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ABSTRACT

Iron formations (IF) were widely deposited in the Archean Eon and Palaeoproterozoic Era and hold potential as an archive of marine biogeochemistry. However, reconstructions are challenging due to their fine-grained nature and complex mineralogy. Recent work has identified greenalite, an Fe(II)-silicate mineral, as an abundant, primary phase in IF. Several depositional mechanisms have been proposed for greenalite precipitation, spanning hydrothermal vent systems and shelf environments. We report new in situ rare earth element and yttrium (REY) data from greenalite in the Palaeoproterozoic Kuruman Iron Formation from the Transvaal Supergroup, South Africa. We use a new approach, cutting samples parallel to banding to expose concentrated greenalite and developed a methodology to quantify the proportion of greenalite in each ablation crater. Greenalite consistently shows heavy REE enrichment (Yb_{SN}/Nd_{SN} 4–21), a small positive Eu anomaly (~1.41), super-chondritic Y/Ho ratios (32–43), and low \sum REE (1.4–13.1), consistent with formation in a shelf environment. While greenalite may have been an abundant precipitate in vent settings, at least some of the greenalite preserved in the rock record formed directly on the shelf. This necessitates another trigger for its formation, which may have included small amounts of Fe³⁺, local increases in pH, or warmer oceans. Our findings suggest that greenalite could provide a valuable archive of local seawater chemistry.

1. Introduction

Iron- and silica-rich chemical sediments (iron formation; IF) are abundant in Archean and Palaeoproterozoic rocks, but their origin remains enigmatic. They are typically characterized by a diverse mineralogy and include both Fe(II) and Fe(III)-bearing minerals (Klein, 2005). Biological or abiotic redox processes may have played an important role in the generation of ferric minerals in banded IF (Johnson et al., 2008). Conventional models proposing the genesis of IF emphasize poorly crystalline ferrihydrite (Fe(OH)₃), which persists as fine-grained "dusty" hematite, as a central component of the depositional model (Konhauser et al., 2017; Sun et al., 2015). Green rust, a mixed-valence Fe(II)-Fe(III) hydroxide, has also been proposed as an important primary phase (Halevy et al., 2017). In this model, Fe(II)-bearing minerals formed during anoxic diagenesis, fuelled by the degradation of organic carbon.

Emerging models challenge this view by proposing that Fe(II)bearing minerals were the principal primary precipitates (Rasmussen et al., 2021). This model is supported by high-resolution imaging that has revealed abundant primary Fe(II)-silicate minerals such as greenalite in IF (Johnson et al., 2018; Rasmussen et al., 2017, 2015). Some proponents have even argued that all hematite in IF is a product of late-stage alteration by oxygen-bearing fluids (Rasmussen et al., 2016, 2014). This perspective raises a number of possibilities, such as the complete absence of O_2 before the Great Oxidation Event (GOE) around 2.43 Ga (Gumsley et al., 2017), which would have far-reaching consequences for the timing of the origin of cyanobacteria and the interpretation of geochemical proxy records. However, current evidence for these two depositional models is mixed, and it is possible that ferric minerals contributed to primary IF (e.g., Sun et al., 2015). Nevertheless, geological evidence underscores the importance of greenalite as a primary phase in these rocks (Rasmussen et al., 2021).

The key question arises: what triggered the precipitation of greenalite? One possibility is that greenalite precipitated in a shallow-water shelf environment. Several triggers for greenalite precipitation have

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been proposed, such as a minor increase in pH (Rasmussen et al., 2017; Tosca et al., 2016). However, greenalite precipitation at ambient temperature requires pH >7.5, and models predict that the average pH in Archean oceans was 6.7-7.0 (Krissansen-Totton et al., 2018). Recent work has shown that the presence of small amounts of Fe^{3+} could have facilitated the precipitation of well-ordered greenalite at the lower pH of 6.5–7 (Hinz et al., 2021). Another pathway for greenalite precipitation on the shelf is the aging of green rust (Halevy et al., 2017). An alternative model proposes that greenalite formed as hot hydrothermal fluids mixed with anoxic, sulfate-free seawater in and around vents, and was subsequently transported laterally and re-deposited on the shelf (Tosca and Tutolo, 2023). This is supported by experiments that show Fe (II)-silicate solubility decreases with temperature, which when extrapolated to the T-pH combinations typically found in vent systems, suggest rapid precipitation (Tostevin and Ahmed, 2023). The lateral transport of greenalite in plumes may have been aided by its relatively low density (Tosca and Tutolo, 2023). This hydrothermal model aligns with some chemical and sedimentological indicators from IF, such as low organic carbon content (Konhauser et al., 2017), and prominent Eu/Eu*

anomalies in bulk IF (Bau and Dulski, 1996).

One method to distinguish between these models for greenalite precipitation is using the relative abundance of rare earth elements and yttrium (REY) in greenalite, because hydrothermal fluids and seawater have distinct shale-normalized REY patterns. Here, we present new mineral-specific REY data from natural greenalite in micro-banded IF from the Transvaal Supergroup, South Africa using laser ablationinductively coupled plasma-mass spectrometry (LA-ICP-MS). Obtaining greenalite-specific data is challenging due to the very fine grain size, low abundance, and fine-grained intergrowths with other minerals. To address this, we strategically cut samples parallel to greenalite-rich micro-bands, maximizing the density of exposed greenalite within a pure chert matrix. We confirmed the identity of greenalite through petrography, X-ray diffraction (XRD), electron probe microanalysis (EPMA), and scanning electron microscopy (SEM) - energy dispersive X-Ray spectroscopy (EDS). We developed a methodology in Matlab® R2019a to quantify the proportion of greenalite versus chert in the analysis area and extract the REY pattern of the greenalite endmember. Additionally, we conducted a comparative analysis of key features in our



Fig. 1. A: Regional setting of the Griqualand West Basin, Transvaal Supergroup, showing the location of the Gasesa drill hole. Modified from the 1:250 000 Geological Map of South Africa, Council for Geosciences, 2019. **B:** Log of the Gasesa drill core. Arrows indicate the positions of samples in this study. BIF = banded iron formation; GIF = granular iron formation.

REY patterns with those of bulk rock iron formation, limestone and other mineral-specific data from the Transvaal Supergroup, as well as the seawater and hydrothermal fluid endmembers to determine the origin of greenalite.

2. Geological setting

The ca. 2.67–2.05 Ga Transvaal Supergroup, situated within the Griqualand West and Transvaal basins on the Kaapvaal Craton (Fig. 1A), spans an area of around 250 000 km². The supergroup comprises diverse lithological assemblages of IF, carbonates, and siliciclastic sediments (Beukes and Klein, 1990), and has experienced peak greenschist facies metamorphism, making it suitable for palaeodepositional investigations (Miyano and Beukes, 1984). The Asbestos Hills Subgroup (~2.5 to 2.46 Ga; Gumsley et al., 2017), which includes the Kuruman and Griquatown Formations (Fig. 1B), hosts the main IF deposits within the Transvaal Supergroup. The Kuruman banded IF shows rhythmic micro-banding and sedimentary characteristics suggest it was deposited in an open-shelf environment below wave base, while the granular Griquatown Formation was deposited in a shallower marine environment (Beukes and Klein, 1990).

3. Methods and results

3.1. Identification of greenalite and mineral paragenesis

Samples for this study were sourced from the Gasesa drill core, which covers the entire Kuruman banded IF and most of the Griquatown IF. Greenalite imparts a dusty pale green colouration to chert layers, and we primarily targeted these laminae in search of greenalite. Samples where greenalite was present were first identified using XRD (Guggenheim et al., 1982) on bulk powders that integrated short intervals (<1 cm; Fig. S1). Samples where greenalite was identified were then prepared as thin sections, which were used to identify larger grains. However, greenalite is below the resolution of optical microscopy, so samples were cut from these sections and mounted in epoxy resin for SEM and BSE imaging using a Nova NanoSEM at the Chemical Engineering Department, University of Cape Town to enable the analysis of textural relationships and mineral paragenesis (fig. S2). The SEM was fitted with an Oxford Instruments XMax EDS, which was used for quantitative and qualitative chemical analysis of mineral grains using AZtec software from Oxford Instruments. The samples were observed and imaged at a 5.5 mm working distance and 20 kV accelerating voltage.

BSE images were used to ascertain the morphological properties of



Fig. 2. Images of samples used in this study from the Kuruman IF, Transvaal Supergroup. A & B: Drill core photos of greenalite-rich banded IF. C & D: BSE images of greenalite, minnesotaite, chert and calcite cut perpendicular to lamination. E - G: BSE images of samples cut parallel to a greenalite-chert laminae. These samples maximize exposure of the greenalite laths, which are suspended in chert and were used for LA-ICP-MS analysis. H - K: SEM-EDS spectra differentiating greenalite (Gre), minnesotaite (Mns), chert (Qz) and calcite (Cal).

minerals, while SEM-EDS provided information on their major element chemistry. Greenalite and minnesotaite have similar chemical compositions, but the former has a higher Fe/Si ratio and contains less Mg, reflected by its brighter appearance in SEM-BSE images (Fig. 2). SEM-EDS analyses can differentiate greenalite $[(Fe^{2+}, Fe^{3+})_{2-3}Si_2O_5(OH)_4]$ from minnesotaite $[(Fe^{2+}, Mg)_3Si_4O_{10}(OH)_2]$, both in terms of morphology and chemical composition (Fig. 2). For example, submicron grains with EDS spectra that show major O, Si and Fe, and minor Mg peaks, but no Al, Na or K peaks, were interpreted to be greenalite (Fig. 2H - K; Muhling and Rasmussen, 2020). Other common Fe-silicates can be excluded because they are associated with additional peaks, for example, stilpnomelane exhibits a K peak and riebeckite displays a Na peak. Morphologically, minnesotaite occurs as larger (5-20 µm long and 2–5 µm wide) 'bow-tie shaped' needles while greenalite laths are smaller (micron-scale) and occur as mottled aggregates. Further confirmation of the mineralogy was achieved with the aid of electron probe microanalysis (EPMA) at Utrecht University, Netherlands (Fig. S4).

Internal lamination in very thinly laminated chert (typical laminae <1 mm thick) is commonly defined by greenalite (Fig. 2A-D). Greenalite is extremely fine-grained, occurring as laths, $<1 \mu m$ in width and $\sim 2-7$ µm in length, which form dense aggregates, which may represent flocs of greenalite nanoparticles that formed in the water column (Rasmussen et al., 2013). The most common greenalite assemblages are chert-calcite-minnesotaite-greenalite, chert-minnesotaite-greenalite, chert-greenalite, and occasionally chert-greenalite-siderite (Fig. S2). In the chert-calcite-minnesotaite-greenalite assemblage, greenalite is cross-cut by calcite, which is in turn crosscut by minnesotaite, suggesting that these grains did not form in equilibrium, and that greenalite was the earliest forming phase (Fig. 2C-D). Experimental work indicates that the primary phase precipitated from seawater was an amorphous Fe (II)-silicate gel, which crystallized to greenalite during heating and burial (Hinz et al., 2023; Tosca et al., 2016; Tostevin and Ahmed, 2023). Since there is no direct evidence for this intermediate phase in the rock record, we refer to greenalite throughout this manuscript.

3.2. Laser ablation ICP-MS

Due to complex mineralogy of banded IF, trace element concentrations determined via dissolution ICP-MS on bulk rocks or micro-drilled horizons integrate multiple phases. Given the high abundance of REY in other phases, such as apatite and siderite, incorporation of even small volumes can skew the average REY trends (Alibert, 2016; Oonk et al., 2018). Laser ablation ICP-MS allows a much smaller region to be targeted in isolation (40 – 120 μ m), but the generally very fine grain size, low abundance, and fine-grained intergrowths of greenalite with other minerals make it challenging to obtain greenalite-specific trace element concentrations. To address this, we selected samples where greenalite is suspended in a pure chert matrix, to the exclusion of other minerals and cut samples parallel to micro-bands to expose the highest possible density of greenalite (Fig. 2E – G). We then made mounts for major and trace element analysis via LA-ICP-MS.

In-situ mineral-specific REY data were obtained by spot analysis using a 193 nm wavelength COMPex 102 ArF excimer LA system (Lambda Physik) connected to an Element 2 sector field ICP-MS (Thermo Scientific) at Utrecht University. The mass spectrometer was operated in low-resolution mode. LA-ICP-MS was performed with an energy density of 10 J/cm^2 and a pulse repetition rate of 10 Hz. Each analysis includes 60-70 s background measurement and 45 s sample signal measurement. The spot size (120 µm) was optimized to ensure that REY values were above the detection limit (sub-ppb). The ablation area was maximized, resulting in signal homogenization across a significant number of greenalite grains (Fig. 3). This approach was taken to enhance the material ablation rate, ultimately leading to improved detection limits, accuracy, and precision. The raw isotope data underwent reduction using a standardized trace element data reduction scheme in iolite v. 3.71 (Paton et al., 2011). ²⁹Si was used as an internal standard for greenalite, assuming 36.49 wt.%, a value constrained by microprobe analysis. Calibration was performed against NIST SRM 612, with results for secondary USGS standard BCR-2 G typically within 5%



Fig. 3. A: SEM-BSE micrographs of selected craters from in situ LA-ICP-MS analyses on aggregates of greenalite laths, Transvaal Supergroup, South Africa, with 120 μ m spot analyses. Greenalite appears white whereas chert is gray, and there are variable proportions of chert in each region. **B**: SEM-BSE image of a laser ablation crater showing a selected region (red circle) used to estimate the chert-to-greenalite proportion, alongside a histogram depicting the estimated proportion of greenalite (bright) to chert (dark) in the analysed area.

of published reference values taken from the GeoReM database (Jochum et al., 2005).

We analysed major elements (Fe, Mg, Si, Ca) and the rare earth elements and yttrium (REY). All REY patterns were normalized to Post-Archean Australian Shale (PAAS) using the values of Pourmand et al. (2012). Promethium does not occur in nature, so values were interpolated based on neighbouring elements. Anomalies such as $(Eu/Eu^*)_{SN}$ and $(Ce/Ce^*)_{SN}$, as well as Y/Ho and \sum REE were calculated using formulas recommended by Lawrence et al. (2006). Diagnostic (average) REY ratios and anomalies related to the lanthanide tetrad effect for IF greenalite are provided in Table S1.

3.3. Isolating the greenalite signal

For each of the three samples, every laser crater represents an independent analysis of a unique group of greenalite laths within a single layer. Targeted laser craters contained both greenalite and chert, but a customized code written in Matlab® R2019a (Mathworks Inc., Natick, MA, USA) allowed us to independently estimate the proportion of greenalite-to-chert around each laser ablation hole. We used SEM-BSE images of laser ablation craters to identify regions that provided an accurate representation of mineral proportions (Fig. 3A). Our code involved image pre-processing, including isolating regions of interest and smoothing the image. Selection of regions of interest was based on the laser analysis spot size and the distribution of minerals closest to the spot. We employed Otsu's method (Otsu, 1979) to automatically determine a global threshold for distinguishing chert and greenalite (dark and bright, respectively). This threshold was applied to segment the image into greenalite and chert, enabling the calculation of the proportions for each phase in the selected area (Fig. 3B). Colors, specifically white and grey, served as proxies for mineralogy in line with the grevscale nature of SEM-BSE images. It assumed a homogeneous average texture on a scale of 10-100 µm, and therefore the region around the crater is representative of the ablated area. The majority of the spots

contained >50% greenalite (Table S1). There is a strong positive correlation between the modelled% greenalite, Fe content and \sum REE in each analysis (Fig. 4), indicating that greenalite is the dominant host of REY and that our script to determine the proportion of greenalite is effective (see supplementary section 2).

3.4. Rare earth element data

The shale-normalized REY trends for greenalite (samples 349–59A and 349–59B) are highly consistent and indicate heavy REE (HREE) enrichment (Yb_{SN}/Nd_{SN} 4–21) with super-chondritic Y/Ho ratios (37.5 \pm 2.0) and low \sum REE (1.4 – 13.1 ppm) (Table 1 and S1, Figs. 4 and S5). They have positive (Eu/Eu*)_{SN} (= 1.41 \pm 0.19) and lack significant positive or negative Ce anomalies (Ce_{SN}/Ce_{SN}* = 1.15 \pm 0.18) or La anomalies (La_{SN}/La _{SN}* = 1.19 \pm 0.34) (Table 1 and S1). The overall

Table 1

Average and Standard Deviation of key REY anomalies in LA-ICP-MS data from the three samples in this study compared with averages for microbial carbonates of the Gamohaan Formation (Kamber and Webb, 2001) and bulk powders from the Kuruman Formation (Bau and Dulski, 1996) (_{SN}: Post-Archean Australian Shale - normalized).

Sample	∑REE	(Eu∕ Eu*) _{SN}	(Ce/ Ce*) _{SN}	(La/ La*) _{SN}	Y/Ho (mass ratio)	(Yb/ Nd) _{SN}
349–59A	5.6 \pm	1.4 \pm	1.1 \pm	$1.2 \ \pm$	$\textbf{38.0} \pm$	9.3 \pm
	0.8	0.1	0.1	0.3	1.7	1.8
349–59B	3.3 \pm	1.4 \pm	1.2 \pm	$1.2~\pm$	37.1 \pm	16.0 \pm
	0.4	0.2	0.2	0.4	2.3	3.3
351-66	6.6 \pm	1.7 \pm	1.2 \pm	1.6 \pm	35.2 \pm	8.3 \pm
	0.4	0.2	0.1	0.3	1.7	1.2
BIF	$8.7~\pm$	$1.9~\pm$	1.1 \pm	1.5 \pm	44.8 \pm	4.6 \pm
	5.3	0.5	0.1	0.2	4.9	1.0
Microbial	4.1 \pm	$2.0~\pm$	1.1 \pm	$2.0~\pm$	77.0 \pm	$2.2 \pm$
carbonates	2.0	0.4	0.1	0.3	13.9	0.5



Fig. 4. LA-ICP-MS REY data from the ~2.46 Ga Kuruman IF, Transvaal Supergroup. **A** – **C:** PAAS-normalised REY patterns from analysis of greenalite for three samples. The only other phase present in samples 349–59B was chert. Sample 351–66 contained greenalite, chert and minor siderite. **D:** cross-plot of \sum REE vs. wt.% Fe, determined by LA-ICP-MS. **E** – **F:** wt.% Fe and \sum REE, determined by LA-ICP-MS, vs. the% greenalite determined by Otsu's method. The black line (*y* = 0.45x) is the hypothetical Fe content of diluted greenalite. Fe content is overestimated by LA-ICP-MS (see supplementary discussion and comparison with EMPA data). In general, analyses with lower \sum REE represent ablation craters that contained a greater proportion of chert.

REY patterns for sample 351-66 are similar, despite the presence of minor siderite (Fig. S3), consistent with evidence that greenalite is the dominant phase and the host for the majority of REE (Fig. 4). However, the REY patterns in sample 351-66 are associated with slightly higher (Eu/Eu*)_{SN} and (La/La*)_{SN} (Table 1). Most of the analyzed craters contained >50 % greenalite (Fig. 4E-F and Table S1). We also analyzed the REY concentrations in greenalite-free chert (<5 % Fe-silicate), which were associated with lower \sum REE (0.67–1.28 ppm; Fig. 5; Table S1). As a consequence, much of the chert data, including Eu, were below the detection limit, resulting in an incomplete REY pattern (Fig. 5). As such, the chert REY signal has little impact on the weighted-average REY pattern or the calculated Eu anomaly, but when the chert component exceeded 40 % of the ablated crater, the drop in REE content can introduce some artefacts into the REY patterns. However, the REY patterns for greenalite-rich craters (<40 % chert) are highly consistent (Fig. 4A–C).

4. Discussion

4.1. A seawater origin for greenalite

In modern, well-oxygenated seawater, the typical REY distribution pattern includes a negative Ce anomaly, HREE enrichment, large positive Y anomalies, small positive La and Gd anomalies and no Eu/Eu* anomaly (Bau et al., 1995). Progressive enrichment in REE across the series is driven by increasing carbonate complexation at higher atomic number and is characteristic of seawater. While there is minor variation in seawater REE patterns driven by water mass mixing, and significant variation in Ce/Ce* in response to local redox conditions, the general shape and features are present globally and are distinct from other fluid sources. Furthermore, the non-redox sensitive aspects of seawater REE patterns are thought to have been conservative over Earth history (Shields and Webb, 2004). In contrast, hydrothermal fluids generally contain higher \sum REE and have a distinct REY pattern, with a flat or even light REE enriched shape and a large positive Eu anomaly (e.g., Eu/Eu* = 25, Bau and Dulski, 1999). Hydrothermal systems occur in diverse settings, including mid-ocean ridges, deep faults on continental margins, and brine systems in sedimentary basins, and due to differences in temperature and host rock, the fluids exhibit variable pH and chemical composition (Tivey, 2007). Some diversity is therefore expected in the REE composition of hydrothermal fluids both geographically and over

geological time. One distinct feature that is commonly present in hydrothermal fluids is the large Eu anomaly, because the highly reducing, high temperature conditions can drive the reduction of Eu^{3+} to Eu^{2+} (Bau and Dulski, 1999).

Our data show that greenalite is a significant host for REY. We assume that greenalite preserves primary geochemical signals for several reasons. Firstly, stratigraphic relationships here and in a range of other Archean and Palaeoproterozoic sediments suggest it was the earliest forming phase (Rasmussen et al., 2021). Secondly, greenalite is encased in early diagenetic chert, which could provide protection from alteration during burial (Rasmussen and Muhling, 2021; Tostevin and Sevgen, 2024). The location of the REY in the primary Fe(II)-silicate gel is not known, but if they are surface bound, they could be susceptible to re-equilibration during transport and settling over a period of weeks-months. This is less likely if the REY are structurally incorporated, as has been demonstrated for several other metals in Fe(II)-silicate (a precursor to greenalite; Tostevin and Ahmed, 2023). We assume uniform partition coefficients (K'_D) for all REY, and while this is broadly true for other authigenic minerals, such as carbonates (Webb and Kamber, 2000), REY partitioning behavior has not been explicitly tested for greenalite.

The most comparable data to ours come from Muhling et al. (2023), who analysed chert samples from a range of depositional settings that span 3.46 - 2.45 Ga. In the majority of samples, greenalite was present in low abundance (10 - 20 %). Many of their samples also contained apatite (1 %), fine-grained siderite, and in some cases, fine-grained hematite. These minerals can be important hosts for REE so inclusion of small amounts can skew average REY signals (Alibert, 2016; Muhling et al., 2023; Oonk et al., 2018). However, their results from the 2.483 Ga Colonial chert of the Mt McRae shale are greenalite-rich (Mitchell2-418 = 28% Fe; Fig. 6), and although the Ca content is high, the strong correlation between REE and Fe suggests greenalite is dominating the average REY signal. The REY pattern for this sample is comparable to our data (Fig. 6), with HREE enrichment (Yb/Nd = 9.94), \sum REE = 5.9 ppm, high Y/Ho ratios (48), small Eu anomalies (2.4), and no Ce anomalies (1.2). In contrast to our data, their results from the Colonial chert show a positive La anomaly $(La/La^* = 1.9)$ (Muhling et al., 2023). These largely comparable trends suggest a similar depositional environment across two different continental cratons. Interestingly, samples from the Marble Bar Chert, which formed in a volcanic exhalative setting, show a distinct REY signal with light REE enrichment and larger



Fig. 5. A: REY data for the greenalite end-member (>99% Greenalite) and greenalite-free chert (<1% Fe). B: Laser ablation crater for greenalite endmember (top) and a representative crater for the chert endmember (bottom), showing the homogeneous mineralogy.



Fig. 6. A and C: Comparison between greenalite (this study) and average bulk rock from IF (orange) and carbonate rocks (gray) in the Transvaal Supergroup (TS). References for Kuruman IF: 1 - Bau and Dulski (1996); 2 - Planavsky et al. (2010); 3 - Oonk et al. (2018). **B and D:** Comparison between greenalite (this study) and other mineral-specific data from the TS as well as chert and greenalite from Australian pre-GOE successions (Muhling et al., 2023). The average greenalite data is calculated from the analyses with >90% greenalite in the ablation area. **A and B:** Comparison of REY patterns using average data for each study. **C & D:** Comparison of (Eu/Eu*)_{SN} and \sum REE for the same samples, demonstrating that greenalite overlaps with the other phases. All data points from each study are plotted.

Eu anomalies (Muhling et al., 2023). This confirms that chemical sediments capture distinct REY trends when they form in vent proximal settings. By extension, chemical sediments formed in or around vent systems, which were subsequently transported to vent-distal shelf settings, would be expected to carry a similar signal, but this is not what we observe in greenalite from the Kuruman Formation.

The REY pattern of greenalite shows typical seawater features such as HREE enrichment and a large positive Y anomaly, but also includes a positive Eu anomaly (mean = 1.41). However, this is small compared with hydrothermal fluids (~25; Bau and Dulski, 1999). Furthermore, the overall patterns and Eu/Eu* overlap with data from bulk IF, which represent an integrated REY pattern from multiple minerals with diverse origins (Fig. 6). None of these minerals are proposed to have formed in hydrothermal vents, but rather on the seafloor or during early diagenesis. More significantly, our REY patterns are similar to microbial carbonate rocks from the Transvaal Supergroup, showing a similar range for many key features such as \sum REE, Ce/Ce*, Eu/Eu* and Yb/Nd. These minerals must have precipitated in shelf environments and are thought to preserve primary REY signals, so should capture the important features of marine REY at this time (Fig. 6B; Kamber and Webb, 2001;

Warke et al., 2020). While REY patterns from greenalite share many of the key features of bulk IF and carbonate rocks, HREE enrichment is more pronounced in greenalite. This could be because REE partition coefficients during carbonate precipitation gradually decrease across the series, resulting in relatively higher incorporation of the light REE, and dampening the magnitude of HREE enrichment relative to seawater (Webb and Kamber, 2000).

The presence of positive Eu/Eu* anomalies in a wide range of minerals in Archean and Palaeoproterozoic sedimentary rocks suggests that, in contrast to modern seawater, small positive Eu/Eu* anomalies were a ubiquitous feature of well-mixed seawater (e.g., Bau and Dulski, 1999; Kamber and Webb, 2001). This may be because hydrothermal fluxes are estimated to have been up to three times higher than the modern day, at 10^{14} Kg yr⁻¹, which may have resulted in higher hydrothermal contributions to the marine REY inventory. In addition, the anoxic nature of seawater may have transported Fe and REY from hydrothermal fluids over long distances as dilute plumes, imparting a hydrothermal over-print on shelf waters.

We conclude that small positive Eu anomalies in greenalite are consistent with a shelf origin. If greenalite precipitated directly as hot, hydrothermal fluids mixed with seawater in and around vent systems, we would expect to see a distinct REY signal with higher \sum REE, a flatter profile, larger (Eu/Eu^{*})_{SN} and light REE enrichment compared to other phases. We calculated the REY pattern anticipated under these conditions at a range of relevant mixing ratios (from 2:1 to 10:1 by mass; Tosca and Tutolo, 2023). Due to the considerably higher REY concentration in vent fluids, the solid retains the characteristic features of vent fluids (Fig. 7). Instead, our REY data support a seawater origin for greenalite and models that invoke precipitation on the shelf. To reproduce the Eu/Eu^{*} observed in greenalite, a dilution factor of 100,000:1 is required (Fig. 7). At this level of dilution, the water mass would be at ambient temperature and pH.

4.2. Redox conditions, pH and temperature in palaeoproterozoic shelf environments

If greenalite was forming on the shelf, then how was its precipitation triggered? Our REY data do not contain any significant positive or negative Ce anomalies. This indicates that greenalite formation occurred under anoxic conditions, which is to be expected in an Fe(II)-bearing mineral. However, experimental work has shown that greenalite precipitation occurs more rapidly in the presence of small amounts of Fe³⁺ (Hinz et al., 2021). Furthermore, natural greenalite commonly contains some Fe(III) in its structure, which has been interpreted to represent Fe^{3+} in ancient seawater (10–20%; Johnson et al., 2018). If this Fe(III) is primary, it could indicate formation close to the chemocline, where Fe could be oxidised by photochemical reactions, iron oxidizing bacteria, or free O2 generated by cyanobacteria. Our Ce/Ce* values do not preclude this scenario, as intermediate redox conditions may have been sufficient to oxidise Fe, but insufficient to initiate the oxidation of Mn and Ce. However, experiments that generated greenalite in the presence of Fe³⁺ produced a mineral assemblage containing magnetite and hematite, which differs from the greenalite-chert-minnesotaite-siderite assemblage in our samples (Hinz et al., 2021). Similarly, when Fe (II)-silicates are generated via in-situ Fe oxidation, they co-precipitate with ferrihydrite, which was not observed in our mineral assemblage



Fig. 7. Mixing between modern seawater (Alibo and Nozaki, 1999), with negative Ce/Ce* removed, and hydrothermal fluids (Bau and Dulski, 1999) at ratios anticipated in and around hydrothermal vent systems (Tosca and Tutolo, 2023) still produces a flat REY pattern dominated by a large Eu anomaly. To produce a REY pattern similar to greenalite, with an Eu/Eu* of 1.5, a mixing ratio of 100,000:1 is required.

(Hinz et al., 2023).

Given the sixth order dependency of greenalite precipitation on H^+ , pH exerts a major control on the precipitation rate of greenalite. The pH range required for greenalite nucleation is similar to the pH range of the modern ocean (Tosca et al., 2016). However, atmospheric CO2 is thought to have been higher in the Precambrian to maintain a clement climate under a faint young sun (Sheldon, 2006). All else being equal, this would have contributed to a lower oceanic pH. Geochemical estimates based on the presence or absence of sulfate evaporites would place seawater at pH 8 or less (Grotzinger and Kasting, 1993). Independent constraints derived from calcium isotope ratios in sedimentary carbonate rocks, assuming a marine Ca^{2+} concentration of 10 – 135 mmolKg⁻¹, place an upper limit on marine pH of <7.8 when pCO₂ is constrained by a palaeosol estimate, and <7.1 when pCO₂ is modelled based on the faint young sun hypothesis (Blättler et al., 2017). Statistical models suggest pH generally increased over geological time and give a 95% chance that pH was <8 at 2.5 Ga (Halevy and Bachan, 2017). Using these constraints, conditions in most of the ocean would not have been conducive to rapid greenalite nucleation. Constraints from carbon cycle models suggest ocean pH was 7.0 at the Archean-Proterozoic boundary, which would have suppressed greenalite precipitation altogether (Krissansen-Totton et al., 2018). The calculated pH range for early seawater is highly dependent on the proportion of CO₂ vs. methane in the early atmosphere, and so a methane-rich greenhouse could allow for a seawater pH that was higher than current models suggest. In addition, elevated pH levels in localized environments, driven by upwelling alkaline water masses or anaerobic respiration of organic carbon, may not be accurately represented in global ocean models (Bergmann et al., 2013; Higgins et al., 2009).

Alternatively, warmer average temperatures in early oceans may have facilitated Fe(II)-silicate precipitation at lower pH. Oxygen isotope records in chert, carbonate and phosphate display an increasing trend over time, which represents a combined record of seawater $\delta^{18}O_{H2O}$ and temperature, as well as potential diagenetic overprinting. Deconvolving these variables in challenging, but if we assume that $\delta^{18}O_{H2O}$ has remained constant over Earth history, seawater temperatures in the Archean Eon and Palaeoproterozoic Era are estimated to have exceeded 70 °C (McGunnigle et al., 2022; Robert and Chaussidon, 2006). Given the temperature dependence of the solubility product of Fe(II)-silicate, this could facilitate precipitation at lower pH (Tostevin and Ahmed, 2023). We use a numerical model to explore this, assuming an Fe²⁺ concentration of 0.1 to 1 mmolKg⁻¹ (Jiang and Tosca, 2019) and a dissolved Si concentration of 2 mmolKg⁻¹. Under these conditions, pH as low as >6.2 to >6.7 could facilitate rapid precipitation of Fe(II)-silicate minerals at 70 °C (Fig. 8). This suggests that seawater would have been sufficiently alkaline to support widespread Fe(II)-silicate precipitation, particularly in low latitude surface waters.

5. Conclusions

We show that well-preserved greenalite in Palaeoproterozoic chert precipitated from seawater in shelf environments, potentially triggered by small changes in pH. The similarity between our data and greenalitechert data from the Colonial Chert Member of the Mt McRae shale in Western Australia suggests that a shelf origin for greenalite preserved in chert was widespread. However, this does not preclude the formation of greenalite in other settings. It is possible that large quantities of greenalite precipitated around hydrothermal vent systems but were rarely transported to the shelf and preserved in the geological record. This would be analogous to many minerals today, such as pyrite, which have diverse origins and precipitate both at hydrothermal vents and in shelf sediments. The preservation of primary REY patterns in chert-hosted greenalite, potentially safeguarded by early silicification, makes this archive a promising candidate to capture other primary geochemical signatures, such as metal contents and isotopes.

CRediT authorship contribution statement

Ansahmbom Y. Nke: Writing – original draft, Visualization, Software, Project administration, Methodology, Investigation, Formal



Fig. 8. Modelled relationship between Fe^{2+} activity and pH at which Fe(II) silicate nucleation will occur for a given temperature (dashed lines), based on experimental constraints on the solubility product at a range of temperatures (Tostevin and Ahmed, 2023). The system has a salinity (S) of 35 g.kg⁻¹ and dissolved silicate concentrations are set by the saturation of amorphous SiO₂. An estimated Fe^{2+} concentration for Precambrian seawater of 0.1–1 mmol.kg⁻¹ (Jiang and Tosca, 2019), suggests that at 70 °C, Fe(II)-silicate minerals could precipitate at pH of 6.2 to 6.7.

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Declaration of competing interest

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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Data availability

Data are available in the online Excel file associated with this article

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Supplementary materials

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