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2 Sedimentary mechanisms of a modern banded iron formation on  
3 Milos Island, Greece

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24 Short title: A modern banded iron formation

25 **Abstract.** An Early Quaternary shallow submarine hydrothermal iron formation (IF)  
26 in the Cape Vani sedimentary basin (CVSB) on Milos Island, Greece, displays banded  
27 rhythmicity similar to Precambrian banded iron formation (BIF). Sedimentary,  
28 stratigraphic reconstruction, biogeochemical analysis and micro-nanoscale  
29 mineralogical characterization confirms the Milos rocks as modern Precambrian BIF  
30 analogues. Spatial coverage of the BIF-type rocks in relation to the economic grade  
31 Mn ore that brought prominence to the CVSB implicates tectonic activity and  
32 changing redox in the deposition of the BIF-type rocks. Field-wide stratigraphic and  
33 biogeochemical reconstruction demonstrates two temporal and spatially isolated iron  
34 deposits in the CVSB with distinct sedimentological character. Petrographic screening  
35 suggest the previously described phototrophic-like microfossil-rich IF (MFIF);  
36 accumulated on basement andesite in a ~150 m wide basin, in the SW margin of the  
37 basin. A strongly banded non-fossiliferous IF (NFIF) caps the Mn-rich sandstones at  
38 the transition to the renowned Mn-rich formation. Geochemical evidence relates the  
39 origin of the NFIF to periodic submarine volcanism and water column oxidation of  
40 released Fe(II) in conditions apparently predominated by anoxia, similar to the MFIF.  
41 This is manifested in the lack of shale-normalized Ce anomalies. Raman spectroscopy  
42 pairs hematite-rich grains in the NFIF with relics of a carbonaceous material carrying  
43 an average  $\delta^{13}\text{C}_{\text{org}}$  signature of ~-25‰. However, a similar  $\delta^{13}\text{C}_{\text{org}}$  signature in the  
44 MFIF is not directly coupled to hematite by mineralogy. The NFIF, which post dates  
45 large-scale Mn deposition in the CVSB, is composed primarily of amorphous Si  
46 (opal-SiO<sub>2</sub>·nH<sub>2</sub>O) while crystalline quartz (SiO<sub>2</sub>) predominates the MFIF. An  
47 intricate interaction between tectonic processes, changing redox, biological activity  
48 and abiotic Si precipitation, formed the unmetamorphosed BIF-type deposits.

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**Keywords:** Banded iron formation; BIF analogue; Hydrothermal activity; Iron  
cycling; Silica cycling.

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## 61 **1 Introduction**

62 Recently, an Early Quaternary iron formation (IF), ~2.0 million years old, displaying  
63  banded rhythmicity typical of Precambrian banded iron formations (BIF) (James,  
64 1954; Gross, 1980; Simonson, 1985, 2003; Bekker et al., 2010), was serendipitously  
65 discovered in the Cape Vani sedimentary basin (CVSB) on Milos Island, Greece (Chi  
66 Fru et al., 2013, 2015). Before this discovery, Cape Vani was long known to host Mn  
67 oxide ores of economic potential (Hein et al., 2000; Liakopoulos et al., 2001; Glasby  
68 et al., 2005; Kiliyas et al., 2007). Milos is an emergent volcano on the Hellenic  
69 Volcanic Arc (HVA) where arc-volcanism and seafloor hydrothermal activity occur  
70 in thinned pre-Alpine to Quaternary continental crust (Kiliyas et al., 2013) (Fig. 1). The  
71 first reported IF from Cape Vani is unmetamorphosed and contains diverse  
72 microfossils encrusted by hematite, with ferrihydrite proposed as a primary precursor  
73 mineral (Chi Fru et al., 2013, 2015). Field stratigraphy,  Rare Earth Elements (REEs),  
74 stable isotopes, petrographic and microfossil studies point to microbial Fe deposition  
75 in a semi-enclosed, shallow submarine basin under conditions analogous to those that  
76 formed the Precambrian Algoma-type BIFs near volcanic centers (Chi Fru et al.,  
77 2015). These earlier reports assumed a one-time basin-wide depositional event and a  
78 common origin for all Fe-rich sedimentary rocks in the CVSB.

79 However, it remains unclear what sedimentary processes caused the distinct  
80 deposition of the BIF-type rocks in a basin where Mn precipitation was apparently  
81 widespread at various intervals. Moreover, it is not known how the Mn ores relate  
82 temporally and spatially to Fe deposition in the ~1 km long CVSB. This knowledge  
83 may provide clues to processes that triggered large-scale deposition of similar  
84 Proterozoic Fe-Mn-rich deposits  (Jy, 2006; Tsikos et al., 2010). Here, new  
85 sedimentological, petrological and biogeochemical evidence describes cycles of

86 periodic precipitation of shallow submarine Si and Fe-rich sedimentary rocks and the  
87 plausible mechanisms that enabled their temporal and spatial separation from the Mn  
88 deposits in the CVSB. The data reveal a much more complex depositional system not  
89 only controlled by microbial Fe(II) oxidation as previously proposed (Chi Fru et al.,  
90 2013, 2015), but illuminates episodic volcanism coupled to changing redox conditions  
91 as a central mechanism in the formation of the banded iron rocks.

92

### 93 **1.1 Geological setting**

94 The geology and iron and manganese mineralization of the CVSB have been  
95 described in detail (Plimer, 2000; Hein et al., 2000; Liakopoulos et al., 2001;  
96 Skarpelis and Koutles, 2004; Glasby et al., 2005; Stewart and McPhie, 2006; Kiliass,  
97 2011; Alfieris et al., 2013; Chi Fru et al., 2013, 2015; Papavassiliou et al., 2017).  
98 Briefly, the Milos IF is part of the CVSB, a recently emergent sedimentary rift basin  
99 located NW of Milos Island, along the HVA in the Aegean Sea, Greece (Fig. 1). It  
100 hosts a fossil analogue of active shallow-submarine hydrothermal activity on the coast  
101 of Milos Island (Dando et al., 1995). The CVSB developed within a 2.7 to 1.8 Ma  
102 shallow-submarine rhyolitic-dacitic volcanic center, filled up mainly by a ~35-50 m  
103 thick stratigraphic succession of volcanoclastic/epiclastic sandstones and sandy tuffs  
104 spanning Upper Pliocene to Lower Pleistocene, 35-40% of which is hydrothermally  
105 mineralized by Mn oxides and barite (Hein et al., 2000; Liakopoulos et al., 2001;  
106 Skarpelis and Koutles, 2004; Papavassiliou et al., 2017). Sedimentologic and  
107 ichnologic data, including sedimentary structures, lamellibranch, echinoid and  
108 brachiopod fossils, the gastropod mollusk fossil, *Haustator biplicatus* (Bronn, 1831),  
109 and microbially induced sedimentary structures (e.g., Kiliass, 2011), suggest that most  
110 of the CVSB sandstones/sandy tuffs hosting the Mn-rich deposit, are foreshore to

111 shoreface shallow submarine deposits, formed at a maximum depth of 200 mbsl. Over  
112 the last 0.8 Myr, fluctuating water depths due to sea-level changes of up to 120 m and  
113 volcanic edifice building, has resulted in tectonic uplift of ~250 m (Papanikolaou et  
114 al., 1990). The CVSB fill, currently 35 m above sea level, is tectonically northbound  
115 by intrusive rhyolite, framed by elevated andesitic-dacitic centres, with the Cape Vani  
116 and the Katsimoutis dacitic lava domes being the most prominent (Fig. 1).

117

## 118 **2 Methodology**

### 119 **2.1 Sample preparation**

120 **Sedimentary structures, grain-size trends, lateral facies variations, vertical stacking**  
121 **trends, and key stratigraphic surfaces form the basis for facies analysis.** Prior to  
122 mineralogical and geochemical analysis, exposed rock surface layers were sawn and  
123 removed. GeoTech Labs (Vancouver, Canada) produced doubly polished thin  
124 sections for mineralogical and textural analysis, while geochemical analysis was  
125 performed on pulverized powders and acid-digests (Chi Fru et al., 2013, 2015).

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### 127 **2.2 Mineralogical analysis**

#### 128 **2.2.1 X-Ray Diffraction analysis**

129 **PANalytical Xpert-pro diffractometer** at room temperature, 45 kV, 40 mA and  
130 1.5406 Å wavelength and Cu-K $\alpha$  radiation and Ni-filter, was used for Powder X-Ray  
131 Diffraction (PXRD) analysis. Samples were analyzed between 5-80° in step sizes of  
132 0.017° with continuous mode scanning step time of 50.1650 s while rotating. **Raman**  
133 **spectroscopy** was performed with a confocal laser Raman spectrometer (Horiba  
134 instrument LabRAM HR 800), equipped with a multichannel air-cooled (-70°C) 1024  
135 x 256 pixel charge-coupled device (CCD) array detector as previously described (Chi

136 Fru et al. 2013, 2015). Spectral resolution was  $\sim 0.3 \text{ cm}^{-1}/\text{pixel}$ . Accuracy was  
137 determined by a repeated silicon wafer calibration standard at a characteristic Raman  
138 line of  $520.7 \text{ cm}^{-1}$ .

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## 140 **2.2.2 Transmission electron microscopy**

141 Specimens for Transmission electron microscopy (TEM) were prepared from the  
142 crushed rock specimen powder. This was followed by dry-dispersal onto a 300 mesh  
143 holey carbon TEM Cu grid. Microscopy was conducted using a JEOL 2100 TEM  
144 with a  $\text{LaB}_6$  source in the School of Chemistry, Cardiff University, operated at  
145 200kV. The X-EDS analysis was performed with an Oxford Instrument SDD detector  
146 X-Max<sup>N</sup> 80 T.

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## 148 **2.2.3 Scanning electron microscopy**

149 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analysis  
150 was done on a FEI QUANTA FEG 650 ESEM. Images were captured at 5 kV and  
151 EDS data collected at 20 kV, using an Oxford T-Max 80 detector (Oxford  
152 Instruments, UK). The analyses were performed in low vacuum to minimize surface  
153 charging of uncoated samples. EDS elemental maps were collected for 30 min or until  
154 the signal had stabilized, indicated by a clear distribution trend. The data were further  
155 processed with the Oxford Aztec software.

156

## 157 **2.3 Geochemical analysis**

### 158 **2.3.1 Laser ablation ICP-MS and trace element analysis**

159 Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) was  
160 performed at Cardiff University on polished thin sections. The LA-ICP-MS system

161 comprised a New Wave Research UP213 laser system coupled to a Thermo X Series  
162 2 ICP-MS. The laser was operated using a frequency of 10 Hz at pulse energy of  
163 ~5mJ for an 80µm diameter beam using lines drawn perpendicular to the layering and  
164 at a movement speed of 26 microns sec<sup>-1</sup>. Samples were analyzed in time resolved  
165 analysis (TRA) mode using acquisition times of between 110 and 250 seconds;  
166 comprising a 20 second gas blank, 80-220 second ablation and 10 second washout.  
167 Dwell times varied from 2 msec for major elements to 35 msec for low abundance  
168 trace elements. Blank subtraction was carried out using the Thermo Plasmalab  
169 software before time resolved data were exported to Excel.

170 Separated and independently pulverized banded layers were digested by lithium  
171 borate fusion followed by major, trace and rare earth element (REE) analyses using  
172  P-ES/MS and XRF at  meLabs® (<http://acmelab.com>). Geochemical data were  
173 compared with previously published results for the more widely investigated Mn  
174 deposits (Hein et al., 2000; Liakopoulos et al., 2001; Glasby et al., 2005).

175

### 176 **2.3.2 Isotope analysis**

177 C, N and S isotopic composition for the pulverized samples was determined as  
178 previously described (Chi Fru et al., 2013, 2015), following combustion in a Carlo  
179 Erba NC2500 analyzer and analyzed in a Finnigan MAT Delta V mass spectrometer,  
180 via a split interface to reduce gas volume. Reproducibility was calculated to be better  
181 than 0.15‰ for δ<sup>13</sup>C and δ<sup>15</sup>N and 0.2‰ for δ<sup>34</sup>S. Total C and N concentrations were  
182 determined simultaneously when measuring the isotope ratios. The relative error was  
183 <1% for both measurements. For carbon isotopic composition of organic carbon,  
184 samples were pre-treated with concentrated HNO<sub>3</sub> prior to analysis.

185

## 186 **2.4 Organic geochemistry analysis**

187 Lipid biomarker and compound specific  $\delta^{13}\text{C}$  analyses were executed on powdered  
188 samples of sectioned bands from which exposed surface layers had been removed.  
189 Modern sediments from Spathi Bay, 36°40'N, 24°31'E, southeast of Milos Island,  
190 collected by push coring at 12.5 m below the seafloor were freeze-dried prior to  
191 extraction to aid the identification of potential syngenetic biomarkers in the  
192 Quaternary rocks. Between 4-6 g of ground samples were ultrasonically extracted  
193 using 3×Methanol, 3×(1:1) Methanol:Dichloromethane (DCM), and 3×DCM and  
194 extracts were combined and dried under  $\text{N}_2$ . Samples were subsequently re-dissolved  
195 in DCM then methylated following the method of Ichihara and Fukubayashi (2010).  
196 The resulting residue was silylated using, 20  $\mu\text{l}$  pyridine and 20  $\mu\text{l}$  TFA and heated  
197 at 60°C for 15 min. Total lipid extracts were analyzed using a Shimadzu QP 2010  
198 Ultra gas chromatography mass spectrometer (GC/MS). Separation was performed on  
199 a Zebron ZB-5HT column (30 m x 0.25 mm x 0.10  $\mu\text{m}$ ) with a helium carrier gas  
200 flow at 1.5 ml  $\text{min}^{-1}$ . Samples were injected splitless, onto the column at 40°C with  
201 the subsequent oven temperature program ramped to 180°C at a rate of 15°C  $\text{min}^{-1}$ ,  
202 followed by ramping to 325°C at a rate of 4°C  $\text{min}^{-1}$  and a final hold for 15 min. The  
203 MS was set to scan from 50 to 800 m/z with an event time of 0.70 sec and a scan  
204 speed of 1111 u/sec. All peaks were background subtracted and identification  
205 confirmed using the NIST GC/MS library and literature spectra. Contamination was  
206 not introduced into the samples, as blank samples worked up concurrently with the  
207 rock fractions had results comparable to the ethyl acetate instrument blank.

208

## 209 **2.5 Chemical weathering analysis**

210 Chemical index of alternation (CIA) was used to determine whether variations in  
211 chemical weathering intensities would in addition to hydrothermal activity deliver  
212 materials into the depositional basin from the continent, according to the  
213 formula:  $CIA = Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O) \times 100$  . Extensively  
214 applied, the CIA index reveals subtle changes in weathering fluxes (Nesbit and  
215 Young, 1982; Maynard, 1993; Bahlburg & Dobrzinski, 2011), where increasing CIA  
216 values generally indicate amplified chemical dissolution of rocks and selective release  
217 of dissolvable CaO, Na<sub>2</sub>O and K<sub>2</sub>O into solution (Nesbit & Young, 1982; Maynard,  
218 1993; Bahlburg & Dobrzinski, 2011). The broken rock particles enriched in the  
219 poorly soluble Al<sub>2</sub>O<sub>3</sub> fraction, settle to the seafloor as weathered sediments carrying a  
220 chemical composition different from the source. In the absence of chemical  
221 dissolution, no net chemical change is expected in the composition of sediments  
222 compared to source and thus a low CIA index. CIA indices for detritus of 0-55, 55-75  
223 and >75, are considered unweathered, unweathered to slightly weathered and  
224 weathered to highly weathered, respectively (Nesbit & Young, 1982; Maynard, 1993;  
225 Bahlburg & Dobrzinski, 2011). The redox conditions under which sediments formed  
226 were obtained from REE composition normalized to the North American Shale  
227 Standard (NASC) (Groment et al., 1984).

228

## 229 **3 Results**

### 230 **3.1 Lithostratigraphy**

231 Field-wide sedimentological and lithostratigraphical mapping of the CVSB in the  
232 summer and fall of 2014, enabled the assessment of the lateral and vertical coverage  
233 of the Milos Mn oxide-rich facies relative to the Mn-rich sandstones that dominate  
234 the Early Quaternary sedimentary basin (Fig. 2). Six stratigraphic sections,

235 representing marine siliciclastic lithofacies sequences, were investigated along a ~1  
236 km SW-NE trending portion of the CVSB infill (Supplementary Figs 1-7). Sequence  
237 stratigraphy was conducted on outcrops and vertical shafts and tunnels left behind by  
238 ~~extinct~~ Mn mining activity. Two of those sections; Section A located at  
239 36°44'17.85''N, 24°21'17.72''E and Section B located at 36°44'35.11''N,  
240 24°21'11.25''E, contain stratigraphic units composed of layered, bedded, or  
241 laminated rocks that contain  $\geq 15$  % Fe, in which the Fe minerals are commonly  
242 interlayered with quartz or chert, in agreement with the definition of Precambrian  
243 BIFs (James, 1954; Gross, 1980; Bekker et al., 2010). These IFs are descriptively  
244 referred to here as microfossiliferous iron formation (MFIF) according to Chi Fru et  
245 al. (2013, 2015), and non-microfossiliferous iron formation (NFIF) (this study),  
246 respectively (Fig. 2). The MFIF and the NFIF occupy at most ~20% of the entire  
247 CVSB infill. The stratigraphy and sedimentary lithofacies are illustrated below,  
248 using lithofacies codes modified after Bouma (1962), Miall (1978, 1985), Lowe  
249 (1982), Mutti (1992) and Shanmugam (2016).

250 Further field stratigraphic survey revealed considerable lithologic variability  
251 within three fault-bounded volcanosedimentary sub-basins in the CVSB (Fig. 2),  
252 which for the sake of simplicity are referred to as Basin 1—host of the MFIF; Basin  
253 2—host of economic grade Mn ore; and Basin 3—host of the NFIF (Fig. 2). Each  
254 section is framed by distinct marginal normal faults that strike in the NW-SE and NE-  
255 SW to NNE-SSW directions, distinguishable by distinct lateral sedimentary facies  
256 exhibiting unique vertical sequence stratigraphy (Fig. 2; Supplementary Figs 1-7).  
257 Faulting in the CVSB is related to major geographical activation of extensional  
258 structures at intervals that shaped Milos into a complex mosaic of neotectonic units  
259 (Papanikolaou et al., 1990).

260

261 **3.1.1 Section A (36°44'17.85''N, 24°21'17.72''E)**

262 Informally known as “Little Vani”, Section A is the type section containing the MFIF  
263 at the base. It crops out in the W-SW edge of the CVSB (Figs 1 & 2) as a ~6-7 m high  
264 cliff resting stratigraphically on submarine dacitic and andesitic lavas and domes.  
265 This section extends laterally in the N-NE direction for an estimated 300–500 m.

266

The MFIF is correlatively interpreted to be in direct stratigraphic contact with

267

Late Pliocene-Early Pleistocene (2.5–1.5 Ma) basement submarine dacitic-andesitic

268

rocks. Lithologically, the MFIF comprises laminated and massive fine-grained red

269 and white weathered ferruginous jaspelitic red chert layers (Chi Fru et al., 2013,  
270 2015). The chert layers contain morphologically distinct Fe minerals dispersed in a  
271 fine-grained siliceous matrix (Fig. 3), marked by the notable absence of pyrite and an  
272 extremely low S content (Chi Fru et al., 2013, 2015). Layers are tabular and typically  
273 laterally continuous at scales of several meters, whereas wave and current structures  
274 (e.g., cross-lamination), are generally absent from the MFIF. The hematite-rich MFIF  
275 laminae (Table 1) are built by massive encrustation of anoxygenic photoferrotrophic-  
276 like microbial biofilms by precipitated Fe (Chi Fru et al., 2013). The base of the MFIF  
277 outcrop, is visibly mineralized by black diffused bands/veins composed of Mn oxides  
278 (Fig. 4 & Table 1).

279 A markedly reddish 2-3 m-thick section immediately overlies the MFIF,  
280 comprising a distinct package of Fe-rich beds that transition up the section from fine  
281 to reddish medium and coarse-grained to pebble–cobble conglomerate volcanoclastic  
282 sandstone beds (Figs 4A & 5). The lower 1-2 m consist of fine-grained sandstone  
283 beds that are well to moderately sorted, containing a 20-40 cm thick portion  
284 dominated by plane parallel-laminated sandstone/sandy tuff, massive to plane

285 parallel-laminated sandstone/sandy tuff, and massive sandstone/sandy tuff lithofacies  
286 (Fig. 5; Supplementary Fig. 1). The fabric of these Fe-rich sandstone facies consists  
287 of sub-angular to sub-rounded and 100–600 µm fine to medium-grained volcanoclastic  
288 K-feldspar grains, making up to 75% of the total rock, with variable amounts of  
289 quartz and clay mineral grains.

290 The latter are overlain by a ~1-1.5 m sequence of poorly-sorted tabular clast-  
291 supported pebble-to-cobble conglomerate beds with an erosional base, grading  
292 upward into coarse to medium-grained **S** beds, arranged in alternating conglomerate  
293 cycles (Fig. 5), averaging 20-40 cm in thickness. The cobble/pebble conglomerate  
294 clasts include intraformational volcanic rocks (dacite, andesite), allochthonous  
295 volcanoclastic sandstone, and volcanoclastic microclasts (e.g. K-feldspar), cemented  
296 by hematite (Fig. 5; Chi Fru et al., 2013; Kiliyas et al., 2013). Towards the  
297 westernmost edge of the “Little Vani” section, there is a facies change from the  
298 graded **m/Sh** rhythms to a predominantly Fe-rich conglomerate Gcm bed (Fig. 4A),  
299 termed the conglomerate-hosted IF (CIF) in Chi Fru et al. (2015), with a maximum  
300 thickness of ~0.5 m and a cobble size range of ~10 cm. The Fe-rich conglomerate bed  
301 transitions upward into medium-grained pebbly reddish ferruginous Sm with thin  
302 volcanic rock and sandstone pebble lenses. ~~This in turn grades~~ upwards into a very-  
303 fine-grained greenish glauconite-bearing plane parallel-laminated sandstone to  
304 siltstone bed; characterized by soft-sediment deformation structures, such as flame  
305 structures, convolute bedding and lamination structures, loop bedding, load casts, and  
306 pseudonodules (Supplementary Figs 1-2).

307 The “Little Vani” section is eventually capped along an erosional surface by  
308 an overlying 1-2 m thick section dominated by medium to fine-grained and  
309 moderately to poorly-sorted reddish Fe-rich tabular sandstone beds, 10–40 cm thick,

310 topped by patchy sub-cm to cm-thick Mn-rich sandstones (Fig. 5; Supplementary Figs  
311 1-2). Dominant lithofacies of the Fe-rich sandstone cap include planar and hummocky  
312 cross-bedding, exhibiting bioturbation in places. The Fe-rich lithofacies cap is  
313 laterally discontinuous, thinning out basinwards towards the N-NE, and can be  
314 observed smoothly grading into a 1-2 m thick section composed of cm to sub-cm-  
315 thick Mn-rich volcanoclastic sandstone lithofacies, described below in Section B. No  
316 Fe-rich hydrothermal feeder veins are obvious ~~in the MFIF, however feeder~~ veins and  
317 Mn horizons can be observed to truncate laminations in the MFIF, and up through the  
318 whole “Little Vani” section (e.g., Figs 4C & 5).

319

### 320 **3.1.2 Interpretation of Section A**

321 The MFIF rests directly on the submarine dacites-andesites that were deposited in  
322 ~~a~~ relatively shallow but dominantly below ~~a~~-wave base submarine setting (Stewart and  
323 McPhie, 2006). The fine-grained, finely laminated nature of the MFIF, and, the lack  
324 of evidence of current or wave structures (e.g., symmetric ripples or hummocky  
325 cross-stratification), coupled to the absence of volcanogenic detrital particles and  
326 intraclast breccia structures, indicate a low energy sedimentation environment at ca.  $\geq$   
327 100-200 m depth, marked by negligible volcanic interference (e.g., Tice and Lowe,  
328 2006; Trower and Lowe, 2016; Konhauser et al., 2017). This interpretation is  
329 supported by the observed enrichment of Fe in the MFIF; a characteristic of relatively  
330 deeper water lithofacies (Trower and Lowe, 2016; Konhauser et al., 2017). This view  
331 is ~~compatible~~ with the proposition that hematite enrichment in the MFIF was under  
332 the control of photoferotrophic biofilms (Chi Fru et al., 2013) known to thrive at  
333 lower light intensities (Kappler et al., 2005; Li et al., 2013; Konhauser et al., 2017).  
334 The quiet environmental conditions would have ensured the formation of such stable

335 photoferrotrophic biofilms over extended periods of time that would have facilitated  
336 the oxidation of hydrothermally released Fe(II) and the deposition of Fe(III) minerals.

337 The overlying lithofacies sequence record a switch to faster accumulation of  
338 volcanoclastic turbidites on the quiet MFIF deposit, with the fine, medium to coarse-  
339 grained sandstone lithofacies typifying deposition during low and high density  
340 turbiditic flows in the middle to inner parts of a turbidite fan-like environment (Lowe,  
341 1982; Mutti 1992; Talling et al., 2012; Orme and Laskowski, 2016; Shanmugam,  
342 2016; Wang et al., 2017). Massive conglomerates containing both allochthonous  
343 sandstone clasts and intraformational andesite-dacite are interpreted as channelized  
344 submarine debris flows or slump deposits sourced from adjacent topographic highs  
345 (Lowe, 1982; Stewart and McPhie, 2006; Orme and Laskowski, 2016). Also,  
346 deposition from a waning low density turbidity current is indicated by the upward  
347 fining bed of pebbly Fe-rich sandstone, greenish glauconite bearing sandstone and  
348 laminated siltstone. Up section, the abundance of parallel and cross stratified Fe-rich  
349 and Mn-rich sandstone facies along an erosional surface, reflect a change in  
350 deposition to a high energy, shallow submarine shoreface/foreshore setting, above a  
351 wave base.

352 In summary, stratigraphic observations in the “Little Vani” section indicate that  
353 the MFIF constitutes the older IF deposited on the CVSB basement lavas. Following  
354 MFIF deposition, there have been a series of upward lithologic changes which reflect  
355 gradual shoaling, accompanied by tectonic instability, topographic growth, submarine  
356 erosion, and massive sediment supply by density/gravity flows of volcanogenic  
357 debris. It is proposed that these changes were controlled by a combination of  
358 submarine volcano-constructional processes, synvolcanic rifting and volcano-tectonic  
359 uplift, resulting in cyclic changes in depositional water depth (Stewart and McPhie,

360 2006; Papanikolaou et al., 1990; Steele et al., 2000; Trower and Lowe, 2016; Wang et  
361 al., 2017).

362

### 363 **3.2 Section B (36°44'35.11''N, 24°21'11.25''E)**

364 This ~8-10 m-thick fault-bounded stratigraphic section, here referred to as “Magnus  
365 Hill”, is the type section that contains the NFIF (Figs 2 & 7; Supplementary Figs 3-4).

366 Two lithostratigraphic units—a lower unit A and an upper unit B—are identified in  
367 this study. Unit A is made up of a lower sandstone facies that is ~4-5 m thick,

368 dominated by a Mn-oxide cement exhibiting a grayish to black, coarse to very coarse-  
369 grained volcanoclastic sandstone beds, overlain by reddish brown Fe-rich massive

370 sandstone beds (Fig. 8 & Supplementary Figs 3-4). Unit B, ~5 m thick,  
371 unconformably overlies unit A and comprises two distinct packages of beds that

372 transition up section from brownish gravel-to-pebble conglomerate beds (0.5-1.0 m  
373 thick), in contact with the very fine-grained NFIF deposit (Supplementary Fig. 8 & 9).

374 The NFIF is capped by patchy cm-thick crustiform Mn oxides. Bifurcating feeder  
375 veins composed of barite, quartz and Mn, and Fe-oxide minerals cut through the

376 underlying sandstone beds (Supplementary Fig. 4).

377 Sandstone beds are moderately to well-sorted and 5-15 cm thick, and Mn-  
378 mineralized lithofacies include plane parallel-laminated sandstone, plane parallel

379 laminated to rippled sandstone, planar cross-bedded sandstone, and massive  
380 sandstone. Secondary lithofacies include thinly bedded (1-5 cm thick) greenish

381 glauconite-bearing heterolithic sandstone and thin (< 5 cm thick) white to pale-brown  
382 sandy tuff beds interbedded with the other Lithofacies. The sandstone facies host the

383 main economic grade Mn-oxide ores in the CVSB, which typically nstruct

384 texturally diverse cements associated with a variety of volcanoclastic detritus (i.e., K-

385 feldspar, lithic fragments, altered volcanic glass, quartz, sericitized plagioclase,  
386 chloritized biotite) and authigenic barite ~~and/or~~ glauconite. This constitutes part of a  
387 separate study devoted to the Mn ores and will not be dealt with further here, as the  
388 focus of the current study is on the IFs. Kiliyas (2011), however, suggested that many  
389 of the sedimentary structures identified within the Mn–mineralized sandstone  
390 lithofacies are associated with microbial mat growth.

391 The NFIF is composed of strongly banded Fe-rich rocks (Fig. 7) exposed on  
392 the topmost part of “Magnus Hill”. About 2-3 m thick, the NFIF consists of mm to  
393 sub-mm thick, dark grey and brown Fe-rich bands, interbanded with reddish brown  
394 Si-rich layers (Figs 7 & 9-11; Supplementary Figs 10-11). Sedimentary structures in  
395 the NFIF are predominantly characterized by rhythmic mm to sub-mm thick bedding  
396 (e.g., Fig. 7). The ~~iron-oxide~~ rich bands made up mainly of hematite (Table 1 & Fig.  
397 10C) are typically composed of very fine-grained angular to sub-angular volcanic dust  
398 material (i.e., fine volcanic ash with particle size under 0.063 mm, K-feldspar,  
399 tridymite and cristobalite (Table 1) in an amorphous Si and crystalline hematite  
400 matrix (Fig. 12). The predominantly amorphous Si-rich bands are typically ~~planar~~  
401 finely laminated and composed of microcrystalline to cryptocrystalline ferruginous  
402 chert.

403 The NFIF is directly overlain by a ~1 m thick laminated to massive well-  
404 indurated, nodular-pisolitic ironstone bed (Fig. 8A, C & D) that locally preserves a  
405 sub-horizontal fabric reflecting the bedding in the original sediment or contain various  
406 ferruginous clasts such as fragments, nodules, pisoliths, and oololiths set in a hematite-  
407 rich siliceous matrix (Fig. 8C). Scattered cm-scale pisoliths display a crude concentric  
408 internal layering, characterized by open and vermiform voids filled by cauliflower-  
409 like Mn ~~oxides overprint~~ (Fig. 8D).

410

### 411 3.2.1 Interpretation of Section B

412 We interpret the ferruginous NFIF lithofacies to represent the deepest water deposits  
413 in the “Magnus Hill” section based on its very fine-grained sedimentary composition,  
414 fine laminations and a paucity of intraclast breccias (e.g., Trower and Lowe, 2016,  
415 and references therein). ~~These combined~~ with the lack of evidence for wave and  
416 current-formed sedimentary structures (e.g., hummocky cross-stratification, trough,  
417 ripple cross-stratification, and erosional contacts), indicate quiet water low energy  
418 sedimentation, below a likely fair-weather wave base (Simonson and Hassler, 1996;  
419 Trendall, 2002; Krapež et al., 2003; Trower and Lowe, 2016; Konhauser et al., 2017).  
420 This interpretation is consistent with ~~(1)~~ up section lithofacies change from  
421 predominantly sandstone facies of the lower unit to conglomerate facies (Fig. 8B),  
422 probably related to a series of channel deposits in an inner-turbidite fan-like setting  
423 (Orme and Laskowski, 2016). This sedimentary sequence shows overall deepening  
424 from a tidal to shoreface zone depositional environment to an offshore zone during  
425 periods of high sea level stand (Trower and Lowe, 2016); ~~(2)~~ conclusions of previous  
426 workers suggest that lithofacies with Fe-rich composition similar to the NFIF, were  
427 deposited from seawater in a basinal settings (Lowe and Byerly, 1999; Tice and  
428 Lowe, 2006). The hypothesized deepening of the “Magnus Hill” section is generally  
429 consistent with the interpretation that active rifting was occurring during the filling of  
430 the CVSB (Papanikolaou et al., 1990; Stewart and McPhie, 2006; Liakopoulos et al.,  
431 2001; Papavassileiou et al., 2017), resulting in the transition from a relatively shallow  
432 and deeper water setting represented by the sandstone and conglomeratic deposits, to  
433 a relatively deeper quiet water environment, characterized by the finely laminated  
434 NFIF facies (Trower and Lowe, 2016).

435 Sedimentary structures and microbial mat fabrics (Kilias et al., 2011) in  
436 lithostratigraphic unit A are interpreted to record a variation between storm-  
437 dominated shallow-marine (lower shoreface), stable shallow-marine environment  
438 with low sedimentation rate in an upper to middle shoreface, and tide-influenced  
439 environments (e.g. Noffke et al., 2003; Ramos et al. 2006; Kilias, 2011; Ossa et al.,  
440 2016).

441 We interpret that each graded Fe oxide-rich band of the NFIF (Supplementary  
442 Figs 8 & 9), represents an individual fallout deposit from a proximal pyroclastic  
443 eruption (Stiegler et al., 2011; Trower and Lowe, 2016). This interpretation is  
444 supported by normal grading in fine volcanic ash content that reflects their likely  
445 origin as pyroclastic fallout deposits in an otherwise quiet water setting (Lowe, 1999).  
446 For example, tridymite is a stable SiO<sub>2</sub> polymorph formed at low pressures of up to  
447 0.4 GPa and at temperatures of ~870-1470 °C (Swamy et al., 1994; Koike et al., 2013;  
448 Morris et al., 2016). The coincidence of tridymite formation with silicic volcanism is  
449 in agreement with the widespread distribution of andesite, dacite and rhyolite lava  
450 domes in the CVSB. For example, vapour phase production of tridymite together with  
451 sanidine identified in this study (Fig. 10) and iron oxides is principally associated  
452 with rhyolite ash flow (Breitkreuz, 2013; Galan et al., 2013). Similarly, Cristobalite is  
453 a SiO<sub>2</sub> polymorph associated with high temperature rhyolitic eruptions (Horwell et al.,  
454 2010). Finally, in situ carbonaceous laminations are absent, suggesting that benthic  
455 microbial mat growth had no influence on deposition of the NFIF (Trower and Lowe,  
456 2016). Ironstones overlying the NFIF are difficult to interpret with the existing data,  
457 but may represent primary granular iron formations (GIF); i.e., a facies transition  
458 from BIF-style to GIF-style IF (e.g., Bekker et al., 2010), or supergene ferruginous  
459 duricrust formation resulting from subaerial weathering (Anand et al., 2002).

460

### 461 3.3 Geochemistry

462 The SEM-EDS-electron micrographs of the NFIF thin sections reveal distinct Fe and  
463 Si-rich layers alternating periodically with each other in a fine sediment matrix as  
464 shown by the grain size (Figs 9 & 11 & Supplementary Figs 9-11). Laser ablation  
465 ICP-MS line analysis indicates Si and Fe count intensities in the Milos BIF-type are  
466 comparable to the 2.5 Ga Precambrian BIF reference from the Kuruman IF formation,  
467 Transvaal Supergroup, South Africa (Fig. 11). The laser ablation ICP-MS data further  
468 show that dramatic fluctuations in Fe concentrations control the Si to Fe ratio in both  
469 types of rocks, despite the thousands of millions of years gap between them.

470 No other Fe(III)(oxyhydr)oxide minerals have been identified in the Cape Vani  
471 Fe-rich facies different from hematite. Electron imaging of the NFIF Fe-rich bands  
472 suggests Si, Al and K-rich phases are mostly associated with the volcanoclastic  
473 material predominated by K-feldspar clasts (Fig. 9; Supplementary Figs 10 & 11). A  
474 unique feature of the NFIF is that the hematite in the Fe-rich bands occurs in tight  
475 association with a carbonaceous material (Fig. 10C), but not for the hematite in the  
476 Fe-rich sandstones and in the MFIF. This is also the case for the CIF overlying the  
477 MFIF. Hematite showing a fluffy texture and at times presenting as framboidal  
478 particles, is sprinkled in the Si-rich cement containing traces of Al and K in the MFIF  
479 rocks (Fig. 3). Lack of association of the framboidal-iron-rich particles with S,  
480 following SEM-EDS analysis, rules out a pyrite affiliation. This is consistent with the  
481 non-sulfidic conditions proposed for the deposition of the Milos BIF-type rocks, as  
482 are their Precambrian predecessors. TEM analysis suggests platy nano-Fe oxide-rich  
483 particles predominate in the NFIF and MFIF, confirmed by overlaid X-ray Energy  
484 Dispersive spectra taken from selected areas (Fig. 12) and consistent with the XRD

485 data showing hematite in both samples. The platy hematite needles in the Milos BIF-  
486 type rocks are morphologically, and by size, comparable to hematite needles reported  
487 in the ~2.5 Ga Kuruman BIFs (Sun et al., 2015).

488 Unlike the ~~iron-rich~~ bands, volcanoclasts in the Si-rich bands are much smaller  
489 in size, occurring mainly  fine-grained (Supplementary Fig. 8-11), signifying  
490 predominant precipitation during periods of ~~weaken~~ hydrothermal activity. The SiO<sub>2</sub>  
491 matrix ~~in both the MFIF~~ are fine-grained, occurring mainly as amorphous opal in the  
492 NFIF ~~and crystalline quartz in the MFIF~~ (Figs 10B & 12A-B), ~~while~~ in the MFIF it is  
493 mainly present as crystalline quartz (Fig. 12C-D). Relative concentrations of Al, K  
494 and Ti in the samples are generally low, with bulk-measured concentrations in both  
495 the Si-/Fe-rich bands, together with the SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> content, strongly covarying  
496 with continental crust concentrations (Fig. 13A). Mn impregnation of the MFIF,  
497 preserved in the form of replacement layers mostly identified as cryptomelane  
498 [K(Mn<sup>4+</sup>, Mn<sup>2+</sup>)<sub>8</sub>O<sub>16</sub>] (Table 1), is below detection in the NFIF. Rare hausmannite  
499 (Mn<sup>2+</sup>Mn<sup>3+</sup><sub>2</sub>O<sub>4</sub>) was detected in a few cases in the MFIF (Fig. 10D).

500 Trends of major elements from which CIA indices were calculated (Fig. 13B),  
501 covary with those of the continental crust (Fig. 13A). Continental crust averages, refer  
502 to the zone from the upper continental crust to the boundary with the mantle (Rudnick  
503 & Gao, 2003). The calculated CIA indices average 52 with one outlier at 22 (Fig.  
504 13B). No distinct relationship could be established between the CIA indices and the  
505 respective IFs or between the distinct alternating Si- and Fe-rich bands (Fig. 13).  
506 Highly weathered clay minerals resulting from the chemical decomposition of  
507 volcanic rocks, e.g., kaolinite representing maximum CIA values of 100 or 75-90 for  
508 illite, are absent in the analyzed materials. The absence of carbonates in the rocks  
509 strengthened the CIA indices, since CIA indices are expected to be lower when Ca

510 carbonates are present (Bahlburg and Dobrzinski, 2011). TiO<sub>2</sub> content—a detrital  
511 proxy—is mostly constant and covaries with the CIA values (Fig. 13B), suggesting  
512 little variability and limited continental weathering input. A fairly strong negative  
513 linear correlation was found between SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> values normalized to TiO<sub>2</sub>  
514 (inset, Fig. 13B).

515 Shale-normalized REE values (REE<sub>(SN)</sub>) for both the MFIF and NFIF are  
516 consistent with previous reports (Chi Fru et al., 2013, 2015), and show patterns  
517 typical of marine sedimentary environments affected by hydrothermal activity  
518 throughout Earth's history (e.g., Planavsky et al., 2010). There is a notable absence of  
519 significant negative Ce<sub>(SN)</sub> anomaly for both the MFIF and NFIF (Fig. 14A-B). These  
520 observations are statistically corroborated by true Ce anomalies, calculated as Ce/Ce\*  
521 ((Ce<sub>(SN)</sub>/0.5Pr<sub>(SN)</sub> + 0.5La<sub>(SN)</sub>) and Pr/Pr\* (Pr<sub>(SN)</sub>/0.5Ce<sub>(SN)</sub> + 0.5Nd<sub>(SN)) and considered  
522 significant when Ce/Ce\* and Pr/Pr\* are less than and greater than 1, respectively (Bau  
523 et al., 1996; Planavsky et al., 2010) (Fig. 14B). Further, the Eu/Eu\* anomalies  
524 averages for the MFIF and NFIF and the distinct Fe-/Si-rich bands, suggest a ~2×  
525 higher Eu/Eu\* signal for the Si-rich bands relative to the Fe-rich bands and between  
526 the MFIF and NFIF deposits (Fig. 14C). Average Pr and Yb shale-normalized ratios  
527 (Pr/Yb\*)—a light vs. heavy REE enrichment proxy (Planavsky et al., 2010)—indicate  
528 similar enrichment levels of light and heavy REE in both the NFIF and MFIF, as well  
529 as in the Fe- and Si-rich bands (Fig. 14C).</sub>

530

### 531 3.4 Lipid biomarker distribution and chemotaxonomy

532 Bulk δ<sup>13</sup>C<sub>org</sub> averaged 5.4‰ (SD:±0.22), -25.2‰ (±0.26) NFIF Fe-/Si-rich bands  
533 and -25.6‰ (SD:±0.12) for bulk MFIF, respectively (Table 2). A fractionation effect  
534 between the alternating Fe-/Si-rich layers (Δ<sup>13</sup>C<sub>Fe-rich NFIF-Si-rich NFIF</sub>) is estimated to be

535  $\sim 0.23\%$  (SD $\pm 0.036$ ), while  $\Delta^{13}\text{C}_{\text{Fe-rich NFIF-MFIF}}$  and  $\Delta^{13}\text{C}_{\text{Si-rich NFIF-bulk MFIF}}$  is  $0.13\%$   
536 (SD: $\pm 0.11$ ) and  $0.36\%$  (SD: $\pm 0.14$ ), respectively. These differences are small and  
537 within the margin of error of analysis, suggesting no strong distinction in  $\delta^{13}\text{C}_{\text{org}}$   
538 preserved in the different IFs and their various facies. They are interpreted to mean  
539 similar carbon fixation processes operated during intervals of predominant Si and  
540 Fe(III)(oxyhydr)oxides deposition in both IFs. Attempts to discriminate between these  
541 environments by lipid biomarker analysis revealed mainly  $\text{C}_{16}\text{-C}_{19}$  fatty acid methyl  
542 esters (FAME) in the Fe-rich NFIF bands and in bulk MFIF, while the Si-rich NFIF  
543 bands contain mainly  $\text{C}_{12}\text{-C}_{21}$  FAMES, suggesting either selective preservation (lipid  
544 recovery was lower in the Fe-rich MFIF bands) or shifts to different potential  
545 biological populations during the deposition of the different layers. Preserved lipids  
546 discriminate against typical microbial lipid biomarkers like hopanoids, while  $\text{C}_3$  plant  
547 FAME are detected in all studied materials (Fig. 15). The anaerobic bacteria indicator,  
548  $10\text{MeC}_{16:0}$  FAME, was ~~however~~ identified in a few bands.

549

## 550 **4 Discussion**

### 551 **4.1 Sedimentological processes**

552 The three sub-basin interpretation of the CVSB is consistent with previous proposals  
553 suggesting that sedimentation within the CVSB was characterized by active  
554 synvolcanic rifting which must have been important in shaping basin topography and  
555 the creation of sub-basin architecture (Papanikolaou et al., 1990; Stewart and McPhie,  
556 2006; Liakopoulos et al., 2001; Papavassiliou et al., 2017). Moreover, this tectonic  
557 regime would suggest that the location(s) of volcanism were continually changing  
558 relative to the two stratigraphic sections, which themselves were also being affected,  
559 i.e. changes in depositional water depth and sedimentation style ~~or~~ and/or that local

560 submarine or subaerial topographic highs impeded the lateral continuity of  
561 sedimentary units (Stewart and McPhie, 2006; Trower and Lowe, 2016). Chi Fru et al.  
562 (2015) have suggested there is an upward deepening of the overall depositional  
563 setting recorded in the “Little Vani” section, consistent with rifting during CVSB  
564 infilling time.

565 The CVSB floored by dacitic/andesitic lava domes and overlain by  
566 volcanoclastic infill, dates back to Upper Pliocene-Lower Pleistocene. A complex  
567 mosaic of lithologically diverse sedimentary units (blocks), confined by neotectonic  
568 marginal faults, characterizes the CVSB (Fig. 2). The most pronounced of these faults  
569 being the NW-trending Vromolimni-Kondaros fault (Papanikolaou et al., 1990) that  
570 has been proposed as the trigger of the hydrothermal activity that deposited Mn ore in  
571 the CVSB (Papanikolaou et al., 1990; Liakopoulos et al., 2001; Alfieris et al., 2013;  
572 Papavassiliou et al., 2017). The stratigraphically tight coupling between Mn and Fe  
573 deposition, linked by Fe oxide minerals in feeder-veins, and positive Eu anomalies  
574 (Fig. 14) indicating vent-sourced Fe (Maynard, 2010), associate Fe mineralization to  
575 fault-triggered hydrothermalism in the CVSB. This is consistent with models of  
576 geothermal fluid circulation along fault lines as conduits for the Mn-rich fluids that  
577 formed the Milos Mn ore deposit (Hein et al., 2000; Liakopoulos et al., 2001; Glasby  
578 et al., 2005; Kiliyas, 2012; Papavassiliou et al., 2017). More importantly, the overall  
579 complex neotectonic structure of the CVSB (Papanikolaou et al., 1990) would explain  
580 the creation of restricted basins, with sedimentological, lithological and geothermal  
581 conditions that enabled the development of unique biogeochemical circumstances in  
582 which the NFIF and MFIF formed.

583 The presence of the three depositional basins is supported by the fact that the  
584 sequence lithologies in each fault-bound unit are characterized exclusively by

585 occurrences of specific and variably thick stratigraphic packages that tend to be  
586 absent in others. For example, the MFIF occurs restricted to basin 1 and the NFIF to  
587 Basin 3. Basin 2 is further distinguished by 35-50 m thick interbedded ore-grade Mn-  
588 mineralized and glauconitic sandstones/sandy tuffs, much less developed in Basins 1  
589 and 3 (Fig. 2). The presence or absence of a stratigraphic sequence, together with its  
590 thickness variation, are interpreted as a result of local syntectonic sediment formation  
591 conditions in each basin as a result of block tectonic movements along fault lines  
592 (Papanikolaou et al., 1990; Nijman et al., 1998). It may also be attributed to unique  
593 basin scale water column redox conditions (e.g. Bekker et al., 2010, and references  
594 therein), post-depositional erosion and changing sea level stand (Cattaneo & Steel,  
595 2000).

596 The lack of hydrothermal feeder veins or seafloor exhalative structures (i.e.,  
597 chimneys) in the MFIF and NFIF lithologies, suggests that hydrothermal Fe(II) was  
598 delivered by diffuse flow and that the Milos-IF formed on the seafloor. Importantly, a  
599 number of studies propose that the main Mn deposit in Basin 2 formed in two stages.  
600 ~~First~~ boiling hydrothermal fluids precipitated sulfide at depth, leading to first  
601 generation microbial-induced deposition of Mn oxides as pyrolusite and ramsdellite.  
602 ~~Tectonic~~ uplift resulted in the replacement of the first generation Mn minerals by  
603 second-generation Mn oxides, including cryptomelane (Hein et al., 2000;  
604 Liakopoulous et al., 2001; Papavassiliou et al., 2017). Cryptomelane replacement of  
605 the original Fe(III)(oxyhydr)oxides in MFIF therefore suggests that deposition of the  
606 MFIF is coeval with first stage Mn deposition in Basin 2. This observation also  
607 indicates that at this time, two active fault-bounded basins probably existed in the  
608 CVSB; i.e., Basins 2 and 3 (Fig. 2). For example, the underlying Mn-enriched  
609 sandstone lithology in Basin 3, stratigraphically correlated to the sandstone Mn

610 deposit in Basin 1 and the MFIF Fe-Si-rich rocks in Basin 2, justify this proposal (Fig.  
611 2).

612 A subsequent geomorphological/chemical reconfiguration formed Basin 3,  
613 orchestrating the deposition of the NFIF in a deeper, small-restricted basin (Fig. 2).

614 The deepening of Basin 3 is strongly demonstrated by an underlying fine upward

615 grading of a transgressive-type Fe-rich lag deposit, that transitions into the NFIF. This

616 uplifting into shallower water event that prompted second generation deposition of

617 Mn oxides in Basin 2 and the substitution of Fe(III)(oxyhydr)oxides by Mn in sub-

618 Basin 1, potentially triggered this environmental change in Basin 3. The MFIF and

619 NFIF sequences are therefore temporally and spatially distinct (Fig. 2).

620

## 621 4.2 Formation Mechanism of The Milos BIFS

### 622 4.2.1 Paragenetic sequence

623 It is stressed that the previously generalized model proposed for biological deposition

624 of the Milos IF, refers exclusively to parts of what is now designated as MFIF (Chi

625 Fru et al., 2013). The NFIF is strongly banded, but does not display the typical

626 microfossils seen in the MFIF, where diffused microbanding apparently relates to the

627 distribution of microbial mats in thin sections (Chi Fru et al., 2013, 2015). The

628 distinction of microcrystalline quartz and amorphous silica phases in the MFIF and

629 NFIF, respectively, together with nano-crystalline hematite particles, suggests a

630 primary amorphous silica origin in both deposits, diagenetically transformed to quartz

631 in the MFIF. The difference in silica crystallinity between the IFs is concurrent with

632 the older age predicted for the MFIF relative to the NFIF, from reconstructed

633 sequence stratigraphy (Fig. 2). Hematite in BIFs is generally interpreted, based on

634 thermodynamic stability, to be a transformation of various primary Fe(III) minerals,

635 with ferrihydrite often proposed as the principal precipitate from the water column  
636 (Glasby and Schulz, 1999; Bekker et al., 2010; Johnson et al., 2008; Percoits et al.,  
637 2009). It is thought that acidic pH yields mainly goethite while hematite is produced  
638 at circumneutral pH (Schwertmann and Murad, 2007). The notable absence of  
639 diagenetic magnetite and Fe carbonates (siderite and ankerite), point to negligible  
640 coupling of primary Fe(III) oxyhydroxides reduction to organic matter oxidation by  
641 the dissimilatory iron-reducing bacteria during burial diagenesis (Johnson et al.,  
642 2008). Minor occurrence of iron-silicate phases (Chi Fru et al., 2015) indicates an  
643 origin of the hematite precursor in seawater independent of the iron silicate proposed  
644 in some cases (Fischer and Knoll, 2009; Rasmussen et al., 2013, 2014). The up to 50  
645 wt% Fe content recorded in the Fe-rich bands, indicate that large amounts of  
646 dissolved Fe(II) was intermittently sourced and deposited as primary Fe(III) minerals,  
647 through various oxidative processes in the depositional basin.

648 Importantly, the CIA ~~index~~ does not support mass weathering and  
649 mineralization of terrestrial Fe and Si, in agreement with the absence of rivers  
650 draining into the CVSB (Chi Fru et al., 2013). The specific identification of plant  
651 biolipids would at face value imply post-depositional contamination. However,  
652 samples were sawn to remove exposed layers and only the laminated bands for the  
653 NFIF were analyzed, while modern sediments from Spathi bay, located Southeast of  
654 Milos Island where hydrothermal activity is presently ensuing at 12.5 m below sea  
655 level, revealed similar plant lipids as recorded in the Quaternary IF (Fig. 15G). Post-  
656 depositional contamination with terrestrial plant lipids is therefore ruled out for the  
657 idea that recalcitrant plant biomass probably entered the sediments via seawater  
658 entrainment at the time of deposition (see Naden et al., 2005). This finding  
659 necessitates the careful interpretation of bulk  $\delta^{13}\text{C}_{\text{org}}$  values obtained from both the

660 modern and ancient Milos sediments, involving in situ and ex situ biological  
661 contributions to  $^{13}\text{C}_{\text{org}}$  fractionation by various known carbon fixation pathways  
662 (Preuß et al., 1989; Berg et al., 2010).

663 Such indication of mixing of the hydrothermal fluids with seawater may be  
664 interpreted to negate a reducing depositional environment as suggested by the Ce  
665 anomalies. However, Pichler & Veizer (1999) demonstrated that in the unconfined  
666 seafloor shallow hydrothermal vent fields at Tatum Bay, Papua New Guinea,  
667 experiencing little or no water column stratification, as low as 11% seawater is  
668 involved in the precipitation of Fe(III)(oxyhydr)oxides from hydrothermal fluids and  
669 at maximum 57%. It is therefore suggested that seawater mixing during deposition  
670 was at the lower limits. This is demonstrated by the REE analysis and the presence of  
671 anaerobic bacteria biomarkers in the NFIF formation, coupled to sediment lithology  
672 and stratigraphy, as explained below.

673

#### 674 **4.2.2 Tectono-sedimentary processes and band formation**

675 Fluctuation in hydrothermal activity is proposed to account for the banding in the  
676 NFIF (Fig. 16), under redox depositional conditions inferred to be mainly reducing  
677 for both investigated IFs, consistent with previous reports (Chi Fru et al., 2013, 2015).  
678 Positive Eu anomalies indicate a hydrothermal origin for all but one of the sample  
679 suite (Fig. 14A). However, statistically calculated Eu/Eu\* anomalies ( $Eu_{(SN)}/$   
680  $(0.66Sm_{(SN)} + 0.33Tb_{(SN)})$ ) to correct for differences in Gd anomalies commonly  
681 encountered in seawater (Planavsky et al., 2010) are in the range of 0.1-0.58,  
682 averaging 0.42. The values are closer to the anoxic water column values calculated for  
683 Archean IFs, compared to Paleoproterozoic IFs (Planavsky et al., 2010), which may  
684 be due to their deposition in an active volcanic center like most of the Archean

5 Agloma BIFs (Bekker et al., 2010; Chi Fru et al., 2015). The lack of statistically  
686 significant true negative Ce anomalies (Fig. 14B) is interpreted to indicate a reducing  
687 depositional environment for both IFs.

688 CIA ~~indices~~ traditionally provide relative information on contributions from  
689 chemical weathering to sediment deposition, linked to operative hydrological and  
690 climatological patterns on land. This information is often gleaned from ancient and  
691 modern soils and from reworked siliclastic deposits in marine basins (Maynard, 1993;  
692 Bahlburg & Dobrzinski, 2011). The calculated CIA ~~indices~~, however, are closer to the  
693 range obtained for unweathered and or only minimally weathered volcanic rocks (e.g.,  
694 Nesbitt & Young, 1982; Bahlburg & Dobrzinski, 2011), thus pointing to a  
695 predominantly volcanic and/or hydrothermal provenance for the clastic sedimentary  
696 materials in the IFs (also see Alfieris et al., 2013).

7 It has been suggested that the release of reduced submarine hydrothermal fluids  
698 contributed towards maintaining water column anoxia during the deposition of  
699 Precambrian BIFs (Bekker et al., 2010). The calculated Eu anomalies (Fig. 14) and  
700 petrographic data showing volcanoclastic detritus (i.e., K-feldspar, sanidine, tridymite,  
701 cristobalite) as key rock components are in agreement with a submarine hydrothermal  
702 source for the investigated IFs. The coarse volcanoclastic detritus embedded in the Fe-  
703 rich bands compared to the finer particles in the Si-rich layers, highlights rapid  
704 oxidation of Fe(II) that coincided with periodic cycles of hydrothermal/volcanic  
705 discharge of new materials into the water column. However, the fine-grained nature  
706 of both the MFIF and NFIF deposits suggests that deposition likely occurred away  
707 from where such activity was occurring or that volcanic/hydrothermal discharge of Fe  
708 and Si was non-eruptive and disruptive. The Fe-rich bands repetitively revealed  
709 hematite grains cementing the denser volcanoclastic fragments that gradually diminish

710 upwards into a zone of fine-grained hematite before transitioning into Si-rich bands  
711 consisting mainly of finer volcanoclastic detritus. These observations provide four  
712 valuable interpretational considerations for proposing a model for the formation of the  
713 alternating Si and Fe-rich bands.

714 1. The Si and ~~Fe oxides-rich~~ bands are a ~~primary precipitate~~ formed in the water  
715 column, by a process in which the precipitation of amorphous Si occurred  
716 during quiescent non-volcanic intervals, ~~after~~ the oxidation and precipitation  
717 of reduced Fe intermittently introduced into the water column by  
718 volcanic/hydrothermal activity to form the Fe oxides.

719 2. The repetitive zonation of distinct particle sizes, suggests density gradient  
720 sedimentation that requires a water column-like environment, rather than  
721 diagenetic alteration of pre-formed sediments by hydrothermal fluids.

722  The lack of  statistically significant Ce anomaly across the Si and Fe-rich units  
723 does not support sediment diagenesis as an alternative model for explaining  
724 the origin of the Milos IF, in favor for a primary water column source. This is  
725 because the oxidation of ferrous Fe supplied by reduced hydrothermal fluids  
726 to iron oxides, requires coincidental interaction with a sizeable pool of  
727 oxygen (Johnson et al., 2008). Otherwise, light-controlled photoferrotrophy—  
728 an extremely rare sediment characteristic—precipitates Fe oxides in the  
729 absence of oxygen (Weber et al., 2006).

730  The style of deposition of the MFIF and NFIF is distinct from the post-  
731 depositional infilling of a porous sandstone sediment matrix during the  
732 formation of the Mn ores. Instead the deposition of the MFIF and NFIF in  
733 restricted portions in the basins not associated with previously accumulated  
734 sandstones, and the difficulty and lack of evidence to provide a viable

735 biogeochemical mechanism for the formation of the even bands of alternating  
736 Si and Fe-rich layers of several meters high and wide, does not support post-  
737 depositional pore filling of a porous sandstone matrix by Fe, as a potential  
738 pathway to the formation of the Milos IF.

739

#### 740 **4.2.3 Biological involvement**

741 Hematite precipitation in the MFIF on microbial filaments (Chi Fru et al., 2013) was  
742 previously used to propose a generalized basin-scale mechanism for the deposition of  
743 Fe-rich rocks in Cape Vani. ~~However such~~ filaments are absent in the NFIF, while  
744 pure hematite grains are tightly bound to relics of an organic matter signal carrying a  
745 maximum  $\delta^{13}\text{C}_{\text{org}}$  signature of -25‰ (Table 2). Similar processes are recorded in  
746 modern marine sediments where interactions between Fe and free organic matter has  
747 been reported to enable the preservation up to 21.5wt% of total organic carbon over  
748 geological time scales (Lalonde et al., 2012). Moreover, Fe generally traps and  
749 preserves organic matter at redox interfaces (Riedel et al., 2013). The data appear to  
750 suggest that the mechanism of Fe(III) (oxyhydr)oxide precipitation and preservation  
751 varied between the two IFs. ~~The lack of similar photoferrotrophic-like~~ filamentous  
752 fossils reported in the MFIF (Chi Fru et al., 2013), ~~in the NFIF, does not however rule~~  
753 out the potential role of microbial involvement in Fe(II) oxidation, ~~since~~ diverse  
754 microbial taxa carry out this process, several of which are non-filamentous (Chi Fru et  
755 al., 2012). However, our data is insufficient to enable clear quantification of the levels  
756 of abiotic vs. biotic contribution to Fe(II) oxidation in the NFIF. Nevertheless, the  
757 inferred predominantly **anoxic depositional conditions as explained above**, together  
758 with the identification of anaerobic bacteria biomarkers in the laminated bands,  
759 intuitively favor significant contribution of anaerobic biological Fe(II) oxidation in

760 the precipitation of primary Fe(III)(oxyhydr)oxides in the NFIF. See Weber et al.,  
761 2006, for a review of potential biological pathways to anaerobic Fe(II) oxidation.

762 Briefly, anaerobic microbial Fe(II) oxidation can proceed via nitrate reduction  
763 and by photoferrotrophy to deposit Fe(III)(oxyhydr)oxides. These mechanisms have  
764 been linked to microbial contribution to BIF formation (Weber et al., 2006; Kappler et  
765 al., 2005) and also for the MFIF (Chi Fru et al., 2013). However, it is also possible  
766 that microaerophilic neutrophilic Fe(II)-oxidizing bacteria likely played an important  
767 role, assuming a depositional setting analogous to the Santorini caldera and Kolumbo  
768 shallow submarine volcanoes, where such low-O<sub>2</sub>-dependent microbial Fe(II)  
769 oxidation has been identified to actively precipitate Fe(III) (oxyhydr)oxides (Kilias et  
770 al., 2013; Camilli et al., 2015). It appears that in the MFIF, precipitating  
771 Fe(III)(oxyhydr)oxide minerals were bound and preserved free of organic carbon or  
772 that such organic carbon was diagenetically degraded. As was previously shown,  
773 Fe(III)(oxyhydr)oxides completely replaced the organic content of the filamentous  
774 microfossils in the MFIF (Chi Fru et al., 2013).

775 The 10MeC<sub>16:0</sub> FAME identified in the rocks has been reported in anaerobic  
776 organisms coupling nitrite reduction to methane oxidation (Kool et al., 2012), in  
777 sulfate and iron-reducing bacterial species such as *Desulfobacter*, *Desulfobacula*  
778 (*Bühning et al., 2005; Dowling et al., 1986; Taylor and Parkes, 1983*), *Geobacter*,  
779 *Marinobacter* and the marine denitrifier, *Pseudomonas nautical* (Kool et al., 2006;  
780 *Bühning et al., 2005; Dowling et al., 1986*). It had previously been proposed that post-  
781 depositional denitrification was a potential pathway for early organic matter removal,  
782 justified by the low rock organic carbon and nitrogen content in the Milos BIF-type  
783 rocks (Chi Fru et al., 2013, 2015; Table 2). Equally, the detected 10MeC<sub>16:0</sub> FAME  
784 has also been found in anaerobic oxidation of methane (AOM) communities (Alain et

785 al., 2006; Blumenberg et al., 2004), originating from sulfate reducing bacteria.  
786 However, bulk sediment  $\delta^{13}\text{C}_{\text{org}}$  of  $-20\text{‰}$  does not reflect AOM activity that is  
787 expected to produce bulk  $\delta^{13}\text{C}_{\text{org}}$  values that are  $\leq -30\text{‰}$ . Low  $10\text{MeC}_{16:0}$  FAME  
788 concentrations frustrated attempts at acquiring its compound specific isotopic  
789 signature to enable further biomolecular level reconstruction of active microbial  
790 metabolisms to explain Fe deposition mechanisms.

791 It is nevertheless puzzling why potential microbial biomarkers typical of marine  
792 or hydrothermal vent environments are hardly preserved in the rocks, given that  
793 microfossil evidence indicates a vast community of diverse prokaryotic assemblages  
794 in the adjacent MFIF (Chi Fru et al., 2013, 2015). Moreover, sediments of the modern  
795 Milos hydrothermal system and elsewhere on the HVA, are ubiquitously colonized by  
796 microbial life, characterized by the marked large-scale absence or low abundance of  
797 higher life forms, including plants (Kiliyas et al., 2013; Camilli et al., 2015; Oulas et  
798 al., 2015). One possibility could be the discriminatory preservation of lipids related to  
799 their selectivity and reactivity towards Fe(III)(oxyhydr)oxides and clays or different  
800 pathways to diagenetic degradation (e.g., Canuel & Martens, 1996; Lü et al., 2010;  
801 Riedel et al., 2013). As noted, the carbonaceous materials in the BIF-type NFIF rocks  
802 occur in tight association with hematite.

803 Importantly, prokaryotic biomarkers are suggested to poorly preserve in these  
804 young BIF analogues. This raises the possibility that this may provide an important  
805 explanation for why lipid biomarkers are yet to be extracted from Precambrian BIFs.

806 Moreover, the data are compatible with low  $\text{C}_{\text{org}}$  recorded in BIFs of all ages. They  
807 suggest these unique BIF features may not be entirely related to metamorphic  
808 degradation of organic matter, since the Milos BIF-type rocks are unmetamorphosed,  
809 yet have vanishing  $\text{C}_{\text{org}}$  levels similar to the ancient metamorphosed BIFs.

810

#### 811 4.2.4 Mn layers and the deposition of the Si-Fe-rich facies

812 ~~Cryptomelane~~  $[K(Mn^{4+}, Mn^{2+})_8O_{16}]$ , ~~commonly occurring in oxidized manganese~~  
813 ~~deposits resulting from mineral replacements and as open space fillings~~  
814 ~~(Papavassiliou et al., 2016), common in MFIF, supports the idea of post-depositional~~  
815 ~~impregnation of the base of the MFIF by Mn-rich fluids.~~ Microscopic analysis  
816 supports the epigenetic origin of the Mn in the MFIF by revealing Mn oxides growing  
817 along fractures, impregnating and replacing Fe minerals (Fig. 4B-F). The  
818 macroscopically evident thinning out to disappearance of such Mn-rich horizons up  
819 the MFIF, coupled by their development along microfractures emphasizes this  
820 epigenetic Mn origin. Mn is not a common feature of the NFIF, even though it sits on  
821 top of a thin sandstone layer impregnated by Mn, that locally forms the cap of the  
822 main Mn ore at Cape Vani. The generally accepted view is that Mn-rich hydrothermal  
823 fluids rose and mineralized the Cape Vani sandstones (Hein et al., 2000; Liakopoulos  
824 et al., 2001; Glasby et al., 2005). Based on the stratigraphic location of the MFIF,  
825 which pre-dates the Mn-rich sandstones, it is proposed that impregnation of the MFIF  
826 by Mn was coeval with large-scale Mn ore mineralization of the Cape Vani  
827 sandstones, implying the entire basin was likely oxygenated at the time. The lack of  
828 Ce anomalies suggests that both the MFIF and the NFIF formed in anoxic settings.  
829 Similar data for the Mn oxides have suggested formation in oxic settings (Glasby et  
830 al., 2005; Chi Fru et al., 2015). However, more sensitive proxies are needed to resolve  
831 and confirm the stratigraphic and REEs-dependent interpretation of potential redox  
832 conditions. This implies that Mn epigenetically replaced the MFIF, either because the  
833 basin was tectonically uplifted into a high-energy oxygenated shallow water setting  
834 or that sea level dropped, leading to partial metasomatism of the base of MFIF, when

5 oxygenated seawater mixed with hydrothermal fluids and precipitated Mn. The lack  
836 of significant Ce anomalies in the dataset also indicates that for the final deposition of  
837 the NFIF, an eventual deepening event or sea level rise, or both, were tectonically  
838 triggered, resulting in deoxygenation of parts of the CVSB.

839 All of this is feasible with the three-basin-fault-bounded hypothesis as a  
840 requirement for movement along fault lines in response to temporal tectonic  
841 activation. Importantly, a deepening event is suggested by the sudden change from the  
842 underlying Mn-rich layer into the conglomeratic deposit (Fig. 8B) often associated  
843 with sedimentary features that form during sea level rise and the landward migration  
844 of the shoreline (Cattaneo & Steel, 2000). The upward sequential transition from the  
845 Mn-rich facies through pebbly to fine-grained sediment to the NFIF, strongly implies  
846 that the underlying Mn-rich facies and NFIF layers formed in shallower and deeper  
847 waters, respectively, or that they are separated by an erosional unconformity. This  
848 study proposes that the NFIF that overlies the transgressive-type conglomeratic lag  
849 along an erosional contact surface was likely deposited during maximum flooding,

850 when the basin became stagnant and stratified, and subsequently was uplifted to  
851 emergence. Similar transgression-type lithologies are indicated to have regulated  
852 primary sedimentation styles during the deposition of nearshore Paleoproterozoic  
853 BIFs (Pufahl and Fralick, 2004; Pufahl et al., 2014). Moreover, deposition of BIFs in  
854 sandstone/grainstone-dominated environments has also been suggested for  
855 Precambrian IFs (Simonson, 1985; Simonson and Goode, 1989; Pufahl and Fralick,  
856 2004).

857 Uplifting is suggested by potential the weathering of the NFIF to form the  
858 ferruginous duricrust cap. Comparable ferruginous layers on Precambrian BIFs are  
859 linked to pervasive subaerial chemical weathering, via the dissolution of the silica-

860 rich layers and precipitation of relatively stable Fe oxides in the spaces between more  
861 resistant hematite crystals (e.g., Dorr, 1964; Shuster et al., 2012; Levett et al., 2016).  
862 This collective evidence supports the existence of a geodynamic tectonic system  
863 capable of producing shallow oxic to deeper anoxic basin conditions at different times  
864 that would explain the existence of Mn and Fe oxide layers within the same  
865 sedimentary sequence. For example, it is common knowledge that both Fe and Mn  
866 oxides will precipitate in the presence of oxygen (Roy, 1997, 2006), with kinetic rates  
867 usually being faster for the oxidation of reduced Fe than reduced Mn. In the Fe(II)-  
868 rich conditions that prevail in anoxic settings, abiotic reactions between Fe(II) and Mn  
869 oxides, produce Fe(III) leading to the dissolution of the Mn oxides to form reduced  
870 Mn, implying Mn oxides should not accumulate (Dieke, 1985). Moreover, under these  
871 conditions, biological precipitation of Fe(III) can occur rapidly, leaving dissolved Mn  
872 in solution to be deposited when oxygen becomes available. Given that the  
873 hydrothermal fluids of the Hellenic Volcanic Arc are commonly enriched in both  
874 reduced Fe and Mn, the deposition of the MFIF and NFIF therefore implies there was  
875 an existing mechanism that enabled the kinetic discrimination and deposition of the  
876 oxides of Fe and Mn into separate settings, most likely dependent on prevailing redox  
877 conditions. The accumulation of the ferruginous duricrust layer, overprinted by redox  
878 sensitive Mn-nodules, above the NFIF indicates a new shallowing event might have  
879 terminated the formation of the NFIF.

880

#### 881 **4.2.5 Modern analogues on the HVA**

882 Mechanistic explanation for the development of potential stratified waters and  
883 reducing conditions during the deposition of the Milos BIF is problematic. However,

884 evidence is available from present shallow submarine hydrothermal analogues in the  
885 central part of the HVA, to which the CVSB belongs. These include:

886 (1) The crater floor of the Kolumbo shallow-submarine volcano (~600×1200  
887 m<sup>3</sup>), which rises from 504 to 18 m below sea level near Santorini, (Sigurdsson et al.,  
888 2006; Carey et al., 2013; Kiliyas et al., 2013).

889 (2) The N part of Santorini's submerged caldera walls, which rises from 390 m  
890 below sea level to over 300 m above sea level (Druitt et al., 1999; Friedrich et al.,  
891 2006; Nomikou et al., 2013; Camilli et al., 2015).

892 (3) The coastal embayments at the Kameni emergent volcanic islands in the  
893 centre of the Santorini caldera (Hanert, 2002; Nomikou et al., 2014; Robbins et al.,  
894 2016).

895 The benthic waters within Kolumbo's crater potentially sustain O<sub>2</sub> depleted  
896 conditions via stable CO<sub>2</sub>-induced water column densification, and accumulation of  
897 acidic water (pH~5), extending ~10 m above the CO<sub>2</sub> venting crater floor (Kiliyas et  
898 al., 2013). This phenomenon is believed to lead not only to obstruction of vertical  
899 mixing of bottom acidic water, but also to O<sub>2</sub> deprivation by precluding efficient  
900 transfer of oxygenated surface seawater into the deeper crater layer. In addition,  
901 diffuse CO<sub>2</sub> degassing is believed to be linked to the formation of Fe microbial mats  
902 and amorphous Fe(III) oxyhydroxides on the entire Kolumbo crater floor (Kiliyas et  
903 al., 2013). Prerequisites for the ~~O<sub>2</sub>-depleted~~ conditions to happen are the closed  
904 geometry of the Kolumbo crater and the virtually pure CO<sub>2</sub> composition of the  
905 released hydrothermal vent fluids that produce ~~oxygen~~ stratification along a stable  
906 CO<sub>2</sub>-pH gradient.

907 A similar scenario is reported for the Santorini caldera, where large (~5 m  
908 diameter) CO<sub>2</sub>-rich, acidic (pH, ~5.93) hydrothermal seafloor pools and flow

909 channels, develop within m-thick microbial Fe-mats on the seafloor slope at 250-230  
910 m below sea level. Persistent hypoxia exists in these pools, representing concentrated  
911 seafloor CO<sub>2</sub> accumulation centers generated by hydrothermal venting (Camilli et al.,  
912 2015). Here, the dissolved O<sub>2</sub> content (~80 μM or less) in the pools is ~40 % depleted  
913 relative to the surrounding ambient seawater (Camilli et al., 2015). These hypoxic  
914 conditions are comparable to or even lower than those measured in the CO<sub>2</sub>-rich  
915 oxygen minimum zones of coastal oceans, relative to seawater existing in equilibrium  
916 with atmospheric pO<sub>2</sub> and pCO<sub>2</sub> pressures (Paulmier et al., 2008, 2011; Franco et al.,  
917 2014). These conditions enable strong redox stratification of the pool waters, in which  
918 unique Si- and Fe-rich microbial mats are associated with amorphous opal and  
919 Fe(III)(oxyhydro)xides (Camilli et al., 2015). Importantly, the Fe microbial mats in  
920 these CO<sub>2</sub>-rich hypoxic pools are affiliated with specific microaerophilic Fe(II)-  
921 oxidizing bacteria that accumulate Fe(III) oxyhydroxides (Camilli et al., 2015; Oulas  
922 et al., 2015). These Fe bacteria are implicated in the deposition of the Precambrian  
923 BIFs (Konhasuer et al., 2002; Planavsky et al., 2009; Bekker et al., 2010).

924 Hypoxia is also associated with the water column of the Fe(III)-rich coastal  
925 embayments and their hydrothermal vents (≤1.0 m water depth), Kameni islands,  
926 considered a modern analogue environment for the precipitation of Precambrian BIFs  
927 (Hanert, 2002; Robbins et al., 2016 and references therein). Venting fluids are warm  
928 (20-40 °C), acidic to circumneutral (pH 5.5-6.9), enriched in CO<sub>2</sub>, Fe and Si  
929 (Georgalas & Liatsikas, 1936, Böstrom et al., 1990; Handley et al., 2010; Robbins et  
930 al., 2016). Water column stratification is expressed as decreasing O<sub>2</sub> with depth that is  
931 positively related to Fe(III)(oxyhydr)oxide density and microaerophilic Fe(II)-  
932 oxidizing bacterial prevalence (Hanert, 2002). Robbins et al. (2016) found that  
933 Fe(III)-rich suspended particulate material in these “Fe bays” may be associated with

934 anoxia, extending up to the air-seawater interface, near the hydrothermal vents  
935 (Hanert, 2002). They consist of ferrihydrite, goethite and microaerophilic Fe(II)  
936 oxidizers.

937 ~~The~~ biogeochemical occurrence of these phenomena within the localized  
938 confines of the Santorini caldera and Kolumbo crater, may ~~however~~ be difficult to  
939 achieve in ordinary shallow submarine hydrothermal settings, such as those occurring  
940 on the coast of present day Milos. The same may be true for Tatum Bay, where non-  
941 volcanic and unconfined diffuse hydrothermalism is widespread (Dando et al., 1996;  
942 Pichler & Dix, 1996; Pichler & Veizer, 1999; Stüben et al., 1999; Rancourt et al.,  
943 2001; Varnavas et al., 2005).

944 In the Kolumbo and Santorini hydrothermal fields, benthic pH averages 5.5 and  
945 the deposition of carbonates is markedly absent (Kilias et al., 2013, Camilli et al.,  
946 2015; Robins et al., 2016). This conforms to observations in the MFIF and NFIF units  
947 where carbonate mineralization is not detected, thereby suggesting a similar low pH  
948 depositional environment for both the MFIF and NFIF. Ubiquitous  
949 Fe(III)(oxyhydr)oxide precipitation and enriched Si content are prevalent in the CO<sub>2</sub>-  
950 rich-hypoxic shallow submarine Santorini caldera slope pools and the Kameni Fe-  
951 embayments where sulfide precipitation is inhibited (Camilli et al., 2015), or  
952 extremely rare (Robbins et al., 2016). Such sulfide-poor conditions are critical for the  
953 formation of BIFs (Bekker et al., 2010). Moreover, the anoxic amorphous Si-  
954 Fe(III)(oxyhydr)oxide-rich-sulfide-poor shallow submarine environments at Kameni  
955 islands, have been independently proposed as a modern analogue environment for  
956 Precambrian BIF precipitation (Hanert, 2002; Robins et al., 2016).

957 A high Si-Fe(III)(oxyhydr)oxide content, absence of carbonate and sulfide  
958 mineralization, coupled to a generally low S content have also been demonstrated for

959 the CVSB Fe formations (Chi Fru et al., 2013, 2015). This depositional situation is  
960 different, for example, from the unconfined shallow submarine hydrothermal systems  
961 in Tatum Bay and Bahia Concepcion Bahia California Sur, Mexico, where authigenic  
962 carbonate deposition is widespread (Canet et al., 2005; Pichler & Dix, 1996, 2005).  
963 Moreover, there is strong geological evidence that within volcanic crater  
964 environments associated with high CO<sub>2</sub> emission, long-term water column redox  
965 stratification is possible under these special conditions. Further evidence is found in  
966 volcanic crater lakes (for example the shallow 205 m deep lake Nyos in Cameroon—  
967 renowned as one of Earth's three CO<sub>2</sub> saturated volcanic lakes (Ozawa et al., 2016;  
968 Kling et al., 2005)). Here CO<sub>2</sub>-induced water column stratification is associated with  
969 bottom reducing conditions characterized by a low sulfate and high Fe bottom water  
970 content relative to surface concentrations (Tiodjio et al., 2014).

971

## 972 **5 Concluding remarks**

973 This study shows the following new insights in light of what was previously known:

- 974 1. At least two distinct IFs (MFIF and NFIF) formed from hydrothermal mud,  
975 within two localized sub-basins in the ~1 km-long CVSB, ~2.66-1.0 Myr ago,  
976 controlled by local tectonism.
- 977 2. A working model that band formation may involve potential  
978 Fe(III)(oxyhydr)oxide filling of sediment pores and fractures during  
979 diagenesis, is not supported by the data. In addition to the lack of observation  
980 of such phenomena, as demonstrated for replacive Mn mineralization,  
981 calculated Ce and Eu anomalies, together with preliminary sequential iron  
982 extraction analysis (Poulton and Canfield, 2011; data not shown), are

983 suggestive of anoxic depositional conditions likely induced by the release of  
984 reduced hydrothermal/volcanic fluids into a cutoff sedimentary basin.

985 3. The precipitation of Fe(III) and Mn oxides require oxygen. In the absence of  
986 oxygen, Mn is not oxidized, while light and photoferrotrophy will oxidize  
987 reduced Fe to Fe(III)(oxyhydr)oxides. Both light and photoferrotrophy are  
988 however extremely rare characteristics of anoxic sediments, but a common  
989 feature of anoxic Fe<sup>2+</sup>-rich waters, where photoferrotrophy is widespread  
990 (Weber et al., 2006). Collectively, these observations provide an important

991 feasible mechanism for the knife sharp separation of the Mn oxide-rich ores  
992 in the CVSB that are also Fe(III)(oxyhydr)oxide-rich, from the highly  
993 localized MFIF and NFIF deposits that are Fe(III)(oxyhydr)oxide-rich but Mn  
994 oxide-poor.

995 4. The mechanism of formation of the MFIF and NFIF therefore most likely  
996 involved exhalative release of reduced hydrothermal/volcanic fluids into a  
997 restricted and deoxygenated seafloor water column where the oxidation of  
998 reduced Fe to Fe(III)(oxyhydr)oxides occurred, most likely by the activity of  
999 photoferrotrophs (Chi Fru et al., 2013).

1000 5. Episodic intensification of hydrothermal activity is identified as a main  
1001 mechanism for the formation of the millimetric BIF bands (Fig. 16), adding to  
1002 the biological mechanism that was inferred from fossil records in the MFIF  
1003 (Chi Fru et al., 2013, 2015).

1004 6. Abiotic Si precipitation was apparently much slower relative to Fe(III)  
1005 precipitation, resulting in Fe-rich bands in the NFIF forming in association  
1006 with large fragments of volcaniclast and the Si-rich bands with fine Si grains.

1007 7. A combination of the above processes produced pulses of Si and Fe in the  
1008 millimetric Si and Fe-rich bands in the NFIF.

1009 8. The Milos rocks fulfill sedimentological, chemical and mineralogical  
1010 characteristics that established them as potentially the youngest known BIFs;  
1011 following the simplistic definition that BIFs are sedimentary rocks composed  
1012 of alternating layers of Fe and Si containing at least 15% iron.

 1013 9. Whether the rocks described here are analogues of Precambrian BIFs or not,  
1014 and whether the proposed formation mechanisms match those that formed the  
1015 ancient rocks, is opened to debate. Nonetheless, the present study provides  
1016 mechanisms by which rocks with Fe and Si-rich bands can be formed in the  
1017 modern oceans.

1018

1019 *Data availability.* Data can be accessed by request from any of the authors

1020

1021 *Author contributions.* ECF, SK and MI designed the study. ECF, SK, KG and MI  
1022 performed fieldwork. ECF, JER, KG, IM and QH performed research. ECF, SK, KG,  
1023 IM, QH and JER interpreted data. ECF and SK wrote paper.

1024

1025 *Competing interests.* The authors declare that they have no conflict of interest.

1026

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1420 Table 1. Results of X-Ray Radiation (XRD) analysis showing major  
 1421 mineralogical compositions. NFIF (non-fossiliferous iron formation) and MFIF  
 1422 (microfossiliferous iron formation), respectively.

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Mineral phase	MFIF1	MFIF2	MFIF3	Fe-rich NFIF2A	Si-rich NFIF2B	Fe-rich NFIF2C	Si-rich NFIFD	Fe-rich NFIF2E	Fe-rich NFIF2F
Hematite	+	+	-	+	+	+	+	+	+
Quartz	+	+	+	-	-	-	-	-	-
Sanidine	-	-	-	+	+	+	+	+	+
Tridymite	-	-	-	-	+	+	+	+	+
Cristobalite	-	-	-	+	-	-	-	-	-
Cryptomelane	-	-	+	-	-	-	-	-	-

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1459 Table 2. Stable isotope results. Letters A-F on the NFIF samples represent respective

1460 bands of the sawn rock in Figure 7E.

Sample	$\delta^{13}\text{C}_{\text{org}}$ vs PDB (‰)	$\text{C}_{\text{org}}$ (%)	$\delta^{15}\text{N}$ vs air (‰)	N (%)	$\delta^{34}\text{S}$ vs CDT (‰)	S (%)
Fe-rich NFIF2A	-25,63	0,061	nd	0,023	nd	0,01
Si-rich NFIF2B	-25,03	0,109	nd	0,017	nd	0,02
Fe-rich NFIF2C	-24,45	0,068	nd	0,013	nd	0,02
Si-rich NFIF2D	-25,04	0,076	nd	0,015	nd	0,02
Fe-rich NFIF2E	-25,19	0,042	nd	0,009	nd	0,01
Si-rich NFIF2F	-25,49	0,050	nd	0,012	nd	0,03
MFIF1	-25,49	0,087	nd	0,017	nd	0,01
MFIF2	-26,25	0,046	nd	0,005	nd	nd
MFIF3	-25,69	0,041	nd	0,006	nd	nd

ND, Not detected

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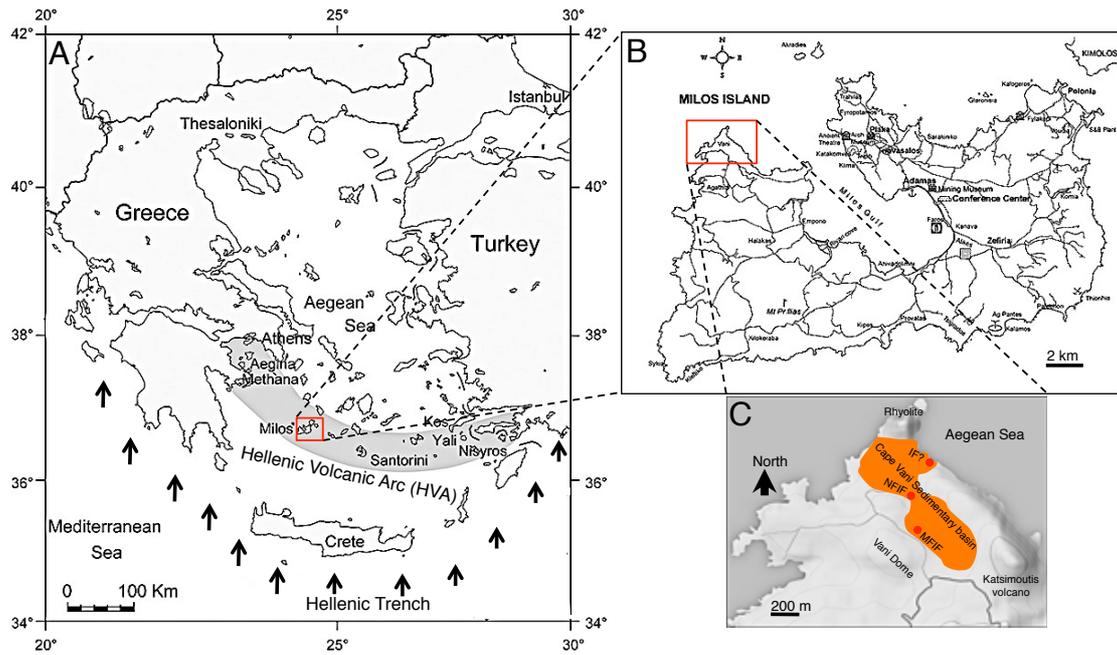
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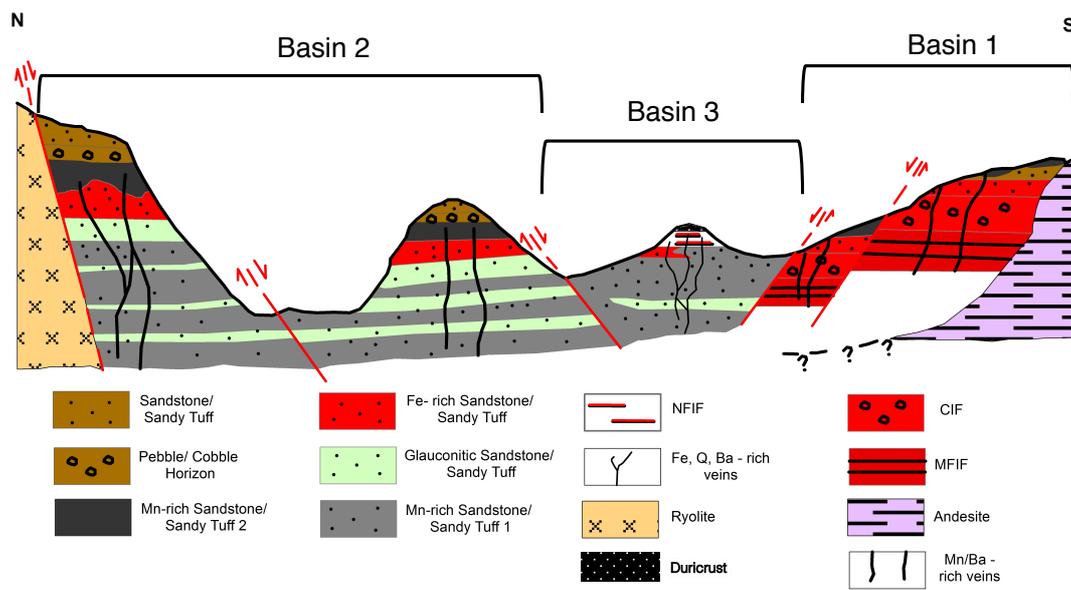


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1481 Fig. 1. Geological map of Milos (redrawn from Marschik et al., 2010). (A),  
 1482 Geotectonic map showing the position of Milos Island, along the Hellenic Volcanic  
 1483 Arc (HVA). Arrows indicate the direction of subduction of the African plate  
 1484 underneath the Eurasian plate. (B) Milos Island. (C), The Milos iron formation is  
 1485 located in the 8-shaped Cape Vani sedimentary basin (CVSB). At least two IFs are  
 1486 present in the CVSB. These are made up of a non-fossiliferous IF (NFIF) at the  
 1487 juncture between the two large sedimentary basins and a microfossiliferous iron  
 1488 formation (MFIF) located at the SW margin in the second basin. A potential third IF  
 1489 (IF?) is located NE, close to the present day Aegean Sea. It is however not certain if  
 1490 this deposit is part of the NFIF or not, because of the open mining pit separating the  
 1491 two.

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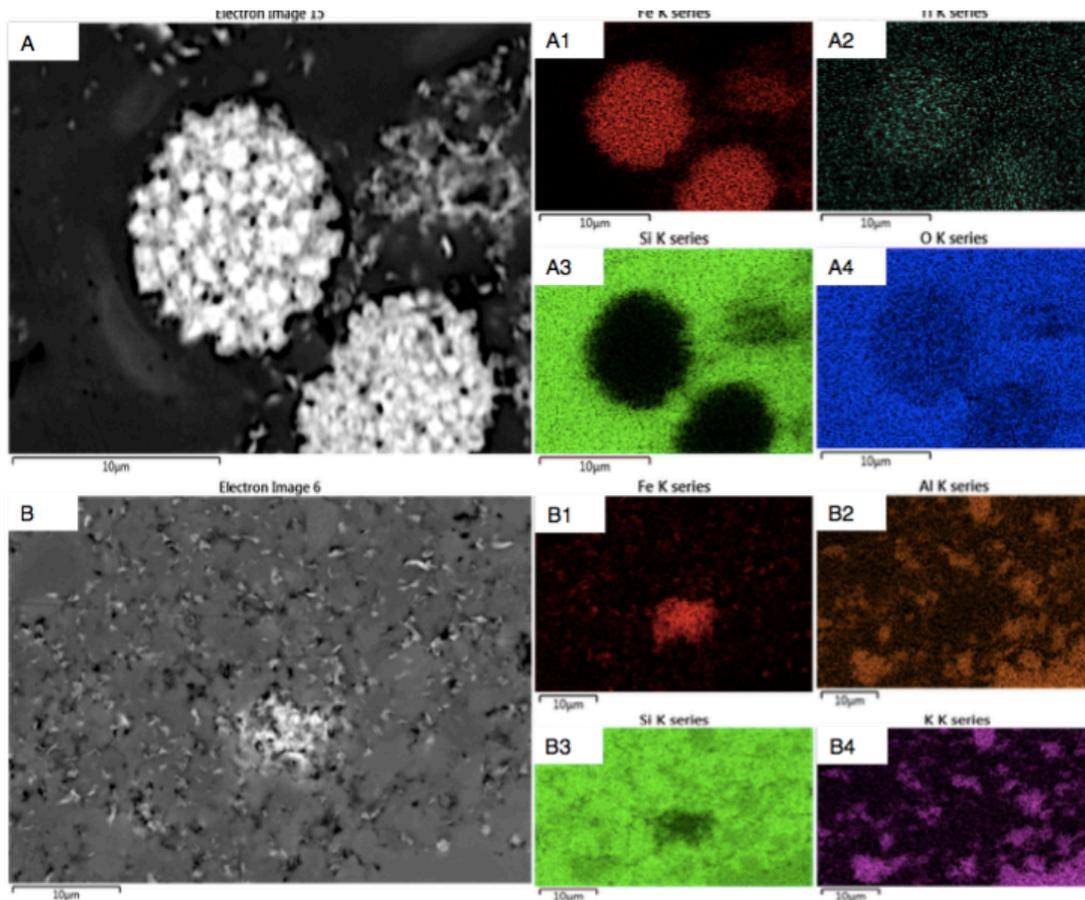


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1495 Fig. 2. Generalized schematic north-south geologic cross section through the ~1 km  
 1496 long CVSB showing interpreted geology, relationships between the main lithofacies,  
 1497 main fault locations, the iron and manganese formations, in support of a proposed  
 1498 three-basin hypothesis. Not drawn to scale. Four types of iron-rich sedimentary rocks  
 1499 occur in the CVSB. These include the iron-rich sandstones, the iron-Mn-rich  
 1500 sandstones, the conglomerate hosted iron formation (CIF) and the MFIF and NFIF  
 1501 formations that are depositionally and chemically distinct from the sandstone  
 1502 deposits.

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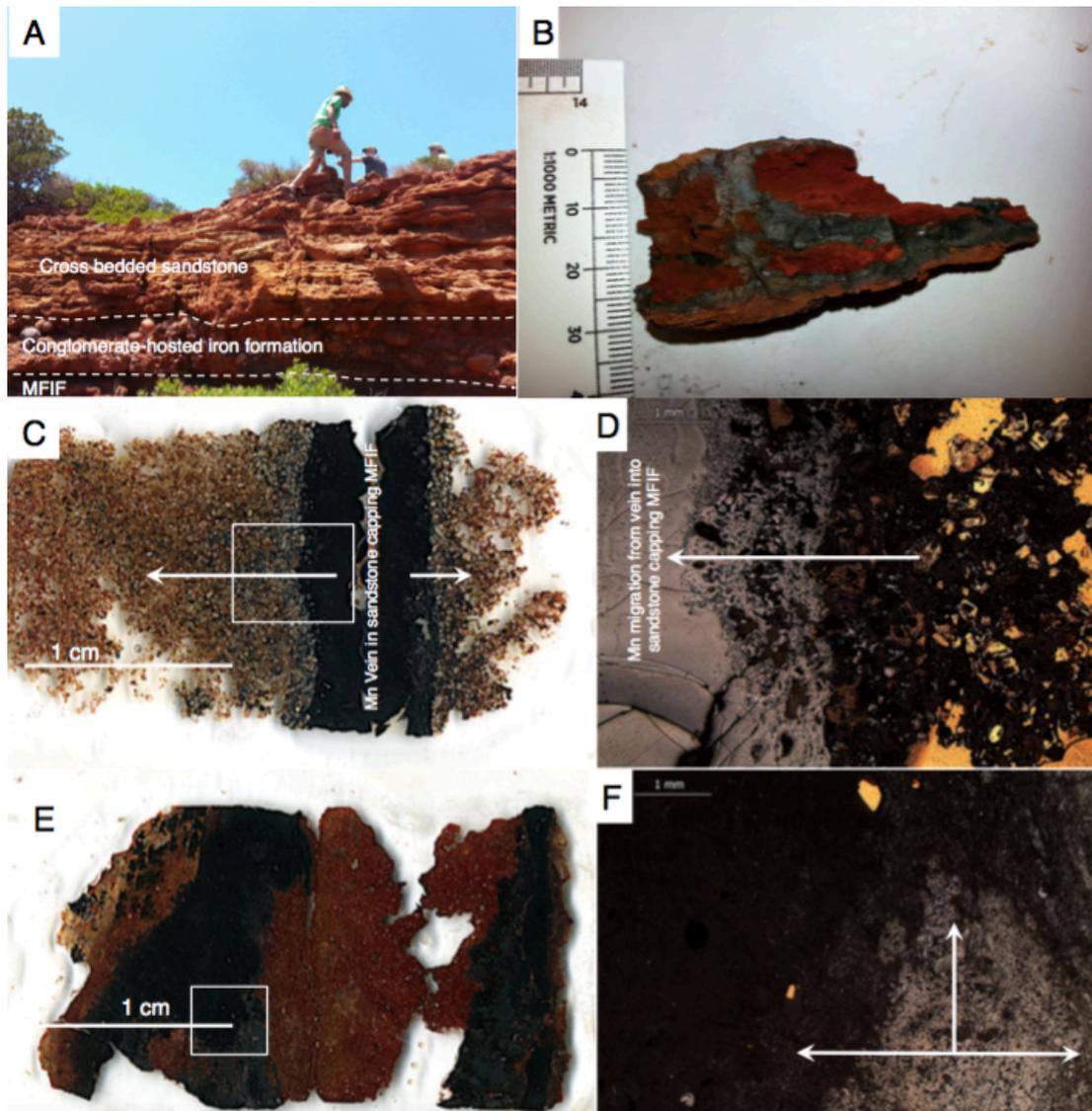
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1506 Fig. 3. EDS-electron image showing different Fe-rich mineral phases in a Si-rich  
 1507 matrix from the MFIF. The bright colours correspond to the analysed elements. (A),  
 1508 framboidal hematite particles. A1-A4, different element compositions associated with  
 1509 framboidal particles in panel A. (B), Dispersed fluffy Fe-rich mineral grains. B1-B4,  
 1510 corresponding elements associated with the micrograph in panel A.  
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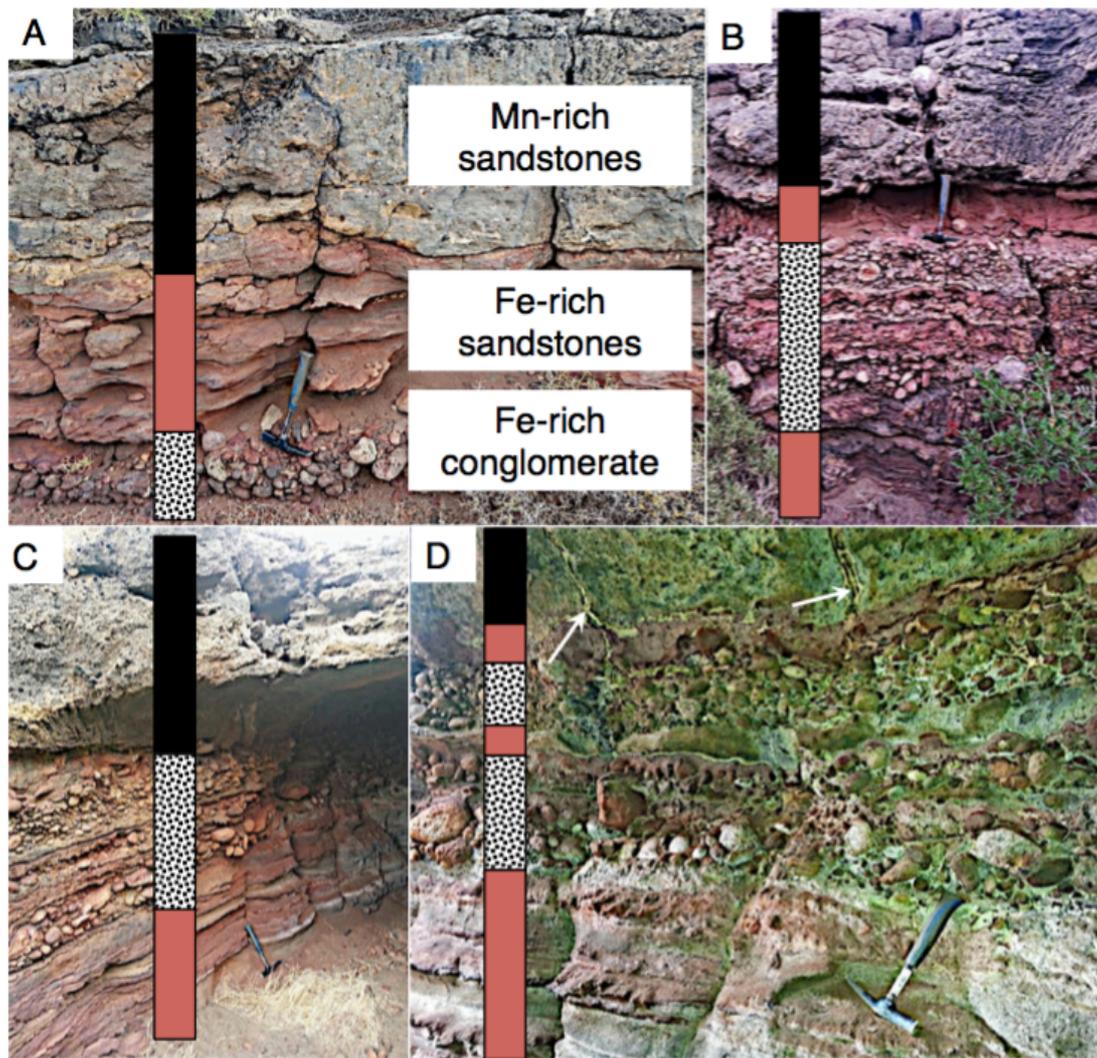


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1514 Fig. 4. Sedimentary profile, thin section scans and optical microscope images of the  
 1515 MFIF. (A), Field photo showing the sedimentary profile of the MFIF characterized by  
 1516 the overlying sandstone cap. (B), Photograph showing black diffused Mn-rich bands  
 1517 near the base of the MFIF. (C), Scanned image of thin section showing a black Mn-  
 1518 rich vein in the overlying MFIF sandstone showing a gradient of Mn migrating into  
 1519 the sandstone matrix (white arrows). (D), Light microscopy images showing details in  
 1520 panel C. (E), Scanned image of an MFIF thin section showing black Mn bands  
 1521 migration into a red iron-rich background. (F), Amplified light microscope image  
 1522 showing gray Mn layers migrating into a black Fe-rich matrix. White arrows show  
 1523 direction of movement. Boxes in C and E are amplified in D and F.

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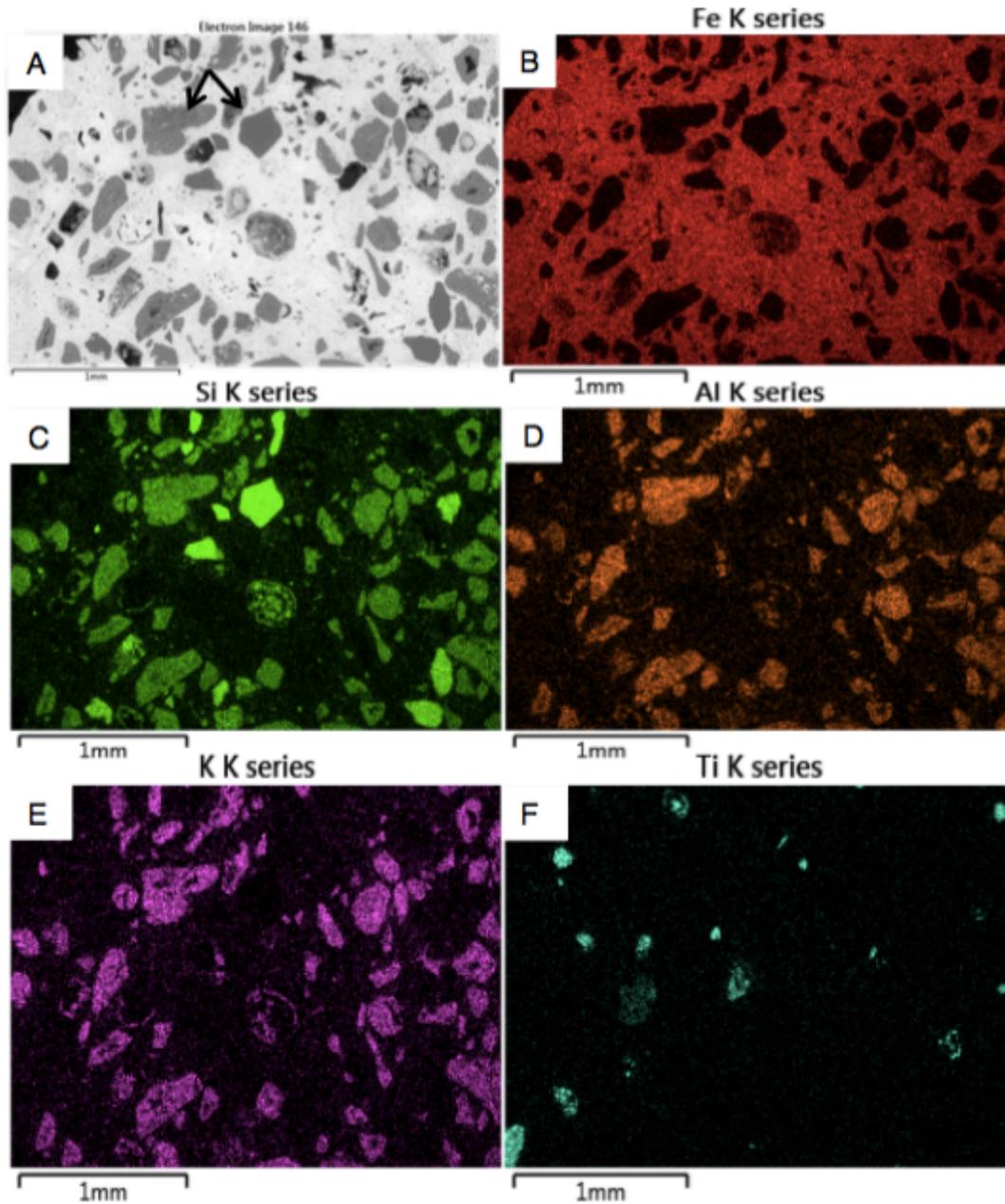


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1527 Fig. 5. Sedimentary sequence overlying the MFIF, consisting of thin (< 0.5 m)  
 1528 polymictic andesite-dacite cobble-pebble, and sandstone-sandy tuff pebble, and Fe-  
 1529 rich conglomerate facies overlain by thinly laminated Fe-rich sandstone beds. This  
 1530 vertical sequence is interpreted to represent a progressively deeper water environment  
 1531 deepening-upward sequence (A) as a result of sea level rise due to tectonic  
 1532 subsidence. The multiple cycles shown in panels B-D signify several potential  
 1533 episodes or sea level rise. Arrows in panel D showing hydrothermal feeder veins  
 1534 feeding the overlying layers. The sequence is overlain by a thin package of parallel  
 1535 and cross-bedded Mn-sandstone cap.

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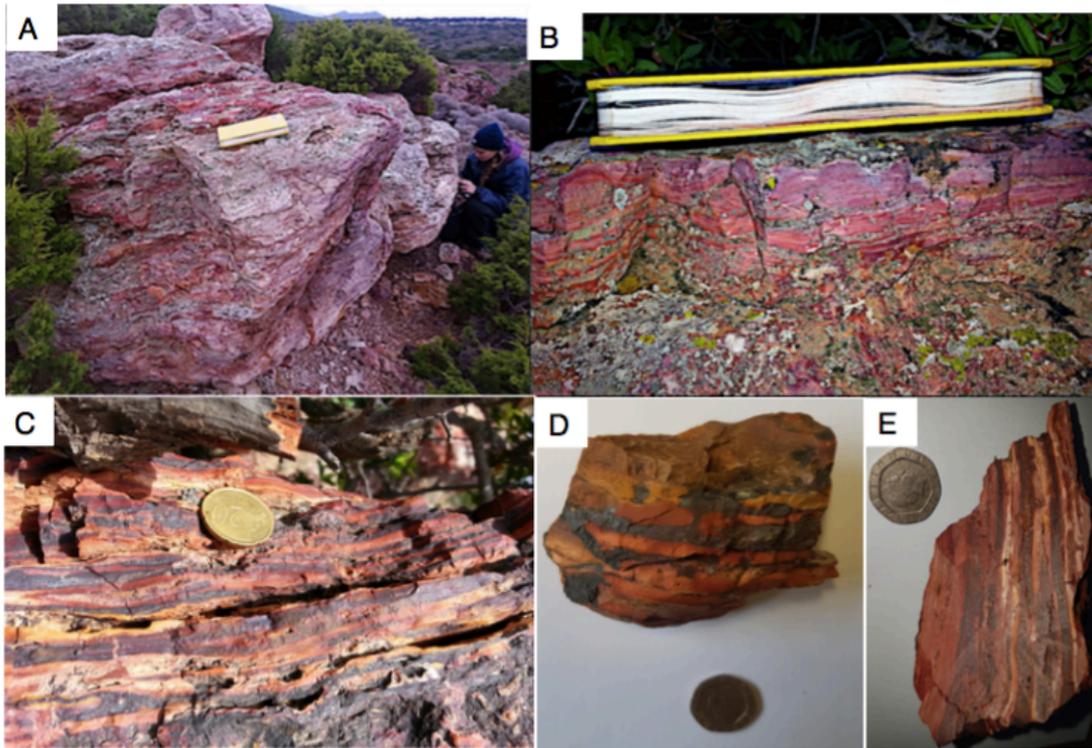


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1539 Fig. 6. Scanning electron microscope electron image of the volcanoclastic (K-  
 1540 feldspar)/ iron-rich sandstone layer overlying the MFIF.

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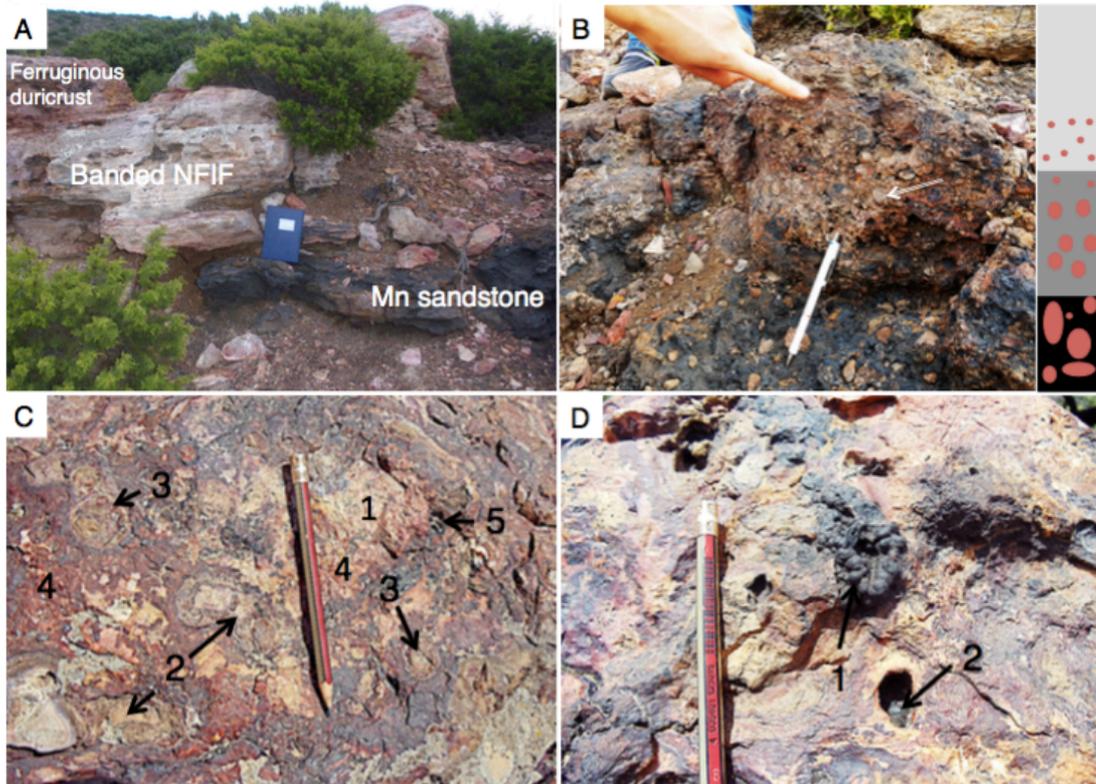


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1544 Fig. 7. Typical NFIF banded iron rocks. (A-C), Field photographs. (D), Handheld  
1545 banded Fe sample. (E), Sawn NFIF sample with laminated Fe-rich bands alternating  
1546 with Si-rich bands.

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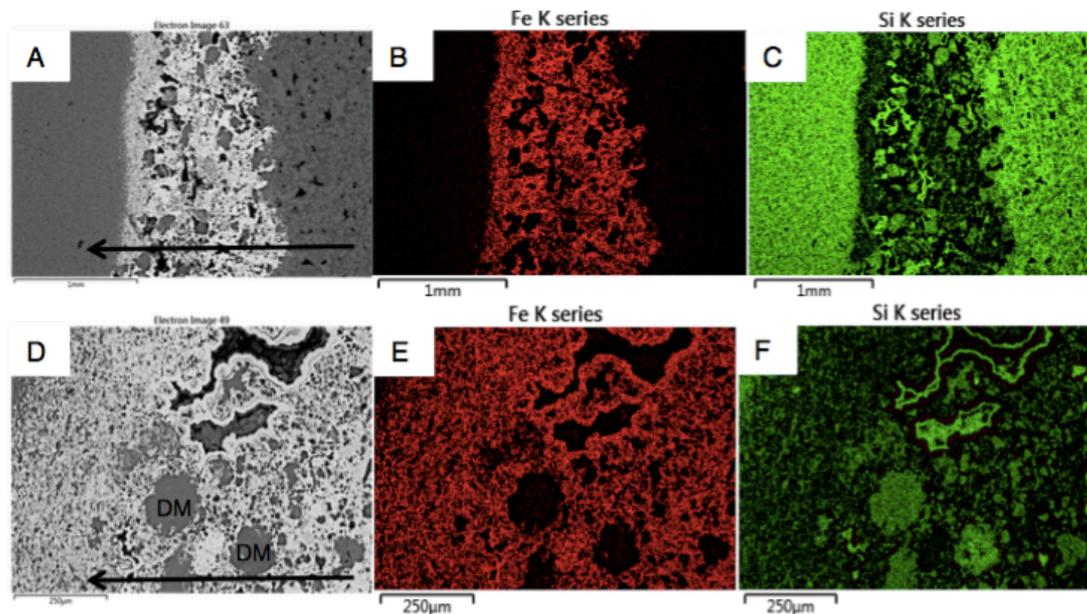


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1550 Fig. 8. Field sedimentology and stratigraphy of Section B sequence containing the  
 1551 NFIF. (A), Sharp boundary between lower Mn sandstone and unconformably  
 1552 overlying NFIF capped by a ferruginous duricrust. (B), Sandstone-sandy tuff pebble  
 1553 to gravel conglomerate lag facies, showing an upward fining character and bored  
 1554 clasts (black), locally overlies the Mn sandstone and capped by a sharp erosional  
 1555 contact with the overlying NFIF. The tip of the pen (7 cm long) rests on late blue-  
 1556 black Mn oxide overprint. (C), Ferruginous duricrust that comprises lithic fragments  
 1557 composed of (1) Fe-nodules (2) and Fe-concretions (3) in a hematite-rich matrix (4).  
 1558 (D), Matrix dissolution resulting in vermiform Mn nodules (1) and cavity black Mn  
 1559 oxide (2) infillings, post-dating the ferruginous duricrust formation.

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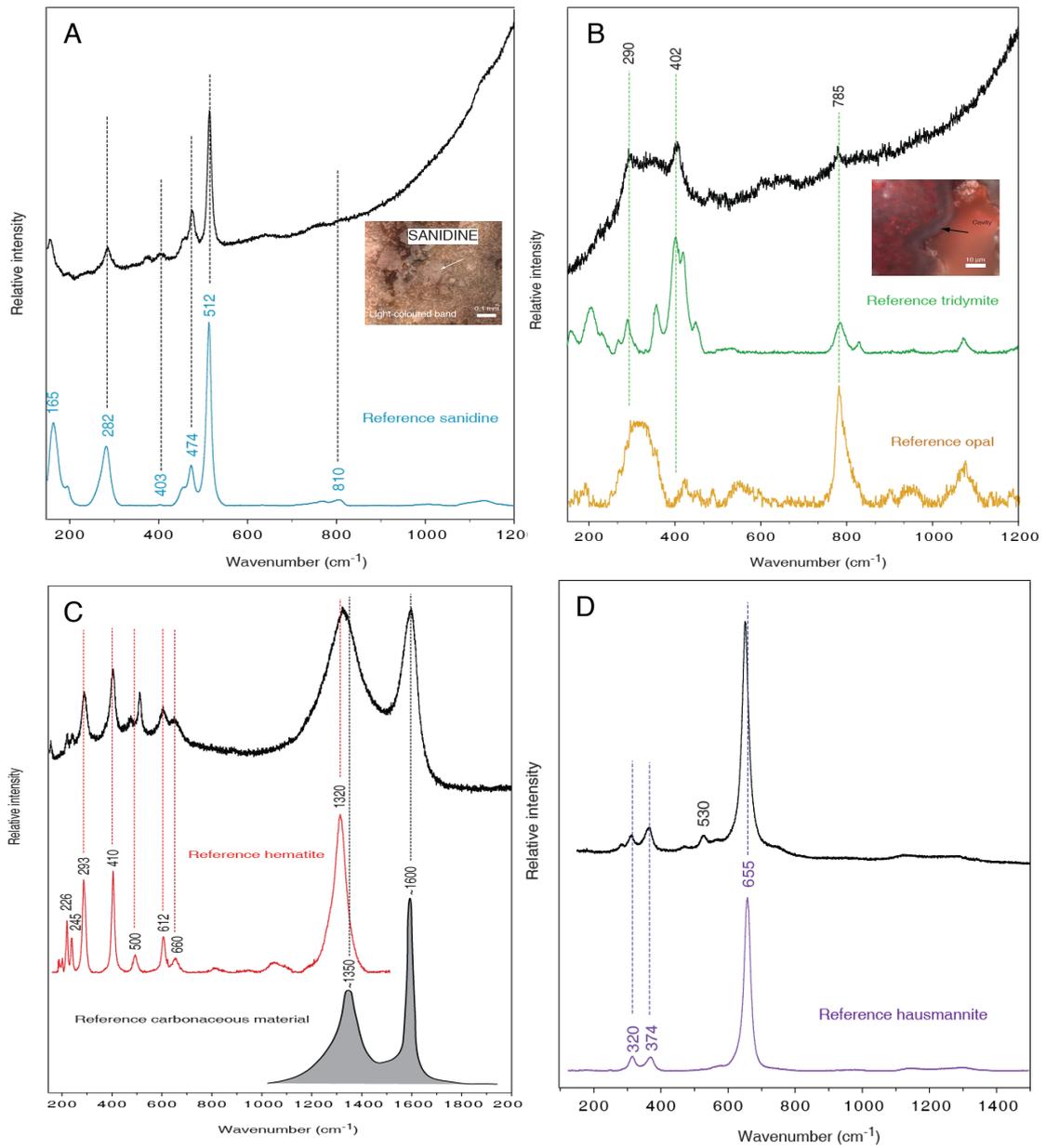
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1563 Fig. 9. EDS-electron image showing major elemental composition of typical Fe bands  
 1564 alternating with Si-rich layers in the NFIF. Volcaniclastic detritus mostly present in  
 1565 the Fe-rich bands, suggests precipitation during active submarine volcanism. To the  
 1566 contrary, the Si-rich bands are composed of more fine-grain, signifying deposition  
 1567 during periods of minimal volcanic activity. Arrows in panels (A) and (B) depict the  
 1568 direction of sedimentation, which was often seen to proceed from an Fe-rich matrix  
 1569 mixed with large grains of volcaniclastic detritus (DM) to one composed essentially  
 1570 of very fine-grained Fe particles before transitioning into the very fine-grained Si-rich  
 1571 layer. An upward fining of the volcaniclastic particles in the Fe-rich layers transitions  
 1572 from one made up of volcaniclastic debris and hematite, to a mainly thin hematite-  
 1573 rich horizon at the top of this mixed layer (see supplementary Figs 8-11 for details).  
 1574 This concurrent occurrence of volcaniclast and Fe oxides and the upward fining  
 1575 nature of the Fe-rich layers, suggest the release and oxidation of Fe(II) coincided with  
 1576 the settling of hydrothermal debris resulting from the introduction of enormous  
 1577 amount of reduced materials into the water column (Bekker et al., 2010). The iron-  
 1578 rich layer ceased forming as hydrothermal/volcanic release of Fe subsided, followed  
 1579 by deposition of the Si-rich layer. This repetitive cycle of events is observed for tens  
 1580 of metres laterally and vertically, stressing that the layers are not single isolated or  
 1581 post-depositional replacement events, but chemical precipitates that sequentially  
 1582 sedimented out of the water column. Red colour in Panels (B) and (C) depict Fe and  
 1583 green in panels (C) and (F), Si.  
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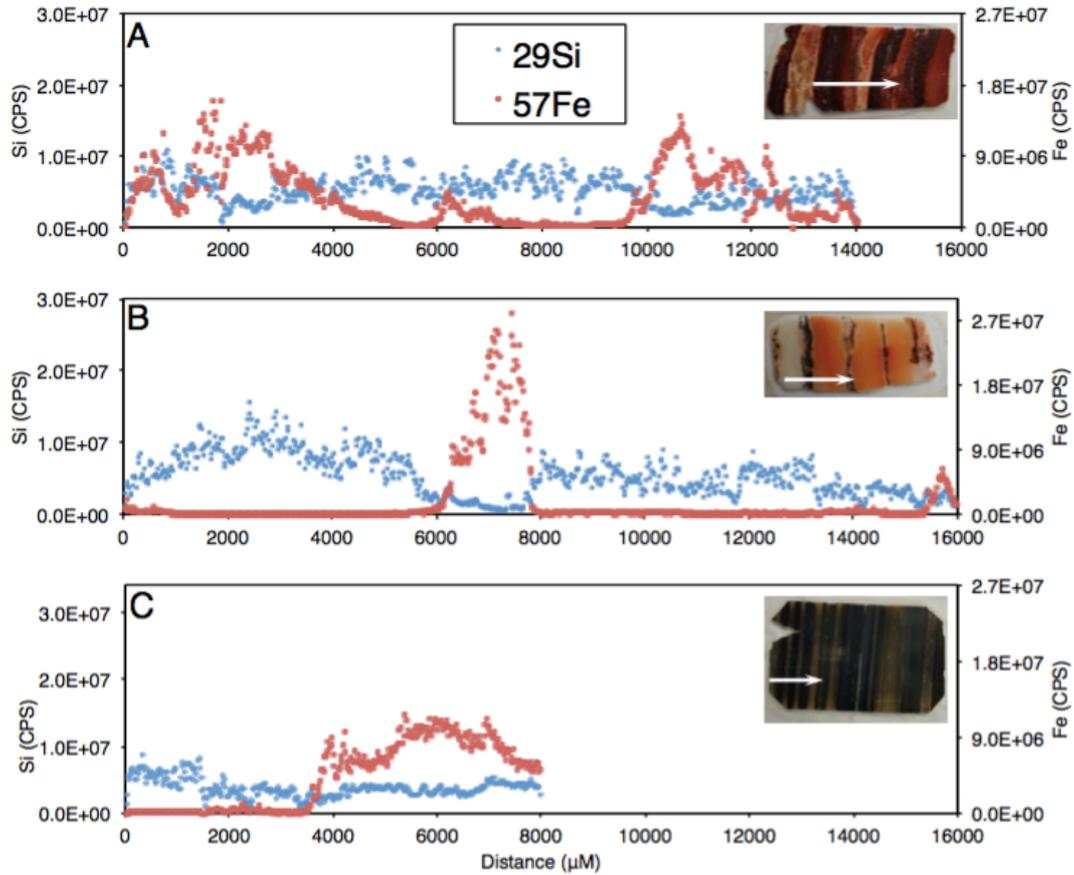
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1587 Fig. 10. Raman spectroscopy of the Fe- and/or Si-rich bands from NFIF.

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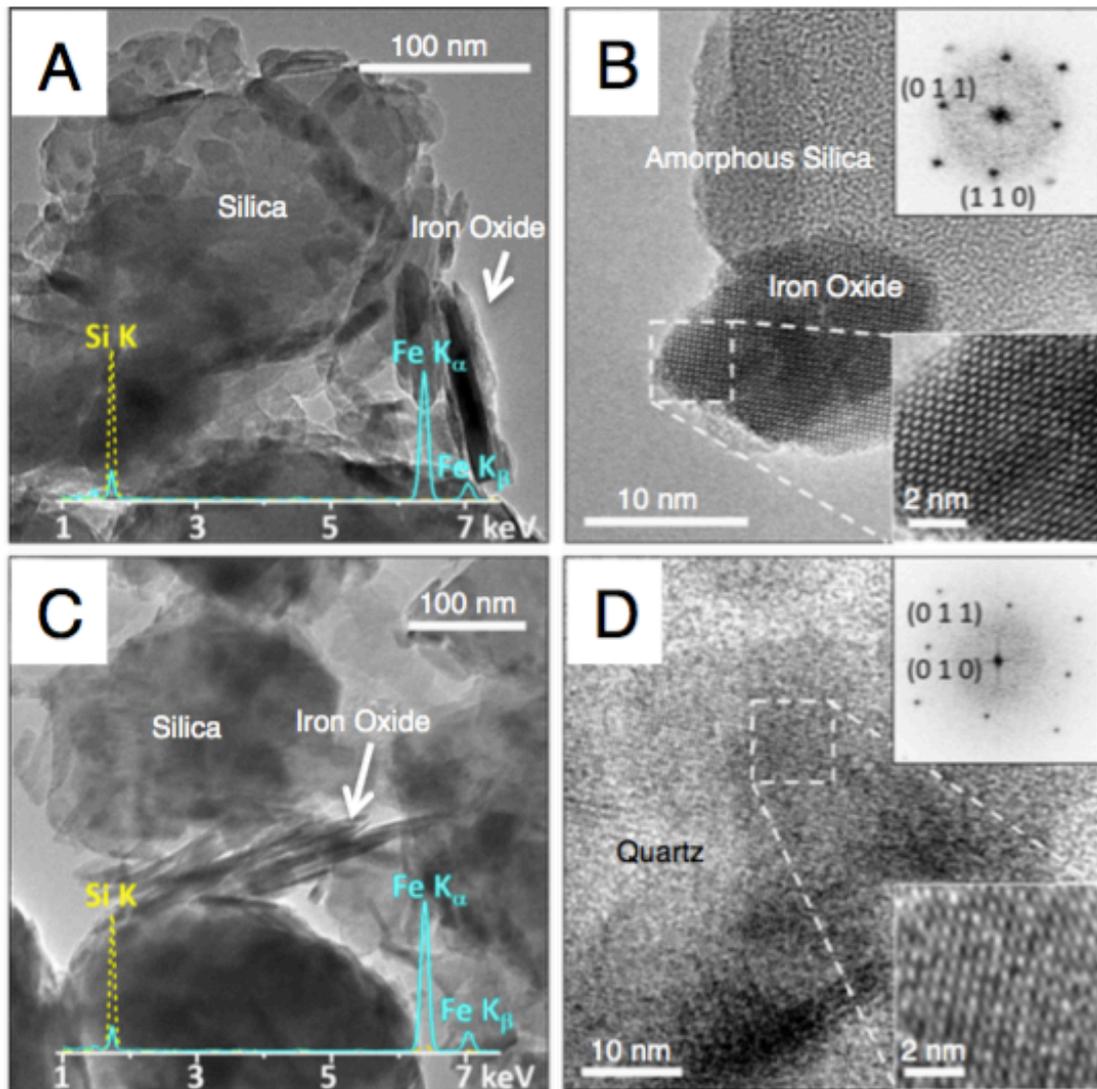


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1590 Fig. 11. Fluctuation in Si and Fe content measured by in situ laser ablation ICP-MS  
 1591 analysis. (A), Milos BIF-type rock with evenly distributed Si and iron rich bands. (B),  
 1592 Milos BIF type rock with large Si bands (whitish-brownish strips) and narrow Fe-rich  
 1593 bands (dark strips). (C), An example for the 2.5 Ga Kuruman BIF. Insets are analyzed  
 1594 thin sections. For scale, each thin section is  $\approx 3.3$  cm long. White arrow on thin section  
 1595 indicates analyzed area.

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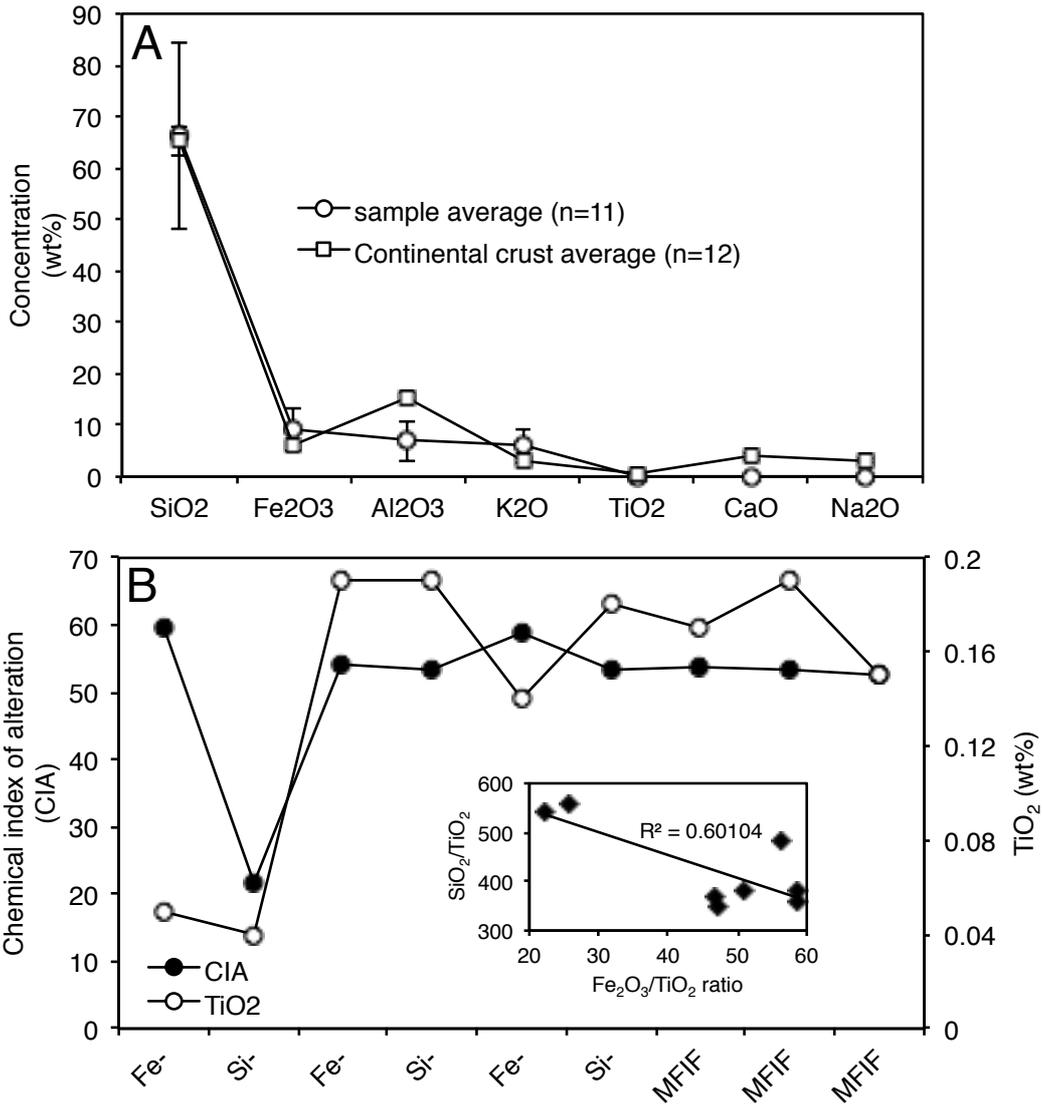


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1599 Fig. 12. TEM characterization of an NFIF and MFIF specimen. (A) lower  
 1600 magnification MFIF TEM-BF image. (B) High resolution images of NFIF showing  
 1601 amorphous Si and iron oxide crystalline lattice structures. Insets highlight a hematite  
 1602 particle viewed from the [1-11] axis (Rhombohedral lattice). (C) Lower magnification  
 1603 MFIF TEM-BF image. (D) High resolution images of MFIF showing crystalline  
 1604 quartz and iron oxide crystalline lattice structures. Insets in (D) show a quartz crystal  
 1605 viewed from the [100] axis. Both samples contain silica with a few hundred nm  
 1606 particle size, and smaller needle-like iron oxide particles. Spectral lines in panels (A)  
 1607 and (C) are X-ray Energy Dispersive elemental profiles of the individual Fe and Si  
 1608 mineral phases.

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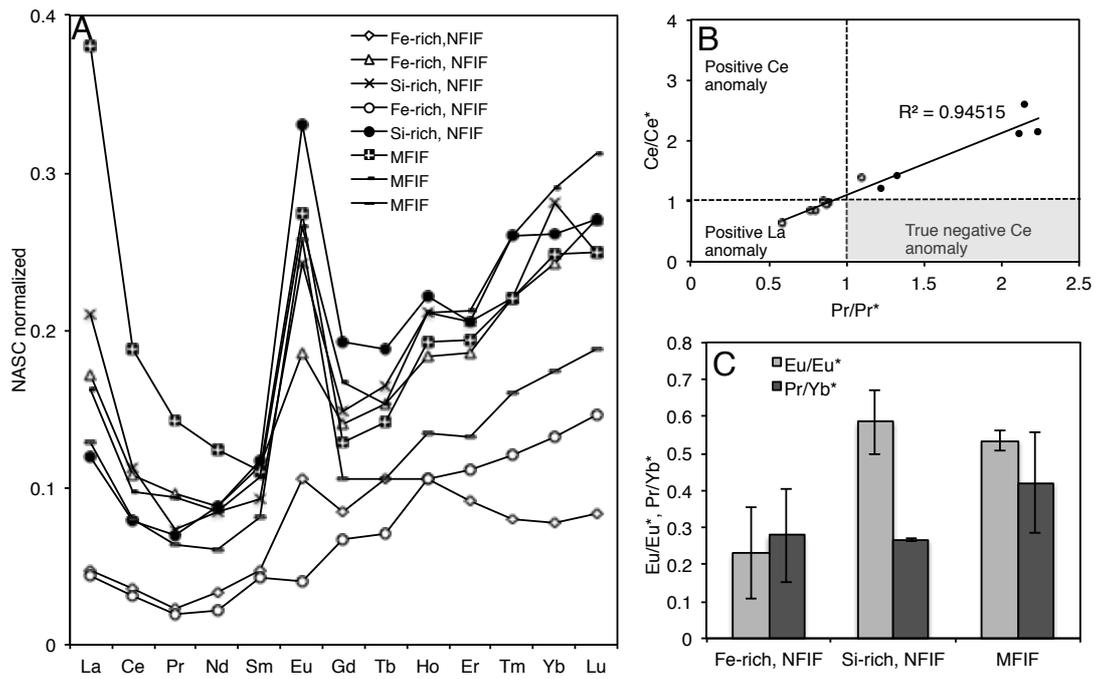
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1612 Fig. 13. Bulk average concentrations of major trace elements and chemical  
 1613 weathering indices. (A), Relationship between average major trace element content  
 1614 and average continental crust (Rudnick and Gao, 2003). (B), Chemical index of  
 1615 alteration (CIA). Inset, relationship between SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>.  
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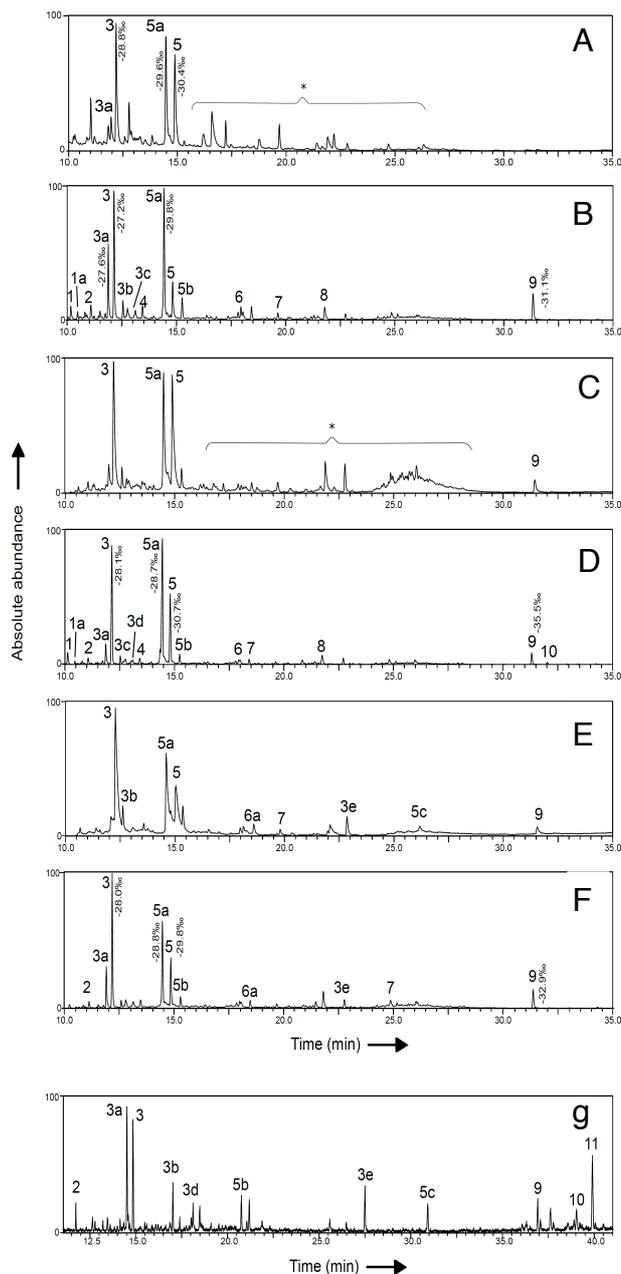
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1619 Fig. 14. Rare Earth Element (REE) distribution in samples and calculated Ce and Eu  
 1620 anomalies. (A), NASC normalized REE distribution in various rock facies. (b), Ce  
 1621 and Eu anomalies. (C), Eu anomalies and light REE (LREE) vs. heavy REE (HREE).  
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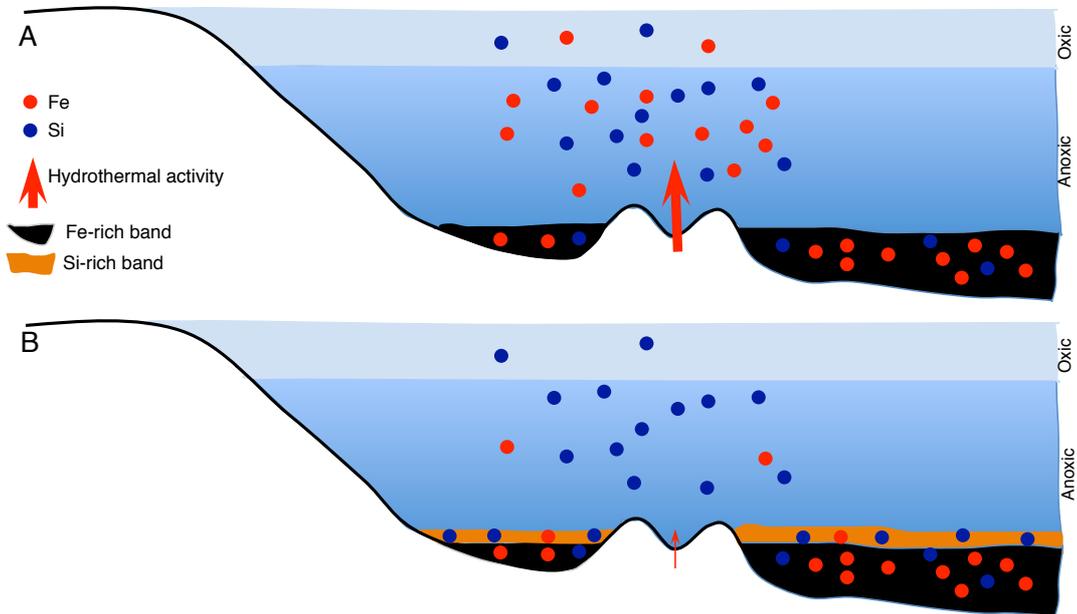


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1625 Fig. 15. GC/MS chromatogram sections of total lipid extracts of the BIF (A-F) for  
 1626 bands excised from the sawn rock in Figure 2c. Panel G illustrates a total lipid extract  
 1627 of modern sediment from the Milos basin. Values beside peaks indicate the lipid  $\delta^{13}\text{C}$   
 1628 values due to the low intensity of the lipids recovered this was not possible for all  
 1629 peaks. Peaks have been annotated as the following compounds (FAME = fatty acid  
 1630 methyl ester, Me = methyl group, TMS = trimethylsilyl, TMSE = trimethylsilyl ester):  
 1631 (1)  $\text{C}_{14:0}$  FAME, (1a)  $\text{C}_{14:0}$  13Me FAME, (2)  $\text{C}_{15:0}$  FAME, (3)  $\text{C}_{16:0}$  FAME, (3a)  $\text{C}_{16:9}$   
 1632 FAME, (3b)  $\text{C}_{16:0}$  TMS, (3c) 10Me  $\text{C}_{16:0}$  FAME, (3d)  $\text{C}_{16:9}$  FAME, (3e)  $\text{C}_{16:0}$  TMSE,  
 1633 (4)  $\text{C}_{17:0}$  TMS, (5)  $\text{C}_{18:0}$  FAME, (5a)  $\text{C}_{18:9}$  FAME, (5b)  $\text{C}_{18:0}$  TMS, (5c)  $\text{C}_{18:0}$  TMSE, (6)

1634 C<sub>19:0</sub> FAME, (6a) C<sub>19:0</sub> 18Me TMS, (7) C<sub>21:0</sub> TMS, (8) C<sub>22:0</sub> TMS, (9) Cholesterol  
1635 TMS, (10) Stigmasterol TMS, (11) beta-Sitosterol (\*) Contaminants e.g. phthalates.  
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1638

1639 Fig. 16. Conceptual model showing the mechanism of band formation in the NFIF  
1640 related to changes in the intensity of hydrothermal activity and chemical oxidation of  
1641 Fe(II) to Fe(III) in the water column, inferred directly from our data. See Chi Fru et  
1642 al. (2013) for a biological model for the formation of the MFIF.