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1 **Post-depositional REE mobility in a Paleoproterozoic banded iron formation**
2 **revealed by La-Ce geochronology: A cautionary tale for signals of ancient**
3 **oxygenation**

4

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23

24 **Abstract**

25 Precambrian banded iron formations (BIF) are chemical sedimentary deposits whose trace
26 element signatures have been widely used to interrogate the chemical composition and redox
27 state of ancient seawater. Here we investigated trace element signatures in BIF of the 3.22 Ga
28 Moodies Group, Barberton Greenstone Belt (South Africa), which are interbedded with near-
29 shore siliciclastic sedimentary rocks and represent one of the oldest known shallow-water
30 occurrences of BIF. Unusual rare earth element signatures, notably with pronounced negative Ce
31 anomalies in shale-normalized spectra, have been previously reported for chemical sediments of
32 the Moodies Group, which we confirm here through an expanded dataset for Moodies BIF
33 spanning three different localities. We find negative Ce anomalies as low as 0.2 Ce/Ce* that are
34 associated with unusual enrichment of LREE relative to HREE in the sample set. While total
35 REE abundances and certain REE features appear strongly related to the concentration of detrital
36 indicators (e.g., Zr), and are likely primary, other features, notably LREE enrichment, cannot be
37 explained as a primary feature of the sediment. This is better explained by later addition of REE
38 from a LREE-enriched but Ce-depleted fluid that generated the significant negative Ce anomalies
39 observed in surface samples of Moodies Group BIF. This REE addition event influenced both
40 Sm-Nd and La-Ce isotope systematics, the latter yielding an isochron of 60 ± 32 Ma, thus
41 constraining the timing of emplacement of the negative Ce anomalies to the past 100 Ma,
42 possibly upon surface exposure of the Barberton Greenstone Belt to wetter conditions during the
43 Cenozoic. Our findings constitute a cautionary tale in that even the most immobile elemental
44 redox proxies may be more sensitive to post-depositional modification than previously thought,
45 and demonstrate the clear advantage offered by paleoredox proxies coupled to radiometric
46 geochronometers to enable the direct dating of ancient signals of Earth surface oxygenation.

47 **Keywords:** Trace element signatures, Ce anomalies, La-Ce geochronology, rare earth element
48 mobility.

49 **1. Introduction**

50 Banded iron formations (BIF) are chemical sediments deposited throughout much of the
51 Precambrian. They consist primarily of iron oxide minerals (hematite, magnetite) and
52 cryptocrystalline quartz (chert), along with lesser amounts of carbonates, iron-rich clays, and
53 other secondary alteration minerals, depending on the metamorphic grade (Bekker et al., 2010;
54 Konhauser et al., 2017). The precursor chemical minerals thought to have initially formed BIF
55 (amorphous Fe(II)- and Fe(III)-hydroxides, carbonates, and silicates) are unstable, and have
56 universally recrystallized to a more stable metamorphic assemblage of dehydrated minerals.
57 Nonetheless, BIF have been widely considered a useful proxy for the chemical composition of
58 ancient seawater and porewaters in which they formed (see Konhauser et al., 2017, for review).
59 Being highly non-porous and impermeable, BIF are conventionally thought to be relatively robust
60 against significant disturbance during metamorphism or metasomatism (e.g., Robbins et al.,
61 2019a. Indeed, millimeter scale variations in trace elements (e.g., Bau, 1993; Bau and Dulski,
62 1996) and in iron isotope compositions in BIF (e.g. Frost et al., 2007), along with experiments
63 simulating BIF diagenesis (e.g. Posth et al., 2013), have been used to argue for general elemental
64 immobility, even for samples that have experienced complete recrystallization during
65 amphibolite-facies metamorphism.

66 Rare earth element (REE) patterns, and in particular anomalies in the abundance of
67 cerium (Ce) relative to its neighbors, are commonly used to interrogate redox conditions of
68 ancient seawater. Cerium is particularly prone to fractionation from other REE because oxidation
69 of Ce(III) to Ce(IV) under mildly oxidizing conditions greatly reduces Ce solubility, resulting in
70 its preferential removal from solution onto Mn(IV)-Fe(III)-oxyhydroxides, organic matter, and
71 clay particles (Byrne and Sholkovitz, 1996). Under oxidizing conditions, seawater is thus

72 characterized by a strong negative Ce anomaly. Accordingly, the presence of negative cerium
73 anomalies in chemical sediments has often been used to infer oxidative conditions during
74 deposition. Despite the potential for significant insight into the primary REE chemistry of ancient
75 seawater, the interpretation of cerium anomalies in ancient sedimentary rocks requires caution.
76 Post-depositional REE modifications have been described in several studies, showing that cerium
77 may behave differently from other REE (Mongelli et al., 1993; Cotton et al., 1995). Hayashi et al.
78 (2004) were the first to use La-Ce isotope systematics in an attempt to constrain the timing of
79 emplacement of a cerium anomaly in ancient sedimentary rocks. Ce-138 is produced by the decay
80 of ^{138}La ($T_{1/2}=292.5$ Ga). The use of ^{138}La - ^{138}Ce systematics is challenging because of the long
81 half-life of ^{138}La but is extremely powerful for dating La/Ce fractionation. The first La-Ce isotope
82 measurements obtained by Hayashi et al. (2004) on samples from the Barberton Greenstone Belt
83 (BGB) show that the presence of cerium anomalies must be interpreted with caution. They
84 attributed Ce anomalies in the BGB, including a single BIF sample from the Moodies Group with
85 $\text{Ce}/\text{Ce}^* = 0.93$ (calculated by Hayashi et al. in the absence of Pr data as the chondrite-normalized
86 projection between La and Nd) to post-depositional remobilization of REE prior to ca. 1.1 Ga
87 (Hayashi et al., 2004).

88 In this paper we present major and trace element measurements in 48 BIF outcrop
89 samples collected at three localities in the Moodies Group, dated at 3.22 Ga (Heubeck et al.,
90 2013). Measurements of the La-Ce and Sm-Nd isotope systematics are presented in samples
91 characterized by a large range of cerium anomalies. This dataset permits (1) direct dating of the
92 formation of the cerium anomaly, and (2) to resolve whether REE spectra represent primary
93 features or were later modified during secondary events, such as surficial weathering of exposed
94 outcrop. Here we demonstrate that the negative cerium anomalies in Moodies BIF were produced

95 by relatively recent fluid addition and that this signature cannot be used to discuss redox
96 conditions during their deposition.

97

98 **2. Geology of Moodies Group BIF**

99

100 The Moodies Group of the BGB is comprised of approximately 3.5 km of sand- and siltstone,
101 subordinate conglomerate and volcanics, and minor ferruginous sediment that were mostly
102 deposited in shallow-water and terrestrial settings (Heubeck, 2019). Dacitic volcanics
103 conformably underlying basal Moodies strata are 3225 ± 3 Ma old (Kröner et al., 1991). The onset
104 of Moodies sedimentation is further constrained by a 3223 ± 1 Ma age for a dacitic tuff in the
105 uppermost Schoongezicht Formation of the underlying Fig Tree Group (Heubeck et al., 2013).
106 Dacitic ash-fall tuffs in the central BGB, approximately mid-section in the stratigraphic column
107 (near the BIF unit Mdl2, Figure 1), yield an age as low as 3219 ± 3 Ma (Heubeck et al., 2013),
108 similar to a porphyritic dike crosscutting the topmost Moodies units dated at 3219 ± 9 Ma
109 (Heubeck et al., 2013). Thus, Moodies deposition occurred between 3223 and 3219 Ma, and
110 likely within a few Ma of 3222 Ma ago (Heubeck et al., 2013). Regional metamorphic grade is
111 lower greenschist facies (Tice et al., 2004), with evidence for metamorphic overprint during
112 emplacement of the Kaap Valley Pluton at 3214 ± 4 Ma, during late granite plutonism at ca. 3100
113 Ma (Toulkeridis et al., 1994), and related to fluid circulation associated with Ventersdorp
114 Supergroup volcanism or the Limpopo orogeny at ca. 2650-2700 Ma ago (Toulkeridis et al.,
115 1998).

116 In the north-central part of BGB, up to four regionally mappable ferruginous units, 2 to 6
117 m thick and comprised of jaspillite and BIF, are interbedded with fine-grained sand- and

118 siltstones (Heubeck and Lowe, 1994). Geological mapping and interpretation of sedimentary
119 structures suggest that deposition of ferruginous units occurred largely in prodelta- and protected
120 bay / lagoonal settings. The BIF samples examined in this study were collected from surface
121 outcrops at three localities in the Moodies Group (Figure 1); (1) unit Mdl2 in the Clutha Creek
122 section of the Eureka Syncline (CC; 25°41'52.81"S, 31°5'10.89"E), (2) unit Mdl2 from the
123 Devil's Staircase Road section of the Moodies Hills Block (DSR; 25°49'55.82"S, 31°0'50.49"E),
124 and (3) unit Mdl1 from the Stolzberg Syncline (SB; 25°54'8.04"S, 30°50'44.90"E). Samples
125 were collected using hammers, chisels, and a sledge, avoiding clear signs of alteration, trimmed
126 for fresh surfaces, and fractured pieces were discarded. All are distal from hydrothermally
127 overprinted brittle-ductile shear zones that are common in the northern BGB. In all three sections,
128 BIF occur in thick, conformable sections of thinly bedded, small-scale-slumped siltstones and
129 very-fine-grained sandstone interbedded with rare laminated shale. See supplemental materials
130 for a more detailed description of each sample site, including photos of the localities and of
131 selected hand samples, as well as a lithological column for the DSR site situating the samples in
132 stratigraphic context.

133

134

135 **3. Methods**

136

137 All samples were prepared using trace-element clean methods (crushing and powdering in pure
138 tungsten carbide and agate, respectively) and all digestions and column separations were
139 performed in clean laboratories at the European Institute for Marine Studies in Brest and at the
140 Laboratoire Magmas et Volcans located at the Université Clermont Auvergne, France. For
141 analysis of major elements, samples were digested at 90° C in PFA vials using concentrated

142 HNO₃ and HF, followed by immediate neutralization with 20 g L⁻¹ H₃BO₃ to retain Si, as per
143 Cotten et al. (1995). After dilution by a factor of 400, samples were analyzed using an Yvon
144 Horiba Ultima 2 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)
145 calibrated against a standard curve comprised of the CRPG reference materials Mica-Fe, UB-N,
146 MORB-E, GB2, IF-G, AC-E, and WS-E digested in the same batch, using the working values of
147 Govindaraju (1995), and with replicates of IF-G and AC-E treated as unknowns to monitor
148 accuracy. Precision based on 5 replicate analyses was better than 4.5% (2 relative standard
149 deviations, RSD) for all major elements except for Mg, Ca, and Na, which showed lower
150 precision (14 to 21%) between replicates due to their low concentrations in iron formation. For
151 analysis of trace elements and Nd isotopes, between 80 and 120 mg of powder was digested
152 sequentially in PFA vials at 90° C using concentrated HF-HNO₃, aqua regia, and 6M HCl. For
153 trace element analysis, aliquots were resuspended in 2% HNO₃ with indium as an internal
154 standard and analyzed using a Thermo Scientific Element2 High-Resolution Inductively Coupled
155 Plasma Mass Spectrometer (ICP-MS) at the Pôle Spectrométrie Océan in Brest, France. The
156 instrument was tuned to minimize oxide production, and mixed mono-elemental Pr-Nd, Ba-Ce,
157 and Sm-Tb solutions were analyzed to quantify potential oxide interferences prior to the session,
158 which were negligible. Calibration was performed against gravimetrically prepared multi-element
159 solutions, and geostandards IF-G and AC-E were analysed in the same session as unknowns to
160 monitor accuracy, which was better than 5% for REE and 10% for most other trace elements (2
161 RSD). For major and trace method analyses, detection limits were determined using blanks
162 prepared alongside samples and are reported in Table S2 as either the detected blank
163 concentration (normalized to the typical amount of rock powder analyzed) or the method
164 detection limit determined by three relative standard deviations of the end-of-rinse intensities that
165 were systematically measured prior to each sample. Sm-Nd and La-Ce parent/daughter ratios

166 were calculated from HR-ICP-MS data of non-spiked samples using $^{147}\text{Sm}/^{144}\text{Nd} = 0.6045$
167 Sm/Nd and $^{138}\text{La}/^{142}\text{Ce} = 0.0080 \text{ La/Ce}$. Propagated relative standard errors on these ratios were
168 constrained to less than 1% by periodic measurements (n=8) of a multi-element solution
169 throughout the session, and to less than 10% for all trace element concentrations, and better than
170 2–3% for most REE, based on the same repeat analyses.

171 To assure complete digestion and confirm the REE data acquired after HF-HNO₃-Aqua
172 Regia digestion in PFA beakers, a selected set of sample powders were re-analyzed by HR-ICP-
173 MS after Na₂O₂-NaOH alkaline fusion in glassy carbon crucibles at 650°C in the presence of a
174 Tm spike, following the protocol and data reduction procedure of Bayon et al. (2009).

175 For Nd isotopes, aliquots were evaporated and re-dissolved in 2.5M HCl for chemical
176 separation of REE using cationic BioRad[®] AG50X8 200-400 mesh columns, followed by further
177 purification on LnSpec Eichrom resin. Nd isotopic measurements were performed during two
178 analytical sessions at the Pôle de Spectrométrie Océan in Brest using a Thermo Scientific
179 Neptune multi-collector ICP-MS and a Thermo Scientific Triton Thermal Ionisation Mass
180 Spectrometer (TIMS, Triton). A $^{146}/^{144}\text{Nd}$ ratio of 0.7219 was used for mass bias correction.
181 Recovered Nd fractions contained between 1266 and 16 ug of Nd (mean 134 ug) while blanks
182 prepared alongside samples contained less than 140 pg of Nd. For TIMS measurements, analyses
183 were made in static mode using 10 blocks of 10 cycles each, with 1 s integration times and
184 baselines measured for 30 s between each block. For MC-ICP-MS measurements, one block of
185 30 cycles with integration times of 4.196 s was employed, preceded by a 30 s baseline
186 measurement. Results obtained on the international standard JNdi-1 are reported in Table S1.
187 JNdi-1 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured during the TIMS session are slightly lower ($0.512086 \pm$
188 0.000017 , 2 s.d., n=5) than the accepted value obtained using a dynamic routine over a period of
189 1.5 years on 3 different Triton mass spectrometers (0.512099 ± 0.000005 , 2 s.d., n=61, Garçon et

190 al., 2018). Thus, the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios have been normalized. Aside from correction
191 for instrumental drift using sample-standard bracketing with JNdi-1, no further correction is
192 applied to the Nd isotope ratios during the MC-ICP-MS session since the JNdi-1 results are in
193 agreement with the accepted value (0.512095 ± 0.000005 , 2 s.d., n=17).

194
195 For Ce isotopes, 100-150 mg of rock powder was digested using a HF-HNO₃ dissolution
196 technique. The chemical separation used to separate the Ce fraction involved four steps of
197 column chemistry (Bonnand et al., 2019). The first step, aimed at removing the Fe fraction, was
198 performed on anionic AG1-X8 resin (100-200 mesh). The sample was loaded onto the resin in
199 strong HCl and Ce was not retained by the resin. The second step was used to separate the REE
200 from other main cations of the matrix. To this end, the samples were loaded in 2.5N HCl onto
201 AG50-X8 resin (200-400 mesh). REE were retained by the resin while major cations were eluted
202 in 2.5N HCl, and REE were then eluted in 6M HCl. The third column procedure was designed to
203 separate Ce⁴⁺ from other REE and was performed using Ln spec resin (Eichrom). The samples
204 were loaded in 10M HNO₃ + NaBrO₃, and Ce⁴⁺ was retained on the column while other REE
205 were not. The Ce⁴⁺ fraction was eluted in 6M HCl + H₂O₂. Finally, the samples were processed
206 through the second step to make sure the Ce fraction was cleaned of any remaining matrix
207 cations. Isotopic measurements were performed on a Thermo Scientific Thermal Ionisation Mass
208 Spectrometer (TIMS) at the Laboratoire Magmas et Volcans as described by Bonnand et al.
209 (2019). Together with the samples, Ce_{AMES} and Ce_{LMV} reference materials were analysed and
210 gave $^{138}\text{Ce}/^{142}\text{Ce}$ values of 0.0225743 ± 0.0000007 (2 s.d.; n=26) and 0.0225705 ± 0.0000006 (2
211 s.d.; n=48), respectively. The values are comparable to previously published values (e.g.
212 Willbold, 2007).

213 4. Results

214

215 **4.1 Major and Trace elements**

216

217 The Moodies Group BIF are composed of chert, magnetite, and hematite, with minor
218 phyllosilicates (likely stilpnomelane and chamosite), goethite, and rare ankerite (see Table S2 for
219 X-ray diffraction method and data). Samples showed a large range in the concentration of detrital
220 indicators, with Al_2O_3 ranging from 8.5 wt.% to <0.1%, and with correlated concentrations of Sc,
221 Zr, Th, and Hf that reached sub-ppm values in the least contaminated samples (see Tables S3 in
222 the supplementary information for complete elemental dataset). Iron concentrations ranged from
223 73.8 wt.% $\text{Fe}_2\text{O}_{3\text{Total}}$ to 5.8 wt.%; 43 out of 54 samples meet the definition of iron formation of
224 >15 wt.% Fe (James, 1954), including two samples with Al_2O_3 between 6 and 8 wt.%.
225 Phosphorus concentrations averaged 0.11 wt.% P_2O_5 and no apatite or other P-rich phases were
226 detected by X-ray diffraction nor by μXRF scanning (data not shown). Redox-sensitive trace
227 elements, such as U and Mo, are present at sub-ppm levels. Transition metals (e.g., V, Cr, Mn,
228 Co, Ni, Cu and Zn) show a variability of approximately one order of magnitude in absolute
229 abundances, similar to other larger BIF datasets (Figure S2; e.g., Konhauser et al., 2011; Robbins
230 et al., 2019b).

231

232 Shale-normalized (SN) spectra for rare earth elements + yttrium (REY_{SN} ; simplified as REE
233 throughout this manuscript) span a wide range in abundances relative to Post-Archean Australian
234 Shale (PAAS; updated values from McLennan, 1989), ranging from below 0.01 to close to 1
235 (Figure 2). Total REE concentrations show strong correlation with detrital indicators, such as Zr
236 concentrations (Figure 3). REE spectra are highly diverse, with some showing light REE (LREE)
237 enrichment relative to heavy REE (HREE) enrichment, while others show the reverse. Nearly all

238 samples show suprachondritic Y/Ho ratios, ranging from 20.5 to 45.5, with an average of 35.0, as
239 well as significant positive La and Eu anomalies, and mild positive Gd anomalies. A striking
240 feature of the spectra are highly variable Ce anomalies, with Ce/Ce* reaching values as low as
241 0.19. A subset of the samples digested by alkaline fusion and analyzed for REE using a Tm spike
242 (Bayon et al., 2009) confirm the large range in La/Ce and Ce/Ce* that is observed for samples
243 digested using concentrated acids in PFA vials (Table S4). The cerium anomaly is calculated here
244 using the formulation of Lawrence et al. (2006) with $Ce/Ce^* = Ce_{SN}/(Pr_{SN} * Pr_{SN}/Nd_{SN})$, where
245 La is not considered in the calculation as to avoid false negative Ce anomalies that may arise
246 simply as the result of La enrichment.

247

248 **4.2 Nd and Ce isotopes**

249

250 Nd isotope compositions ($^{143}Nd/^{144}Nd$) of 22 selected samples from all three localities range from
251 0.510836 to 0.511459, while $^{147}Sm/^{144}Nd$ ratios range from 0.0911 to 0.1453. Nd isotope model
252 ages span 3597 to 2246 Ma, with a mean value of 3161 Ma, assuming a source with CHUR
253 composition ($^{147}Sm/^{144}Nd=0.1960$ and $^{143}Nd/^{144}Nd=0.512630$; Bouvier et al., 2008). Three
254 samples, all from the SB locality, show significantly younger model ages than the rest of the
255 dataset (mean $\tau_{Nd\ CHUR} = 2487$ Ma); when these three samples are excluded, mean $\tau_{Nd\ CHUR}$ value
256 of the rest of the dataset average 3267 Ma. On a $^{147}Sm/^{144}Nd - ^{143}Nd/^{144}Nd$ plot, samples from the
257 SB locality do not show any correlation. Samples from the DSR locality are tightly clustered.
258 With such a small range of Sm/Nd ratios, it is not possible to calculate a robust isochron. Samples
259 from the CC locality show a positive correlation that yields an errorchron with an apparent age of
260 2770 ± 530 Ma (MSWD=16), considering measured uncertainties.

261

262 $^{138}\text{La}/^{142}\text{Ce}$ ratios for the five DSR samples analyzed range from 0.004 to 0.013, while the SB
263 sample analyzed showed a value of 0.004 (Figure 4b). Cerium isotope compositions ($^{138}\text{Ce}/^{142}\text{Ce}$)
264 ranged from 0.02257053 to 0.02257522 (Table S5). On a $^{138}\text{La}/^{142}\text{Ce}$ vs. $^{138}\text{Ce}/^{142}\text{Ce}$ plot, the five
265 analyzed DSR samples define an isochron that yields an apparent age of 60 ± 32 Ma based on
266 measured uncertainties. The single analyzed SB sample overlaps the range defined by the DSR
267 samples.

268

269

270 **5. Discussion**

271

272

273 **5.1 Unusual REE signatures in Moodies Group BIF**

274

275 Samples of the shallow-water BIF of the Moodies Group analyzed here show some rather
276 unusual characteristics in their REE systematics. Most striking is the presence of strong Ce
277 anomalies, ranging down to $\text{Ce}/\text{Ce}^* = 0.19$. Because cerium is readily oxidized from Ce(III) to
278 Ce(IV) in the presence of free oxygen, this process leaves oxic waters depleted in Ce, creating
279 characteristic negative Ce anomalies in oxygenated seawater (shale-normalized Ce anomalies,
280 Ce/Ce^* , of about 0.3 – 0.1; e.g., German et al., 1995). BIF deposited before the GOE generally
281 lack Ce anomalies, a feature attributed to the prevalence of anoxic water column conditions (e.g.,
282 Bau and Dulski, 1996; Kato et al., 1998). Moodies Group BIF samples show significant Ce
283 anomalies at all three sample locations ($\text{Ce}/\text{Ce}^*=0.2 - 0.95$; Figure S2), with samples from DSR
284 and SB localities showing the most pronounced anomalies. The magnitude of Ce anomalies
285 observed in our dataset reaches significantly more extreme values than those observed by

286 Hayashi et al. (2004) in three samples from the Moodies and underlying Fig Tree Groups. One
287 might be tempted to equate these anomalies with oxic Ce cycling at the time of deposition;
288 however, Hayashi et al. (2004) suggested that such anomalies may instead represent post-
289 depositional mobilization of REE with a maximum age of 1.1 Ga.

290
291 Another unusual feature of the REE spectra is the highly variable degree of LREE vs. HREE
292 enrichment. Modern seawater, and most detritus-free ancient chemical sediments (both BIF and
293 carbonates; e.g., Bohlar et al., 2004), generally shows HREE enrichment relative to LREE due to
294 lanthanide contraction and the decrease in ionic radii going from LREE to HREE as the result of
295 an increasingly filled f-electron shell. This contraction results in a more important extent of
296 aqueous carbonate complexation for HREE relative to LREE (Lee et al., 1992), leaving a greater
297 proportion of LREE available for adsorption to reactive particle surfaces, thus decreasing their
298 concentration in seawater relative to the more strongly carbonate-complexed HREE. Another
299 consequence of the lanthanide contraction is that LREE are more efficiently mobilized by
300 alteration fluids bearing important REE ligands such as fluoride, phosphate, and carbonate (e.g.,
301 Wood, 1990; Bilal and Langer, 1989).

302
303 Both syn-depositional and post-depositional processes may influence REE systematics. BIF,
304 however, have generally been considered robust against post-depositional alteration of their REE
305 signatures (Bau, 1993), even by protracted high-grade metamorphism (Bolhar et al., 2004).
306 Nonetheless, the highly atypical nature of the REE signatures observed in this study, and the fact
307 that all samples were obtained from surface outcrop, lead us to examine these assumptions more
308 closely. We first consider controls over REE systematics that can be confidently linked to syn-
309 depositional processes, such as the seawater precipitation of iron and silica chemical components

310 and the admixture of detrital contaminants, before examining alternative explanations for
311 chemical features that are difficult to explain as primary.

312

313

314 **5.1 Syn-depositional control over REE signatures: chemical sedimentation vs. detrital** 315 **contamination**

316

317 For the original protolith, prior to any post-depositional alteration, it is reasonable to assume that
318 REE were derived from two contrasting sources; (1) those scavenged directly from seawater onto
319 the surface of the original chemical precipitates, and (2) those delivered physically in association
320 with detrital components. Distinguishing these two sources can be difficult as both primary
321 depositional processes and post-depositional alteration processes have the potential to generate
322 correlations that do not imply causation. For example, total REE concentrations in this dataset
323 show mild but notable correlations with major elements which are typically associated with a
324 predominately chemical sedimentary origin (e.g., Fe, Si, Mn, P; Pearson's correlation coefficients
325 of 0.21, -0.41, 0.28, and 0.59, respectively). However, even stronger correlations are observed
326 between total REE concentrations and the concentrations of detrital indicators (e.g., Al, Ti, Zr,
327 Hf, Th; Pearson's correlation coefficients of 0.91, 0.86, 0.94, 0.91, and 0.95, respectively). A
328 variety of processes may induce such correlations. These include early depositional and
329 diagenetic processes such as REE adsorption to iron oxide precipitates or sequestration of REE
330 into early diagenetic phosphate minerals. However, multiple features of the REE spectra show no
331 relation to the inferred chemical sedimentary component. For instance, there exists no good
332 correlation between Ce/Ce* nor LREE/HREE (evaluated as Nd/Yb, for example) and the
333 concentrations of Fe, Si, Mn, or P.

334

335 On the other hand, some features of the REE spectra can be explained by the admixture of detrital
336 components. In order to assess the influence of detrital contributions on REE spectra of the
337 Moodies BIF, we modelled the addition of detrital components to a detritus-poor sample. The
338 chemical composition of the Archean continental crust, used as a detrital component in our
339 model, is highly debated (e.g. Martin et al., 2005). We chose to use an average composition of
340 TTG and Sanukitoids presented in Halla et al. (2017) as representative of the Archean crust and
341 as a material most likely to increase the LREE/HREE slope. The models are presented in Figure 5
342 and the chemical composition of the detrital component is given in Table S6. As shown in Figure
343 5a, Moodies samples are characterized by large variations in La/Yb ratios. The addition of detrital
344 material to a detritus-poor sample results in an increase in the La/Yb ratio as shown in Fig. 5a.
345 The model succeeds in reproducing the general trends observed in CC and SB samples but not
346 the high La/Yb ratios in detritus-poor DSR samples. The model also explains variations observed
347 in Yb and Th concentrations (Fig. 5b). This suggests that the increase in Yb in the Moodies
348 samples is primarily controlled by the addition of detrital material. During the addition of detrital
349 material to a detritus-poor sample, the chemical signatures of the REE spectra are modified (Fig.
350 5c). For example, the LREE depletion, characteristic of detritus-poor samples, is erased by the
351 addition of about 10-15% detrital material. The addition of detrital material also results in the
352 suppression of the positive Y anomaly (Fig. 5c). However, during the addition of detrital material,
353 the positive Eu anomaly is not affected and remains a characteristic feature of detrital-rich
354 samples (Fig. 2). This indicates that the chemical composition of the crustal component is
355 characterized by a positive Eu anomaly, evidence for which is also apparent in Barberton TTG
356 rocks (Moyen et al., 2019, their supplementary data). During the addition of detrital components,
357 the La/Ce and Sm/Nd ratios both decrease slightly.

358
359 Detrital contributions can explain large variations in total REE concentrations and also the
360 correlation between Yb and Zr, but fail to explain certain features in the dataset, notably the high
361 La/Yb ratios seen in DSR samples at low Zr abundances, as well as the presence of Ce anomalies
362 in general. As discussed in the next section, these are better explained by post-depositional
363 alteration processes. Detrital contributions appeared to have modified the sensitivity of both of
364 these features (La/Yb and Ce anomalies) to post-depositional alteration.

365

366

367 **5.2 Fluid addition**

368

369 REE spectra have been clearly affected by a secondary process that resulted in differential
370 REE mobilization. Two distinct mechanisms of REE mobilization could be proposed to explain
371 such variations; (1) removal of REE during chemical weathering, and/or (2) addition of REE by
372 fluid circulation. The REE concentrations in aqueous solutions are affected by several
373 parameters, including the original composition of the protolith, the chemical composition of the
374 fluid, and physicochemical conditions during the fluid-rock interaction. For example, during
375 chemical weathering and leaching of REE in basalts, it has been shown that LREE are
376 preferentially mobilized compared to HREE (Cotten et al., 1995). This process results in REE
377 spectra for the fluid that show elevated LREE/HREE ratios relative to the protolith. However, it's
378 important to note that the relative enrichment of LREE and HREE can be highly variable as a
379 function of protolith, fluid chemistry, degree of alteration, . Importantly, during chemical
380 weathering and fluid-rock interaction in tropical environments, Ce is oxidized to Ce⁴⁺ and
381 becomes insoluble, leaving the fluid with a strong negative anomaly (Cotten et al. 1995). The

382 removal of REE by chemical weathering would thus result in depletion of the total REE
383 concentration of the protolith, leaving a strong LREE depletion in the residual altered rock and a
384 strong positive Ce anomaly, which is the opposite of what is observed in Moodies BIF. Instead,
385 we propose that fluid addition is largely responsible for generating the unusual REE spectra in the
386 samples. As discussed below, the initial REE content of the iron formations themselves also
387 appears to have played a role in the modification of REE spectra features during fluid addition.

388
389 To further explore the possible impact of fluid addition, we have developed two fluid addition
390 models (Fig. 6). The fluid used in these models bears deliberately simple REE spectra and shows
391 two main features; (1) a positive linear enrichment from Lu to La, and (2) a strong negative Ce
392 anomaly ($Ce/Ce^* = 0.27$). The REE concentrations in the model fluid presented in Figure 6 are
393 listed in Table S6. The two models presented in Figure 6 represent the admixing of REE from
394 fluids of the same composition to rocks of differing initial compositions. Two end-member cases
395 are presented where the starting compositions were either detritus-poor or detritus-rich,
396 respectively. During fluid addition, the total REE concentration increases, the REE spectra
397 become progressively enriched in LREE, and negative Ce/Ce^* values are produced (Fig. 6).
398 Importantly, the Ce/Yb ratio will either increase or decrease, depending on the composition of the
399 protolith (i.e., detritus-rich or -poor). Similarly, in the case of La/Yb (Figure 5a), detritally
400 contaminated samples (high Zr) do not reach La/Yb ratios above crustal values, whereas detritus-
401 free samples (low Zr) show both high and low La/Yb values. Samples showing low La/Yb values
402 appear to retain the light REE depletion expected for seawater precipitates. However, samples
403 with high La/Yb ratios cannot be explained by a seawater origin nor by detrital contamination;
404 the best explanation for samples found above crustal La/Yb values is late LREE addition.

405

406 The REE concentration in the fluid is unknown which prevents us from determining the amount
407 of fluid addition necessary to explain the observed variations. Nevertheless, it is clear that the
408 amount of inherited REE required to alter spectra will be greater for a detritus-rich sample than
409 for a detritus-poor sample. The model we present illustrates the late generation of multiple
410 features of the unusual REE spectra using relatively simple and plausible assumptions, notably a
411 preferential mobility of LREE compared to HREE. It is possible that the source of the mobilized
412 REE is the host rock itself, in which case the fluid would be expected to carry pre-existing
413 anomalies, such as a positive Eu anomaly. However, when considering fluids of different
414 compositions and relative REE mobilities, it quickly becomes apparent that the system is poorly
415 constrained and that diverse fluid compositions may be evoked to explain any given alteration
416 pattern, regardless of the protolith from which REE in the fluids derived. What is apparent,
417 however, is that these fluids were enriched in LREE while at the same time depleted in Ce.

418
419 Groundwaters today are characterized by REE concentrations that are generally low, in the
420 nanomolar to picomolar range, including deeper (~200m) groundwaters draining REE-rich
421 lithologies such as granite (Janssen and Verweij, 2003; Noack et al., 2014; Munemoto et al.,
422 2015). Mean iron formation Ce and Pr concentrations observed in our dataset are 10 and 1.3 ppm,
423 respectively. Mass balance indicates that to supply an equivalent amount of REE from
424 groundwater, volumes ranging from as little as 200L per Kg of iron formation, to as much as ten
425 million liters, are implied. Acidic geothermal waters may carry higher REE loads, up to ~0.1 ppm
426 (Wood, 2006), and could supply the necessary REE in as little as 100L per Kg of iron formation.
427 Crucially, the BGB already contains evidence of significant REE mobility during the formation
428 of “ironstone pods” as the result of iron dissolution and reprecipitation in shallow groundwater
429 systems (Lowe and Byerly, 2007). Contrary to the samples studied herein, these pods show a

430 range of features that are inconsistent with an Archean origin, namely a lack of deformation,
431 stratification aligned with modern topographic slopes, abundant cavities, and goethite drip
432 features. Importantly, these ironstone pods bear both positive and negative Ce anomalies,
433 reaching as low as 0.2 Ce/Ce*, and bear concentrations of REE that are similar to those reported
434 here for the Moodies BIF (Hren et al., 2006). They thus offering an attractive analogue for how
435 significant quantities of REE may have been mobilized under near-surface conditions and with
436 sufficient oxygen exposure to generate large Ce anomalies in markedly older rocks.

437

438

439 **5.3 Applicability of Sm-Nd and La-Ce geochronometers for dating fluid addition**

440

441 As discussed above, fluid addition likely had a strong influence on REE elemental ratios. In
442 Figure 7, we present the impact of our fluid addition model on the La/Ce and Sm/Nd ratios. The
443 La/Ce ratio is most strongly affected because the added fluid is heavily depleted in Ce. This
444 results in an increase in the La/Ce ratio of the altered samples. In the models presented in Figure
445 7a, the $^{138}\text{La}/^{142}\text{Ce}$ ratio evolves from 0.004 to 0.015. During fluid addition, the Sm/Nd ratios are
446 also affected and slightly decrease from 0.13 to 0.10 (Fig. 7b). The modification of
447 parent/daughter elemental ratios during fluid addition has strong implications for the time-
448 dependent evolution of Ce and Nd isotopic compositions because the relatively large variations in
449 La/Ce produced during alteration means that it is possible to use Ce isotopes to constrain the
450 timing of fluid addition.

451

452 A large spread in La/Ce ratios, if ancient, should give rise to a corresponding large spread in the
453 $^{138}\text{Ce}/^{142}\text{Ce}$ ratio, as sufficient time has passed for ingrowth of ^{138}Ce from ^{138}La decay to occur.

454 However, if the fractionation of La and Ce is more recent, ingrowth of ^{138}Ce will be small,
455 considering the long half-life of ^{138}La , and samples will show a restricted range in $^{138}\text{Ce}/^{142}\text{Ce}$
456 despite a large apparent range in La/Ce. We have measured the Ce isotopic compositions of six
457 samples with varying $^{138}\text{La}/^{142}\text{Ce}$ ratios (from 0.004 to 0.012), and a plot of $^{138}\text{Ce}/^{142}\text{Ce}$ versus
458 $^{138}\text{La}/^{142}\text{Ce}$ gives an isochron age of 60 ± 32 Ma (Figure 4b). This suggests that the La-Ce
459 elemental fractionation occurred considerably more recently than deposition of the Moodies BIF.
460 In Figure 8a, we report the theoretical isochrons for two fractionation ages (the known 3.2 Ga
461 U/Pb zircon-constrained depositional age, and the La/Ce fractionation age of 1.1 Ga suggested as
462 a maximum age by Hayashi et al., 2004), anchored for simplicity at the same initial $^{138}\text{Ce}/^{142}\text{Ce}$
463 value as indicated by our data. As is clearly evident, the data reported in this study does not show
464 the expected ^{138}Ce ingrowth predicted by a 3.2 Ga isochron, but rather shows a restricted range in
465 $^{138}\text{Ce}/^{142}\text{Ce}$, consistent with a suite of sediments that possessed similar La/Ce ratios for most of
466 their history. This confirms that the La/Ce fractionation is not a primary feature of the Moodies
467 BIF, and crucially, the negative Ce anomalies were generated post-depositionally. Our data also
468 show a less inclined slope than the 1.1 Ga isochron, which contradicts the La/Ce fractionation
469 ages proposed by Hayashi et al. (2004). This maximum age was essentially proposed to explain
470 the radiogenic Ce isotopic composition of a banded ferruginous chert from the Fig Tree Group
471 ($\epsilon\text{Ce}=9.2$). All our samples, on the contrary, plot on the terrestrial Ce-Nd array defined by Israel
472 et al. (2020) with present day ϵCe and ϵNd mean values for the less-perturbed DSR samples of
473 3.9 and -33.1, respectively.

474
475 The fractionation of La from Ce, and thus the generation of negative Ce anomalies, is more
476 recent than proposed by Hayashi et al. (2004). However, considering the long half-life of ^{138}La ,
477 we emphasize that the geochronological resolution of our dataset is limited. It is safe to say that

478 La/Ce fractionation likely occurred in the last 100 Ma. This is consistent with the findings of
479 Lowe and Byerly (2007), who inferred that the “ironstone pods” found in multiple localities in
480 the Barberton Greenstone Belt formed during the Cenozoic, most likely during the Pleistocene.
481 These ironstone pods are composed largely of goethite that would not have survived
482 metamorphic temperatures exceeding ~100 °C without recrystallization to hematite. The BIF
483 sampled in this study also contain a small, but non-negligible, quantity of goethite in some
484 samples (Table S2). This similarly indicates that some hydrological modification must have
485 occurred at near-surface conditions. There appears to be no correlation between the magnitude of
486 the Ce anomaly and any feature of sample mineralogy that would indicate a consistent
487 mineralogical pattern of post-depositional alteration (Table S2). While the Moodies BIF show
488 multiple features consistent with an Archean origin (deformation, strike and dip consistent with
489 adjacent siliciclastic units, mineral assemblages consistent with metamorphosed BIF), it is likely
490 that these units were also subject to hydrological modification during wetter periods of the
491 Cenozoic.

492 Fluid addition also played a role in the Sm/Nd variations measured in the Moodies BIF,
493 with consequences for Sm-Nd geochronology. In a plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$, the
494 samples from the CC locality lie on an isochron with an age of 2770 ± 530 Ma whereas the other
495 localities either plot outside of the isochron (most SB samples) or show little variation (DSR). In
496 order to test the influence of fluid addition on the Sm/Nd isochron, we calculated the theoretical
497 3.2 Ga isochron anchored by the sample with the highest Sm/Nd ratio because this sample was
498 least affected by detrital input or fluid addition, which both act to decrease the Sm/Nd ratio
499 (Figure 8b). It can be clearly seen that the majority of points lie to the left of the theoretical
500 isochron. This is consistent with the models presented where fluid addition is shown to decrease
501 the Sm/Nd ratio and move points to the left of the isochron. The deviation from the 3.2 Ga

502 isochron can be calculated (as the difference in Sm/Nd ratio expressed in %) and plotted as a
503 function of the magnitude of the cerium anomaly (Figure 9). This deviation scales positively with
504 the magnitudes of negative Ce anomalies in the same samples and is consistent with Sm/Nd ratios
505 that have been affected by fluid addition. However, this fluid delivery did not change the Nd
506 isotope composition. SB samples that are the most affected by the suspected fluid addition show
507 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in a narrow range ($<2\epsilon$), showing that the fluid may have been internal to the
508 examined BIF units.

509 It is important to note that Sm/Nd ratios are less susceptible to fractionation relative to
510 La/Ce ratios because neither undergo redox transformation under surface or upper-mantle
511 conditions. The shifts in Sm/Nd produced by fluid addition are thus small, and while perceptible
512 on an isochron plot, may still give an isochron age that is within error of the known depositional
513 age (which is the case of the isochron coinciding with the CC samples in Figure 4). Ultimately,
514 while the influence of fluid addition on Sm-Nd geochronology may be apparent, it is unsuitable
515 for resolving the timing of fluid addition due to the muted effects on the Sm/Nd ratio. Sm-Nd
516 geochronology should thus not be used to constrain the timing of emplacement of Ce anomalies
517 in ancient rocks, metasedimentary or otherwise.

518

519 **5.4 Implications for geochemical proxy reconstruction of Archean redox conditions**

520 Redox-sensitive geochemical proxies such as Ce/Ce* are widely applied to reconstruct the
521 history of Earth surface oxygenation. In Archean black shales, enrichments in redox-sensitive
522 elements (S, Mo, Re, Os), as well as Fe, Mo and C isotopes, all suggest that O₂-rich niches
523 already existed ca. 2.6 to 3.0 Ga (e.g., Wille et al., 2007; Czaja et al., 2012; Stüeken et al., 2012;
524 Thomazo et al., 2013). In diverse metasediments of the Pongola Supergroup, isotope

525 compositions of S, Fe, Cr, Mo, and U have all similarly been used to indicate the presence of
526 some free O₂ ca. 2.96 Ga ago (Crowe et al., 2013; Planavsky et al., 2014; Wang et al., 2018;
527 Eickmann et al., 2018). Sedimentary Fe isotope composition and U enrichment have also been
528 used to argue for oxygenated surface waters as far back as 3.2 Ga ago (Satkoski et al., 2015).

529 Nevertheless, a Paleo- to Mesoarchean origin for oxygenic photosynthesis remains
530 controversial (e.g., Johnson et al., 2013; Ward et al., 2016). Part of this controversy is related to
531 alternative interpretations of geochemical records suggested as proxies for O₂ in deep time,
532 especially emerging metal isotope proxies (e.g., Konhauser et al., 2011; Kaufman, 2014) and to
533 uncertainty in the robustness and syngenicity of these signals (Kirschvink et al., 2012; Kaufman,
534 2014). Indeed, post-depositional oxidation of originally reduced Archean metasediments has been
535 widely demonstrated (e.g., Li et al., 2012; Rasmussen et al., 2014a; Albut et al., 2018). For
536 instance, Hoashi et al. (2009) hypothesized that hematite in the 3.46 Ga Marble Bar chert (Pilbara
537 Supergroup, Australia) occurred as a primary precipitate formed in the presence of seawater, yet
538 this was later discounted on petrographic grounds (Rasmussen et al., 2014b). Similarly, Cr
539 isotope fractionation in the 2.96 Ga Sinqeni IF (Pongola Supergroup, South Africa) that was used
540 to suggest transient atmospheric oxygenation ca. 3.0 Ga (Crowe et al., 2013) was later shown to
541 be present in surface samples but not in fresh drill core (Albut et al., 2018), and since confirmed
542 using U-series isotopic disequilibrium to represent modern weathering (Albut et al., 2019). Due
543 to the uncertainties surrounding the timing of oxidation, it appears that geochemical proxy
544 evidence indicating the former presence of O₂ in water may not alone be sufficient to resolve the
545 debate surrounding the origin of oxygenic photosynthesis.

546 Several geochemical proxies for O₂ form radiogenic systems that are amenable to dating,
547 and radiogenic approaches for constraining the timing of oxidation have now been successfully

548 applied using Re-Os (Kendall et al., 2015) and U-Th-Pb (Li et al., 2012; Satkoski et al., 2015).
549 The latter approach provides the only direct geochronological support to date for an oxidative
550 proxy signal dating as far back as 3.2 Ga ago. Our study underlines the necessity of such an
551 approach. Ce/Ce* is considered one of the most robust redox proxies due to the general
552 insolubility of REE at Earth surface conditions, by their immobility during greenschist- and
553 amphibolite-facies metamorphism, and by the fact that Ce becomes even more immobile when
554 oxidized. Indeed, with the exception of the Hayashi et al. (2004) study and this work, we are
555 unaware of any reports of confirmed late emplacement of negative Ce anomalies in Archean-aged
556 metasedimentary rocks. However, several published datasets in Archean rocks warrant
557 reexamination of the inferred syn-depositional origin of negative Ce anomalies. For example, an
558 Archean paleosol from the Singhbhum Craton displays strongly negative Ce anomalies that were
559 used to suggest transient atmospheric oxygenation sometime prior to 3.02 Ga, yet iron loss and U
560 immobility within the paleosol, as well as the presence of redox-sensitive detrital pyrite and
561 uraninite in overlying sediments, indicate reducing conditions (Mukhopadhyay et al., 2014).
562 Furthermore, the sample showing the most pronounced Ce anomaly conspicuously shows
563 pronounced LREE enrichment but comparable Ce abundance relative to other samples. In a study
564 compiling REE data from multiple studies, Kato et al. (2006) highlighted that several different
565 BIF occurrences deposited prior to 2.5 Ga are characterized by negative Ce anomalies. It would
566 be prudent to re-examine these samples for telltale signs of REE mobilization and the generation
567 of Ce anomalies by fluid addition, which may be indicated by LREE enrichment. While late
568 emplacement of a negative Ce anomaly by an alteration fluid simply requires oxic conditions at
569 some point during the fluid's trajectory, it's important to note that this anomaly could persist if
570 conditions became anoxic further along the flow path. Contrary to some redox indicators such as
571 uranium that are rapidly scrubbed out of solution at reductive redox boundaries (c.f. Abdelouas et

572 al., 2000, and reference therein), only dilution by non-fractionated REE, or possibly reductive
573 dissolution of minerals that already bore a positive Ce anomaly, would erase a negative Ce
574 anomaly from an alteration fluid. Such a scenario may lead to the emplacement of negative Ce
575 anomalies in rocks that simultaneously bear indicators of anoxia, such as U immobility.

576 This work constitutes a cautionary tale in that even the most robust (e.g., least easily
577 reset) elemental and isotopic proxies for ancient oxygenation, such as REE and their isotopes, are
578 susceptible to post-depositional alteration. In the case of REE-based proxies, as described here,
579 there are a variety of supplemental indicators that can be used to reveal such processes, such as
580 modifications to the REE spectra and perturbation to Nd and Ce isotope systematics. This is not
581 the case for all elemental and isotopic redox proxies. Therefore, when inferring the ancient
582 presence of O₂ from elemental and isotopic redox proxies, additional confirmatory information
583 regarding the syn-depositional nature of the signal is required.

584

585

586 **6. Conclusion**

587

588 Some BIF of the Moodies Group show unusual features in their shale-normalized REE spectra,
589 most notably pronounced negative Ce anomalies and variable LREE vs. HREE enrichment, with
590 some samples possessing LREE that are enriched compared to HREE. We examined the origin of
591 these features with respect to potential syn- and post-depositional processes that may have
592 influenced the REE spectra. While total REE abundances scale weakly with the concentrations of
593 elements that were likely derived from the chemical components of the sediment (Fe, Si, Mn, P),
594 there appears to be little relation between their concentrations and the features of the REE spectra

595 themselves. By contrast, total REE abundances scaled strongly in a positive fashion with the
596 concentrations of indicators of detrital contamination, notably Al, Ti, Hf, Th, and Zr. Detrital
597 contamination clearly exerted control over REE features in these samples but cannot explain the
598 presence of significant negative Ce anomalies nor extreme LREE enrichments relative to HREE,
599 which we attribute to post-depositional mobilization of REE and addition of REE by alteration
600 fluids. A simple model for the late addition of REE can explain these unusual spectral features for
601 both detritus-rich and detritus-poor samples. The influence of this late REE addition is also
602 evident in the Ce and Nd isotope systematics of these samples. La/Ce ratios were significantly
603 altered by fluid addition, and the samples form a La-Ce isochron that constrains the timing of
604 fluid addition to within the last 100 Ma. This is consistent with previous suggestions that negative
605 Ce anomalies in ferruginous sediments of the Barberton Greenstone Belt are not primary features
606 and confirms the utility of the La-Ce isotope approach for constraining the timing of oxidation as
607 expressed by the Ce anomaly redox proxy. Sm/Nd ratios were less perturbed by fluid addition;
608 nevertheless, the effect of fluid addition is evident in the Nd isotopic compositions of the
609 samples, with deviation of both the sample set Sm-Nd isochron, as well as Nd model ages, that is
610 proportional to the importance of fluid addition, as inferred by the magnitude of the negative Ce
611 anomaly. This work highlights the need for careful consideration of the potential for post-
612 depositional alteration to modify elemental and isotopic redox proxies. Caution is warranted
613 when inferring the ancient presence of O₂ in the absence of direct geochronological constraints
614 on the age of the proxy signal.

615

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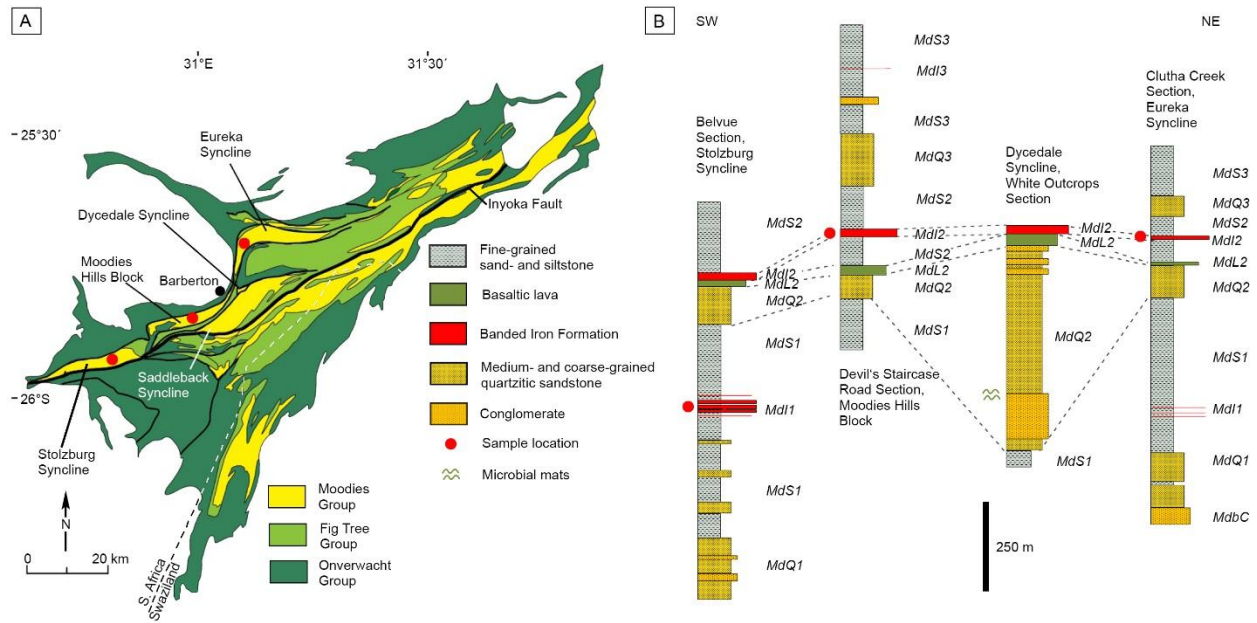
817 **Declaration of competing interest:**

818 We have no competing financial interests or personal relationship that could have appeared to
819 influence the work reported in this paper.

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822 **Figures**



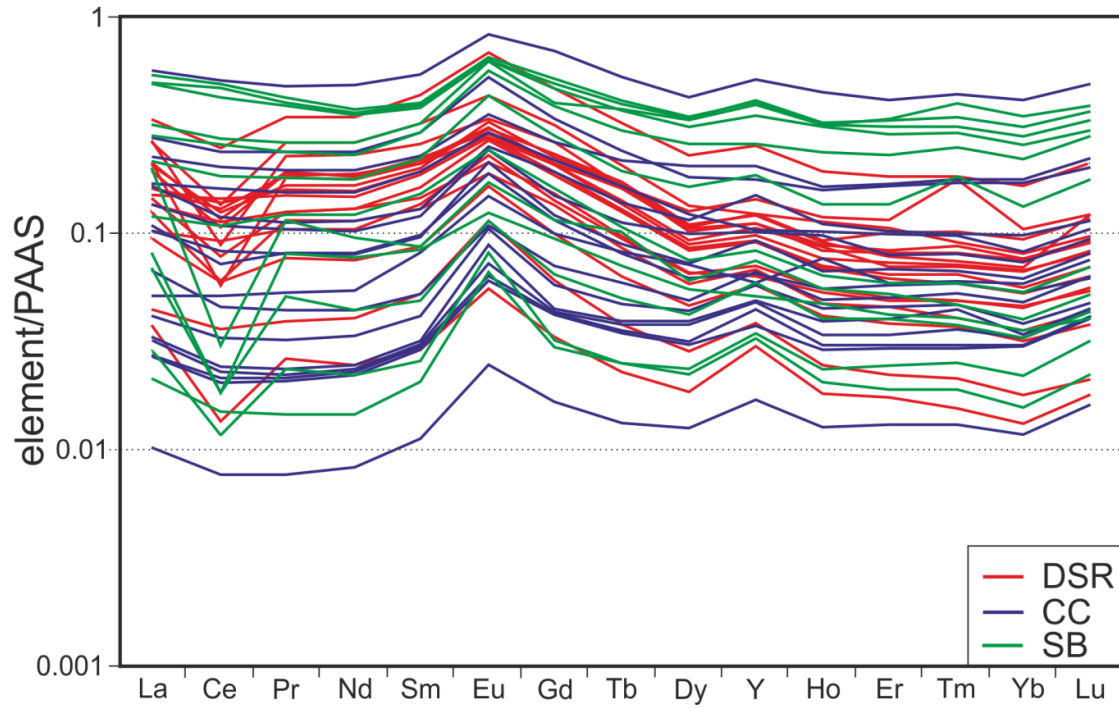
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 824 **Figure 1.** Location and stratigraphy of Moodies Group BIF in the Barberton Greenstone Belt. (A) Map
 825 showing sampling locations. (B) Stratigraphic columns of the Stolzburg Syncline, Moodies Hills Block,
 826 Dycedale Syncline and Eureka Syncline. Abbreviations of stratigraphic units follow Anhaeusser (1976).

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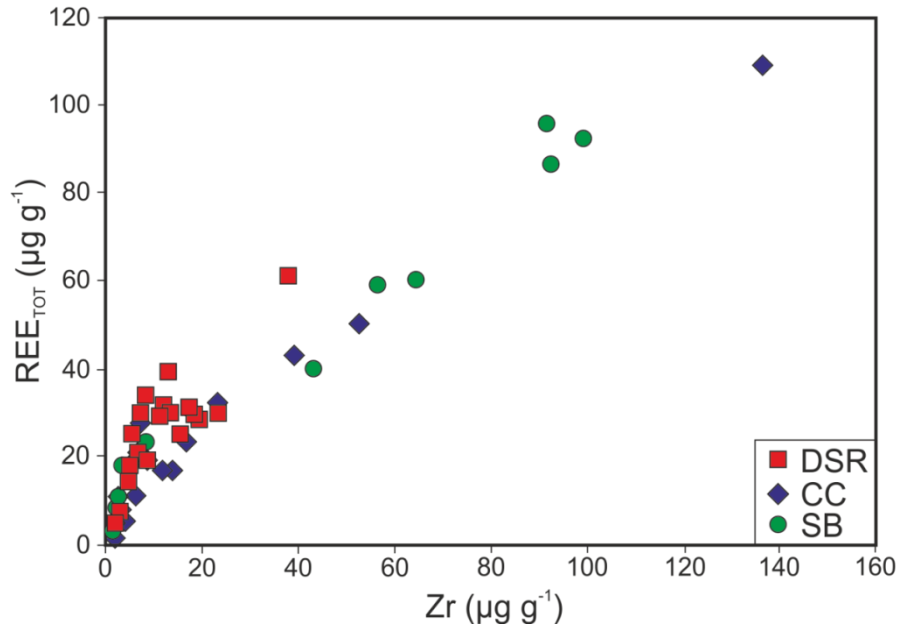
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 832 **Figure 2.** PAAS-normalized REE patterns of Moodies BIF analysed in this study (DSR = Devil's
 833 Staircase Road of the Moodies Hills block, CC = Clutha Creek section of the Eureka Syncline, SB =
 834 eastern Stolzberg Syncline).

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844 **Figure 3.** Total REE content versus Zr content in the Moodies BIF. Abbreviations as in Fig. 2.

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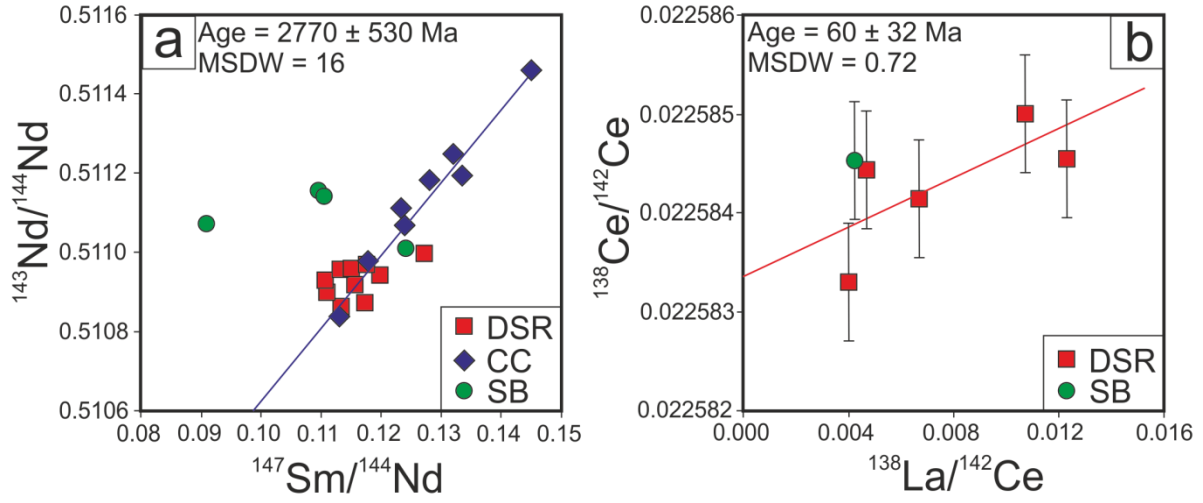
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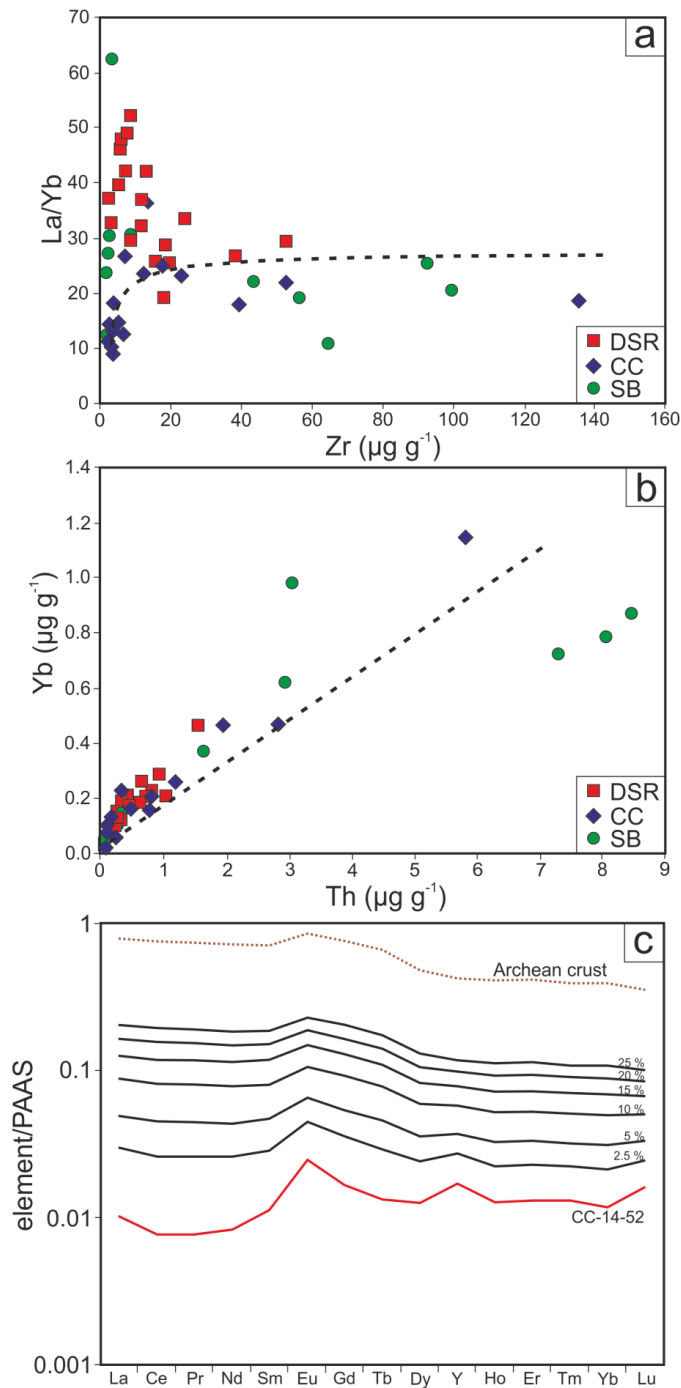
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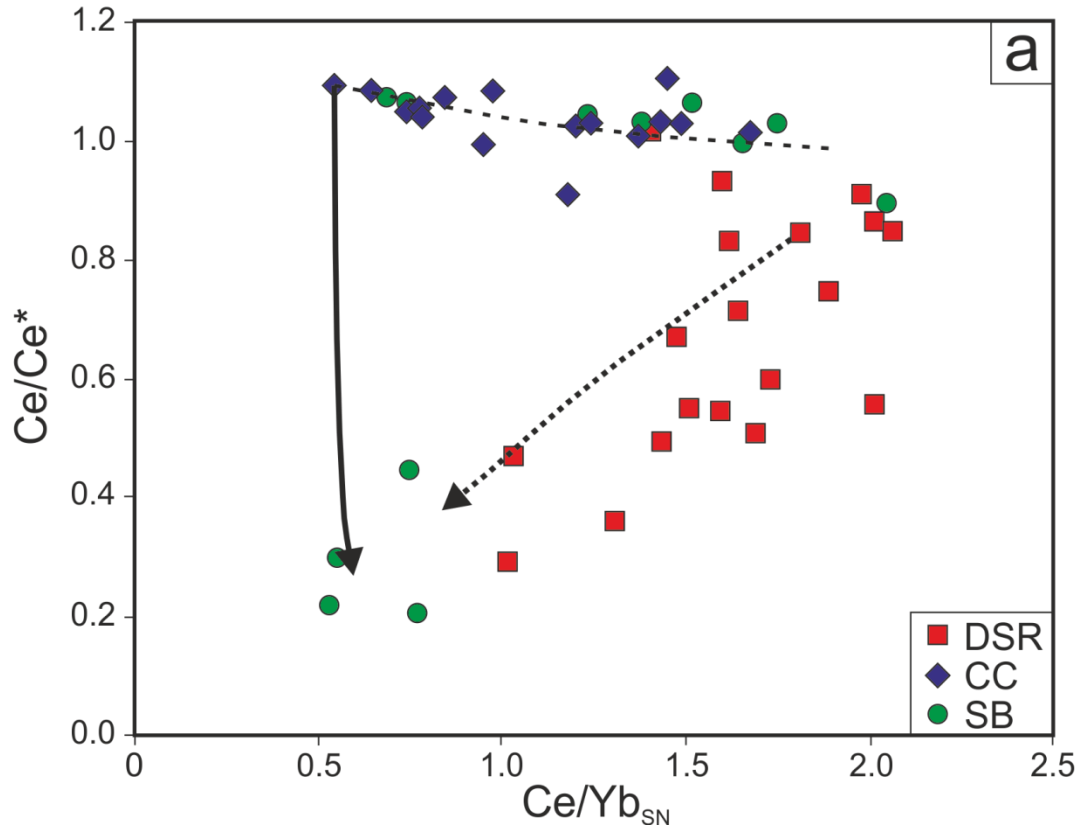
857 **Figure 4.** (a) Sm-Nd isotope composition of Moodies Group BIF analysed in this study. (b) La-Ce isotope

858 composition of selected samples from the SB and DSR localities.



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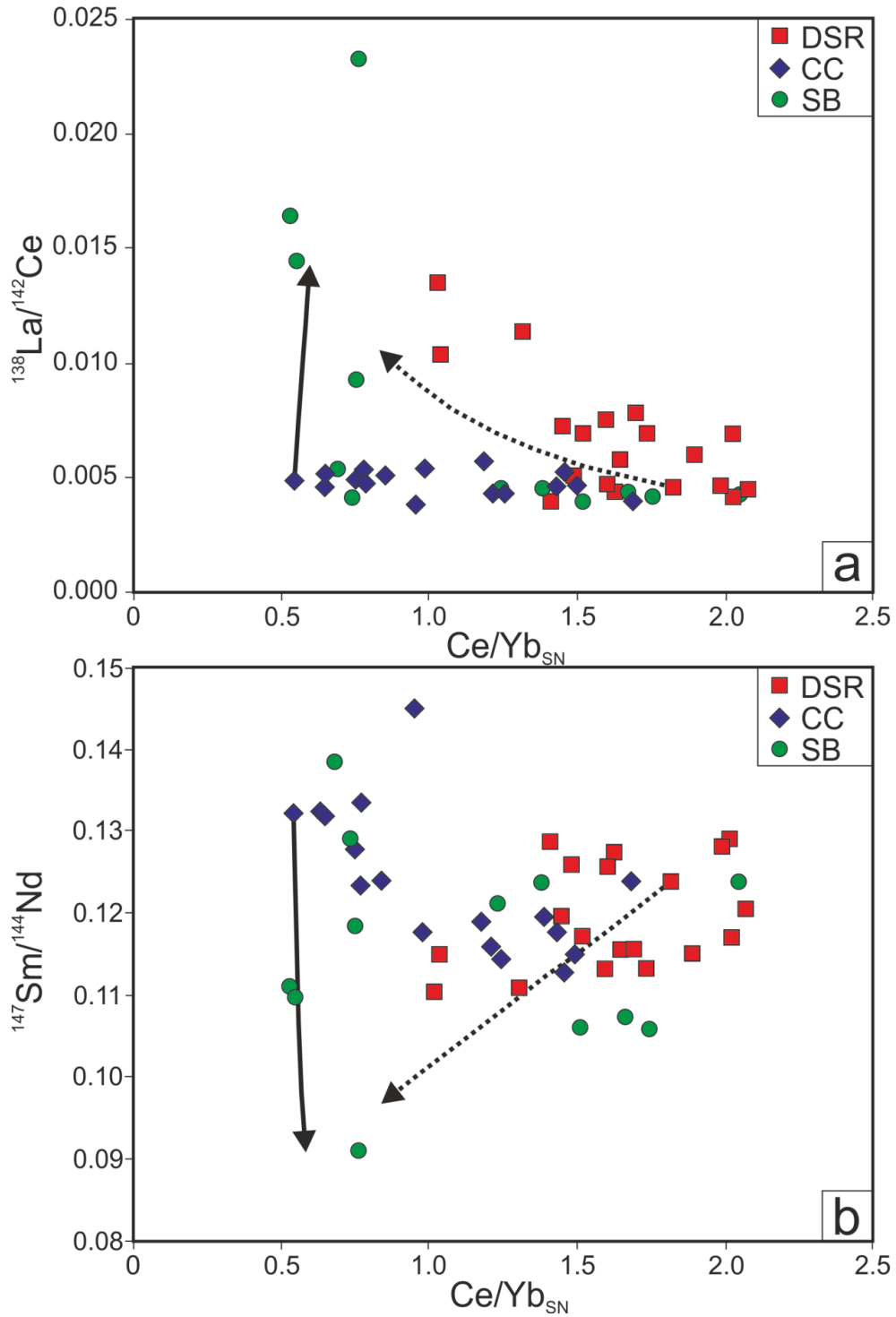
860 **Figure 5.** (a) La/Yb ratio versus Zr concentrations for Moodies Group BIF. (b) Yb concentration versus
 861 Th concentration of the Moodies Group BIF. (c) PAAS-normalized REE patterns for a detritus-poor
 862 sample (CC-14-52) together with models of admixture of detrital input. Dashed lines in (a) and (b)
 863 represent the admixing model of detrital material. Values for Archean Crust in (c) are from Halla et al.
 864 (2017) (Table S6). The values given in (c) show the amount of detrital material added to the detritus-poor
 865 sample. See text for details.



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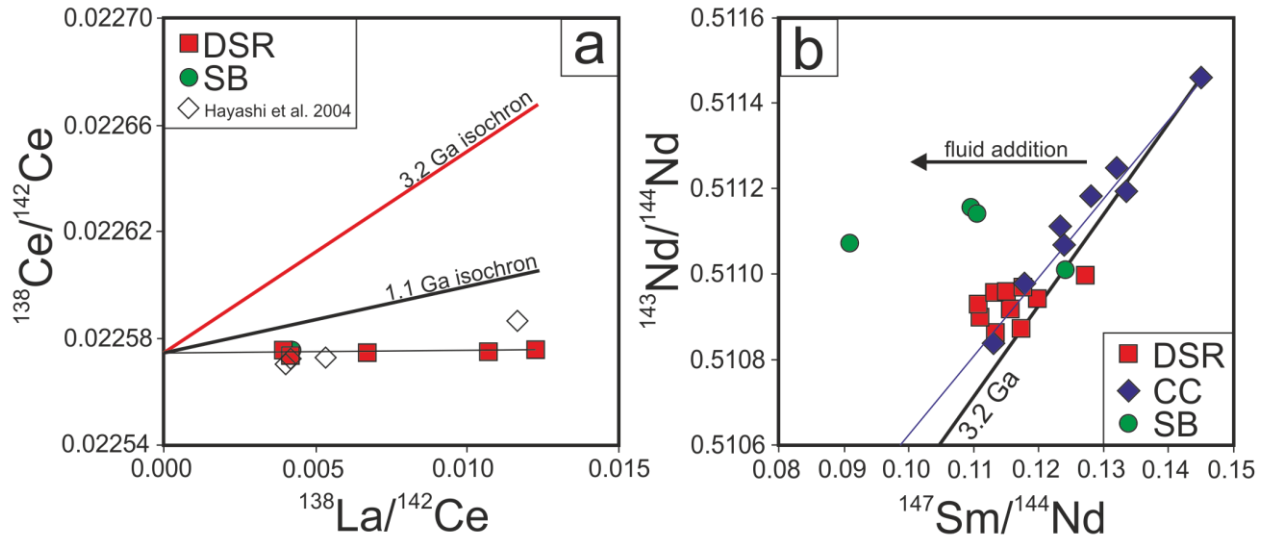
867 **Figure 6.** Ce anomaly versus shale-normalised Ce/Yb ratio in Moodies Group BIF. The dashed line
 868 represents the admixing model; arrow indicates increasing admixture of detrital material. The dotted and
 869 solid lines show fluid addition models with detritus-poor and detritus-rich starting composition,
 870 respectively. See text for details.

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873 **Figure 7.** (a) $^{138}Ce/^{142}Ce$ versus shale-normalized Ce/Yb ratio. (b) $^{147}Sm/^{144}Nd$ versus shale-normalized
 874 Ce/Yb ratio in the Moodies Group BIF analysed in this study. The dotted and solid lines show fluid
 875 addition models with a detritus-poor and detritus-rich starting composition, respectively. See text for
 876 details.



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878 **Figure 8.** (a) La-Ce isotope composition of selected samples from the SB and DSR localities; (b) Sm-Nd
 879 isotope composition of Moodies Group BIF analysed in this study. In (a), the black and red lines are
 880 theoretical Sm-Nd isochrons at 1.1 Ga and 3.2 Ga, respectively. In (b), the blue line is the isochron
 881 calculated using samples from the CC locality only; the black line is a theoretical isochron calculated
 882 using the U/Pb-constrained depositional age. The arrow in (b) indicates the modification induced by fluid
 883 addition.

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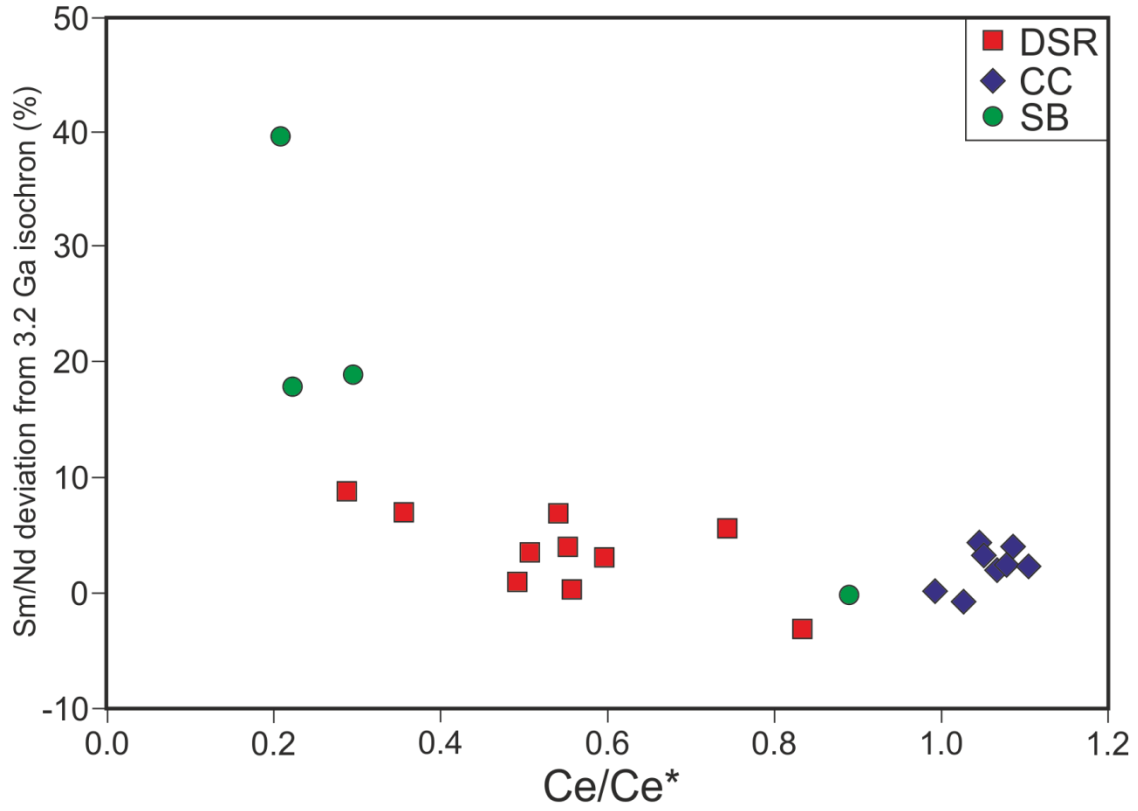
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893 **Figure 9.** Degree of Sm/Nd-ratio deviation from the 3.2 Ga isochron (in %) versus magnitude of the Ce
 894 anomaly of Moodies Group BIF. See text for details.

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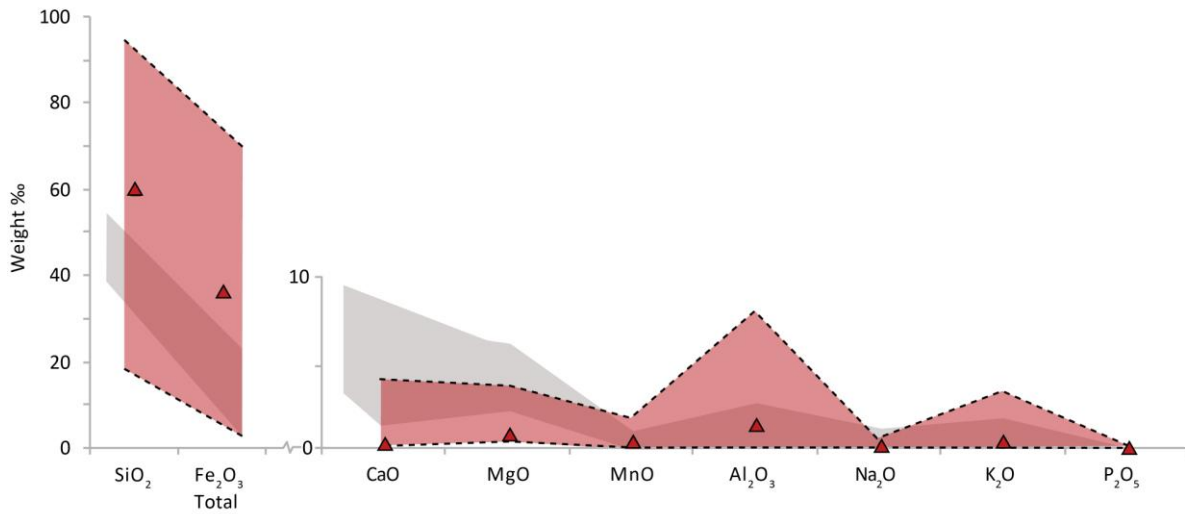
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908 **Supplementary Figures**

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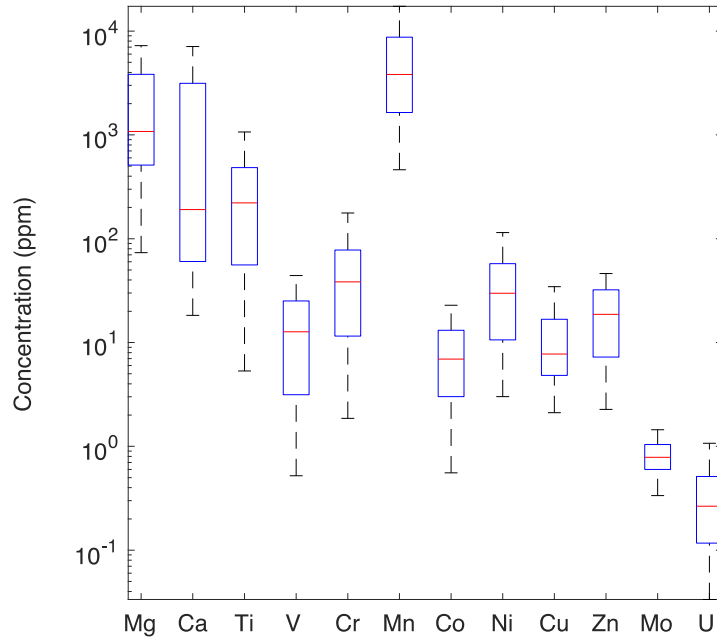
912 **Figure S1.** Mean (triangles) as well as maximum and minimum concentrations (red shaded area) of major
913 elements in Moodies Group BIF (n=48). For comparison (gray shaded area), the range of values provided
914 by Klein (2005) for a large compilation of Archean and Paleoproterozoic BIF (n=90).

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 920 **Figure S2.** Box-and-whisker plot of selected major elements and transition metals in Moodies Group BIF
 921 (n=51). Red lines represent mean values, box limits denote 75th and 25th percentiles, and whiskers show
 922 the full range of values.

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