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Insights from modern diffuse-flow hydrothermal systems into the origin of post-GOE deep-water Fe-Si precipitates

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Abstract: Post-GOE deep-water Fe-Si precipitates associated with volcanogenic massive sulfide deposits are an important feature of the Proterozoic rock record. Although it is clear that these enigmatic deposits formed in oxygen-deficient and hydrothermally influenced deep-water settings, the oxidation mechanism(s) resulting in their precipitation remain(s) unclear. Whilst existing genetic models typically couple direct and/or bacterially-mediated iron oxidation with abiotic silica precipitation, low temperature diffuse hydrothermal fluids offer a potential mechanistic alternative to explain the observed layering. Herein, via combination of petrographic observations with elemental and isotopic data (Fe, Si, and O), we explore the genesis of the primary mineral phases present within recent Fe-Si precipitates obtained from the Southwest Indian Ridge. Formation of ferrihydrite and opal-A in these precipitates provides insight into the genesis of widely invoked precursor minerals to post-GOE deep-water Fe-Si precipitates. Specifically, we find that the mineralogical layers that typify these Fe-Si precipitates may have originated via biologically mediated ferrihydrite precipitation and abiotic precipitation of opal-A from oversaturated fluids during diffuse flow. By analogy, we propose that diffuse hydrothermal fluid flow played an important role in the formation of post-GOE deep-water Fe-Si precipitates.

Key Words

Iron Formation, Fe-Si Precipitates, Diffuse Hydrothermal Flow, Iron Isotopes, Silicon Isotopes

1. Introduction

The Great Oxidation Episode (GOE) at ~2.43–2.06 Ga corresponds to a protracted period of fluctuating atmospheric oxygen levels that ultimately resulted in the permanent rise of atmospheric O_2 to appreciable concentrations (e.g., Bekker et al., 2004; Lyons et al., 2014; Gumsley et al., 2017; Poulton et al., 2021). After the GOE, the redox state of Proterozoic deep waters is debated, and likely varied in space and time between anoxic ferruginous and suboxic conditions (Slack et al., 2009; Poulton et al., 2010; Planavsky et al., 2011; Little et al., 2021). Some Fe-Si precipitates, such as deep-water iron Formations (IFs) and jaspers deposited in volcanically influenced marine settings in association with volcanogenic massive sulfide deposits, have been used to inform on the prevailing seawater chemistry and background redox conditions (e.g., Grenne and Slack, 2003a; Slack et al., 2007, 2009; Bekker et al., 2014). Filamentous microstructures, interpreted as iron-oxidizing bacteria, have also been observed in some jasper deposits (Duhig et al., 1992; Juniper and Fouquet, 1998; Grenne and Slack, 2003b; Slack et al., 2007; Dodd et al., 2017; Little et al., 2021). Slack et al. (2007) and Little et al. (2021) suggested a suboxic or weakly oxygenated deep-ocean redox state at ~1.7 Ga based on petrological and geochemical study of IFs and jaspers. Thus, deep-water IFs and jaspers represent an important sedimentary archive for inferring the redox state of deep seawater after the GOE.

Algoma-type IFs, which are deep-water Fe-Si precipitates and one of two dominant types of IF, represent a hydrothermally-associated deep-water lithotype that features characteristic banding defined by alternations between iron- and silica-rich layers (e.g., Bekker et al., 2010, 2014; Konhauser et al., 2017). Numerous studies have proposed different potential depositional models for pre-GOE Algoma-type IFs (reviewed in Bekker et al., 2014). The prevalent depositional models infer “ferrihydrite rain” to the seafloor, with ferrihydrite formed in the seawater via different oxidation processes (Bekker et al., 2014; Konhauser et al., 2017). Sinking ferrihydrite particles would scavenge dissolved Si from seawater to form an Fe-Si gel before reaching the seafloor (Konhauser et al., 2017). However, there has been limited research on post-GOE Algoma-type IFs, and the origin of the iron- and silica-rich bands in these younger Algoma-type IFs remains unclear. In particular, since most post-GOE Algoma-type IFs developed in anoxic deep-water basins (Bekker et al., 2014), the mechanism(s) that drove iron precipitation, ultimately resulting in laminae with high concentrations of hematite (Fe_2O_3) and/or magnetite (Fe_3O_4), have proven particularly difficult to unravel.

A conventional explanation invokes the oxidation of aqueous ferrous iron upon mixing between hydrothermal fluid and seawater, resulting in precipitation of poorly crystalline ferrihydrite ($5Fe_2O_3{\cdot}9H_2O$; e.g., Bekker et al., 2014). This model, however, neglects the lability of ferrihydrite, which, upon transit through a ferruginous water column, would be expected to either undergo conversion to another mineral phase (e.g., green rust or magnetite; Zegeye et al., 2012; Halevy et al., 2017; Li et al., 2017) or be reduced to aqueous ferrous iron upon reaction with dissolved organic carbon and/or other reductants. Indeed, the transformation of ferrihydrite to green rust, a known magnetite precursor, has been observed in a modern ferruginous water column (Zegeye et al., 2012). Hence, while water column oxidation has the potential to explain the presence of magnetite, it cannot readily account for the high concentrations of hematite observed in Algoma-type IFs, nor can it provide an explanation for closely associated magnetite and hematite banding often observed within the same sections of IFs.

Contrasting models have also been proposed to explain the silicon enrichment in Algoma-type IFs (Posth et al., 2008; Konhauser et al., 2017; Schad et al., 2019), with the most critical explanations informed by Si isotope datasets (Bekker et al., 2014; Konhauser et al., 2017). The Si isotope difference between IF-hosted cherts and other Precambrian Fe-poor cherts has been used to argue for primary precipitation of IFs as an Fe(III)-Si gel (Grenne and Slack, 2003a, 2005; Bekker et al., 2014; Konhauser et al., 2017). Nevertheless, consensus regarding the mechanism responsible for producing alternating layers of Fe- and Si-rich minerals in post-GOE Algoma-type IFs has not been reached.

Although the utility of contemporary hydrothermal Fe-Si precipitates as modern analogues for IF deposition is debated (Bekker et al., 2010, 2014; Moeller et al., 2014; Sun et al., 2015; Konhauser et al., 2017; Rouxel et al., 2018), these chemical precipitates certainly display features that could provide valuable insight into the genesis of similar features in post-GOE, deep-water Fe-Si precipitates (Moeller et al., 2014; Sun et al., 2015; Rouxel et al., 2018). In modern hydrothermal settings, Fe-Si-precipitates are thought to form progressively via precipitation from high-temperature hydrothermal plumes as they disperse from the vent site (focused flow; German and Seyfried, 2014; Rouxel et al., 2016) or, alternatively, in association with microbial mats as low-temperature fluids emerge from the subsurface (diffuse flow; Sun et al., 2015; Rouxel et al., 2018). While focused flow is frequently implicated in genetic models of modern Fe-Si precipitates (Sun et al., 2015; Rouxel et al., 2018), diffuse flow has received far less attention. Nonetheless, total chemical fluxes (CH_4, CO_2, H_2 and dissolved Fe) and heat flow associated with modern low-temperature diffuse flow are of at least equal magnitude to those associated with high-temperature focused flow (Schultz et al., 1992; Elderfield and Schultz, 1996; Wankel et al., 2011). Thus, a better understanding of the origin of Fe-Si deposits in modern diffuse-flow hydrothermal settings is critical for evaluating hypotheses concerning the origin of post-GOE deep-water Fe-Si precipitates (i.e., deep-water IFs and volcanically influenced jaspers) and the wider significance of their geochemical archives.

Iron, silicon and oxygen are all major elements in hydrothermally precipitated chemical sediments. Accordingly, the isotopic compositions of these elements serve as important geochemical tracers, capable of elucidating the depositional setting, prevailing environmental conditions and the specific depositional mechanisms active within a given setting. Employing a multi-isotope (Fe, O and Si) approach, combined with petrographic and elemental abundance data, here we examine the origin of a suite of Fe-Si precipitates recovered along the Southwest Indian Ridge (SWIR; Fig. 1). These data are then used to evaluate the mechanisms responsible for Fe and Si precipitation in these modern deposits and, by extension, the origin of the Fe- and Si-rich mineral banding preserved in older post-GOE deep-water Fe-Si precipitates. Importantly, we stress that the implications of this study are restricted to a subset of post GOE, deep-water Fe-Si precipitates such as the 1.7 Ga jasper and IFs of central Arizona, USA (Slack et al., 2007; Little et al., 2021), and are not necessarily relevant to all large VMS deposits associated with Fe-Si exhalates. Accordingly, we caution against the over-zealous application of a unifying model.

2. Geological setting and sampling strategy

The Southwest Indian Ridge (SWIR) intersects the Mid-Atlantic and American-Antarctic Ridges at the Bouvet Triple Junction, as well as the Central Indian Ridge and the Southeast Indian Ridge at the Rodriguez Triple Junction (Fig. 1). The SWIR formed after the breakup of Gondwana and the eventual separation of the African and Antarctic tectonic plates during the Late Cretaceous. Among the world's slowest spreading ridges, with a spreading rate of ~14 mm year^{-1} along most of its length (German et al., 1998; Tao et al., 2012), hydrothermally active fields are limited along the SWIR and only eight extant hydrothermal fields have been identified (Tao et al., 2012, 2014).

Data for twenty-three Fe-Si precipitates, combined with contextual data derived from associated sediments and sulfides obtained in proximity to the hydrothermally active SWIR, are presented herein. These samples were collected from three separate hydrothermal fields — Longqi, Duanqiao and Tiancheng — by TV-guided grab sampling as part of expedition DY115-20 conducted by R/V *DaYang YiHao* (October 2008 to March 2009).

The Longqi hydrothermal field (37°47'S, 49°39'E; Table S1) marks the intersection between small ridge-housed non-transform faults and the main mid-ridge rift fault, manifest as a dome on the southeast slope of the axial rift at 2755 m water depth (Fig. 1; Table S1). Here, basalt and oceanic core complexes were observed without sediment cover, and abundant detachment faults offer potentially important conduits for focusing hydrothermal circulation (Tao et al., 2012, 2014). The Longqi hydrothermal field, with high-temperature active vents, features abundant sulfide chimneys and massive sulfide deposits, supporting complex and dense hydrothermal communities comprising scaly-foot gastropods and stalked barnacles, among other large epifauna (Tao et al., 2012; Chen et al., 2015). Six samples, from three stations, were collected from the Longqi hydrothermal field.

The Duanqiao hydrothermal field (37°39'S, 50°28'E; Table S1) is located on the ridge axis at a water depth of 1700 m (Fig. 1). No temperature or turbidity anomalies were observed within the Duanqiao field, implying the absence of high-temperature hydrothermal activity. Indeed, ^{230}Th/^{238}U dating of Duanqiao massive sulfides and chimney precipitates places the termination of hydrothermal activity about 700 years ago (Yang et al., 2017). Within the Duanqiao field, thirteen samples were collected from five separate stations, displaying variable morphology and structure (Tao et al., 2012, 2014).

The Tiancheng hydrothermal field (27°57'S, 63°33'E; Table S1) is located between the Melville transform fault on the SWIR and the Rodriguez Triple Junction (Fig. 1). The mid-ridge rift has an average water depth of 4730 m, representing the deepest part of the SWIR. Both temperature and turbidity anomalies were detected, which, together with abundant hydrothermal mussels, demonstrates contemporary hydrothermal activity (Tao et al., 2012, 2014). Two samples, from two stations, were collected from the Tiancheng hydrothermal field.

3. Methods

3.1. X-Ray Diffraction, Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectrometry

Samples were dried at ~60°C and ground to < 74 µm using an agate pestle and mortar. X-ray diffraction analysis was performed using an X-ray diffractometer (D/max2550VB3, Rigaku Corporation, Tokyo, Japan) with Cu K-α radiation (35 kV, 30 mA). Diffraction angles (2θ) corresponding to the unique crystal structure of each mineral phase were measured during a 50 second scan time at a resolution of 0.02°.

For scanning electron microscopy, dried subsamples were fixed onto aluminum stubs with two-way adhesive tabs and allowed to dry overnight. These were then sputter-coated with gold for 2–3 minutes prior to analysis. All samples were examined using a Philips XL-30 scanning electron microscope (SEM) equipped with an EDAX energy-dispersive X-ray spectrometer (EDS) at the State Key Laboratory of Marine Geology, Qingdao, China. The SEM was operated at 15 kV, with a working distance of 10 mm, providing optimum imaging capability while minimizing sample charging. To obtain sufficient X-ray counts, an accelerating voltage of 20 kV was used.

3.2. Mössbauer Spectroscopy

A ^{57}Fe Mössbauer spectrometer at Lanzhou University (Lanzhou, China) was used to further probe the mineralogy of samples XNZ1 and XNX1. Mössbauer spectra were recorded using a Wissel conventional constant acceleration-type spectrometer, exploiting transmission geometry and a Co/Rh γ-ray source maintained at ambient temperature. The absorbers were cooled by a Janis model CCS-850 closed cycle refrigerator with vibration damping. The drive velocity was calibrated using α-Fe foil at ambient temperature and the isomer shift (IS) was quoted relative to the α-Fe foil. All spectra were fitted using the commercial software package MossWinn. The Mössbauer spectra of the XNX1 and XNZ1 samples at ambient temperatures of 77K and 20K are illustrated in Fig. S4 (Table S2).

3.3. Elemental Analysis

Bulk major element abundances were measured by X-ray fluorescence (XRF) spectroscopy by Australian Laboratory Services. Each powdered sample was fused with a mixed lithium metaborate and tetraborate flux containing an oxidizing agent (lithium nitrate). Sample glasses were set in a platinum mould for analysis. Replicate analyses of rock standards (e.g., BCR-2 and AGV-2) and samples demonstrate that the relative reproducibility is within 5% for all major element oxides. Loss on ignition (LOI) was determined by combustion of separate 1 g aliquots of sample powders at 1100°C for 1 hr (Dong et al., 2016).

Trace element concentrations were measured by inductively coupled plasma mass-spectrometry (ICP-MS, Finnigan MAT Element) at the Institute of Geochemistry, Chinese

Academy of Sciences, Guiyang, China. Here, ~100 mg of whole-rock powder was digested in a mixture of concentrated HNO_3 and HF in screw-top PTFE-lined stainless steel bombs at 190°C, following the methodology described by Dong et al. (2016). Based on analyses of rock standards (e.g., BCR-2 and AGV-2) and duplicate samples, the analytical precision was found to be better than 10% for all reported elements.

Total organic carbon (TOC) was measured using a CE Elantech Flash 1112 Elemental Analyzer. Before analysis, samples were treated with dilute HCl (10% vol/vol) to remove the carbonate fraction. Subsequently, the carbonate-free residues were encapsulated in tin and combusted at 900°C under a stream of oxygen, converting the remaining C, H and N to CO_2, H_2O and NO_2, which were quantified and converted to atomic weight percentages. The analytical uncertainty was less than 5% of the measured value and the detection limit was 0.07%.

3.4. Iron Isotope Analysis

Iron isotope analyses were performed at ALS Scandinavia AB, Luleå, Sweden, and the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences (CAGS). At ALS, Fe isotope analysis followed the protocol described in Malinovsky et al. (2003). Briefly, the powdered sample was digested in a mixture of concentrated HNO_3, HCl and HF in a clean room. Iron was separated from its matrix via anion-exchange (AG MP-1) chromatography, whereby the matrix elements (e.g., Ca, Mg and Na) were eluted in 12 mL of 7 M HCl and Fe was collected in 10 mL of 1 M HNO_3 after discarding the first 0.4 mL of eluent.

At ALS, Fe isotope ratios were measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Thermo Scientific Neptune) operated in high-resolution mode. A standard-sample bracketing (SSB) approach was employed to correct for instrumental mass bias. Samples and standards were prepared in a 0.14 M HNO_3 solution and introduced to the plasma via a micro-concentric PFA nebulizer connected to a tandem quartz spray chamber (cyclone 1 Scott double pass) at a flow rate of ~0.2 ml min^{-1}. All samples and standards were analyzed in duplicate, giving a per sample analytical time of ~20 min. Compiled data for IRMM-014 and geological reference materials (e.g., USGS basalt standard BCR-2) over eight measurement sessions, demonstrate that the external reproducibility for all iron isotope ratios was better than 0.10‰ at the 2σ level. The Fe isotopic compositions of the samples are reported relative to reference material IRMM-014, as follows:

$\delta^{i}Fe$ (‰) = [(^{i}Fe / ^{54}Fe)$_{sample}$ / (^{i}Fe / ^{54}Fe)$_{IRMM\text{-}014}$ – 1] × 1000;

where i is either ^{56}Fe or ^{57}Fe.

To further ensure the quality of Fe isotope measurements, several samples were also analyzed at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences, following the protocol described by Dong et al. (2017). Here, Fe isotope ratios were determined using a Nu Plasma MC-ICP-MS operated in high-resolution mode, using a SSB approach to correct for instrumental mass bias. During this study, the $\delta^{56}Fe$ value of the Chinese basaltic reference standard CAGSR-1 (GBW-07105; n = 1) and USGS basalt standard BCR-2 (n = 1) were found to be statistically indistinguishable from reported values (Dong et al., 2017). Importantly, the samples that were analyzed in both laboratories yielded consistent results, thus precluding inter-laboratory bias.

3.5. Silicon and Oxygen Isotope Analysis

The Si and O isotope compositions of silicates were determined from same sample aliquot after fluorination and cryogenic purification at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (Clayton and Mayeda, 1963; Ding et al., 1996). Before Si and O isotope analysis, carbonates and Fe-Mn oxides were removed with 10% acetic acid (v/v) over 12 h, followed by a mixture of 1 M hydroxylamine hydrochloride and 25% acetic acid (v/v) over 3 h. The residues were used for subsequent analyses. Approximately 10 mg of leached residue was then reacted with BrF_5 at 550°C in a Ni reaction vessel to produce O_2 and SiF_4. The fluorinated products (SiF_4 and BrF_5) were then frozen using liquid nitrogen (LN_2), allowing the headspace O_2 to be converted to CO_2 via reaction with a carbon electrode at 700°C. Replacing the LN_2 with a dry ice-acetone slurry at −78°C separated SiF_4 from the majority of the remaining impurities, allowing the SiF_4 to be collected at LN_2 temperatures. This cryogenic distillation was performed in triplicate and the remaining BrF_5 and other active fluorides were removed by reaction with Zn granules at 70°C, yielding pure SiF_4 gas for mass spectrometric analysis.

Measurements of oxygen and silicon isotope ratios were performed using a Finnigan MAT 253 mass spectrometer. The results are expressed in conventional delta notation relative to the respective V-SMOW and NBS-28 standards, as follows:

$$\delta^{18}O_{V\text{-}SMOW}\ (‰) = [(^{18}O\ /\ ^{16}O)_{sample}\ /\ (^{18}O\ /\ ^{16}O)_{V\text{-}SMOW} - 1] \times 1000$$

$$\delta^{30}Si_{NBS\text{-}28}\ (‰) = [(^{30}Si\ /\ ^{28}Si)_{sample}\ /\ (^{30}Si\ /\ ^{28}Si)_{NBS\text{-}28} - 1] \times 1000$$

Based on replicate measurements of quartz standards (NBS-28 and GBW04421), the external precision of the $\delta^{18}O$ and $\delta^{30}Si$ measurements was 0.4‰ (2σ) and 0.2‰ (2σ), respectively.

3.6. Oxygen Isotope Paleothermometry

The fractionation factor (α) between amorphous silica and fluids is given by the following equation:

$$\alpha = (1 + 10^{-3} \times \delta^{18}O_{silica})/\ (1 + 10^{-3} \times \delta^{18}O_{fluid})$$

The temperature was calculated using the following equations for opal-A and nontronite (Clayton and Mayeda, 1963; Li et al., 2013), respectively:

$$10^3 \ln\alpha_{nontronite\text{-}water} = 2.67 \times (10^6 \times T^{-2}) - 4.82$$

$$10^3 \ln\alpha_{opal\text{-}water} = 3.52 \times (10^6 \times T^{-2}) - 4.35$$

In the absence of $\delta^{18}O$ data from the hydrothermal fluids at the newly discovered SWIR hydrothermal fields, we adopted the seawater ($\delta^{18}O_{seawater}$ = 0‰) value instead. Generally, $\delta^{18}O$ values of the hydrothermal fluids from sediment-starved settings are ~1.4‰ (e.g., East Pacific Rise (13°N and 21°N), Mid-Atlantic Ridge (Mark, TAG, Logatchev, and Nibelungen), and Central Indian Ridge (Kairei); Li et al., 2013; Rouxel et al., 2016) and are slightly higher than that of seawater. Given the above $\delta^{18}O$ value for hydrothermal fluids and the intense mixing between hydrothermal fluid and seawater, it is reasonable to infer that the $\delta^{18}O$ value of the fluid from which amorphous silica precipitated would be close to the value of seawater. Therefore, the seawater value ($\delta^{18}O_{seawater}$ = 0‰) was used in our calculations.

4. Results

4.1. Mineralogy

The majority of the analysed samples are massive and yellow–brown coloured unlithified sediments. However, several samples contain black layers or hard-surface encrustations (Fig. S1). Initial mineralogical work revealed that these SWIR Fe-Si precipitates predominantly comprise opal-A, nontronite, 2-line ferrihydrite and birnessite, displaying broadly similar mineralogical characteristics to those found at other hydrothermal vent deposits (e.g., Rouxel et al., 2018; Sun et al., 2015). Based on macroscopic and microscopic observations, X-ray diffraction patterns and EDS-derived elemental abundances of the Fe-rich and Si-rich minerals (Figs. 2, S1–S3), the examined samples were subdivided into two mineralogically distinct groups: the first dominated by opal-A and ferrihydrite (F-O-type), and the second dominated by nontronite and ferrihydrite (F-N-type). Scanning electron microscopy reveals that opal-A and ferrihydrite display twisted filamentous textures with smooth surfaces (Figs. 2, S1, S5), whereas nontronite principally forms granular aggregates with a scaly appearance (Figs. 2, S1).

The presence of nontronite and ferrihydrite was confirmed by Mössbauer spectroscopy (Fig. S4, Table S2). The room temperature (RT) Mössbauer spectrum of sample XNZ1 features a paramagnetic doublet with a broad humped background, requiring a doublet and a sextet to adequately fit the data. The isomer shift (IS) of the doublet was determined to be 0.338(9) mm s^{-1} and quadrupole splitting (QS) was 0.690(9) mm s^{-1}, in agreement with published data for ferrihydrite (Murad, 1988). Generally, sample XNZ1 is magnetically ordered at low temperature, with the 77K and 20K spectra displaying six-line shapes that are approximated by two sextets. The two sextets are similar in IS and QS, but with different hyperfine fields at both 77K and 20K, consistent with the reported idealized magnetic structure of poorly crystalline ferrihydrite

(Murad, 1988). By contrast, the RT Mössbauer spectrum for sample XNX1 is well approximated by a doublet, whereas the low-temperature (20K and 77K) spectra require an additional doublet. Here, the obtained hyperfine parameters resemble those reported for nontronite (Rouxel et al., 2016). At reduced temperature (20K and 77K), the inner doublet and the outer doublet are assigned to Fe atoms occupying two separate octahedral sites that, due to poor crystallinity, cannot be resolved at room temperature.

Traditional light and scanning electron microscopy reveal that all F-O-type samples feature abundant mineralized filaments. Morphologically, these twisted filaments (Fig. S5) resemble neutrophilic Fe-oxidizing bacteria that are common at modern hydrothermal fields (e.g., Emerson and Moyer, 2010; Chan et al., 2016). Elemental analysis (EDS) shows that these filaments are rich in Fe and Si, with additional C and P enrichments (Figs. 2, S3).

4.2. Elemental and Total Organic Carbon Abundance

The elemental composition of the SWIR Fe-Si precipitates is tabulated in Tables S3 and S4. The samples are rich in Si (SiO_2: 44.9 ± 58.0 wt. %; 2σ) and Fe (Fe_2O_3: 20.2 ± 27.6 wt. %, 2σ). Manganese abundances (MnO) are variable, ranging from 0.11 to 46.1 wt. %, averaging 11.0 ± 27.5 wt. % (2σ). By contrast, concentrations of Al (Al_2O_3: 0.36 ± 1.22 wt. %; 2σ), Ca (CaO: 0.84 ± 1.26 wt. %; 2σ), Mg (MgO: 1.07 ± 1.88 wt. %; 2σ), Na (Na_2O: 1.46 ± 2.62 wt. %; 2σ) and K (K_2O: 0.43 ± 0.65 wt. %; 2σ) are very low, consistent with the limited terrestrial influence expected at the open-ocean location of the SWIR. The organic-carbon content of all samples is relatively low, ranging from 0.05 to 0.63 wt. %, averaging 0.21 ± 0.30 wt. % (2σ; Table S3). Phosphorus and vanadium concentrations display a positive correlation with Fe/Si ratios, consistent with P and V adsorption onto iron-bearing minerals. These elemental correlations are stronger in the F-O-type samples when compared to the F-N-type precipitates (Figs. 3B, 4A).

4.3. Rare Earth Element Abundances and Distributions

Total rare earth element and yttrium (ΣREY) concentrations of the SWIR Fe-Si precipitates range from 2.02 to 53.90 mg kg^{-1}, with an average of 20.44 mg kg^{-1} (n = 17; Table S5). These values are lower than those for Post-Archean Average Shale (PAAS; McLennan, 1989), but are higher than those of modern seawater, resembling the abundances reported from ancient IFs (Planavsky et al., 2010). The Y/Ho ratios of the SWIR Fe-Si precipitates have sub-chondritic to super-chondritic values, ranging from 18.6 to 36.0 (with an average of 27.9), again, falling into the range of post-GOE IFs (Planavsky etl al., 2010). The low Y/Ho ratios for post-GOE IFs have been related to the dissolution of Mn-(oxyhydr)oxides in anoxic deep-waters and deposition of Fe-(oxyhydr)oxides at the redoxcline (Planavsky et al., 2010). The Sm/Yb ratio of the SWIR Fe-Si precipitates range from 0.54 to 1.36, with an average of 0.94, implying a slight heavy REY enrichment. The SWIR Fe-Si precipitates display significant positive Eu anomalies ($Eu_N/Eu_N^*= Eu_N/[0.67\ Sm_N + 0.33\ Tb_N]$), with an average value of 3.0 ± 1.3 ($n = 17$). Except for a single sample (XNZ9), samples from the SWIR exhibit weak negative Ce anomalies ($Ce_N/Ce_N^* = Ce_N/[0.5Pr_N+0.5La_N]$), with an average value of 0.67 ± 0.31 ($n = 17$). In general, the F-N-type Fe-Si precipitates have marginally lower Ce_N/Ce_N^* values (0.42–0.67; $n = 8$) compared to their F-O counterparts (0.58–1.05; $n = 9$). In summary, the shale-normalized REY patterns of the SWIR Fe-Si precipitates (Fig. 5) are slightly enriched in heavy REY, with typically weak negative Ce anomalies and prominent positive Eu anomalies.

The pronounced positive Eu anomalies seen in the SWIR Fe-Si precipitates reflect reduction of Eu^{3+} to Eu^{2+}, decoupling the behavior of di- and trivalent REYs (Bau and Dulski, 1996). Conditions conducive to Eu^{3+} reduction are frequently encountered in high-temperature hydrothermal systems. At the SWIR, the Eu_N/Eu_N^* values resemble those reported from mid-ocean ridges (Bau and Dulski, 1999) and many ancient iron formations (Planavsky et al., 2010). Given that contemporary seawater lacks an Eu anomaly (Bau and Dulski, 1996), the elevated Eu_N/Eu_N^* values must have been inherited from hydrothermal fluids. Combining these observations with REY distribution patterns suggests that at least the REY chemistry of the SWIR Fe-Si precipitates was derived from mixing between seawater and hydrothermal fluids.

Cerium anomalies result from cerium oxidation (Bau and Dulski, 1999). In oxygenated aqueous solutions, particulate Fe-Mn (oxyhydr)oxides absorb and catalyze Ce oxidation, depleting seawater of insoluble Ce(IV), resulting in a negative Ce anomaly ($Ce_N/Ce_N^* < 1$; Bau and Dulski, 1999). Given that anomalous La enrichment could affect the Ce anomaly, we combined Ce and Pr anomalies ($Pr_N/Pr_N^* = Pr_N/[0.5Ce_N+0.5Nd_N]$) to evaluate the Ce anomaly in the SWIR samples (Bau and Dulski, 1996). Here, the F-O-type Fe-Si precipitates display weak or negligible negative Ce anomalies, whereas the F-N-type samples have significant negative Ce anomalies (Fig. 6). We explain these data in terms of subtle differences in the mixing ratio between hydrothermal fluid and seawater, with the negligible to weak negative Ce anomalies seen in the F-O-type samples reflecting precipitation from solutions with a lower component of seawater compared to the F-N-type samples. Further, we reconcile these observations with the locus of precipitation and hypothesize that the F-O-type precipitates were formed within the sediment pile, which limited the influence of oxygenated seawater compared to their F-N counterparts that may have formed in the water column.

4.4. Oxygen Isotopic Composition

The $\delta^{18}O$ values of SWIR silicates range between 8.3 and 39.2‰, with an average of 26.3 ± 19.6‰ (2σ, $n = 21$). These data are dependent on mineralogy: F-N-type samples carry $\delta^{18}O$ values that range between 8.3 and 25.8‰, with an average of 18.1 ± 1.8‰ (2σ, $n = 10$); while the $\delta^{18}O$ values of F-O-type samples are statistically more positive (33.7 ± 11.7‰; 2σ, $n = 11$), with $\delta^{18}O$ values ranging from 19.8 to 39.2‰. Using these $\delta^{18}O$ data as a paleothermometer reveals variable and mineral-dependent precipitation temperatures, with nontronite (79 ± 105°C; 2σ) precipitating from apparently hotter fluids than opal-A (36 ± 57°C; 2σ). This difference in precipitation temperature, however, is insignificant at the 2σ level. Equations used for these calculations can be found in Section 3.6.

4.5. Iron Isotopic Composition

The $\delta^{56}Fe$ values of SWIR Fe-Si precipitates range from –2.02 to 0.75‰, with an average of –0.26 ± 0.02‰ (2σ, $n = 21$). All data are tabulated in Table 1. These $\delta^{56}Fe$ values are significantly different from basalts (δ^{56}Fe ~0.1‰) and modern hydrothermal fluids (–0.8 to –0.1‰), but overlap with the range reported for Precambrian IFs (Fig. 7). F-N-type Fe-Si precipitates have δ^{56}Fe values ranging from –2.02 to 0.43‰ (*n* = 10), whereas F-O-type samples have δ^{56}Fe values ranging from −1.11 to 0.75‰ (*n* = 11). At first glance, F-N-type samples (–0.64 ± 1.32‰; 2σ) display lower δ^{56}Fe values when compared to F-O-type samples (0.04 ± 1.10‰; 2σ); however, this difference is also insignificant at the 2σ level.

4.6. Silicon Isotopic Composition

The Si isotopic composition of the Fe-Si precipitates ranges from −2.2 to 0.2‰, with an average value of −1.0 ± 1.3‰ (2σ, *n* = 21; Table 1, Fig. 8). F-N-type Fe-Si precipitates have δ^{30}Si values ranging from −2.2 to −0.6‰ (*n* = 10), while the F-O-type Fe-Si precipitates display δ^{30}Si values ranging from −1.8 to 0.2‰ (*n* = 11). The average δ^{30}Si values of the F-N-type (–1.3 ± 1.0‰) and F-O-type (–0.9 ± 1.4‰) samples are indistinguishable at the 2σ level.

5. Discussion

5.1. Mineralogical and elemental composition of SWIR Fe-Si precipitates

Based on mineralogical and textural observations (Figs. 2, S2–S4), the SWIR samples have been divided into two distinct groups: the first group, termed F-O-type samples, is dominated by opal-A and ferrihydrite, whereas the second group, labelled F-N-type samples, is dominated by nontronite and ferrihydrite. Given that ferrihydrite typically contains nanometer-sized particles and poorly ordered crystals (e.g., Gloter et al., 2004), Mössbauer spectroscopy was employed to confirm its presence (Figs. 2, S4). Scanning electron microscopy also revealed a pronounced textural difference between these mineralogically distinct sample types; with the F-O-type samples displaying a twisted filamentous texture with smooth surfaces that strongly contrast with the granular and scaly texture possessed by the F-N-type samples (Figs. 2, S3, S5).

Regardless of sample type, shale-normalized REY patterns display muted heavy REY enrichments and strong positive Eu anomalies, requiring an appreciable contribution from hydrothermal fluids (Fig. 5). By contrast, Ce anomalies appear sample-type dependent, with the F-O-type samples displaying negligible Ce anomalies compared with the F-N-type subset, which feature pronounced negative Ce anomalies (Fig. 6). Given that modern deep marine water masses carry a pronounced negative Ce anomaly that is absent in hydrothermal fluids (Bau and Dulski, 1999), the variable Ce anomalies observed within the SWIR Fe-Si precipitates presumably reflects subtle differences in the mixing ratio of the precursor fluids.

Oxygen isotope paleothermometery reveals variable formation temperatures for nontronite (24 to 179°C) and opal-A (14 to 110°C) that, in turn, implies different genetic and fluid circulation pathways for the mineralogically distinct sample subsets. Indeed, contrasting Fe-P systematics (Fig. 3, Tables S3) fortify this stance, again implicating different genetic pathways for the F-O- and F-N-type samples. Iron-associated phosphorus enrichments are common in modern hydrothermal systems and are thought to reflect water-column scavenging by freshly precipitated ferrihydrite (Feely et al., 1998). Considering that the P content of hydrothermal fluid is typically less than 25% of ambient seawater (Feely et al., 1998), the lower P content of the F-O-type samples (Fig. 3B, Tables S3) potentially records limited interaction between the hydrothermal fluids and seawater. Moreover, the high Si concentrations within diffuse hydrothermal fluids may have also hindered P adsorption to ferrihydrite via direct competition (cf. Konhauser et al., 2007; Planavsky et al., 2010). Assimilating these mineralogical, elemental and isotopic observations, we conclude that the F-O-type samples were derived from diffuse hydrothermal fluids.

By contrast, F-N-type samples feature abundant ferrihydrite and nontronite that might be genetically related to more focused-flow. A point injection of hydrothermal fluids into seawater results in an initially buoyant plume that loses its buoyancy as it dissipates (German et al., 2014). Supported by the high P contents and positive Eu anomalies in the bulk samples, the ferrihydrite observed in the F-N-type samples could have resulted from such a non-buoyant plume. Similarly, the nontronite may have also precipitated directly from seawater or, alternatively, formed at the sediment–water interface through the alteration of clay minerals and Fe oxides (cf. Dekov et al., 2007). Consequently, F-N-type samples could potentially record a combination of precipitation from a non-buoyant plume and/or a diffuse-flow system, with subsequent alteration at the seafloor.

Given that F-O-type samples were most likely precipitated from diffuse-flow, they likely formed in the subsurface or at the sediment-seawater interface of microbial mats with low dissolved O_2 (based on Ce data). Similar environments must have existed at the ancient seafloor, even in the Precambrian oceans. Fe-oxidation and Si-precipitation mechanisms recorded by the F-O-type samples at the SWIR may therefore shed light on formation of Fe-Si precipitates in post-GOE weakly oxygenated deep oceans. In the following discussion, we mainly focus on the F-O-type samples as potential analogues to post-GOE deep-water Fe-Si precipitates.

5.2. The role of bacteria in ferrihydrite precipitation

Partial oxidation of dissolved ferrous iron and the precipitation of ferric precipitates impart a distinctive isotope effect due to preferential removal of heavy Fe isotopes from solution, which correspondingly decreases the δ^{56}Fe value of the residual dissolved iron pool (e.g., Balci et al., 2006). The ensuing Rayleigh effect can induce significant δ^{56}Fe variability in the precipitate, yielding strongly negative δ^{56}Fe values in the fluid and precipitate once a majority of the ferrous iron has been removed from the iron pool (Fig. 3A). Mass balance, however, dictates that quantitative iron oxidation eliminates δ^{56}Fe variability, and the precipitate then inherits the composition of the initial fluid (Rouxel et al., 2018). In addition, hydrothermal sulfides possess low δ^{56}Fe values, as demonstrated by data from the East Pacific Rise (Rouxel et al., 2008) and the SWIR (Table 1).

Ferric iron precipitates derived from diffuse-flow are formed below the sediment-water interface and are therefore sheltered from full exchange with oxic seawater. Consequently, where diffuse fluids travel through the sediment pile, significant Fe isotopic fractionation due to partial ferrous iron oxidation should be expected. At the SWIR, the δ^{56}Fe values of F-O-type samples range from −1.11 to 0.75‰, with an average value of −0.04 ± 1.10‰ (2σ, $n = 11$; Table

1, Fig. 7), which overlaps with values reported for modern near-vent hydrothermal oxides (Severmann et al., 2004; Wu et al., 2013; Rouxel et al., 2018), Phanerozoic jaspers (Moeller et al., 2014), Precambrian IFs (Dauphas et al., 2004; Frost et al., 2006; Hyslop et al., 2008; Haugaard et al., 2016), and hydrothermal sulfides (Rouxel et al., 2008).

The δ^{56}Fe values of F-O-type samples could have been generated via one or more of the following three redox scenarios. **(i)** Ferrous iron from diffuse flow is almost quantitatively oxidized on the seafloor. Considering that hydrothermal fluids have a limited range of δ^{56}Fe values (−0.5 to 0.0‰; Rouxel et al., 2016), the four F-O-type samples with δ^{56}Fe values from −0.56 to -0.08‰ could conceivably have been produced by near-quantitative ferrous iron oxidation (Fig. 3C). A similar process has been suggested for the Rainbow vent site, Mid-Atlantic Ridge (Severmann et al., 2004). **(ii)** During diffuse flow in the subsurface, partial ferrihydrite precipitation occurs as the diffuse fluids travel in the subsurface, possibly causing the residual dissolved iron pool to evolve towards lower δ^{56}Fe values as ^{56}Fe is preferentially incorporated into ferrihydrite. When the diffuse-flow fluid vents to the seafloor, near-quantitative oxidation of the isotopically light residual ferrous iron results in ferrihydrite with negative δ^{56}Fe values (e.g., −1.11‰ in one F-O-type sample). Alternatively, iron-reducing bacteria, such as members of *Firmicutes* and *Burkholderiaceae* observed at SWIR (Li et al., 2013), could have partially re-dissolved iron minerals, preferentially releasing ^{54}Fe to the ambient seawater. The dissolved ferrous iron with negative δ^{56}Fe values could have been quantitatively precipitated again, thus producing F-O precipitates with δ^{56}Fe values as low as −1.11‰. **(iii)** Where the diffuse flow passed through bacterial mats on the seafloor, the dissolved ferrous iron may have been partially oxidized and then precipitated as ferrihydrite. Given an Fe isotopic fractionation of ~2.9‰ between ferrihydrite and the fluid (Balci et al., 2006), the six F-O-type samples with δ^{56}Fe values ranging from 0.20 to 0.75‰ could be explained by 43 to 53% of ferrous-iron oxidation in the fluid (Fig. 3A). Limited interaction with ambient seawater within the bacterial mats may have hindered abiotic oxidation, requiring a biological role. Bacterially-mediated iron oxidation is supported by the presence of abundant twisted filamentous microbial structures seen in F-O-type samples (Fig. 2), combined with previous microbiological assays of samples from the SWIR that validate the presence of iron-oxidising bacteria, such as *ζ-Proteobacteria* and *Pseudoalteromonas* (Li et al., 2013; Chan et al., 2016). Similar bacterial mats were also documented at Loihi Seamount, Juan de Fuca Ridge, and Vailulu'u Seamount in the Pacific Ocean (Emerson et al., 2010; Rouxel et al., 2018), extending their presence beyond the SWIR.

Thus, in summary, considering that (1) the average δ^{56}Fe value of F-O-type samples is close to that of hydrothermal vent fluids (Rouxel et al., 2016), (2) these samples show a negative correlation between δ^{56}Fe values and Mn/Fe ratios (with the exception of a single outlier; Fig. 4D), and (3) twisted filamentous microbial structures and iron-oxidising bacteria are preserved in these samples (Fig. S5), it is reasonable to infer that oxidation of ferrous iron to form F-O-type samples at the SWIR was biologically mediated at the seafloor.

5.3. Inorganic silica precipitation from diffuse-fluid flow

The δ^{30}Si values of the Fe-Si deposits from the SWIR range from −2.2 to 0.2‰ (average = −1.0 ± 1.3‰; 2σ, $n = 21$, Table 1, Fig. 8), which approximates the range of δ^{30}Si values reported from modern hot-spring sinters (Ding et al., 1996; Douthitt, 1982) and ancient IFs (André et al., 2006; Heck et al., 2011; Hou et al., 2014; Steinhoefel et al., 2009). These values, however, are significantly lower than those carried by contemporary seawater (Cao et al., 2012) or fluids from active hot springs and hydrothermal vents (Douthitt, 1982). Recent experiments indicate that the equilibrium Si isotope fractionation factor between amorphous silica and aqueous fluids ($\Delta^{30}Si_{amorphous\text{-}aqueous}$) at 25°C is *ca.*0.45‰ at pH 6, increasing to *ca.*1.63‰ at pH 9.9 (Stamm et al., 2019), signaling that amorphous silica will be enriched in ^{30}Si at equilibrium. The δ^{30}Si values for the F-O-type samples are negative (average = −0.9 ± 1.4‰; 2σ, $n = 11$) and show a positive correlation with depositional temperatures inferred from δ^{18}O thermometry (Fig. 3D). Clearly, equilibrium Si isotope fractionation cannot fully explain the δ^{30}Si values of our F-O-type samples.

Alternatively, previous experimental work has suggested that silica precipitation is associated with a temperature-dependent kinetic isotope fractionation that preferentially removes ^{28}Si from the dissolved phase (Ding et al., 1996; Geilert et al., 2015). The negative δ^{30}Si values (< –0.3‰), therefore, must reflect the kinetic isotope fractionation associated with partial precipitation of dissolved Si from the diffuse-flow-derived fluid. A negative correlation between δ^{30}Si and δ^{56}Fe values, and positive correlation between the depositional temperature and either δ^{30}Si values or Si/Fe ratios (Fig. 4), further support temperature-dependent kinetic Si isotope fractionation during mineral precipitation as the cause of the negative and highly variable δ^{30}Si values seen in the SWIR Fe-Si precipitates. The slightly positive δ^{30}Si values (0.2‰) of some F-O-type samples, therefore, require near-quantitative precipitation of silica from hydrothermal fluids, and thus reflect the δ^{30}Si value of the parent hydrothermal fluid.

Precipitation of Si-rich minerals requires the precursor solution to be supersaturated with respect to the specific silicon-bearing mineral phase (Juniper and Fouquet, 1988). Given that the silica concentration of modern seawater (0.05 mM) is much lower than that of diffuse hydrothermal fluids (7.0–18.1 mM; Elderfield and Schultz, 1996; Proskurowski et al., 2008), a high degree of mixing between the seawater and hydrothermal fluid is required to prevent the precipitation of Si minerals. Silica precipitation from diffuse-flow hydrothermal fluid is thus ultimately associated with the formation of microbial mats, which limits the interaction between the seawater and the diffuse hydrothermal fluid. Precipitated ferrihydrite electrostatically adsorbed onto the surface of microbial mats could limit exchange between subsurface derived diffuse hydrothermal fluids and seawater. In our model, gradually decreasing temperatures as the diffuse hydrothermal fluid slowly began to mix with seawater led to silica supersaturation, promoting opal-A precipitation (Juniper and Fouquet, 1988; Sun et al., 2015). In this scenario, Fe-Si co-precipitation is an expected outcome in diffuse-flow-dominated systems housed within Fe-oxidizing microbial mats.

5.4. Implications for the genesis of Fe- and Si-rich mineral bands in post-GOE Fe-Si precipitates

The genetic mechanism(s) responsible for the distinct Fe- and Si-rich mineral bands seen in IFs remains unclear, particularly within post-GOE deep-water Fe-Si precipitates (Posth et al., 2008; Bekker et al., 2010, 2014; Konhauser et al., 2017; Li et al., 2017). Prior to the permanent oxygenation of the atmosphere during the GOE, the surface and deep oceans were presumably largely devoid of dissolved O_2. After the accumulation of atmospheric O_2 during the GOE, the deep oceans remained O_2-deficient and capable of harbouring a substantial, hydrothermally-sourced dissolved iron reservoir (Lyons et al., 2014), with the spatial and temporal extent of recently inferred, weakly oxygenated conditions as yet unresolved (Slack et al., 2007; Little et al., 2021). Under weakly oxygenated and ferruginous conditions, microaerophilic and anaerobic Fe-oxidizing and Fe-reducing bacteria would have proliferated in benthic microbial communities, while planktonic Fe-oxidizing bacteria would have prevailed within the water column (Emerson et al., 2010). Bacterially mediated Fe-oxidation, as dissolved iron entered the aerated mixed-layer of the ocean, would have precipitated ferrihydrite. Commonly, water-column-derived 'ferrihydrite rain' is inferred to be the dominant source of oxidized Fe to the seafloor. However, when considering the prevailing geochemical conditions, its importance has likely been overemphasized. Transit via a weakly oxygenated water column, with plentiful dissolved organic matter and other reductants, would have most likely promoted ferrihydrite dissolution and/or transformation into other mineral phases such as green rust and/or magnetite (Zegeye et al., 2012; Halevy et al., 2017; Li et al., 2017).

If a suboxic deep-ocean redox state prevailed, as inferred from the 1.74 Ga jasper and Algoma-type IFs from the Jerome area in central Arizona, USA (Slack et al., 2007), then ferrous iron released from focused-flow should have been oxidized to ferrihydrite directly in the water column as hydrothermal plumes dissipated. In the case of diffuse-flow systems, Fe-Si precipitates could have formed in the subsurface and at the sediment-water interface as low-temperature hydrothermal fluids seeped into the deep ocean and mixed with seawater, with partial iron oxidation mediated by Fe-oxidizing microaerophilic bacteria (Little et al., 2021). Here, we propose that the ferrihydrite precursor for the hematite preserved in some Algoma-type IFs and jaspers originated from diffuse-flow hydrothermal fluids that percolated through bacterial mats on the seafloor beneath a weakly oxygenated water column.

Previous studies have argued that the Si enrichment seen in IFs originated via three main pathways: (i) evaporation and/or ocean water temperature changes that affected silica saturation, resulting in episodic precipitation (Posth et al., 2008); (ii) direct Si absorption to ferrihydrite shuttling Si to the seafloor, or (iii) co-precipitation of an Fe-Si gel at the sediment–water interface (Grenne and Slack, 2003a; Fischer and Knoll, 2009; Bekker et al., 2014; Konhauser et al., 2017; Schad et al., 2019). Here we advocate for an alternate explanation, whereby direct precipitation of hydrated silica (such as opal-A) at, or immediately below, the sediment-water interface in microbial mats provides a direct precursor for the Si-rich minerals preserved in some post-GOE Fe-Si precipitates. Specifically, we envisage that the microbially-induced ferrihydrite precipitation within benthic microbial mats limited exchange between seawater and percolating hydrothermal fluids in the subsurface. This limited exchange would then have allowed the hydrothermal fluids to cool gradually, triggering the precipitation of Si-rich minerals, such as opal-A, once silica supersaturation was reached. Additionally, the elevated Si concentrations inferred for Precambrian seawater (>0.67 mM; Konhauser et al., 2007; Siever et al., 1992) and Cambrian to Early Cretaceous seawater (Grenne and Slack, 2003a) would have further enhanced silica precipitation as hydrothermal fluids approached the seafloor and mixed with cold seawater. Fluctuations in hydrothermal activity would have produced bands of Si-rich minerals with variable thicknesses. Ultimately, diagenetic overprinting and modification of ferrihydrite, magnetite (or green rust), and opal-A would have converted these primary Fe-Si precipitates into the mineral assemblages preserved in post-GOE, deep-water Algoma-type IFs and jaspers associated with volcanogenic massive sulfide deposits, an interpretation consistent with textural observations of Fe-oxide and chert bands preserved in Algoma-type IFs.

Importantly, our data do not exclude the role of water-column Fe-oxidation, nor do they preclude seawater abiotic silica precipitation or Fe-Si co-precipitation (Fischer and Knoll, 2009; Bekker et al., 2010, 2014; Konhauser et al., 2017). Rather, we suggest that hydrothermal diffuse-flow would have operated in parallel with water-column oxidative processes. In this perspective, post-GOE Fe-Si precipitates, derived from the water-column, were likely modified after deposition by biogeochemical processing in sediments, resulting in the diagenetic neomorphism of Si-rich minerals as diffuse-flow, hydrothermal fluids circulated in the subsurface. In short, we argue that the co-existence of microbial iron oxidation and abiotic silica precipitation, as a result of low-temperature hydrothermal-fluid flow through the seabed, presents a potential explanation for the characteristic Fe- and Si-rich bands seen in many post-GOE deep-water Fe-Si precipitates associated with volcanogenic massive sulfide deposits, including Algoma-type IFs and jaspers.

6. Conclusions

A set of Fe-Si precipitates, sediments and sulfides were examined from the Southwest Indian Ridge. Assimilating their mineralogical macro-scale textural observations, the formation of samples dominated by opal-A and ferrihydrite (F-O-type precipitates) is attributed to precipitation from diffuse hydrothermal fluids at or below the subsurface. The δ^{56}Fe values of these F-O-type samples implicate biologically-mediated iron oxidation at the SWIR. Negative and highly variable δ^{30}Si values in the F-O-type precipitates are explained by temperature-dependent kinetic Si isotope fractionation during mineral precipitation. Formation of ferrihydrite and opal-A in these F-O-type precipitates provides insight into the genesis of widely invoked precursor minerals for post-GOE deep-water Fe-Si precipitates associated with volcanogenic massive sulfide deposits, including some Algoma-type IFs and jaspers. By analogy, we suggest that the mineralogical banding in post-GOE Fe-Si precipitates could have formed by biologically mediated ferrihydrite precipitation and abiotic precipitation of opal-A from oversaturated fluids during diffuse hydrothermal fluid flow. We thus propose that low-temperature diffuse hydrothermal flow may have played an important role in the deposition of these enigmatic lithotypes.

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Competing interests

The authors declare they have no competing interests.

Supplementary materials

The appended supplementary material related to this article can be found online at

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Figure captions

Fig. 1. Distribution of hydrothermal fields along the Southwest Indian Ridge (SWIR).

Fig. 2. Textural, elemental and Mössbauer spectroscopic images and data for selected Fe-Si precipitates from the SWIR. Transmitted light (**A–B**) and scanning electron photomicrographs (**C–D**), coupled with energy dispersive X-ray spectroscopy (EDS; **E–F**), reveal textural and chemical difference between F-O-type (sample XNZ7, **A;** sample XNZ12, **C & E**) and F-N-type

(sample XNZ10, B; sample XNX1, **D** & **F**) precipitates. Clear difference in the low-temperature (20°K) Mössbauer spectra derived from F-O-type (**G**) and F-N-type (**H**) Fe-Si precipitates confirm their mineralogical distinction. Specifically, the prominent sextet shown by the F-O-type precipitate (XNZ1, **G**) requires a magnetically ordered and poorly crystalline Fe phase (i.e., ferrihydrite), while the summed doublets seen in the spectrum of the F-N-type sample (XNX1, **H**) requires for Fe atoms to be arranged in two different octahedral sites. These observations, combined with the measured hyperfine parameters, identify Fe-bearing mineral in F-N-type precipitates as nontronite (Supplementary Material). Wt.% and At.% stand for weight % and atomic %, respectively.

Fig. 3. Measured and modelled elemental and isotopic variability displayed by the SWIR Fe-Si precipitates. (**A**) Modelled Rayleigh fractionation between an aqueous ferrous phase and a ferric precipitate at 22°C; (**B**) P_2O_5 content *versus* Fe/Si ratio; (**C**) Fe_2O_3 content *versus* δ^{56}Fe values; and (**D**) precipitation temperature *versus* δ^{30}Si values. In panel (**A**) curve I shows the evolving δ^{56}Fe value of the dissolved phase, curve II denotes the δ^{56}Fe composition of an instantaneous Fe^{3+} precipitate, and curve III reflects the cumulative δ^{56}Fe value of the Fe^{3+} precipitate. The dashed line represents the δ^{56}Fe value of the initial hydrothermal solution (δ^{56}Fe = −0.5‰ from Rouxel et al., 2008). The fractionation factor (α) between the aqueous ferrous iron phase and precipitated ferric iron phase is 1.0029 at 22°C (Balci et al., 2006). Iron and silicon isotope data are reported as per mill (‰) deviations relative to IRMM014 and NBS-28, respectively. Wt.% is weight %.

Fig. 4. Cross-plots of selected elemental abundances, ratios and Fe-Si-O isotope systematics of Fe-Si precipitates from the SWIR: (**A**) [V] *vs* Fe/Si, (**B**) Temperature *vs* Si/Fe, (**C**) δ^{30}Si *vs* δ^{56}Fe, (**D**) Mn/Fe *vs* δ^{56}Fe. Red and blue datapoints distinguish data from F-O- and F-N-type samples, respectively.

Fig. 5. Rare earth element and yttrium distribution patterns for the SWIR Fe-Si precipitates. Data have been normalized to post-Archean average shale (PAAS), arranged according to the

type (F-N-type = A, F-O-type =B) and colour-coded for each frame.

Fig. 6. Cross-plot of calculated Ce_N and Pr_N anomalies by the SWIR Fe-Si precipitates. Red and blue datapoints refer to F-O- and F-N-type samples, respectively. Discrimination between positive La and true negative Ce anomalies follows Bau and Dulski (1996).

Fig. 7. **New Fe isotope data from the SWIR contextualized within a compilation of δ^{56}Fe data sourced from modern–Ordovician-aged Fe-Si precipitates, Archean–Paleoproterozoic-aged Superior- and Algoma-type IFs, modern hydrothermal sulfides and hydrothermal/spring fluids.** The vertical grey bar represents the δ^{56}Fe value of the Bulk Silicate Earth. IRMM014 is the reference standard for expressing Fe isotope data in delta notation. Ga is giga-annum (10^9 years). Iron isotope data are denoted: A1 from Wu et al (2013), A2 from Moeller et al (2014); A3 and A4 from Severmann et al (2004); A5–A8 from Rouxel et al (2008); A9 from Dauphas et al (2004); A10 from Haugaard et al (2016); A11–A12 from Frost et al (2006); Hyslop et al (2008); A13 from Moeller et al (2014); A14 from Wu et al (2013); A15 from Severmann et al (2004); A16 from Moeller et al (2014); A17 and A18 from this study.

Fig. 8. **A Si isotope compilation, featuring data derived from Archean–Paleoproterozoic-aged Superior- and Algoma-type IFs, modern hydrothermal sulfides, contemporary sinter precipitates, fluids sourced from active hydrothermal springs and the studied SWIR Fe-SI precipitates.** NBS-28 is the reference standard for expressing Si isotope data in delta notation. Ga is giga-annum (10^9 years). Silicon isotope data are denoted: B1 from Cao et al (2012); B2 from Douthitt (1982); B3 from Ding et al (1996); B4 from André et al (2006); B5 from Steinhoefel et al (2009); B6 from Hou et al (2014); B7 from Heck et al (2011); B8 from Ding et al (1996); Douthitt (1982); B9 and B10 are from this study.

Table captions

Table 1: Elemental and isotopic data for the SWIR Fe-Si precipitates, sediments and sulphides. Stable isotope (Fe, Si, and O) data are expressed in delta notion as per mill (‰) deviations from the appropriate reference standard. Elemental abundances are expressed in weight percent

(Wt. %). Calculated temperatures are in degrees Celsius (°C). N.D. not determined.