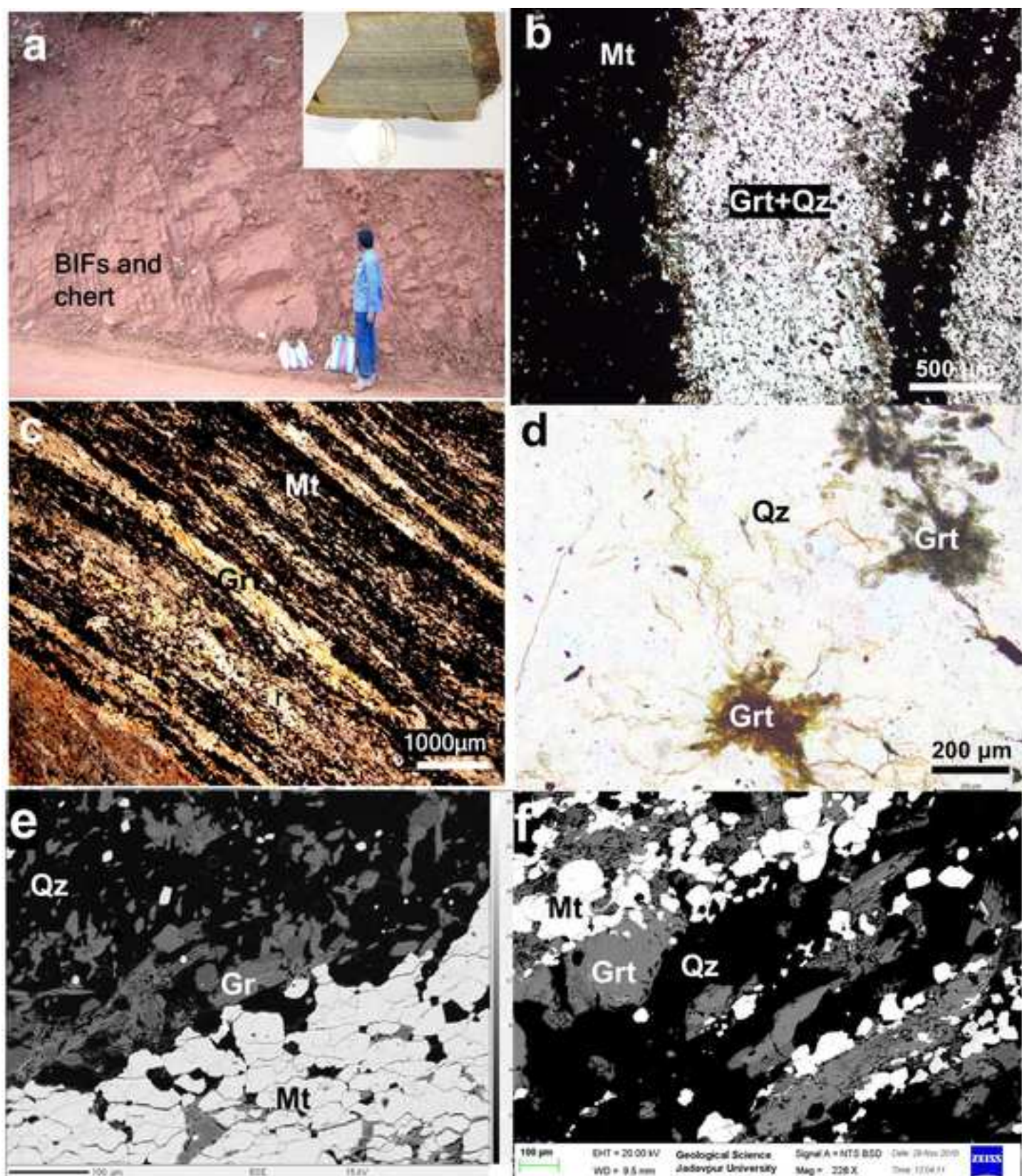
Table 3. Fe k-edge XANES spectra linear combination best fit results of experimental samples.

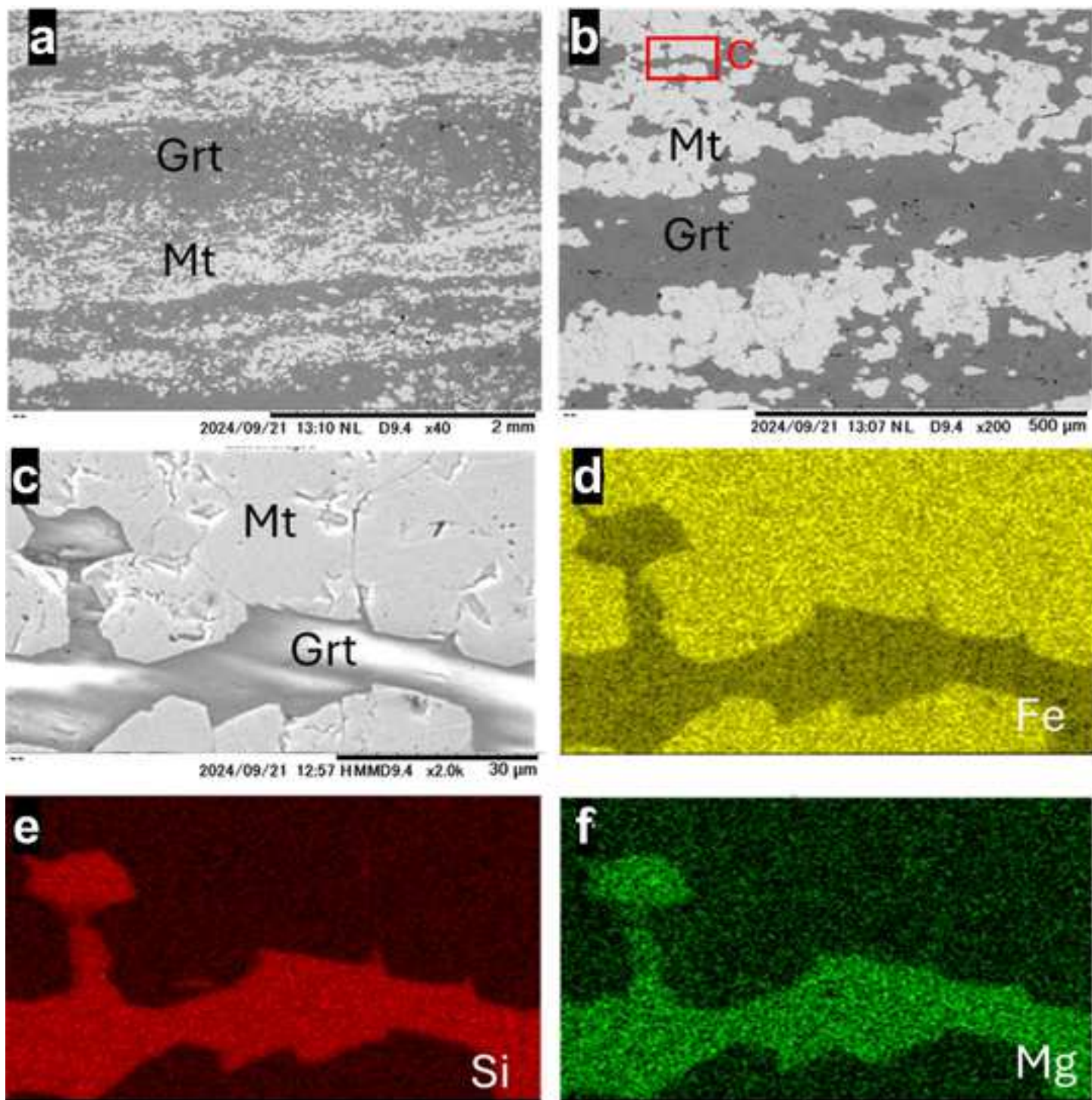
Table 4. Composition of ambient seawater calculated from average Archean BIF magnetite and Fe silicates. Full composition ranges are in bracket.

Supplementary Data

Supplementary data 1: Contains supplementary text S1, Figures S1-S5 and Table S1.

Supplementary data 2: Contains supplementary dataset as Tables 1-3.





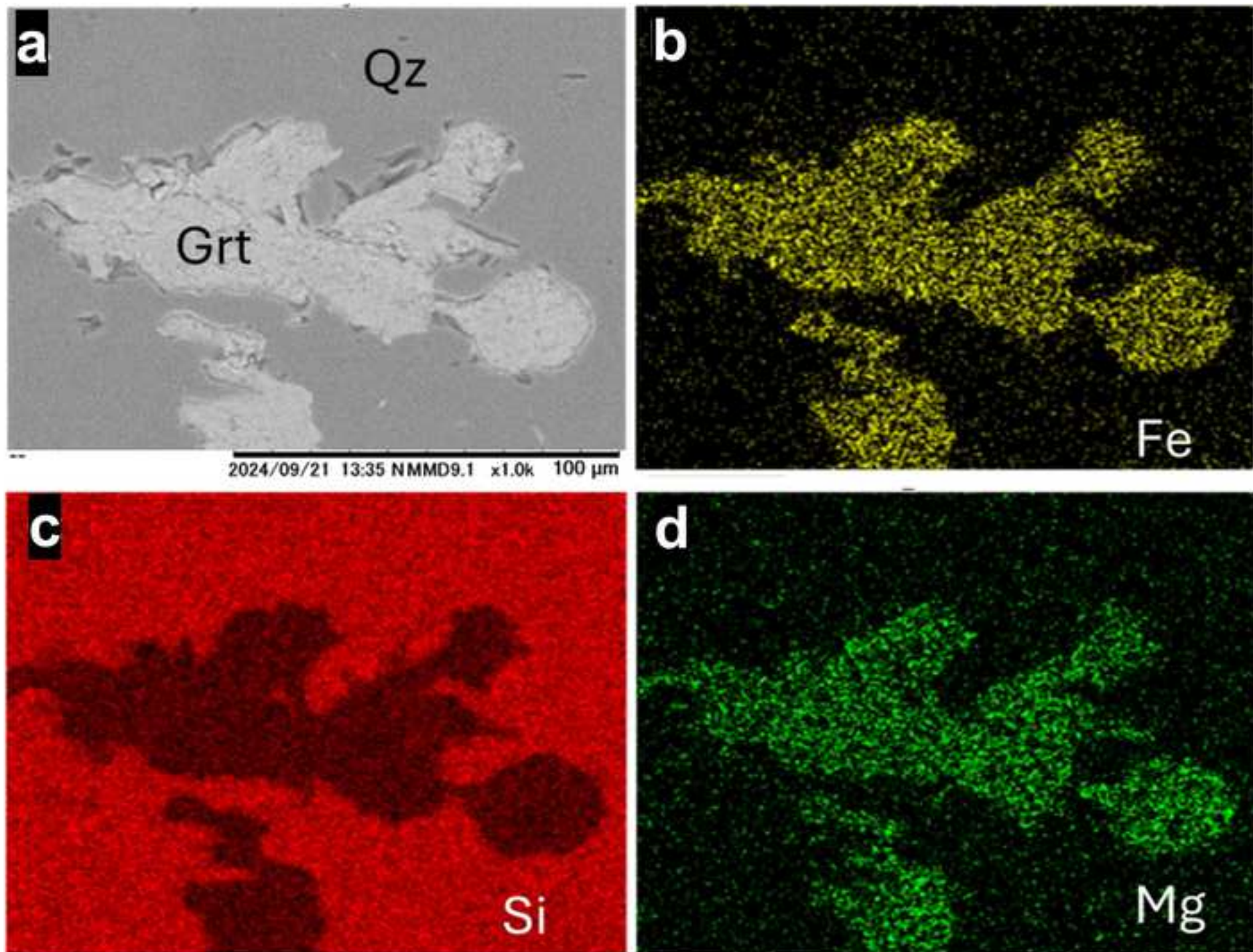


Fig 4

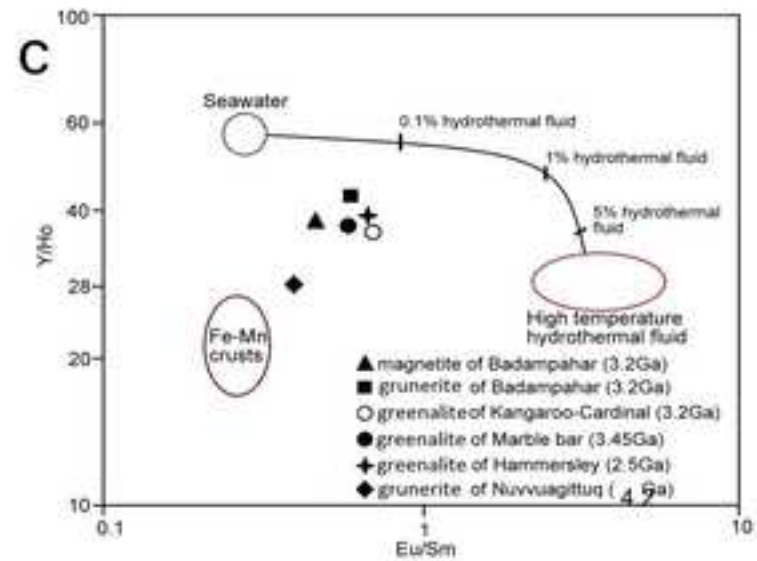
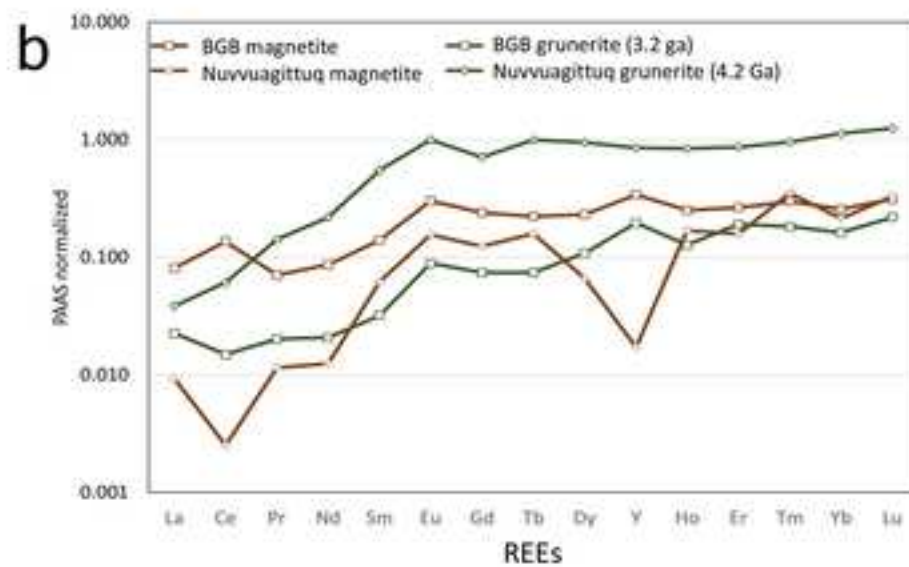
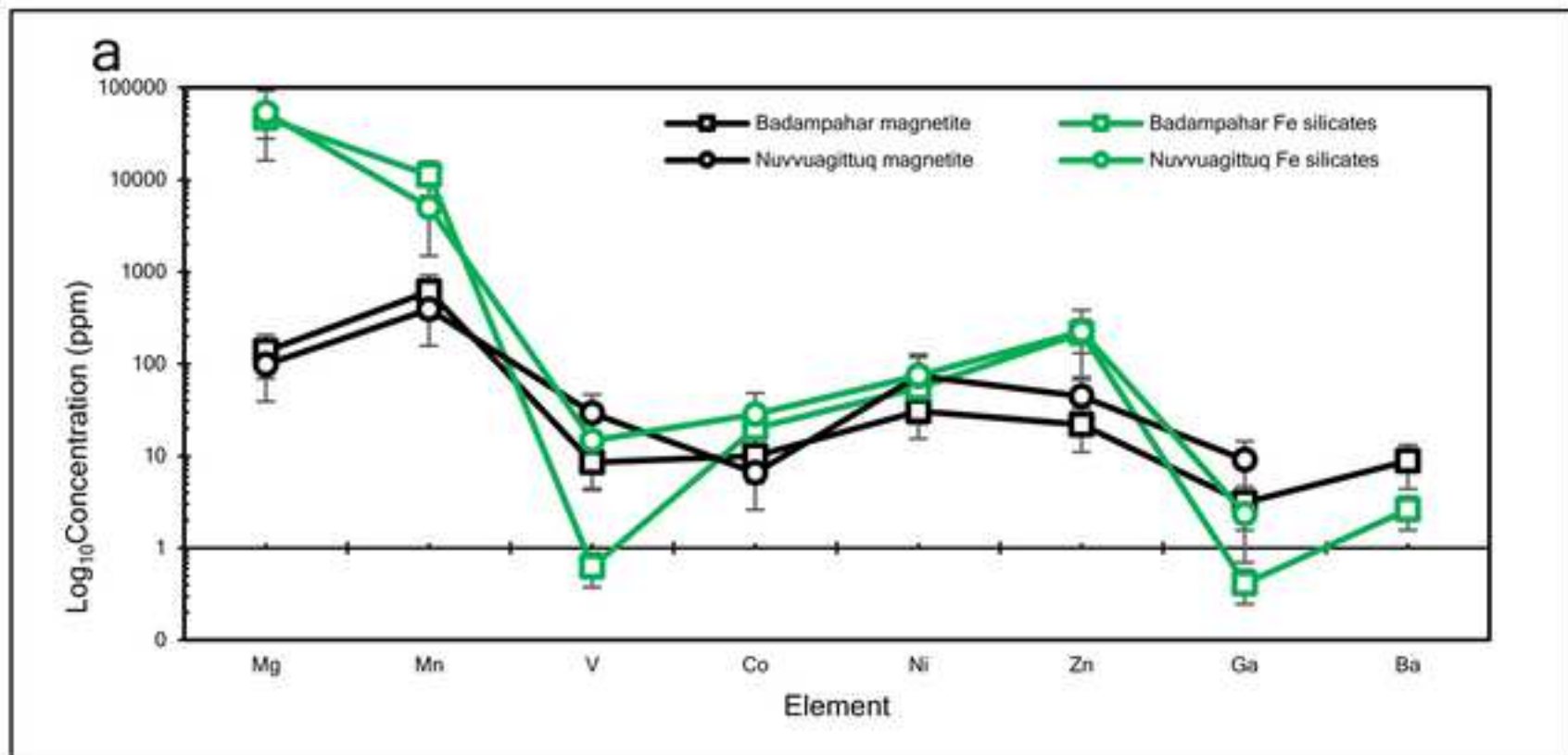


Fig 5

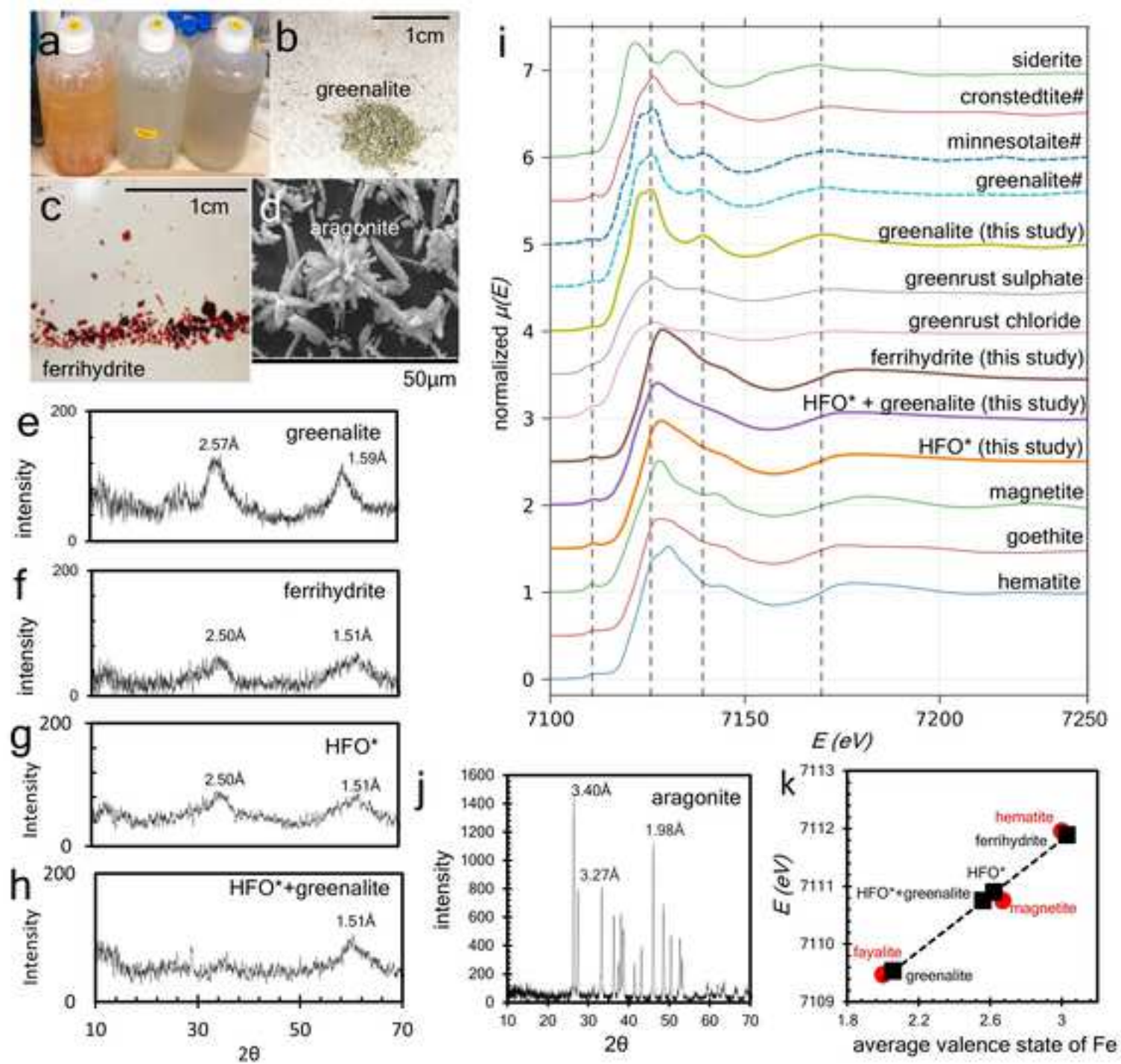
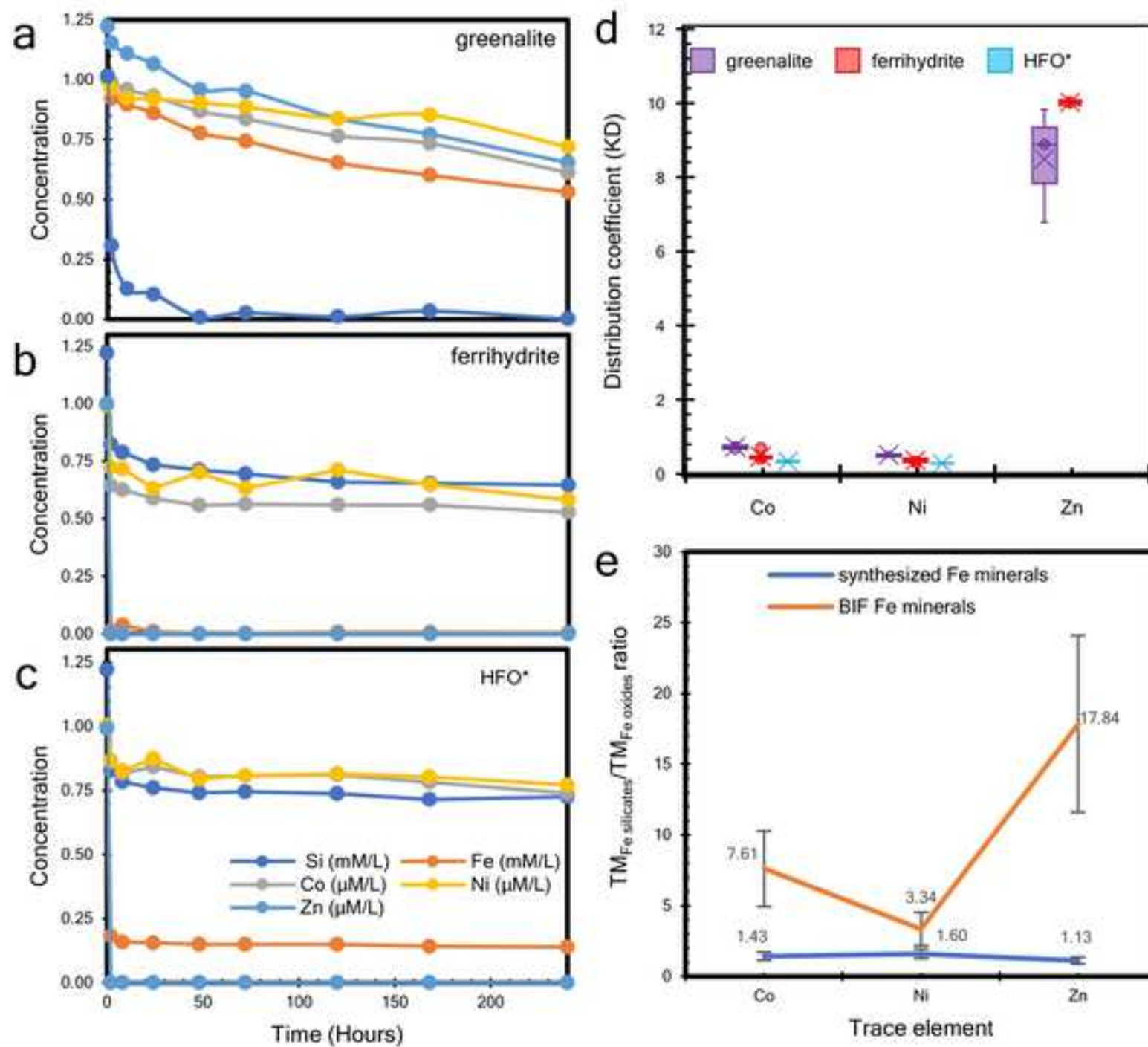


Fig 6



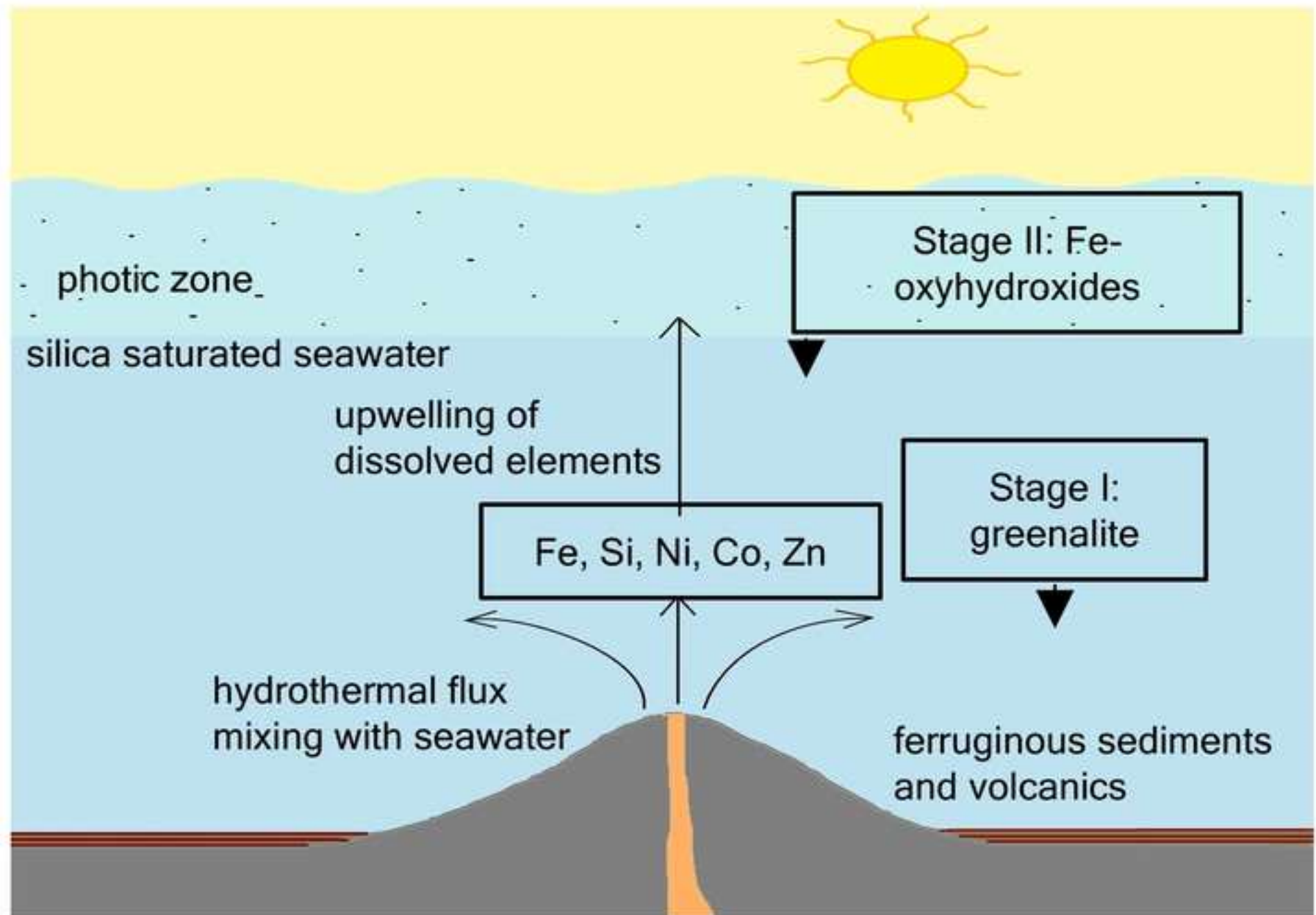


Table 1. Summary of experiments, compositions of solid phases and distribution coefficients (K_D).

Coprecipitation+adsorption experiments											
Experiment #	#1				#2				#3	#4	#5
Conditions:											
pH	7.8-7.5				7.8-7.5				7.8-7.5	7.8-7.5	7.8-7.5
T (°C)	25				25				25	25	25
oxygen	No				No				Yes	No	No
Fe redox state											
in starting solution	2				3				2	2.67	2.33
HCO ₃ (mM)	0	2	5	10	0	2	5	10	0	0	0
Replication	3	1	1	1	2	1	1	1	5	2	1
Compositions:											
Minerals formed	greenalite (+aragonite at 5-10mM HCO ₃)				ferrihydrite (+aragonite at 5-10mM HCO ₃)				ferrihydrite	Mixed valent HFO*	Mixed valent HFO* + greenalite
^{Co} K _D	0.736				0.474					0.334	0.558
^{Ni} K _D	0.506				0.359					0.276	0.389
^{Zn} K _D	8.53				10					nd	nd

nd: not determined.

TMK_D (distribution coefficient)= [(M_{TM})/[SW_{TM}], where M_{TM} is molar trace metal/Fe ratios in mineral and SW_{TM} is molar trace metal/Fe ratios in seawater.

Table 2. Elemental compositions of average Fe minerals in different BIFs and chert.

Minerals	Fe minerals in silicate-BIFs				Grunerite of BGB (3.2 Ga) chert	Greenalite of Kangaroo-Cardinal formations (3.2 Ga) ³ chert	Magnetite of Hammersley (2.5 Ga) ⁴ BIF
	Badampahar (3.2 Ga)		Nuvvuagittuq (4.2 Ga) ¹				
	Mt (n=134)	Grt±Act (n=86)	Mt (n=199)	Grt±Act (n=66)			
Metamorphic grade	Greenschist to lower amphibolite		Upper amphibolite		Greenschist to lower amphibolite	greenschist	sub-greenschist
(ppm)							
Mg	137	46503	98.0	53839	71033	31254	1917
Mn	612	11189	391	4972	1167	6356	155
P	101	2.95	nd	nd	1.77	434	338
V	8.47	0.626	29.0	14.7	406	6.69	3.25
Co	9.98	20.0	6.53	28.3	20.7	20.6	1.91
Ni	30.8	54.7	74.1	74.7	151	72.7	10.02
Zn	21.9	216	44.6	224	305	196	15.04
Ga	3.11	0.411	9.00	2.33	58	-	-
Ba	8.78	2.60	nd	nd	4.08	123	24.19
Zr	0.226	1.11	0.620	1.39	0.087	2.79	2.30
Hf	0.028	0.293	0.403	0.116	-	-	1.22
Ta	0.035	0.056	0.265	0.202	0.006	-	-
Th	0.097	0.646	0.146	0.160	0.001	-	0.40

Mt=magnetite; Grt=grunerite; Act=ferroactinolite; SN=shale normalized (Taylor and McLennan, 1985); nd=not determined

¹ Nuvvuagittuq greenstone belt; Mloszewska et al. (2012)

² Badampahar greenstone belt; Ghosh and Baidya (2017)

³ Kangaroo caves and Cardinal formation; Muhling et al. (2023); recalculated to standard greenalite composition having 42 wt. % Fe.

⁴ Dales Gorge, Hammersley Supergroup; Pecoits et al. (2009)

Table 3. Fe k-edge XANES spectra linear combination best fit results of experimental samples.

Average Fe redox state	2	3	2.62	2.55
Mineral standards (wt. %))				
hematite	0	0.664	0.256	0
goethite	0	0.164	0.439	0.028
ferrihydrite	0	0.166	0.334	0.134
magnetite	0	0	0	0
green rust-Cl	0	0	0	0
green rust-SO ₄	0	0	0	0
green rust-CO ₃	0	0	0	0
greenalite	0.962	0	0	0.205
cronstedtite	0	0	0	0.039
siderite	0	0	0	0
HFO*	X	X	X	0.577
Total	0.962	0.994	1.029	0.982
Identified mineral	greenalite	aged ferrihydrite	HFO*	HFO*+greenalite

Table 4. Composition of ambient seawater calculated from average Archean BIF magnetite and Fe silicates assuming 1mM dissolved Fe in seawater. Full composition ranges are in bracket.

Reference samples	Reconstructed Archean seawater chemistry					
	Nuvvuagittuq BIFs (4.2 Ga) ¹		Badampahar BIFs (3.2 Ga) ²		Kangaroo-Cardinal chert (3.2 Ga) ³	Archean BIFs
	magnetite	grunerite	magnetite	grunerite	greenalite	magnetite
Co (nM)	19.5 (2.1-144)	133 (49.3-260)	29.7 (15.2-55.6)	94.2 (49-154)	63.2	nd
Ni (nM)	287 (141-961)	513 (246-1027)	119 (54-263)	376 (113-899)	325	200-400 ^a
Zn (nM)	5.26 (1.76-24.4)	82.1 (36.9-234)	2.58 (1.14-6.56)	78.9 (38.7-116)	46.7	~10 ^b

¹Nuvvuagittuq greenstone belt, Canada (Mloszewska et al., 2012)

²Badampahar greenstone belt, India (current data)

³Kangaroo Caves and Cardinal formation, Australia (Muhling et al., 2023)

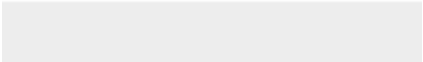
^aKonhauser et al. (2009)

^bRobbins et al. (2013)

'nd' = not determined.



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