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A critical evaluation of copper isotopes in Precambrian Iron Formations as a paleoceanographic proxy

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Abstract

Trace metals in Iron Formations (IF) have been widely used as proxies for oceanic redox processes and oxygen evolution leading to the Great Oxidation Event (GOE). Copper has hitherto received comparatively little attention, with a single study reporting variation in $\delta^{65}\text{Cu}$ between pre- and post-GOE black shales. This is attributed to postulated isotope fractionation effects in the pre-GOE ocean during widespread iron oxide deposition in IF. Here we focus on the application of Cu isotopes in two classic IF-containing sequences of the Neoproterozoic-Paleoproterozoic, namely the Hamersley (Australia) and Transvaal (South Africa) Supergroups. We specifically targeted the oxide-rich Joffre and Kuruman IF, the carbonate-rich Griquatown IF, and the Mn-rich Hotazel IF, which collectively record over 100 Ma of sustained IF deposition in the pre-GOE ocean. The aim was to assess the utility of Cu isotopes

25 in IF as a paleoceanographic proxy in view of existing oxygen evolution models. Iron formation
26 Cu concentrations are low compared to average crust and modern oceanic Fe-Mn oxide
27 deposits, with average values between 1 and 5 ppm for all four IF data sets. Copper
28 concentrations show no systematic variability with mineralogy, no statistical correlation with
29 bulk Fe and Mn contents, good correlations with Ti ($r_{\text{Cu-Ti}} = 0.73$) for the Joffre data set and
30 with Cr, Ni, and V for the South African data sets, and shale-like Cu/Ti ratios. Isotopic results
31 show statistically invariant average $\delta^{65}\text{Cu}$ values very close to 0 ‰ for all but the Joffre IF
32 which has a marginally negative average $\delta^{65}\text{Cu}$ value (-0.24 ± 0.22 ‰). Combined with other
33 trace transition metal systematics, the Cu isotope data point to a Cu source that was
34 controlled largely by inputs of fine volcanic-derived particles (ash), thus placing limitations on
35 its utility as a paleoceanographic redox proxy during IF genesis.

36

37 **Keywords**

38 Iron formation; Great Oxidation Event; Copper isotopes; Ocean chemistry; Transvaal
39 Supergroup; Hamersley Supergroup

40

41 **1. Introduction**

42 The concentrations and stable isotope ratios (where applicable) of trace metals in
43 Precambrian marine sedimentary rocks (iron formations-IF, carbonates, black shales) and
44 paleosols have been variously utilised as key records for the reconstruction and redox
45 evolution of the marine and terrestrial realms of the early Earth (Anbar and Rouxel, 2007).
46 Constraints on a Neoproterozoic onset of oxygenic photosynthesis have been gleaned from the

47 isotopic records of several redox-sensitive elements such as Mo (e.g. Planavsky et al. (2014)),
48 Cr (Crowe et al., 2013), and, more recently, U (Wang et al., 2018), and Tl (Ostrander et al.,
49 2019). The use of Cr fractionation as a proxy of Mesoarchean oxidative weathering has,
50 however, been questioned because of uncertain preservation of the rocks (Albut et al., 2018).
51 Complementing the isotopic record is a number of independent studies applying trace metal
52 geochemistry which has further illuminated the processes and effects leading to the first
53 appearance of oxygen in the atmosphere, the so-called Great Oxidation Event (GOE).
54 Konhauser et al. (2009) used declining molar Ni/Fe ratios in IF, while Swanner et al. (2014)
55 focused on secular variations in Co abundance in marine shales and IF, in both instances as
56 tracers of oxygen evolution through time. Similar constraints on the GOE have been provided
57 through the U record of IF (Partin et al., 2013), the Zn/Fe ratio of marine carbonates (Liu et
58 al., 2015b), and the Cu isotopic record of marine black shales (Chi Fru et al., 2016). Proxies for
59 oxidative weathering in the Archean prior to the GOE include Mo and Re concentrations, and
60 Re/Mo ratios in marine shales (Anbar and Rouxel, 2007; Kendall et al., 2010; Scott et al., 2008;
61 Sheen et al., 2018), and Cr isotopes in IF and paleosols alike (Crowe et al., 2013; Frei et al.,
62 2016; Frei et al., 2011).

63 In terms of Precambrian IF, the fundamental premises for the use of a given trace metal as a
64 reliable proxy for water-column processes is that the residence time of the element in
65 question in the ocean is long enough with respect to the time interval averaged by the sample
66 size or that multiple coeval sedimentary pathways compete for the sedimentary output. From
67 the record of Fe isotopes in pre-GOE IF drill cores, Thibon et al. (2019) demonstrated that Fe
68 has a residence time in the Archean ocean in the million year range, which makes Fe a good
69 redox paleoproxy. Iron formations are widely thought to represent the products of primary,
70 cyclic marine iron oxyhydroxide and silica precipitation (Posth et al., 2008) that was

71 subsequently transformed into the present assemblages, mainly through diagenetic bacterial
72 iron reduction (e.g. DIR) (Heimann et al., 2010). Diagenesis would have produced
73 predominantly ferrous assemblages from the ferric precursors in the presence of an electron
74 donor, a role widely thought to have been played by co-precipitated organic matter
75 (Konhauser et al., 2017). Ferrous minerals in IF are mainly carbonates and silicates of iron,
76 with magnetite essentially being the chief Fe(III) host (Oonk et al., 2017). Therefore, in
77 principle, the more iron carbonate and silicate-rich an IF is, the more diagenetically modified
78 it is from the original oxyhydroxide precursor. Consequently, carbonate-silicate facies IF may
79 have been the comparatively more likely candidates for open-system fractionation effects
80 during diagenesis, with high potential for alteration of their primary signals in absolute
81 concentrations and stable isotope ratios of contained trace metals.

82 It follows that for trace metal concentrations and stable isotope ratios to work as effective
83 proxies, the assumption has to be made that diagenesis would have operated as a closed
84 system with respect to the elements of choice. Alternatively, the water-column isotope ratio
85 signature must have been fortuitously retained in the sediment during open system
86 diagenetic transformations. For closed system conservation of isotopic signals to have
87 occurred, the added condition would be that either the trace metals formed discrete
88 authigenic mineral phases stable under the new conditions, or they systematically and
89 quantitatively entered the structure of newly-formed mineral phases that dominate the
90 composition of IF, such as magnetite, iron carbonates, and iron silicates (Oonk et al., 2017).

91 A recently introduced complexity with respect to partly or wholly reduced Fe minerals in IF is
92 the growing body of evidence that some of them may have formed as primary precipitates
93 under high oceanic alkalinity in the form of greenalite (Johnson et al., 2018) or magnetite

94 (Thibon et al., 2019). Primary precipitation of such minerals means that sequestration and
95 isotopic fractionation of associated trace metals would be guided in each case by
96 correspondingly distinct physico-chemical principles and parameters, which may differ
97 markedly from those pertaining to ferric oxyhydroxide nucleation and precipitation. Here, we
98 will employ the traditionally prevailing view in the published literature that the sedimentary
99 precursor in IF was predominantly ferric oxyhydroxide (such as ferrihydrite; Konhauser et al.
100 (2007)). This would occasionally have been accompanied by co-precipitation of Mn(IV) oxides,
101 which presumably would have been driven by transient periods of increased redox potential
102 in the ocean (e.g. “oxygen whiffs”; see Anbar et al. (2007); Kurzweil et al. (2016)).

103 Copper is arguably one of the metals that has received the least attention as a redox proxy
104 for Paleoproterozoic oceanography. To the best of our knowledge, there are hitherto no
105 published studies utilising Cu and its isotopes in IF. The recent study by Chi Fru et al. (2016) is
106 the only work that focuses on Cu isotopes as a record of the GOE, albeit entirely on results
107 from black shales deposited before and after the GOE. Nevertheless, Chi Fru et al. (2016)
108 postulate global IF deposition in the pre-GOE ocean as a driver for effective sequestration of
109 isotopically heavy Cu (^{65}Cu) out of seawater, by virtue of the expected positive fractionation
110 effect linked to the sorption of Cu onto precursor ferric oxyhydroxides (Balistrieri et al., 2008).
111 The resultant reservoir effect in terms of negative Cu isotope fractionation in the oceans
112 would have been quantitatively captured in pre-GOE black shales. At post-GOE times, paucity
113 of IF deposition along with corresponding changes in sources and sinks of Cu in the terrestrial
114 and marine environments would have resulted in black shale deposition recording positive

115 values of $\delta^{65}\text{Cu} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST 976}}} - 1 \right]$.

116 NIST 976 stands for the isotopic Standard Reference Material (SRM) (copper metal) provided
117 by the National Institute of Standards and Technology (NIST). In this work, we provide the first
118 comprehensive record of the Cu isotopic composition of four major IF sequences from the
119 Transvaal and Hamersley Supergroups in South Africa and Australia, respectively, that span
120 over 100 million years of chemical iron deposition immediately before the GOE. We critically
121 assess our results against the broader mineralogical and geochemical characteristics of the
122 examined IF, and provide constraints on the sources and sinks of Cu during deposition and
123 diagenesis. We then evaluate the potential of Cu isotopes for constraining redox processes in
124 the pre-GOE ocean through time, in light of both existing models and in more general terms.
125 Finally, we highlight some of the caveats in the wider application of trace metal geochemistry
126 of IF as a paleoenvironmental proxy, especially when the speciation and mineralogical
127 distribution of these metals in the primary sedimentary environment are neither adequately
128 understood nor rigorously constrained.

129

130 **2. Samples and analytical techniques**

131 Four drill cores capturing representative sections of IF from the Transvaal Supergroup of
132 South Africa and the Hamersley Supergroup of Australia were sampled for the purpose of this
133 work. Detailed information on the geological settings and full descriptions of the samples are
134 given in the Electronic Supplement of Thibon et al. (2019). The three South African drill cores,
135 referred to as GAS, LO1, and MP56, capture, respectively, the Kuruman, Griquatown, and
136 Hotazel IF, which collectively span the time interval between 2521 and 2394 Ma (Gumsley et
137 al., 2017). The fourth drill core, GW, from Hamersley captures part of the Joffre member of
138 the Brockman IF, which has been dated at 2463 to 2449 Ma (Pickard, 2002). The IF deposition

139 rates have been independently assessed by U-Pb chronology and Co deposition rates (Thibon
140 et al., 2019). The rates of 4-30 m/Ma obtained by the two methods are consistent and have
141 received further support from the comparison of stratigraphy with orbital periods (Lantink et
142 al., 2019).

143 One of the issues associated with laminated samples is the chemical variability induced by
144 mineral grain size and banding. A total of 156 samples were collected from the four drill cores
145 in the form of 10 to 20 cm-long quartered cores every one to five meters on average along
146 the entire length of each core (MP56: 362.46-458.80 meters depth; LO1: 122.35-355.60
147 meters depth; GAS: 0-522.70 meters depth; GW: 40-101 meters depth). The length was
148 chosen to correspond to a moving average, or, equivalently, to a low-pass filter, removing
149 fluctuations shorter than about 10,000 years. Unfortunately, the range of variations of Cu
150 isotopes is too small to apply the technique of Thibon et al. (2019) for determining the Cu
151 oceanic residence time. Thibon et al. (2019) also reported Fe isotope data on samples from
152 the LO1 core collected on the cm-scale. Although the major and trace element and Fe isotopic
153 compositions of these centimetric samples averaged over 10-20 cm are fully consistent with
154 the values obtained on the corresponding decimetric samples, they are significantly noisier.
155 We therefore concluded that short-range fluctuations reflect mineral abundances and, hence,
156 for the remainder of the study focused on the decimetric samples collected every 10 to 20 cm
157 along the cores.

158 Each sample was crushed into small fragments and approximately a quarter of each was
159 pulverized into fine powder in order to provide a bulk average of the sample mineralogy on a
160 10 to 20 cm length scale. Approximately 100 mg of sample powder for each sample was
161 digested in concentrated distilled HF:HNO₃, evaporated to dryness, then redissolved in

162 concentrated distilled 3:1 HCl:HNO₃ (*aqua regia*). After another round of evaporation to
163 dryness, the samples were taken up in 6 M HCl. Two aliquots were prepared: the first aliquot,
164 consisting of 5% of the sample solution, was dedicated to elemental analyses; the second
165 aliquot (i.e. the remaining 95% of the sample) was dedicated to Cu isotopic measurements. A
166 key requirement for the latter is the elimination of most of the iron of the sample solution as
167 it will otherwise saturate the resin used for copper purification. Copper, therefore, was first
168 eluted with the sample matrix using 25 mL of 4 M HCl on a column filled with 3mL AG1-X8
169 resin, while >90% of the Fe was retained on the column. Copper was then separated from the
170 sample matrix and remaining Fe following the procedure of Maréchal et al. (1999), which uses
171 1.8 mL of AG-MP1 resin and 7 M HCl with 0.001 % H₂O₂. Further details of the chemical
172 purification protocol, yields, blanks, and reference values can be found in Maréchal et al.
173 (1999) and a number of later references from several groups who adopted the “Maréchal” Cu
174 separation procedure.

175 Elemental concentration analyses were done on a Thermo-Scientific ICAP ICP-OES for major
176 elements and a Thermo-Scientific ELEMENT2 ICP-MS for minor and trace elements, both at
177 the Ecole Normale Supérieure de Lyon (ENS de Lyon). The analyses followed a 22-sample
178 batch procedure with each batch containing 20 samples (unknowns), the IF reference material
179 IF-G, and a blank, the latter two of which had been through all the same steps as the samples
180 so as to provide measures of the total procedural blank and the reproducibility of the
181 technique. All eight total procedural blanks fell below the level of detection for all elements
182 analysed. The mean external reproducibility of the IF-G reference material was ~10% for
183 major element concentrations and ~30% for minor and trace element concentrations. Most
184 of this variability is ascribed to the inherent heterogeneity of the reference material itself.

185 Our elemental measurements are in excellent agreement with the published values of
186 Govindaraju (1995) (see Electronic Supplement, Fig. S1).

187 Copper isotopic compositions were measured on a Nu Instrument 500 HR MC-ICP-MS, also at
188 ENS de Lyon. Again, all eight total procedural blanks for Cu fell below the level of detection.
189 Samples and standards (SRM NIST 976) were analyzed in wet plasma conditions in low-
190 resolution mode ($R \sim 300$) with SRM NIST 976 run systematically every two samples. With
191 optimal Cu purification as described above, low-resolution mode is sufficient to resolve all Cu
192 interferences (Xe^{++} , Te^{++} , $^{31}\text{P}^{16}\text{O}_2^+$, $^{40}\text{Ar}^{23}\text{Na}^+$, and $^{47}\text{Ti}^{16}\text{O}^+$ for ^{63}Cu , and Xe^{++} , Te^{++} , Ba^{++} , $^{49}\text{Ti}^{16}\text{O}^+$,
193 $^{40}\text{Ar}^{25}\text{Mg}^+$, $^{32}\text{S}^{33}\text{S}^+$, $^{32}\text{S}^{16}\text{O}^{17}\text{O}^+$, $^{33}\text{S}^{16}\text{O}_2^+$, and $^{31}\text{P}^{16}\text{O}^{18}\text{O}^+$ for ^{65}Cu). The optimum Cu
194 concentration for isotopic measurement is 0.3 mg/L, which gives a maximum intensity of 3V
195 of Cu, but concentrations down to 0.05 mg/L are acceptable in good running conditions.
196 Instrumental mass bias correction was done by combining external correction (i.e. sample-
197 standard bracketing using SRM NIST 976) with internal correction using the exponential
198 fractionation law applied to a Zn solution added to both the samples and bracketing
199 standards. The mean value and reproducibility of 19 replicate measurements of the IF-G
200 reference material typically used in IF geochemical studies gave $\delta^{65}\text{Cu}_{\text{IFG}} = -0.23 \pm 0.20 \text{‰}$ (2σ).
201 Precision, therefore, is 0.10 ‰ per amu. To the best of our knowledge, no other $\delta^{65}\text{Cu}_{\text{IFG}}$
202 measurements of this reference standard material have been published so far.

203

204 **3. Results**

205 Bulk-rock major, minor, and trace element data and $\delta^{65}\text{Cu}$ values of all samples, accompanied
206 by tabulated correlation coefficients for each of the four IF sample sets analysed, are archived
207 in the Electronic Supplement (Tables S1 and S2). The elemental data were previously

208 published in Thibon et al. (2019), but for the reader's convenience we include them here as
209 well. In general, the mineralogy and bulk geochemistry of the targeted IF have recently been
210 studied or reviewed comprehensively (Joffre IF: Haugaard et al. (2016); Kuruman/Griquatown
211 IF: Oonk et al. (2017); Hotazel IF: Tsikos et al. (2003); Tsikos et al. (2010)). Hence, the main
212 emphasis in this section will be placed on the behavior of Cu, both its abundances and its
213 isotopic compositions, in connection with the gross mineralogical and geochemical
214 characteristics of the rocks.

215 One of the geochemical parameters that provides a close approximation of the modal
216 mineralogy for all IF is the bulk average Mn/Fe ratio, multiplied here for convenience by a
217 factor of 10^3 and hereinafter referred to as Mn*/Fe. As previously demonstrated, Mn in at
218 least the South African IF is hosted almost exclusively (>90%) in the carbonate fraction and
219 specifically in the minerals siderite and ankerite in the Kuruman and Griquatown IF (Oonk et
220 al., 2017) and in kuthahorite and Mn-calcite in hematite lutites of the Hotazel IF (Tsikos et al.,
221 2003). By contrast, Fe is contained dominantly in the mineral magnetite (and hematite in the
222 case of the Hotazel hematite lutite samples), although a fraction of the bulk Fe is also
223 invariably contained in the aforementioned carbonate minerals and in iron silicate species.
224 The parameter Mn*/Fe can therefore effectively serve as the approximate ratio of bulk
225 carbonate *versus* bulk oxide in IF, while at the same time constituting a measure of the relative
226 role of Mn *versus* Fe on the speciation of trace metals such as Cu.

227 Based on the Mn*/Fe ratio, the selected IF sample sets complement each other well in terms
228 of bulk mineralogy and geochemistry (Fig. 1a): the Joffre IF is the most oxide (magnetite)-rich
229 member, with a Mn*/Fe ratio of 4.2, while the slightly more carbonate-rich Kuruman IF has a
230 Mn*/Fe ratio of 8.4. The Griquatown IF is the most carbonate (ankerite+siderite)-rich

231 member, with a bulk Mn*/Fe ratio of 24.8. The Hotazel IF sample set has a far more
232 heterogeneous composition as it comprises Mn-poor, magnetite+Fe carbonate facies IF, as
233 well as a manganese carbonate-rich sub-facies containing abundant hematite (hematite
234 lutite). This compositional heterogeneity gives rise to an exceptionally high average Mn*/Fe
235 ratio of 317. Exclusion of the hematite lutite samples still results in a high mean Mn*/Fe of
236 46.1.

237 The concentration of Cu in the samples from the Transvaal Supergroup IF is low and compares
238 well with literature data, ranging between 1 and 10 ppm for >95% of all samples analysed.
239 There is, however, no statistical correlation between average Cu abundance from each IF and
240 bulk-rock Fe, bulk-rock Mn, or the ratio thereof, with correlation coefficients always lower
241 than 0.3. When average bulk-rock Cu values are normalised to bulk average Fe for each
242 sample set, the only notable relationship that emerges is a subtle increase in the ratio of
243 $\text{Cu} \cdot 10^6 / \text{Fe}$ (hereinafter referred to as Cu*/Fe) from the Joffre IF (13.9), to the Kuruman IF
244 (14.9) and ultimately the Griquatown IF (18.8) (Fig. 1b). This relationship is crudely correlated
245 with the increasing Mn*/Fe ratio across these three IF sample suites, pointing to a broadly
246 inverse relationship between bulk Fe and Cu.

247 Contrary to the aforementioned lack of correlation between Cu and Fe or Mn, each IF displays
248 its own weak to moderate positive correlations of Cu with other major and/or trace elements,
249 and specifically with transition metal concentrations (Fig. 2). In the Transvaal IF sample sets,
250 correlation coefficients between Cu and Ni, Cr, and V (Figs. 2a-c) are – with one single
251 exception – higher than 0.5, with the highest values observed in the Kuruman formation data
252 set (Table 1). By contrast, Cu concentrations in the Joffre IF correlate well with Ti, with a
253 correlation coefficient of 0.73. This is in agreement with previously published Ti and Cu

254 concentration data of the Joffre IF (Chi Fru et al., 2016), which show a correlation coefficient
255 as high as 0.85 (Fig. 2d).

256 Copper isotope compositions are displayed in Fig. 1c. Copper isotope ratios exhibit very low
257 variability within each IF, at a maximum standard deviation of ± 0.2 ‰. Specifically, the Joffre
258 IF has average $\delta^{65}\text{Cu} = -0.24 \pm 0.22$ ‰; the Kuruman IF $\delta^{65}\text{Cu} = 0.02 \pm 0.13$ ‰; the Griquatown
259 IF $\delta^{65}\text{Cu} = 0.01 \pm 0.09$ ‰; and the Hotazel IF $\delta^{65}\text{Cu} = -0.01 \pm 0.12$ ‰. It is evident from the
260 above data that the Transvaal IF show no statistical difference in average $\delta^{65}\text{Cu}$ among the
261 three data sets (p-value = 0.7) with average values extremely close to 0 ‰, whereas the Joffre
262 IF has a statistically distinct and marginally lower $\delta^{65}\text{Cu}$ average value than those of the South
263 African IF (p-value <0.001).

264

265 **4. Discussion**

266 *4.1. Iron formations as a Cu sink*

267 Copper and Fe variations are visibly decoupled (Fig. 3), which indicates that the two elements
268 are controlled by different processes. The determination of Fe residence time (~2 Ma) in the
269 Archean ocean by Thibon et al. (2019) is based on Fe isotopes and therefore is robust.
270 Although Fe isotopes are a good paleoceanographic proxy, the same may not be the case for
271 Cu isotopes. The lack of large $\delta^{65}\text{Cu}$ fluctuations in the present IF cores indicates that either
272 Cu residence time in the ocean is <10,000 years (fast transfer from input to sediments,
273 fluctuations averaged out) or input $\delta^{65}\text{Cu}$ did not change much over long time intervals.

274 An additional key parameter that would inform the utility of Cu and its stable isotopes as a
275 palaeoceanographic proxy, but is hitherto unconstrained, is the average $\delta^{65}\text{Cu}$ of the
276 Neoproterozoic-Paleoproterozoic oceanic Cu inventory. Given the uncertainties, we first

277 evaluate the abundance of Cu as registered in the bulk-rock composition of the IF analysed
278 here. In terms of average trace metal concentrations, all four IF data sets are clearly low with
279 respect to the average crust, and between one and three orders of magnitude lower than the
280 abundances recorded in Mn nodules in the modern ocean (with the single exception of Cr;
281 Fig. 4). The situation does not change in any major way when the concentrations of Cu are
282 considered as ratios against Fe ($\text{Cu/Fe} \sim 10^{-5}$, this work, *versus* 5×10^{-4} , Rudnick and Gao
283 (2003)). In their oceanic Cu model around the GOE, Chi Fru et al. (2016) postulate a relative
284 Cu/Fe sedimentation rate equivalent to approximately 1/4500 (Konhauser et al., 2002) which,
285 if multiplied by 10^6 for direct comparison with the Cu^*/Fe parameter used earlier (Fig. 1),
286 would result in a value as high as 220. This value is at least an order of magnitude higher than
287 each of the average Cu/Fe ratios for the four IF analysed in this study.

288 Further insights into IF as an effective (or not) Cu sink can be derived from the use of Cu/Ti
289 ratios. Here, Cu concentrations are assessed against Ti, which is widely regarded as a proxy of
290 the terrigenous detrital fraction in marine sediments. A key postulate in previous studies (Chi
291 Fru et al., 2016) is that IF deposited prior to the GOE constituted a sustained and effective
292 oceanic Cu sink by comparison to black shale deposits. We have plotted our entire data set of
293 molar Cu/Ti ratios against time for our four selected IF (Fig. 5, adapted from Chi Fru et al.
294 (2016)), on the contention that our data represent two of the classic and most voluminous
295 pre-GOE IF sequences globally. Contrary to earlier suggestions of Chi Fru et al. (2016) that at
296 least the pre-GOE IF are relatively more enriched sedimentary Cu sinks than coeval black
297 shales, we observe that all four formation averages and >95% of the data plot well into the
298 black shale field. This clearly indicates that at least the IF targeted here were comparatively
299 no more or less important than organic-rich siliciclastic deposits in terms of net precipitation
300 of Cu in the primary sedimentary environment.

301 Understanding Cu behavior requires an assessment of its speciation in Archean seawater.
302 Under the reducing conditions prevailing to maintain positive Eu anomalies, the redox
303 potential of the environment must be negative (Danielson et al., 1992) and, therefore, Cu
304 must be in its reduced form. In addition, Cu⁺ is strongly chelated by chlorine, notably CuCl₃²⁻
305 (Dekov et al. (2013), Fig. 6), which reduces the sedimentary Cu output rate and makes the
306 residence time of Cu dissolved in the ocean longer.

307

308 *4.2. Sources and fate of Cu during IF deposition and diagenesis*

309 The very low concentrations of Cu presented in this paper can be fundamentally explained
310 either by much lower fluxes of Cu in association with primary Fe oxyhydroxide precipitation
311 than postulated elsewhere (e.g. Konhauser et al. (2002)), and/or remobilisation of most of
312 the deposited Cu and loss from the sediment during diagenetic recycling. Irrespective of the
313 exact process or combination of processes, some further conclusions can be drawn from our
314 new Cu isotope results in conjunction with selected bulk geochemical characteristics of the
315 rocks in question.

316 In terms of average Cu isotope ratios, the Joffre IF has a marginally lower $\delta^{65}\text{Cu}$ value than the
317 other three IF from South Africa. The positive correlation between Cu and Ti in Fig. 2d can be
318 interpreted as an association with fine-grained clastic input from a terrigenous or volcanic
319 source. This association is further supported by the comparable range of Cu/Ti values of the
320 Joffre IF samples with those defining the shale field of Fig. 5. In the absence of any statistical
321 correlation of Cu with bulk Fe, we propose that the Cu isotope signal captured in the Joffre IF
322 is essentially the signal of co-precipitated Cu-bearing particles that are genetically unrelated
323 to processes of primary Fe-oxyhydroxide precipitation out of the oceanic water column.

324 The situation with the Cu isotope signal of the three South African IF is somewhat less clear.
325 The Kuruman IF is closely comparable to the Joffre IF in terms of the dominance of magnetite
326 and low modal abundance of carbonate minerals. Assuming that magnetite is the
327 compositionally closest diagenetic mineral to precursor ferric oxyhydroxide, our expectation
328 is that it would have been the most likely candidate to retain primary Cu in the sediment
329 during diagenesis. However, again there is no statistical correlation between Cu and bulk-rock
330 Fe in the Kuruman IF; instead, there are strong positive correlations between Cu and Cr, Ni
331 and V (Fig. 2). Previous studies on the trace metal speciation of the Kuruman and Griquatown
332 IF (Oonk et al. (2017); see also Fig. 7) have indicated that Cr is associated with the IF detrital
333 fraction and shows a good correlation with bulk-rock Zr. By extension, and in the absence of
334 Zr measurements on our current samples, we are inclined to interpret the Cu isotopic
335 signature of the Kuruman IF as also reflecting mainly the fine-grained clastic (i.e. non-
336 chemical) fraction of the original sediment.

337 The Griquatown and Hotazel Formations add important additional dimensions not only with
338 regard to the origin of Cu but also the fate of Cu during diagenetic processes. The Griquatown
339 IF is thought to have been deposited in a relatively shallower environment (above wave base)
340 than the Kuruman IF. It is therefore dominated by Fe carbonate minerals relative to
341 magnetite, and it also has a marginally higher modal detrital component of a presumed
342 terrigenous source (Oonk et al., 2017). Furthermore, the mean of Mn^*/Fe and Cu^*/Fe ratios
343 of the Griquatown IF are clearly higher than those of the Kuruman IF. Previously published
344 speciation results for Cu and other trace metals (Fig. 7) indicate that the carbonate and silicate
345 mineral fractions are the main hosts for Cu, while Mn is almost entirely hosted in the
346 carbonate fraction. Whereas the weakly positive correlation of Cu with Cr (Fig. 2a) suggests
347 that some of the Cu is probably hosted in fine-grained particles of a non-chemical origin (as

348 for the Kuruman IF), a fraction of the Cu in the Griquatown IF may be associated with primary
349 Mn oxide that is now recycled – partly or wholly – into Mn-rich iron carbonates during
350 anaerobic diagenesis. Studies of Mn(IV)-rich deposits in the modern ocean (Little et al., 2014a;
351 Little et al., 2014b) have demonstrated an affinity to the isotopically light Cu isotope (^{63}Cu).
352 In view of this association, the increased Mn/Fe ratio in the Griquatown IF could be expected
353 to record a relatively low $\delta^{65}\text{Cu}$, certainly lower than seen in the Kuruman IF; this is, however,
354 clearly not the case, as the $\delta^{65}\text{Cu}$ average of the Griquatown IF is statistically indistinguishable
355 from that of the Kuruman IF.

356 The Hotazel sample set provides an even better candidate to assess the relative role of high
357 primary fluxes of Mn in controlling primary Cu isotope variations. The selected Hotazel
358 samples range from Mn-poor, magnetite+carbonate-rich IF to hematite-rich lutites with a
359 high abundance of Mn in carbonate minerals, again widely interpreted to represent
360 diagenetic products of MnO_2 reduction (Tsikos et al., 2003; Tsikos et al., 2010). The probability
361 is high, therefore, that the Hotazel samples would capture low $\delta^{65}\text{Cu}$ signatures directly
362 associated with elevated Mn/Fe ratios.

363 The potential for the Hotazel samples to record the lowest $\delta^{65}\text{Cu}$ signatures could in fact be
364 augmented further for an additional reason: very low $\delta^{56}\text{Fe}$ data in the Hotazel IF have been
365 previously interpreted as a highly evolved signature during Rayleigh fractionation of heavy Fe
366 isotopes into Mn-poor BIF in the pre-GOE ocean (Tsikos et al., 2010). If the same principle is
367 applied in the case of Cu and its isotopes, as also put forward by Chi Fru et al. (2016), then
368 highly fractionated $\delta^{65}\text{Cu}$ ought to have been recorded in the most Mn-enriched portions of
369 the Hotazel IF (i.e. lower than the Mn-poor samples). The essentially invariant $\delta^{65}\text{Cu}$ data
370 across the entire Hotazel sample suite irrespective of the large variations displayed by Mn/Fe

371 suggests that, again, the anticipated low Cu isotope signal linked to putative primary MnO₂
372 deposition was either absent in the primary environment, or has been completely erased
373 during diagenetic mineral transformations. It therefore becomes increasingly likely that the
374 very close similarity between the Hotazel, Griquatown, and Kuruman IF in terms of $\delta^{65}\text{Cu}$ data,
375 is simply a manifestation of Cu having a common, isotopically homogeneous fine-grained
376 clastic provenance.

377 In an attempt to constrain further the source of Cu-bearing particulates in the investigated IF,
378 we have plotted spidergrams of the range and average transition metal abundances for each
379 IF normalised relative to the respective average data for arc tholeiite (Lodders and Fegley,
380 1998) (Fig. 8). We have included in our considerations corresponding average data and
381 compositional ranges for four stilpnomelane lutite samples from the Transvaal IF stratigraphy.
382 These lutites are commonly intercalated with the IF in distinct cm- to dm-thick layers, and are
383 widely considered to represent the lithified products of mixed chemical sedimentation with
384 contemporaneous episodes of volcanic ash deposition (Oonk, et al., 2017). We interpret the
385 comparably “flat” nature of all spidergrams with respect to all trace transition metals
386 (excepting Fe and Mn) as consistent with a common – albeit highly diluted in the case of IF –
387 volcanic ash source, especially for the three South African IF which are isotopically
388 indistinguishable in terms of their Cu isotopic signatures. Specifically, this signature recalls
389 that of igneous rocks, especially arc basalts (~0‰, Liu et al. (2015a)). We note that an anoxic
390 pre-GOE atmosphere and ocean would probably have been associated with lower dissolved
391 Cu river fluxes from continents because of sulphide stability and weaker break-down of
392 silicates with Cu in mafic rocks (e.g. pyroxenes) during weathering. In such case, the
393 particulate flux of Cu-bearing minerals would have been the relatively more dominant Cu

394 source to the global ocean at pre-GOE times, augmented by the simultaneous lack of plant
395 cover on the continents (Martin and Whitfield, 1983).

396 The lack of Fe-Cu correlation in the present IF cores requires that the two elements followed
397 different pathways. Iron in the Archean ocean is dominated by hydrothermal input (Thibon
398 et al., 2019). In contrast, Cu in IF is dominated by a volcanogenic “detrital” component and,
399 regardless of the residence time of Cu dissolved in the ocean, the output in the form of
400 “chemical” Cu precipitated from the ocean is minor.

401

402 **5. Conclusions and implications**

403 The following points summarize the key results of the present study with regard to Cu and its
404 isotopes in IF as a paleoceanographic proxy:

- 405 • Copper, and most other trace metals contained in IF, are present in vanishingly low
406 concentrations by comparison to the bulk-rock iron content. They are also very low by
407 comparison to transition metal contents in modern oceanic ferromanganese deposits and
408 to the corresponding concentrations of average continental crust.
- 409 • The average $\delta^{65}\text{Cu}$ value of the Joffre IF is slightly negative (-0.24 ‰) but statistically
410 invariant within analytical error. The good positive correlation between Cu and Ti
411 abundances suggests that Cu and its isotopic signature in the Joffre IF most likely is derived
412 from a terrigenous or volcanic detrital source and therefore is unrelated to water-column
413 iron oxyhydroxide deposition.
- 414 • The average $\delta^{65}\text{Cu}$ data of all three of the South African IF (Kuruman, Griquatown, and
415 Hotazel) are very close to 0 ‰ and are also essentially invariant within analytical error.

416 The average $\delta^{65}\text{Cu}$ values are thus independent of the relative age relationships of the
417 three IF, pointing to no obvious oceanic reservoir effects related to Cu isotope
418 fractionation through time.

- 419 • The $\delta^{65}\text{Cu}$ values of the South African IF are independent of first-order mineralogical
420 variations from oxide- to carbonate-dominated assemblages (Kuruman-Griquatown IF).
421 They are also independent of high bulk-rock Mn abundances and Mn/Fe ratios which
422 characterise particularly the youngest Hotazel IF.
- 423 • Different associations between Cu and detritally-derived transition metals for the three
424 South African IF and the Joffre IF of Australia, and correspondingly slight isotopic
425 differences in average Cu isotope compositions, can most easily be interpreted as
426 reflecting different sources of Cu-bearing particulates carrying a largely homogenous
427 isotopic fingerprint in each case.

428 In view of our results and interpretations, we conclude that Cu and its stable isotope
429 composition in IF are unsuitable records to reconstruct trends in redox evolution of the
430 Archean-Proterozoic oceans and atmosphere, particularly with respect to the GOE. Iron
431 formations are demonstrably poor reservoirs of primary oceanic Cu by comparison to Fe or
432 Mn. They also record no apparent Cu isotope fractionation effects that could be linked to
433 primary deposition of Fe or Mn oxyhydroxides; instead, they reflect principally different
434 provenance controls in the minor Cu-bearing particulate fraction of the primary sediments,
435 likely derived from fine volcanic ash, probably of arc origin. The lack of any clear association
436 between Cu and primary Fe and Mn oxyhydroxides may also lend support to recent studies
437 suggesting that primary Fe (and Mn) precipitation in IF did not necessarily take place in the
438 form of high-valence oxides and hydroxides, but chiefly in reduced mineral species such as
439 greenalite (Johnson et al., 2018).

440 We consider it possible that other trace transition metals in IF are likely to suffer from exactly
441 the same limitations that apply to Cu, especially when they are characterised by very low bulk-
442 rock concentrations and erratic speciation behavior. We therefore propose that rigorous
443 understanding of the trace metal speciation in IF is an imperative for the robust utility of
444 corresponding bulk-rock concentration data and/or isotope ratios in paleoenvironmental
445 studies.

446

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453

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578

579 **Figure captions**

580 Figure 1. Boxplots of (a) Mn/Fe x 10², (b) Cu/Fe x 10⁶, and (c) δ⁶⁵Cu for each of the four IF of
581 this study (Joffre, Kuruman, Griquatown, and Hotazel). The pink line in (b) represents the
582 Cu/Fe ratio assumed in the oceanic Cu model of Chi Fru et al. (2016). Included for comparison
583 in (c) are the δ⁶⁵Cu data of pre- and post-GOE black shales from Chi Fru et al. (2016). These
584 boxplots represent the entire data range obtained for each IF, with the interquartile range

585 (between the 25th and 75th percentile) of the data defining the coloured areas, the lines
586 representing the corresponding median values, and the small black dots being outliers.

587 Figure 2. Correlation plots between Cu and trace metal concentrations of (a) Cr, (b) Ni, and
588 (c) V in the Transvaal IF; and (d) Ti in the Joffre IF. Joffre IF data include those from Chi Fru et
589 al. (2016).

590 Figure 3. Correlation plot between Cu and Fe concentrations in the Transvaal and Joffre IF.

591 Figure 4. Spidergram of average trace metal concentrations normalised relative to continental
592 crust (Rudnick and Gao, 2005) for all four IF of this study (Hotazel, Griquatown, Kuruman, and
593 Joffre). Included for comparison are compositional data for modern seawater (Millero, 2005),
594 manganese nodules (Calvert and Price, 1977; Piper and Williamson, 1977), and hydrothermal
595 fluids (Seward et al., 2014; Von Damm, 1990).

596 Figure 5. Color-coded Cu/Ti ratios of all IF samples (small circles) and corresponding averages
597 (large squares) obtained in this study, superimposed on the fields for IF (red), shale (green),
598 and continental crust (white line), as a function of geological time (modified after Chi Fru et
599 al. (2016)).

600 Figure 6. Fraction of Cu(I) chloride complexes at different chloride concentrations. The blue
601 vertical line represents the assumed concentration of chloride ions in the pre-GOE ocean.
602 Calculations done using the stability constant of Meng and Bard (2015).

603 Figure 7. Distribution of selected major elements and trace metals on a ternary diagram
604 depicting oxide, carbonate, and silicate fractions of IF from South Africa (adapted from Oonk
605 et al. (2017)).

606 Figure 8. Spidergram of the logarithm of average transition metal concentrations and ranges
607 (in grey), normalized to arc tholeiite (Lodders and Fegley, 1998) and assuming 0.7% TiO₂, for
608 all four IF of this study (Hotazel, Griquatown, Kuruman, and Joffre). Included for comparison
609 are corresponding compositional data and ranges (in purple) for stilpomelane lutite layers
610 from the Griquatown IF (Oonk et al., 2017).

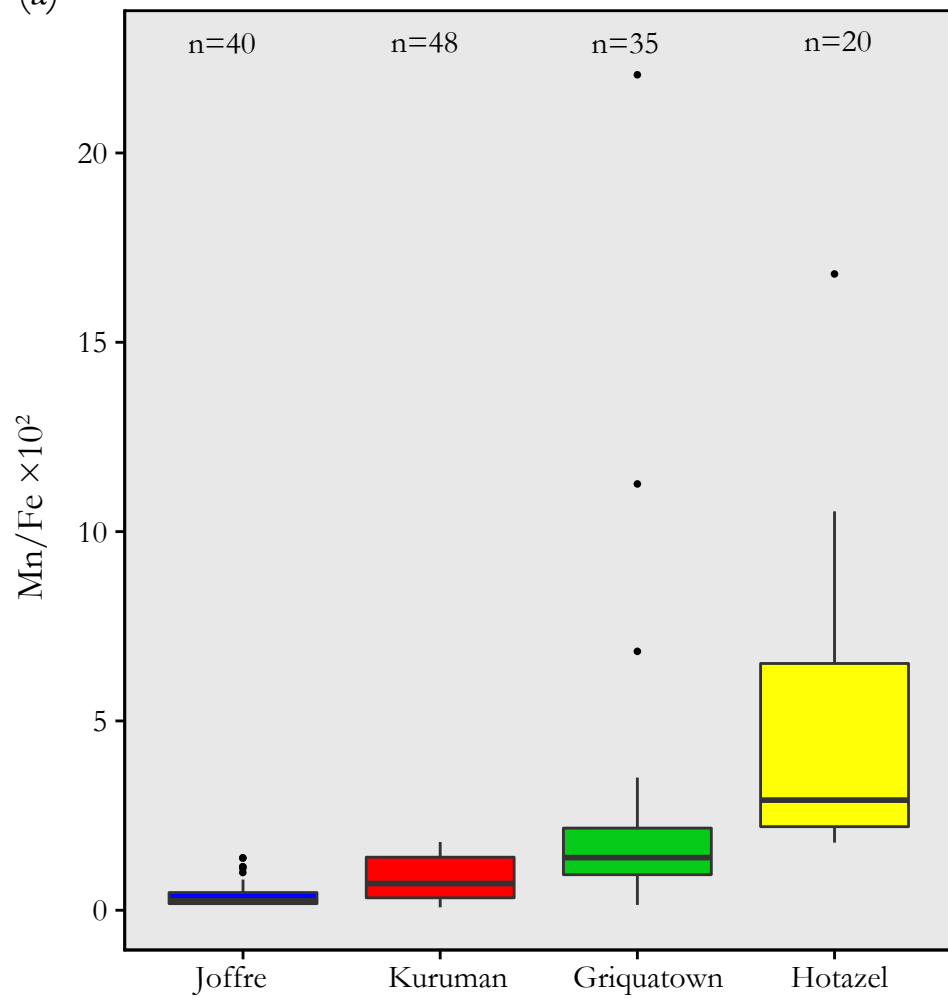
611

612 **Table captions**

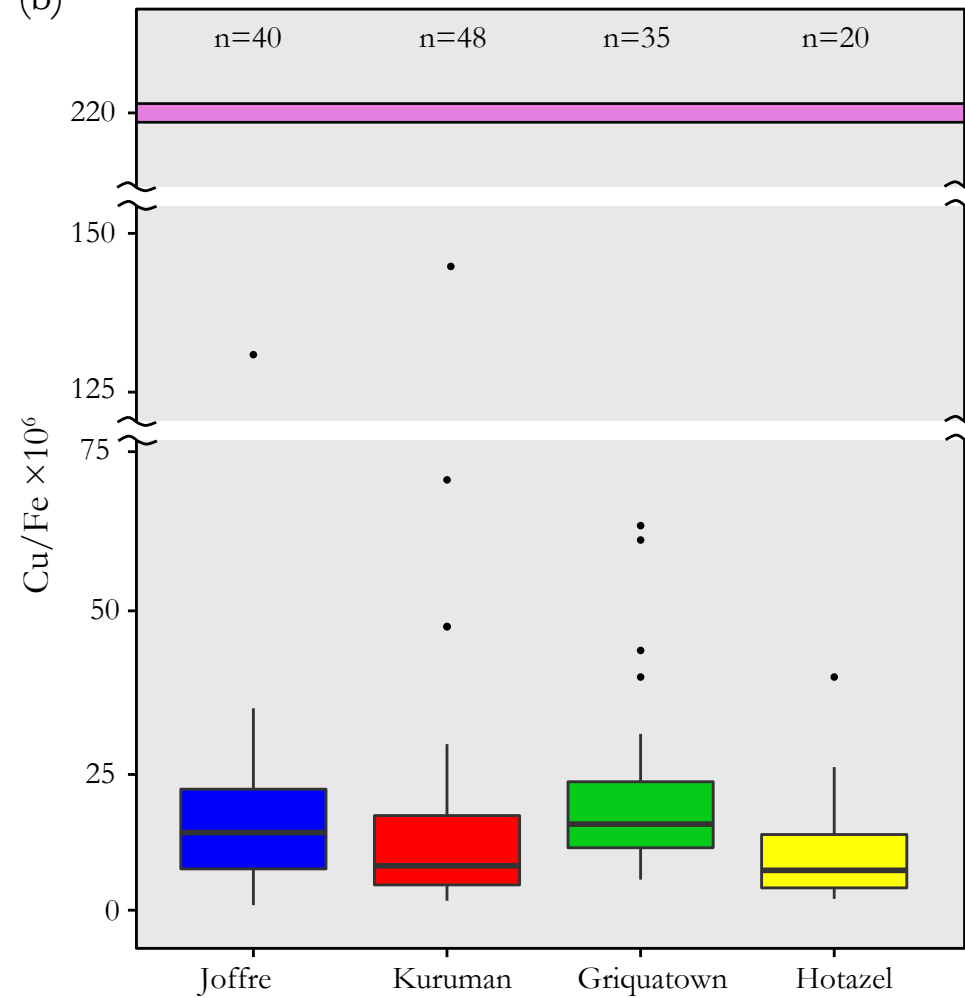
613 Table 1. Correlation coefficients between Cu and Cr, Ni, and V concentrations of the Transvaal
614 IF.

615

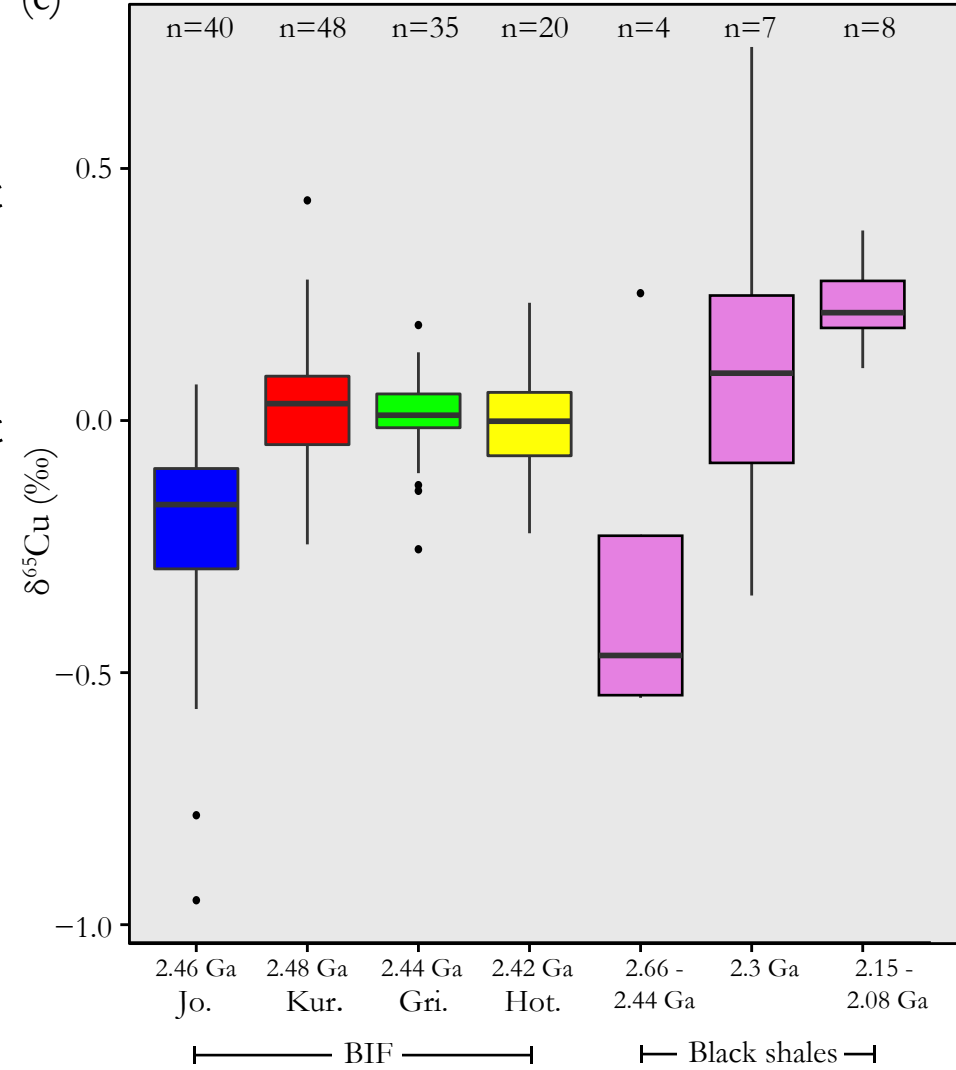
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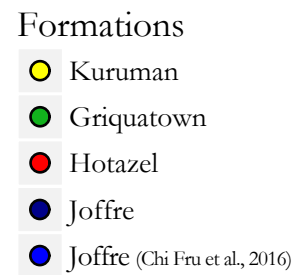
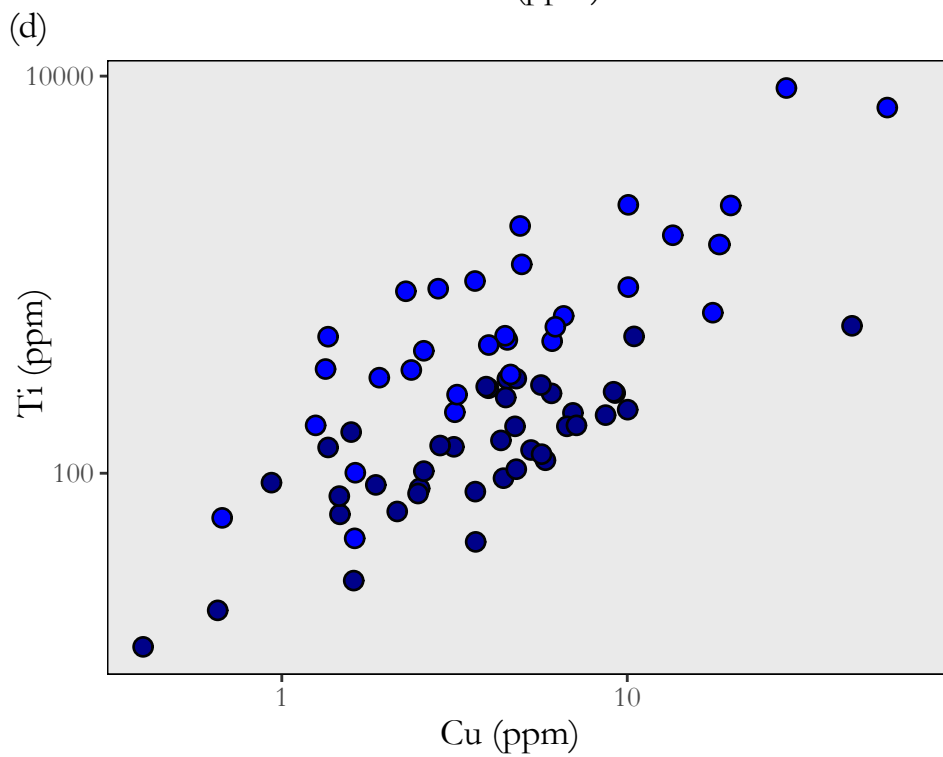
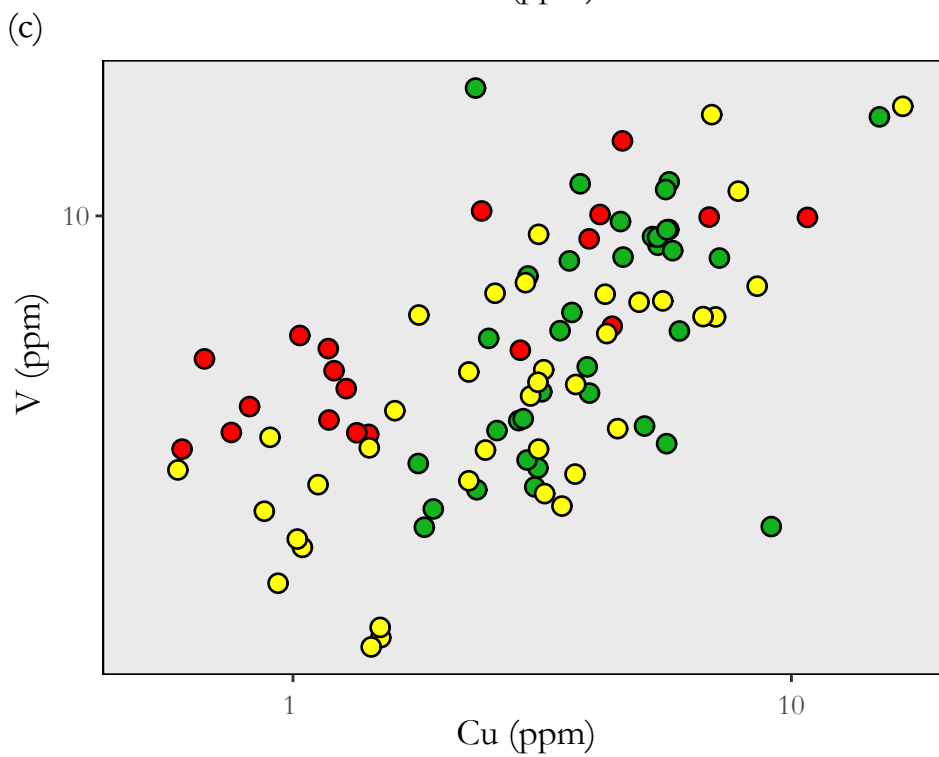
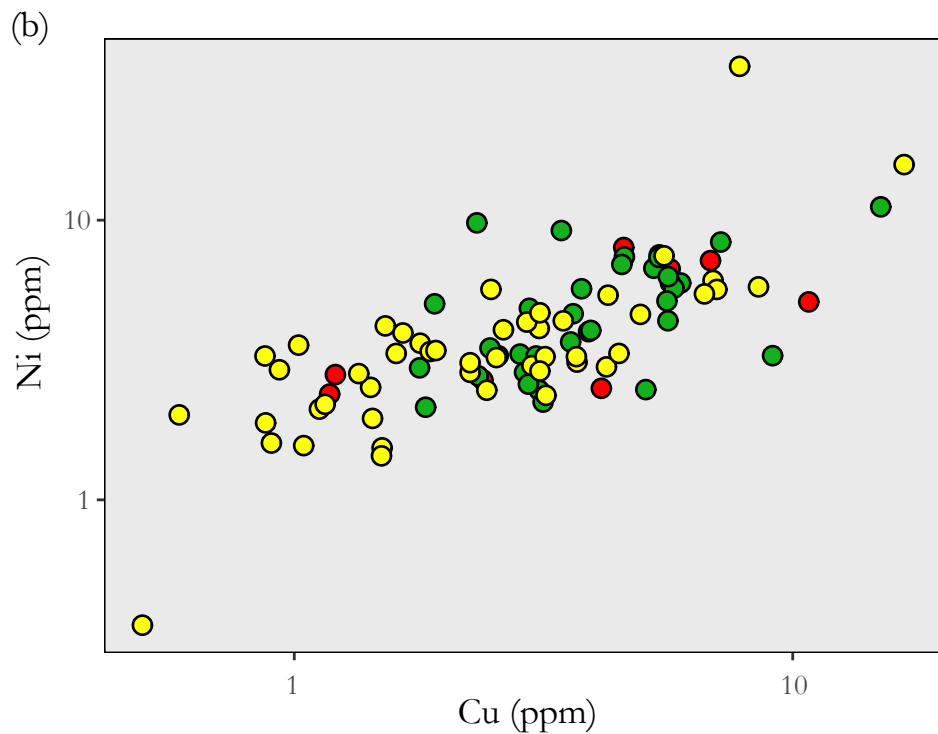
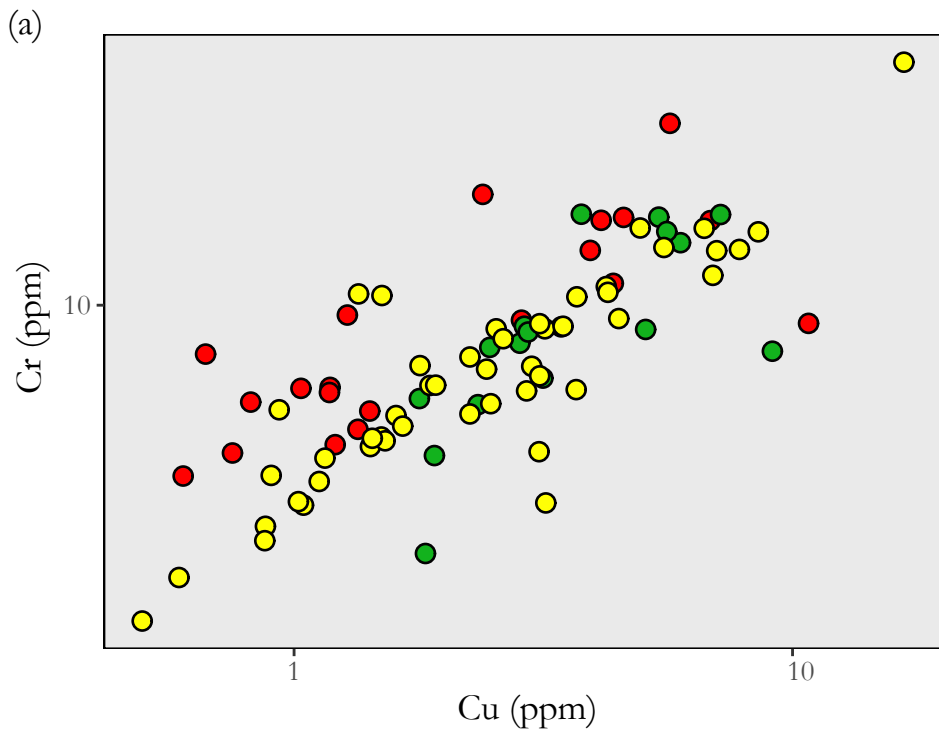


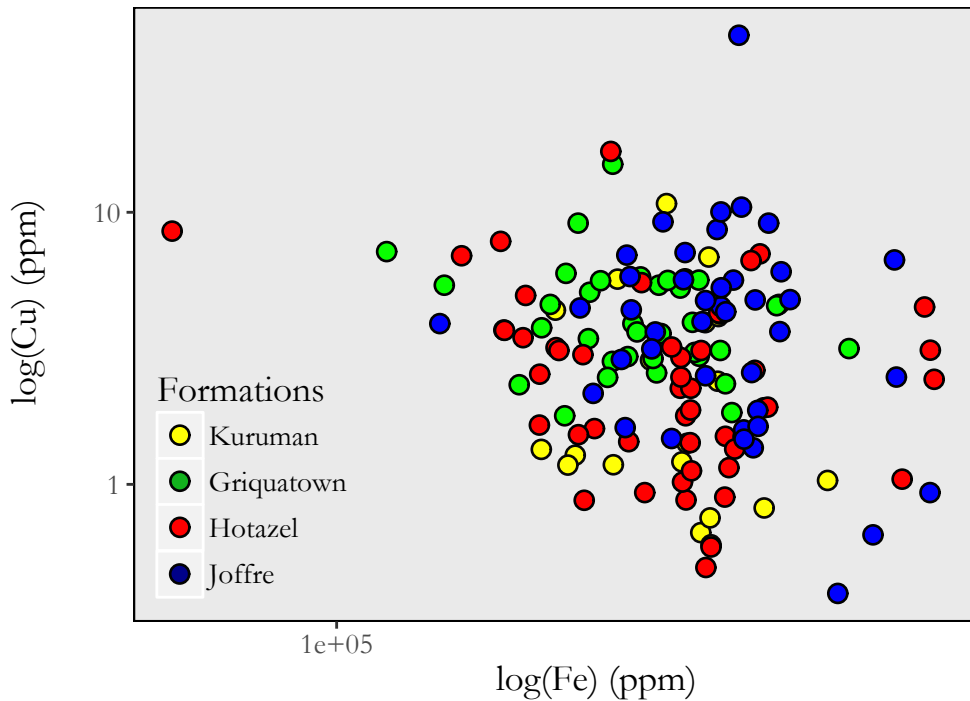
(b)



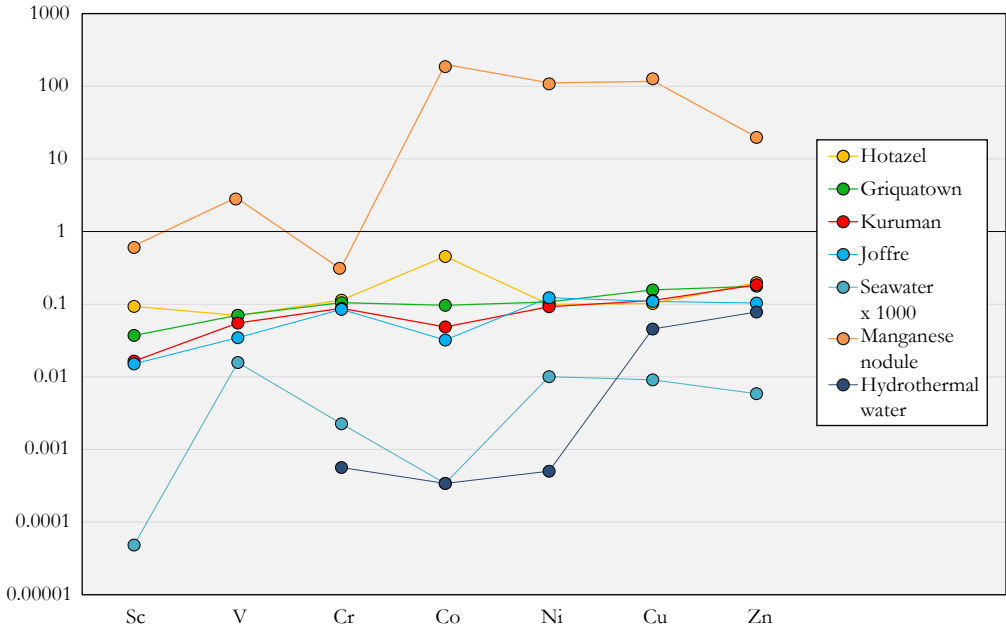
(c)

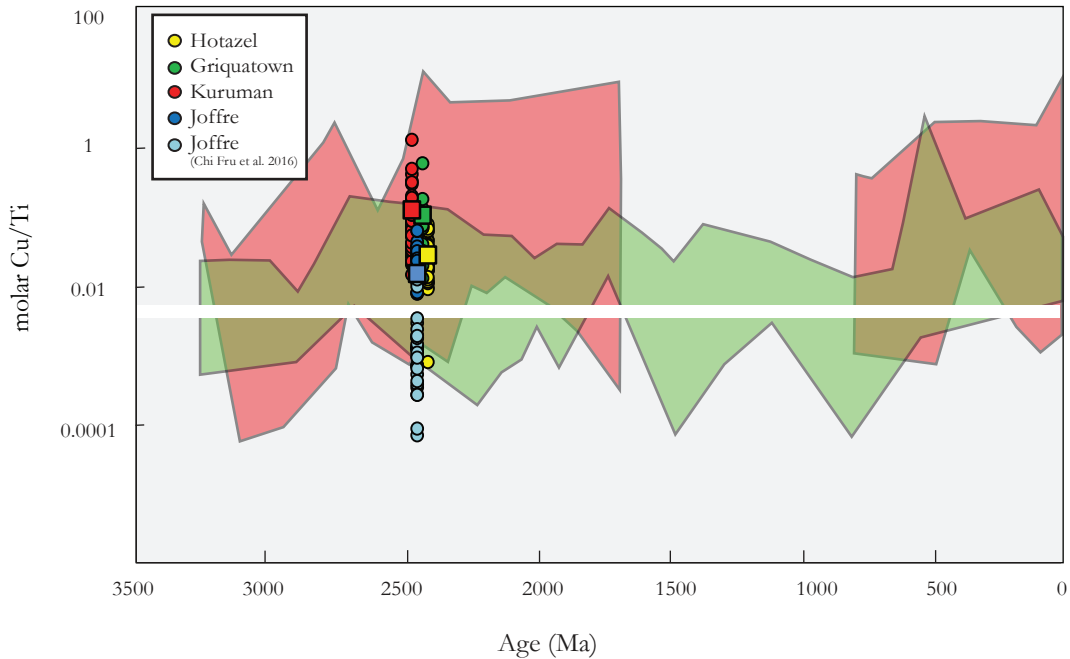


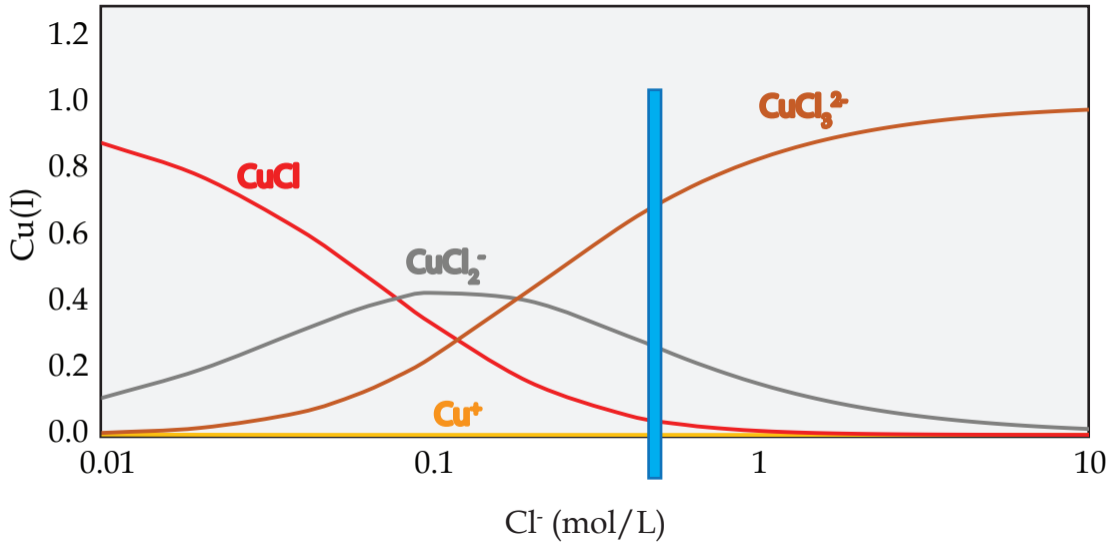


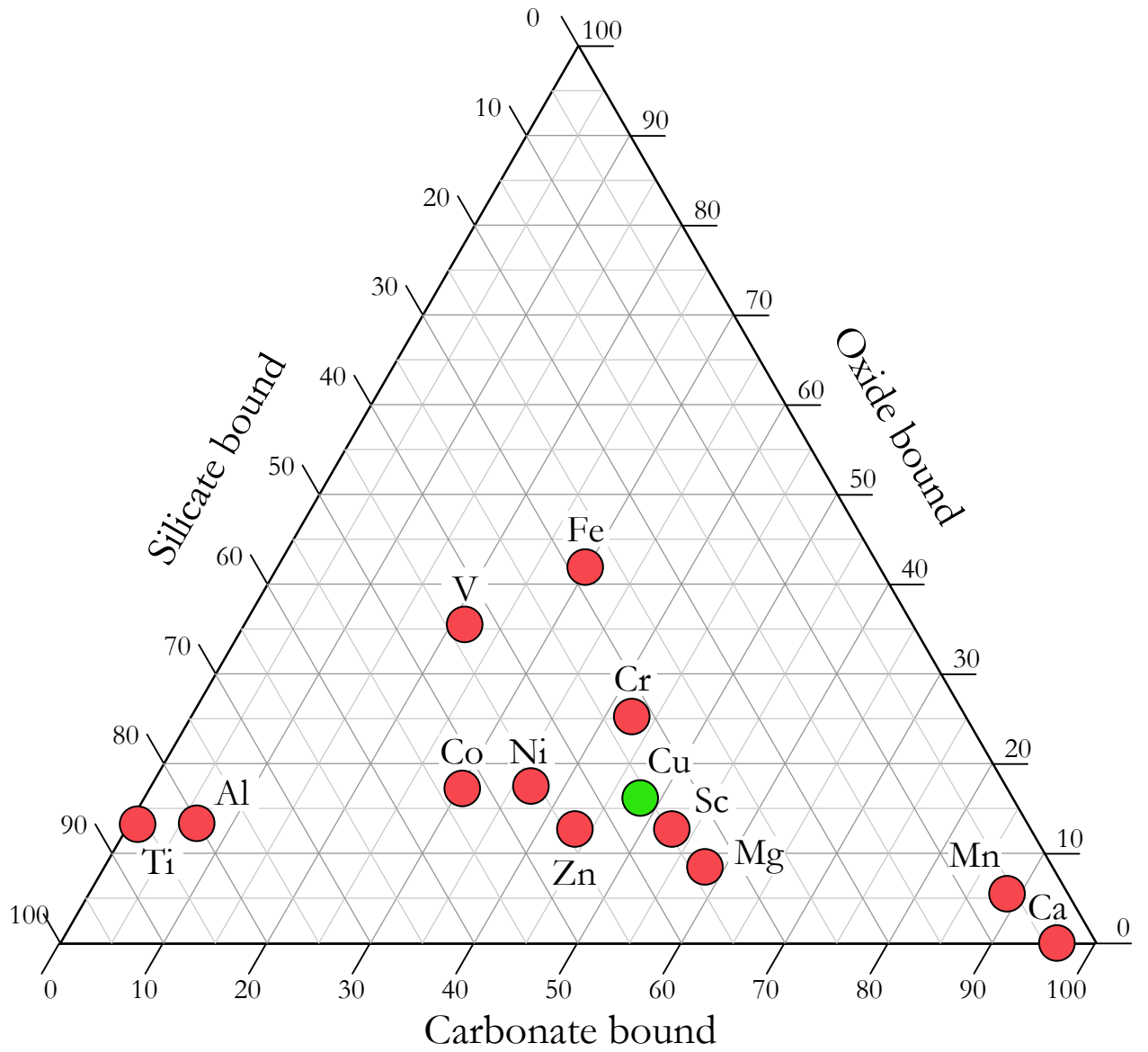


Mean concentration (ppm)
normalized to continental crust

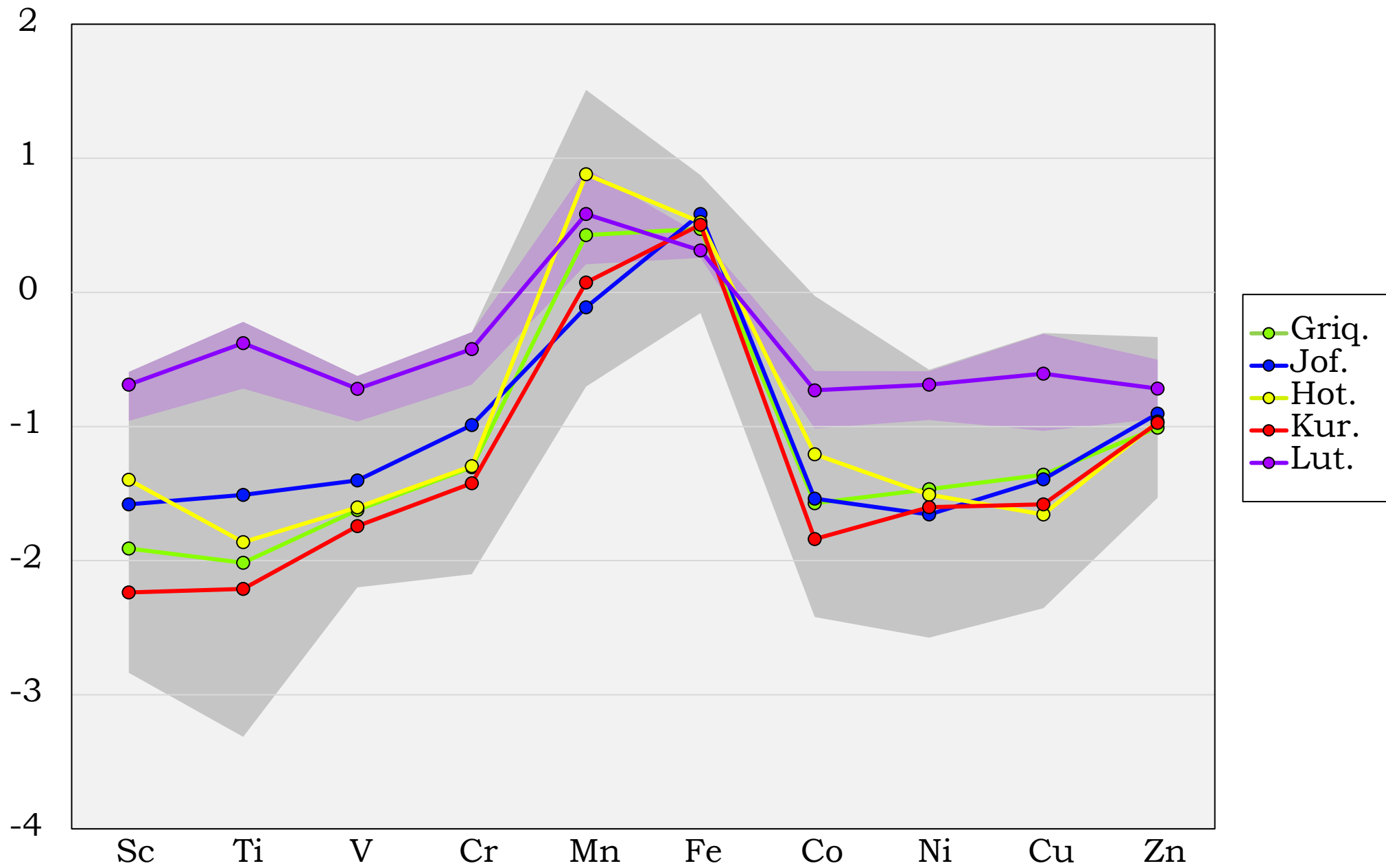








log of trace metal abundances in IF
normalized to arc tholeiite



	Cu-Cr	Cu-Ni	Cu-V
Hotazel	0.54	0.56	0.71
Griquatown	0.58	0.54	0.44
Kuruman	0.93	0.60	0.80