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REVISION 1

The composition of mackinawite

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ABSTRACT

The composition of a mineral is a defining characteristic. The various compositions listed for mackinawite in current mineralogical databases and reference books, such as $\text{Fe}(\text{Ni})\text{S}$ and Fe_{1+x}S , are both wrong and misleading. Statistical analyses of over 100 mackinawite analyses reported over the last 50 years show a mean composition of $\text{Me}_{1.0}\text{S}$ where $\text{Me} = \text{Fe} + \text{Co} + \text{Ni} + \text{Cu}$. Mackinawite is stoichiometric FeS . As with many sulfide minerals, Ni-, Co- and, possibly, Cu – rich varieties occur in addition to the simple iron monosulfide. These varieties are best referred to as nickelian mackinawite, cobaltian mackinawite and cupriferous mackinawite. The results confirm that these metals substitute for Fe in the mackinawite structure rather than being contained in the interstices between the Fe-S layers. Most compositional data on mackinawites derives from electron probe microanalyses of small grains in magmatic/hydrothermal associations. The result means that there is no dichotomy between the composition of ambient temperature synthetic mackinawite (which is supposed to be equivalent to sedimentary mackinawite) and mackinawites from higher temperature associations. The correct representation of the composition of mackinawite has implications for a wide swathe of fundamental science, including the origin of life, the genesis of magmatic ore deposits, the provenance of meteorites as well as industrial applications such as water treatment and steel corrosion. The stoichiometric formulation permits the mackinawite formula to be balanced electronically using conventional Fe and S ionic species. It also enables simple balanced chemical equations involving mackinawite.

Keywords: mackinawite, iron sulfide, composition, formula, mineralogy

INTRODUCTION

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A cogent argument can be made that mackinawite, the tetragonal iron monosulfide, was the last widespread simple mineral to be discovered on Earth. It has been identified as a major component of the global sulfur cycle (e.g. Rickard, 2012) and intimately associated with microorganisms (e.g. Posfai et al., 1998), and has been widely implicated as a necessary mineral for the origin of life (Russell and Ponce, 2020). The mineral has been discovered in soils (e.g. Burton et al., 2006), sediments (Berner, 1962), magmatic (Evans et al., 1964) and hydrothermal (e.g. Krupp, 1994) ore deposits, serpentinised ultrabasic rocks (e.g. Ashley, 1975), meteorites (Ramdohr, 1973) and even diamonds (Agrosi et al., 2017). Synthetic analogs have proven to be important corrosion products in the petroleum industry (e.g. Meyer et al., 1958), wastewater treatment (e.g. Yang et al., 2017), and the Girdler-sulfide process for making heavy water in the nuclear industry (Shoesmith et al., 1980). It is widely believed to play a key role in the environment, controlling deleterious minor and trace elements concentrations in natural waters (e.g. Rickard and Morse, 2005).

Its composition is, however, often presented as (Fe,Ni)S or Fe_{1+x}S or some variant of these formulations, which is wrong. These formulations may derive from the fact that the type mackinawite from the Mackinaw Mine WA was a nickelian mackinawite with an apparent composition $\text{Fe}_{0.96}\text{Ni}_{0.04}\text{S}$ (Evans et al., 1964). The uncertainties in the analyses were considerable: ± 8 relative wt% for Fe, ± 16 relative wt% for Ni and ± 12 relative wt% for S, resulting in a total analytic uncertainty of 9.5 wt%. It is apparent that the totals were corrected to produce a stoichiometric MeS composition (where Me = Fe + Ni + Co + Cu). By contrast, the co-discoverers of the mineral in Outokumpu, Finland, (Kuovo et al., 1963) tried to separate

69 sufficient quantities mechanically for wet chemical analyses. Unfortunately, this was not entirely
70 successful and the result was subject to errors due to inclusions of silicates and other metal
71 sulfides in the separates. Even so, it appeared that the Outokumpu mackinawites were also
72 nickelian with trace Co giving compositions like $\text{Fe}_{0.92}\text{Ni}_{0.13}\text{Co}_{0.01}\text{S}$ resulting in a non-
73 stoichiometric formula $\text{Me}_{1.06}\text{S}$. In both cases, these early workers assumed that the S
74 concentration was equivalent to 1.00 apfu (atoms per formula unit).

75 Although definitions of what constitutes a mineral are legion, most would agree that a
76 mineral is naturally occurring material with a defined crystal structure and a particular chemical
77 composition. The problem with current definitions of mackinawite is that although the crystal
78 structure is defined, its particular chemical composition is not. This means that, at least in detail,
79 it is uncertain what is meant – at least chemically- when someone refers to mackinawite. The
80 present report aims to rectify this lacuna and define the composition of mackinawite.

81 **[Table 1 here]**

82 Table 1 gives examples of mackinawite compositions as defined by some current widespread
83 – and otherwise authoritative – mineralogical databases. The only one which gives some clue to
84 the actual compositions in the listing in the *Handbook of Mineralogy* published by the *American*
85 *Mineralogical Society*, which at least gives examples of Ni-, Co- and Cu- bearing mackinawites
86 even though the title gives a composition $(\text{Fe,Ni})_{1+x}\text{S}$ ($x = 0$ to 0.11), which seems odd. Fe_{1+x}S
87 may have been a nod to the other popular and equally misleading formula for mackinawite.

88 Kuovo et al. (1963) and Clark (1966) recommended that the composition of mackinawite
89 should be presented as Me_{1+x}S . However, Babkine and Conqu  r   (1968 p.270) concluded that:

90 *L'  tablissement d'une formule telle que $M_{1+x}\text{S}$ ($x=0,05$    $0,07$) para  t pr  matur   compte*
91 *tenu du peu de pr  cision des donn  es analytiques. Il serait alors pr  f  rable de conserver pour la*

92 *mackinawite la formule stoïchiométrique MS.*¹

93 Unfortunately, this caveat was generally missed by later workers. Fe_{1+x}S became popular
94 since it appeared to distinguish mackinawite chemically from other iron monosulfide minerals
95 such as the pyrrhotites (Fe_{1-x}S) and troilite (FeS).

96 Berner (1962) originally described a tetragonal FeS from an iron trash dump in the Mystic
97 River, MA. This was not accepted as a mineral since the IMAA did not deem it a natural
98 occurrence. Berner reported that analyses of this material gave an average composition of
99 $\text{Fe}_{1.05}\text{S}$. However, he concluded – and this might have been again subsequently missed by later
100 researchers – that the composition of the phase “was essentially FeS ”. Berner noted that the
101 phase was identical to the synthetic FeS commonly produced in the laboratory through the
102 reaction between aqueous sulfide and iron salts at ambient temperatures. Subsequent wet
103 chemical analyses of bulk synthetic mackinawites also gave varying results (Table 2).

104 **[Table 2 here]**

105 Ward (1970), reviewing the literature up until that date, reported that mackinawite analyses
106 varied between $\text{Me}_{0.994}\text{S}$ and $\text{Me}_{1.023}\text{S}$ and concluded that mackinawite was a pure iron
107 monosulfide with composition of $\text{Fe}_{1.06}\text{S}$, although this appears to be outwith the range of $\text{Me}:\text{S}$
108 ratios he reported. The problem was solved by Rickard et al. (2006) who showed that errors in
109 the analytic protocols led to the apparent non-stoichiometry of synthetic mackinawite. Pure
110 synthetic mackinawite is stoichiometric $\text{Fe}_{1.00}\text{S}$. This is consistent with the results from a detailed
111 Rietveld investigation of the structure of synthetic crystalline mackinawite by Lennie et al.
112 (1995) which showed that any vacancy occupancy or surplus Fe occupancy was below the
113 detection limit of the method and concluded that the Fe/S ratio of mackinawite closely

¹ *The establishment of a formula such as $M_{1+x}\text{S}$ ($x=0.05$ to 0.07) seems premature given the low precision of the analytical data. It would be preferable to keep the MS stoichiometric formula for mackinawite.*

114 approaches unity.

115 However, the problem of the reported compositions of natural mackinawites remain. These
116 compositions are almost exclusively for mackinawites occurring in higher temperature sulfide
117 mineral associations. The mackinawites in these occurrences are fine grained and the
118 mackinawites occur mainly as apparent exsolution or hydrothermal alteration products in
119 chalcopyrite, pyrrhotite and pentlandite. Because of their microscopic nature, their compositions
120 are almost entirely determined by Electron Probe Microanalysis (EPMA). Indeed, the
121 identification of mackinawite and its distinction from valleriite (a complex mineral consisting of
122 alternating Mg(OH)₂ - and (Cu,Fe)₂S- dominated layers) was one of the great triumphs of the
123 early deployment of EPMA in mineralogy (Evans et al., 1964).

124 I refer to these mackinawites as magmatic/hydrothermal mackinawites since they occur in
125 high temperature ores associated, either directly or indirectly, with magmatism. These
126 mackinawites include the type minerals and are the main source of the present misleading
127 compositional information in the literature.

128 *Mindat* (Anonymous, 2022b) lists over 500 localities worldwide where mackinawite has
129 been recorded including 48 stony meteorites listed by Ramdohr (1973) or about a third of the
130 chondrites he examined. However, the Ramdohr's volume was submitted to the publishers in
131 some years before 1973 and the content was essentially pre-EPMA but post-Evans et al. (1964),
132 which is cited and originally distinguished mackinawite from valleriite. Ramdohr stated that it
133 was virtually impossible to distinguish mackinawite from valleriite by optical properties alone
134 and, mainly on the basis of Evans et al's report, appears to have renamed all of his earlier
135 meteoritic valleriites, mackinawite.

136 The purpose of this paper is to present a statistical re-evaluation of published chemical

137 analyses of natural mackinawites worldwide with a view to establishing the chemical
138 composition of this mineral.

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METHODS

142 The analytic method used for mackinawite analysis is Electron Probe Microanalysis
143 (EPMA). Since the early years of mackinawite analyses, EPMA has undergone major
144 developments, including the introduction of field emission electron guns with sub-micron beams.
145 However, the methods used for the analyses of the magmatic/hydrothermal mackinawites appear
146 to have been carried out universally on older EPMA systems (Table 3). These had tungsten
147 filaments with spot diameters of 2 μm – 10 μm depending on the material being analysed. The
148 electron beam also excited a sub-surface volume which may be $\sim 5\mu\text{m}$ in depth and similar in
149 width depending on the element atomic mass. Even a more modern Cameca SX-100 from 2008
150 as used by Baidya et al. (2018) samples volumes typically of 10-30 μm^3 . Mackinawite
151 commonly occurs as inclusion in other sulfides and the EPMA analyses may therefore be
152 affected by the composition of the enclosing mineral (Adams and Bishop, 1986). Mücke (2017)
153 acknowledged this and noted that corrections were made to the analyses to account for this error.
154 Vavtar (1995) and Baidya et al. (2018) noted that mackinawite inclusions in chalcopyrite showed
155 apparent high Cu contents as a result of this effect and these analyses have been excluded from
156 this analysis. The uncertainties in Cu concentrations in these samples are further increased by
157 the secondary fluorescence effects due to the relatively high energy and low attenuation of
158 $\text{CuK}\alpha$. Jennings et al. (2019), for example, showed that high Cu concentrations (0.5-1.2 wt%
159 Cu) could be generated in Cu-free materials by secondary fluorescence from the Cu- sample
160 holder.

161 **[Table 3 here]**

162 Stoichiometric FeS contains 63.525 wt% Fe and 36.475 wt% S, assuming an average S
163 isotope ratio. An Fe-deficient mackinawite with a composition $\text{Fe}_{0.9}\text{S}$ contains 61.05 wt% Fe and
164 38.95 wt% S. Each 0.1apfu of Fe deficiency involves an S increase of 2.475 wt%. Estimates of
165 the analytic uncertainties are usually around 0.1 on the S/Fe ratio even after multiple
166 measurements on relatively pure synthetic sulfide crystals (e.g. Voigt et al., 2019). The result is
167 that the reported non-stoichiometry of magmatic/hydrothermal mackinawites is at or beyond the
168 limits of accuracy of the EPMA.

169 The situation is complicated because the result is usually presented by the ratio of the total of
170 divalent metals including Fe, Cu, Co, and Ni versus S. This is generally an apparent composition
171 since the actual analyses are often presented as ratios in the form of MeS, where Me includes Fe,
172 Cu, Co, Cr and Ni; the totals are not always accessible. In Table 1, the American Mineralogical
173 Society notes that the metal: sulfur (Me:S) ratios in the three examples they list vary between
174 1.11 and 1.02. This suggests that the Me:S ratios of these mackinawites cannot be confidently
175 distinguished from unity. It may well be that increased precision in mass discrimination in
176 inductively coupled plasma mass spectrometry may lead to better probes of
177 magmatic/hydrothermal mackinawite.

178 The parameters for including analyses in this study were that analytic totals should be
179 available and some reports were therefore not included. (e.g. Clark and Clark, 1968). Some
180 examples were omitted because S analyses were not reported (e.g. Vaughan, 1969). Many of the
181 reports were published in the last century before computerized manuscript preparation, electronic
182 submission and publication were universally available. Reported analyses in which transcription
183 errors occurred (e.g. errors in analytical totals, transposition of numbers) were not included in

184 this study. There is no *a priori* reason that separate mackinawite grains from the same deposit
185 should show similar compositions and the analyses are for individual grains, with no averaging
186 of the composition of a group of analyses. An exception might be the cohesive group of
187 mackinawite analyses reported by Spiridinov et al. (2008) from late veins in the Noril'sk ore
188 field. The 8 analyses, which are included in the listing in Table A1, show an average
189 composition (\bar{x}) and standard deviation (σ) of $\text{Fe}_{1.05(0.01)}\text{Ni}_{0.07(0.01)}\text{S}$, but these are treated as
190 separate analyses in this report.

191 There are very few repeat analyses on the same mackinawite grain because of their small
192 sizes although analytic scans across grains were reported by Zôka et al. (1973). The intra-grain
193 variations in compositional analyses they reported were mainly due to local variations in grain
194 thicknesses and near-edge effects: there is no evidence for intra-grain variations in mackinawite
195 compositions. Likewise, Clark (1970) reported occasional compositional zonation in larger
196 mackinawite crystals from Kilembe, Uganda (as preliminary observations with no listed
197 analyses) although most of the mackinawites he analyzed were homogeneous. Clark (1969) also
198 reported zonation in Cr- mackinawites he described from the Abessedo deposit in Portugal but,
199 as noted below, this was a preliminary report which has not been confirmed. There are,
200 however, sufficient indications to suggest that zoned mackinawite crystals occur. Certainly,
201 mackinawite analyses with field emission electron guns or atom probe tomography providing
202 nanometer spot diameters would provide more accurate information about the composition – and
203 the variations in composition - in these tiny mackinawite grains.

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RESULTS

Mackinawite compositions

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210 The results are detailed in the Tables A1 - A3 and Figure A1 in the supplementary files
211 attached to this paper. The compositions of 103 mackinawites reported in the literature are listed
212 in Table A1. The occurrences listed in Table A1 refer almost exclusively to mackinawites
213 associated with magmatic or hydrothermal ore assemblages. There are very few published
214 analyses of mackinawites in sediments. Bonev et al. (1989) listed two microprobe analyses of
215 mackinawite from concretions from Black Sea sediments. Unfortunately, no totals were listed
216 but a small S-deficit in the element ratios was reported (0.05 apfu). Morin et al. (2016) reported
217 that mackinawite nodules from the river Seine, France, have compositions approaching FeS as
218 measured by energy dispersive methods. Berner (1962) originally noted that it proved impossible
219 to separate mackinawite from sediments and this has remained the situation to date. Indeed, it
220 appears that the assumption that mackinawite is widely present in sediments may be mistaken
221 (cf. Rickard and Morse, 2005).

222 It is possible – and indeed probable- that the mackinawites associated with the high
223 temperature monosulfide solid solution or intermediate solid solution, which appear as
224 anomalous pseudo-exsolution features in chalcopyrite, pentlandite and pyrrhotite are the result of
225 lower temperature reactions of late stage convecting sulfidic solutions with the original
226 exsolution products. There is, therefore, a continuum between the magmatic mackinawites and
227 the hydrothermal mackinawites, typically exemplified by the association widely observed in the
228 Kuroko ores of Japan. At the extreme lower end of this continuum are the mackinawites in the
229 remarkable vein ores of the Moschellandsberg Hg deposits described by Krupp (1994). The
230 mackinawites occurring in this association occur as distinct euhedral crystals up to 100 μm in
231 size. These formed during late-stage activity in the hydrothermal system when the temperature
232 reached as low as 50°C. The average composition of the 8 pure iron monosulfides is $\text{Fe}_{1.00}\text{S}$ with

233 $\sigma = 0.01$ apfu. Two samples had trace Ni (<0.03 apfu) but the Me:S ratio is still unity.

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235 **Statistical analysis of the results.**

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237 Table A1 lists 103 published mackinawite analyses which meet the analytic criteria
238 mentioned above. As pointed out by Limpert et al. (2001) and Rickard (2019) most natural
239 distributions follow log-normal distributions. This results from the multiplicative hypothesis of
240 elementary errors which states that if a random variation is the product of several random effects,
241 a log-normal distribution must result (Heath, 1967). The average of a log-normal distribution is
242 the geometric mean (\bar{x}^*). The geometric mean composition of the 103 mackinawite analyses
243 listed in Table A1 is $\text{Me}_{1.0}\text{S}$. This is similar to the arithmetic mean (\bar{x}) and the total data can
244 conveniently be treated with the more familiar additive rather than multiplicative statistics.

245 The approximation to the normal distribution also suggests that the variables are random and
246 not systematic. One area of potential systematic errors in these EPMA analyses is the
247 uncertainties in the analyses of the lightest constituent, sulfur. The problem here, especially with
248 early EPMA analyses, is that S is a relatively light element and that the standard often used was
249 pyrite, which has both considerable variation from mackinawite and also uncertainties in its
250 composition (cf. Rickard, 2021). In order to test this hypothesis, all total analytic errors are
251 loaded on to the S analyses in Table A2 and the statistical parameters for the corrected data are
252 compared with the original data in Table 4.

253 **[Table 4 here]**

254 The results show that the variation in the individual metal concentrations and therefore
255 mackinawite formulae, is small but that the Me:S ratio condenses to 1.00 for both the arithmetic

256 and geometric means. The 1σ error increases from 0.05 apfu to 0.06 apfu. This suggests that
257 there is a systematic error in the data but that its effect is small. Dispensing the total error across
258 all the analyses, and not just S, does not, of course, change the results measurably.

259 The uncertainties in the EPMA analyses are not presented in the papers which reported the
260 mackinawite analyses listed in Table A1. The errors in the analytic totals are ± 2 wt% for 2σ and
261 this is taken as a minimum measure of the uncertainties in the analytic data. Uncertainties
262 commonly used in EPMA analyses are ± 5 wt% and this appears to derive from Heinrich and
263 Yakowitz (1975). Applying this error to the minor element analyses gives an uncertainty of
264 about ± 0.1 apfu for each element.

265 **[Table 5 here]**

266 The areas where the use of geometric means and standard deviations becomes important is in
267 the minor element analyses. Statistical parameters for the metal analyses in the data listed in
268 Table A1 are summarized in Table 5. The arithmetic average of the reported Cu analyses is 1.00
269 wt% and 1σ is 1.27. However, a large number of samples (59 of the listed 103) have no reported
270 Cu concentrations. This does not equate to zero wt% literally but merely means that the Cu
271 contents of the samples were below the EPMA detection limits. The arithmetic average value (\bar{x})
272 for all the listed mackinawites, including those with Cu concentrations below the detection limit,
273 is 0.45 wt % Cu and the arithmetic standard deviation (σ) is 0.98. This means that the range of
274 *ca.* 70% of the Cu values ($\pm 1\sigma$) is -0.53 wt% to 1.43 wt%. The negative value is obviously
275 impossible so the arithmetic average – which assumes a normal distribution - is invalid. The
276 distribution is thus highly skewed and the mean Cu value is better described by the multiplicative
277 or geometric mean. The weakness of the geometric mean is that analytic totals of 0 cannot be
278 included in the analysis. However, there is a work-around that avoids guessing the actual

279 concentration which relates the geometric means and standard deviations to their arithmetic
280 counterparts (Rickard, 2019). This suggests that the geometric mean value (\bar{x}^*) of the Cu
281 analyses is 0.18 wt% and the geometric standard deviation (σ^*) is 3.78. The range of Cu analyses
282 then described by the 95% confidence interval ($\bar{x}^* \pm (\sigma^*)^2$) is 0.01-2.64 wt%. The statistical
283 parameters for the Cu distribution diverge considerably from those for Co and Ni. (Table 5).

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DISCUSSION

287 The results show that mackinawite is $\text{Fe}_{1.0}\text{S}$ and that apparent deviations from this
288 stoichiometry are well within the range of analytic errors of the methods used. Where additional
289 exotic metals, such as Ni, Co and Cu occur, the metal:sulfur ratio (MeS) remains at unity.

290 The mackinawites can be conveniently classified as mackinawite, cobaltian mackinawite,
291 nickelian mackinawite and cupriferous mackinawite dependent on their dominant minor element,
292 which is consistent with other sulfide minerals. In this I use a conventional lower concentration
293 of 0.1wt% (which converts to ~ 0.01 apfu) to distinguish minor from trace elements but insist on
294 no upper limit. All the mackinawites show average stoichiometric $\text{Me}_{1.0}\text{S}$ compositions.

295 **Cobaltian mackinawite**

296 Cobaltian mackinawite is defined as mackinawite where Co is the dominant minor metal and
297 where its concentration is greater than 0.1wt%. Clark (1970) reported 18.5 wt% Co in large
298 mackinawite crystals ($\leq 500\mu\text{m}$) from the Kilembe Cu-Co deposit, Uganda but no further details
299 have been presented. Otherwise the maximum amount of Co in these data is 12.68 wt% (0.19
300 apfu) in a mackinawite from the Shimokama deposit, Japan (Mariko, 1988). This is a Kuroko -
301 style volcanogenic massive sulfide deposit in Hokkaido and is a 13Ma old equivalent of current
302 deep ocean hydrothermal vent deposits. The mackinawite occurs as a herringbone replacement

303 of chalcopyrite with cubanite and pyrrhotite (Bamba and Motoyoshi, 1985). Bamba and
304 Motoyoshi (1985) also listed two EPMA analyses of Co-rich mackinawites from the Shimokama
305 mine but these seem to have been contaminated with Cu from the enclosing chalcopyrite,
306 although one large grain which appears to be about 100 μm long and up to 20 μm wide may be
307 the source of the virtually Cu-free analysis listed in Table A1.

308 **Nickelian mackinawite.**

309 Nickelian mackinawite is defined as mackinawite where Ni is the dominant minor metal and
310 where its concentration is greater than 0.1wt%. As long ago as 1969, Ni-rich mackinawites were
311 reported. For example, Vaughan (1969) reported 18.7 wt% Ni in a mackinawite from
312 Vlakfontein, RSA. Unfortunately, there are no S analyses listed and the totals are also missing.
313 Papunen (1970) reported that mackinawite was locally the main Ni-bearing mineral in the Hitura
314 Ni deposit, Finland. These early reports may have helped establish the mistaken view that
315 mackinawite was an iron nickel sulfide. The maximum amount of Ni in nickelian mackinawite in
316 Table A1 is 22.7 wt% (Lorand, 1989).

317 **Cupriferous mackinawite**

318 Cupriferous mackinawite is defined as mackinawite where Cu is the dominant minor metal
319 and where its concentration is greater than 0.1wt%. The problem here is that cupriferous
320 mackinawites are often reported from mackinawite inclusions within chalcopyrite. As noted
321 above, with the older EPMA's a relatively large volume of the section may have been
322 interrogated by the beam and the analyses may include Cu from the enclosing chalcopyrite. Zôka
323 et al. (1973) specifically addressed this problem and concluded that the EPMA analyses of 5 of
324 their mackinawite samples (including one from the Mackinaw type locality) were unsafe since
325 the reported Cu values were undoubtedly due to excitation of the enclosing chalcopyrite. The

326 highest Cu contents reported for mackinawite are both from Zôka et al's analyses and refer to
327 mackinawites enclosed by chalcopyrite. These two analyses, from the Shimokama (8.80 wt%)
328 and Kawayama (6.80 wt%) mines from the Japanese Kuroko deposits are the only mackinawites
329 listed having $\text{Cu} \geq 0.1$ apfu. Analyses of mackinawites from these deposits by Takeno (1965)
330 and Mariko (1988) did not report similarly high Cu contents. It appears that Cu is not an
331 abundant minor element in mackinawite.

332 **Other minor elements in mackinawite**

333 A large number of other elements have been reported as being associated chemically with
334 mackinawite – or at least with the H_2S produced by acid treatment of sediments which may
335 evidence the presence of iron monosulfides. Widespread experimentation with various forms of
336 nanoparticulate FeS has evidenced that many elements, including deleterious compounds like As
337 for example, can be removed from solution by a variety of processes involving FeS including
338 surface redox reactions (Cr, Se, U), adsorption (Mn, As, U), and coprecipitation (Mn, Co, Ni,
339 Cu, Zn, As, Tc, Cd, Re, Hg, Pb) (see Rickard, 2012 for a review). However, there is little
340 evidence that these elements are significant in mackinawite minerals.

341 One of the most egregious minor elements reported in mackinawite is Cr (Clark, 1969). Here
342 up to 9 wt% Cr was reported in preliminary analyses of apparently compositionally zoned
343 mackinawite grains up to 1-5 μm in diameter in serpentinites from Portugal. The mackinawite
344 grains were analyzed with an early Cameca Microsonde Mark 1 at University College, London
345 University. The analyses have not been confirmed.

346 Small quantities of silver (0.02-0.07 wt %) were reported in 2 mackinawite samples for the
347 Noril'sk ores in parkerite ($\text{Ni}_3\text{Bi}_2\text{S}_2$)-bearing veins by Spiridinov et al. (2008). The mineral
348 association also includes native Ag but the mackinawite seems mostly associated with

349 chalcopyrite and magnetite. High concentrations of Ag (7.1 wt %) were also reported from EDS
350 (energy dispersive) analyses of mackinawite, associated with chalcopyrite and pyrrhotite from
351 the Zona Basal shear zone gold deposit, SE Brasil (Alves et al., 2022) but no other information
352 on the mackinawite composition was recorded.

353 **Substitution versus addition**

354 The electronic consequences of excess metal being included in the mackinawite structure as
355 suggested by the formulation Fe_{1+x}S has been studied theoretically by Brgoch and Miller (2012).
356 However, their model of interstitial metal atoms contrasts with the data of Kwon et al. (2015)
357 which suggests that exotic metal atoms substitute for Fe rather than are added interstitially
358 between the Fe-S sheets. In fact, Brgoch and Miller (2012) only considered reports of
359 mackinawite compositions between $\text{Fe}_{1.00}\text{S}$ and $\text{Fe}_{1.15}\text{S}$ and appear to have ignored reported
360 compositions between $\text{Fe}_{0.9}\text{S}$ and $\text{Fe}_{1.0}\text{S}$. The difference between the two theories is that the idea
361 that exotic metal ions are included between the Fe-S sheets in the mackinawite structure will
362 produce non-stoichiometry so that mackinawite will have a Me_{1+x}S composition. The hypothesis
363 that the exotic metals substitute for Fe in the structure will tend to produce a more stoichiometric
364 MeS composition. Kwon et al. (2015) neatly divided the two hypotheses into two mackinawite
365 formulae:

366 (1) $(\text{Fe}_{1-x}\text{M}_x)\text{S}$ where $\text{M} = \text{Cu} + \text{Co} + \text{Ni}$ substitute for Fe

367 (2) FeM_xS where $\text{M} = \text{Cu} + \text{Co} + \text{Ni}$ are added to mackinawite intercalated between the Fe-
368 S sheets.

369 The data listed in Table A1 have been interrogated statistically and the results are
370 summarized in FIGURE 1 and in Figure A1.

371 **[Figure 1 here]**

372 Obviously, if Co +Ni (+Cu) substitute for Fe in the mackinawite formula there will be a
373 negative correlation between the atoms per formula unit (apfu) for Fe and the apfu for Co +Ni
374 (+Cu) and a plot of these variables will give a slope of -1 and an intersect at the Fe axis of 1.00 if
375 the mackinawite formula is indeed $Me_{1.00}S$. FIGURE 1 shows that this is indeed the case – at
376 least within the uncertainty of the EPMA data (± 5 wt% or ± 0.1 apfu). The results show that the
377 best fit to the data shows a slope of -0.81 and an intercept of 0.84 with a regression coefficient
378 (R^2) of 0.71 which is quite surprising considering the probable uncertainties in the data. Indeed,
379 forcing the regression line through $Fe_{1.00}S$ gives a slope of -0.99 although R^2 is just 0.68. The
380 analysis supports Kwon et al's (2015) conclusion based on molecular modelling, that Co + Ni
381 (+Cu) are substituted for Fe in mackinawite. It also suggests that mackinawite composition is
382 stoichiometric and indistinguishable from $Me_{1.0}S$.

383 The question of whether the Cu analyses presented in the mackinawite analyses are real or a
384 function of contamination of the mackinawite analyses through the EPMA exciting Cu from
385 enclosing chalcopyrite is also examined in FIGURE 1. The regression coefficients and the slopes
386 of the lines forced through $Fe_{1.00}S$ are very similar whether (Co + Ni) or (Co + Ni +Cu) are
387 considered. However, the plot of Cu apfu versus Fe apfu (Figure A1(a)) is a pure scattergram.
388 This suggests that Cu can substitute for Fe in mackinawite but that there is substantial analytical
389 uncertainty in the Cu data, as discussed above. There is, furthermore, no correlation between
390 (Co + Ni) and Cu.

391 The data in Table A3 also show that there is no significant correlation between the Co and
392 Ni contents of mackinawite. However, the plot of Co versus Ni (Fig.A1(d)) suggests a
393 correlation between Co and Ni in cobaltian mackinawites with Co > 0.01 apfu (>6.8 wt%) and
394 Ni. Eighteen of the 103 reported mackinawites are Co-rich and they reveal a regression

395 coefficient for Co versus Ni of 0.87 with a negative slope of the trend line of 3.4. If Co replaced
396 Ni in the mackinawite structure on an atom for atom basis then we might expect a slope
397 approaching -1. The observed correlation between Co and Ni for these Co- rich mackinawites
398 most probably reflects the composition of the solutions in which the mackinawite crystals grew
399 combined with molecular effects of Co and Ni substituting for Fe the mackinawite structure. It
400 might be an interesting area of research. Overall, however, the data suggests that cobaltian and
401 nickelian mackinawites are essentially unrelated species: there are a similar number of nickelian
402 mackinawites with no detectable Co.

403

404

IMPLICATIONS

405

406 The composition of a mineral is a fundamental property and, in the absence of a definitive
407 formulation, mineral identification is impossible. This means that both the reporter of the
408 mineral and the reader of the report will be uncertain about what is actually being described. In
409 the case of mackinawite, the formulation (Fe,Ni)S often seen in origin of life discussions, for
410 example, is not necessarily wrong – since nickelian mackinawites exist – but it does raise
411 questions why this particular variant is chosen and how it forms in competition with other
412 compositional variants. This is especially the case in the absence of any chemical analyses. The
413 processes involved in the formation of mackinawite in magmatic settings will remain unclear in
414 the absence of an appreciation of the intrinsic stoichiometry of the phase. That is that Ni and Co
415 – and possibly Cu – substitute for Fe in the mackinawite structure rather than being intercalated
416 between Fe-S layers.

417 Even simple balanced chemical equations involving mackinawite are likely to be wrong if
418 the composition of mackinawite is assumed to be non-stoichiometric. It is obvious, for

419 example, that the composition Fe_{1+x}S cannot be balanced electronically with normally charged
420 Fe and S ions. By contrast, Fe_{1-x}S , the usual representation of pyrrhotite compositions, is
421 readily electronically balanced with oxidized Fe^{3+} and $\text{S}_n(-\text{II})$ ions. The finding that
422 mackinawite is stoichiometric has considerable implications in thermodynamic modelling of
423 geologic processes involving mackinawite as well as understanding the chemistry of a number
424 of key industrial processes. This has been long realized by the compilers of the thermodynamic
425 datasets used in popular geochemical modelling programs, such as Geochemist's Workbench
426 TM , where the composition of mackinawite is listed in their thermodynamic database as
427 stoichiometric FeS.

428 The result of this study that the composition of mackinawite in higher temperature
429 associations is the same as that reported for synthetic ambient temperature mackinawite – and
430 thus, by extension, to sedimentary mackinawite – resolves an uncomfortable anomaly in the
431 mineralogical and geochemical literature. It is obvious that, a priori, a mineral must have the
432 same composition at low temperatures as at high temperatures – otherwise they are distinct
433 phases. Chemical composition is the more fundamental characteristic of a mineral for, whereas
434 minerals with the same composition and different crystal structures are widespread, minerals
435 with different compositions and the same structure are defined as different species.

436 Mackinawites often contain substantial amounts of Ni and Co and these are better described
437 as nickelian and cobaltian mackinawites depending on their dominant minor element. The
438 amounts of Ni and Co range up to a little over 10 wt% except for one outlier Ni analysis of 22.7
439 wt % (Lorand 1989). The analytic data show that these mackinawites retain their metal: sulfur
440 stoichiometry confirming molecular modelling data which suggests that Ni and Co substitute for
441 Fe in mackinawite rather than being trapped in the interstices between the Fe-S sheets in the

442 mackinawite structure.

443 This result suggests that crystallization of mackinawite is accompanied by the permanent
444 removal of the large variety of exotic ions that have been reported to be absorbed onto
445 mackinawite experimentally and, by inductive reasoning, assumed to be sequestered by
446 mackinawite in natural waters. However, there are little data on the concentration of anions, such
447 as As and Se, in natural mackinawite. Even so, it would be expected that, if such variants were
448 widespread, they would have been detected by the microprobe analyses. The implication is that
449 sequestering of deleterious exotic ions by mackinawite in water treatment systems, for example,
450 does not result in their permanent removal.

451 The reported amounts of Cu in mackinawite during EPMA analyses are often affected by
452 excitation of Cu in enclosing Cu minerals such as chalcopyrite. The amounts of Cu reported
453 ranges up to around 3 wt% with occasional outliers such as the early analysis of 4.70 wt % Cu by
454 Chamberlain and Delabio (1965). Even so, this equates to < 0.1 apfu Cu in the mackinawite
455 formula and has little effect on the mineral's stoichiometry. The question of whether Cu
456 substitutes for Fe in mackinawite cannot be directly resolved by the analytic data collected in this
457 study: the data are subject to substantial potential analytic errors and the amounts of Cu are
458 relatively small and have little effect on the mineral stoichiometry.

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460

461

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612

613

614 **Figure captions**

615

616

617 FIGURE 1.

618 Plots of **(a)** Co+Ni (afpu) versus Fe (afpu) and **(b)** Cu+Ni+Co (afpu) and versus Fe (afpu). The

619 solid lines and their equations and regression coefficients (R^2) are the best fit for the data; the

620 dashed lines and their equations and regression coefficients (R^2) are for a best fit line forced

621 through $Fe_{1.00}S$. Error bars for the data are not shown.

622

623 FIGURE A1.

624 **(a-c)** Plots of Cu, Ni and Co afpu versus Fe afpu for mackinawites listed in Table A3 showing

625 scattergrams. **(d)** Plot of Co versus Ni afpu for mackinawites listed in Supplementary Data 3

626 showing lack of any correlation. **(e)** Scattergram of Cu versus (Co+Ni) afpu for mackinawites

627 listed in Table A3.

628

Tables

TABLE 1. Examples in common current mineralogical reference databases of definitions composition of mackinawite.

Mackinawite	Source	
composition		
$(\text{Fe,Ni})_{1+x}\text{S}$	<i>Wikipedia</i>	Anonymous (2022a)
$(\text{Fe,Ni})_9\text{S}_8$	<i>Mindat.org</i>	Anonymous (2022b)
$(\text{Fe,Ni})\text{S}_{0.9}$	<i>Webmineral.com</i>	Barthelmy (2022)
$(\text{Fe,Ni})\text{S}_{0.9}$	<i>Dana's New Mineralogy</i>	Gaines <i>et al.</i> (1997)
$(\text{Fe,Ni})_{1+x}\text{S}(x = 0 \text{ to } 0.11)$	<i>Handbook of Mineralogy</i>	Anthony <i>et al.</i> (2003)

TABLE 2. Examples of wet chemical analyses of synthetic mackinawite

formulation	source
Fe _{0.91} S	Berner (1962)
Fe _{0.91} S	Rickard (1969)
Fe _{1.09} S - Fe _{1.15} S	Sweeney and Kaplan (1973)
Fe _{0.995} S - Fe _{1.023} S	Ward (1970)
Fe _{1.00} S	Rickard et al. (2006)

TABLE 3. Electron probe microanalytic systems used by some cited investigations of mackinawite compositions.

Citation	Model number	Manufacturer	Year introduced
Mukherjee and Sen (1991)	EMX-SM	ARL	1960
Mariko (1988)	JXA-50A	JEOL	1971
Mücke (2017)	SEMQ-II	ARL	1978
Krupp (1994)	CAMEBAX MICROBEAM	CAMECA	1982
Baidya et al. (2018)	SX-100	CAMECA	1994

TABLE 4. Evidence for systematic error in sulfur analyses. Weight percentage (wt %) and metal:S) in atoms per formula unit (apfu) sulfur analyses corrected for divergence from 100 wt% for total analyses (S*) compared with uncorrected, reported S analyses (S). Data extracted from Appendices 1 and 3. Arithmetic average (\bar{x}) and standard deviation (σ) compared with geometric mean (\bar{x}^*) and geometric standard deviations (σ^*) and ranges at the 95% confidence interval ($\bar{x}^* \times / (\sigma^*)^2$ where $\times /$ is the multiplicative equivalent of the arithmetic \pm).

	S wt %	S* wt %	Me:S apfu	Me:S* apfu
\bar{x}	35.72	36.32	1.02	1.00
σ	1.17	1.39	0.05	0.06
\bar{x}^*	35.70	36.32	1.01	1.00
σ^*	1.03	1.04	1.05	1.06
95% range	33.44-38.11	33.65-39.21	0.92-1.12	0.89-1.13

TABLE 5. Summary statistical parameters for mackinawite compositions for data listed in Table A1 ($n = 103$). The range for a log normal distribution is $\bar{x}^* \pm (\sigma^*)^2$ and includes around 95% of the data.

			wt% Cu	wt% Co	wt% Ni
arithmetic	average	\bar{x}	0.45	3.11	2.67
	standard deviation	σ	0.98	4.34	3.34
geometric	mean	\bar{x}^*	0.18	1.81	1.67
	standard deviation	σ^*	3.78	2.83	2.64
	95% range		0.01-2.64	0.23-14.50	0.24-11.62

Figure 1(a)

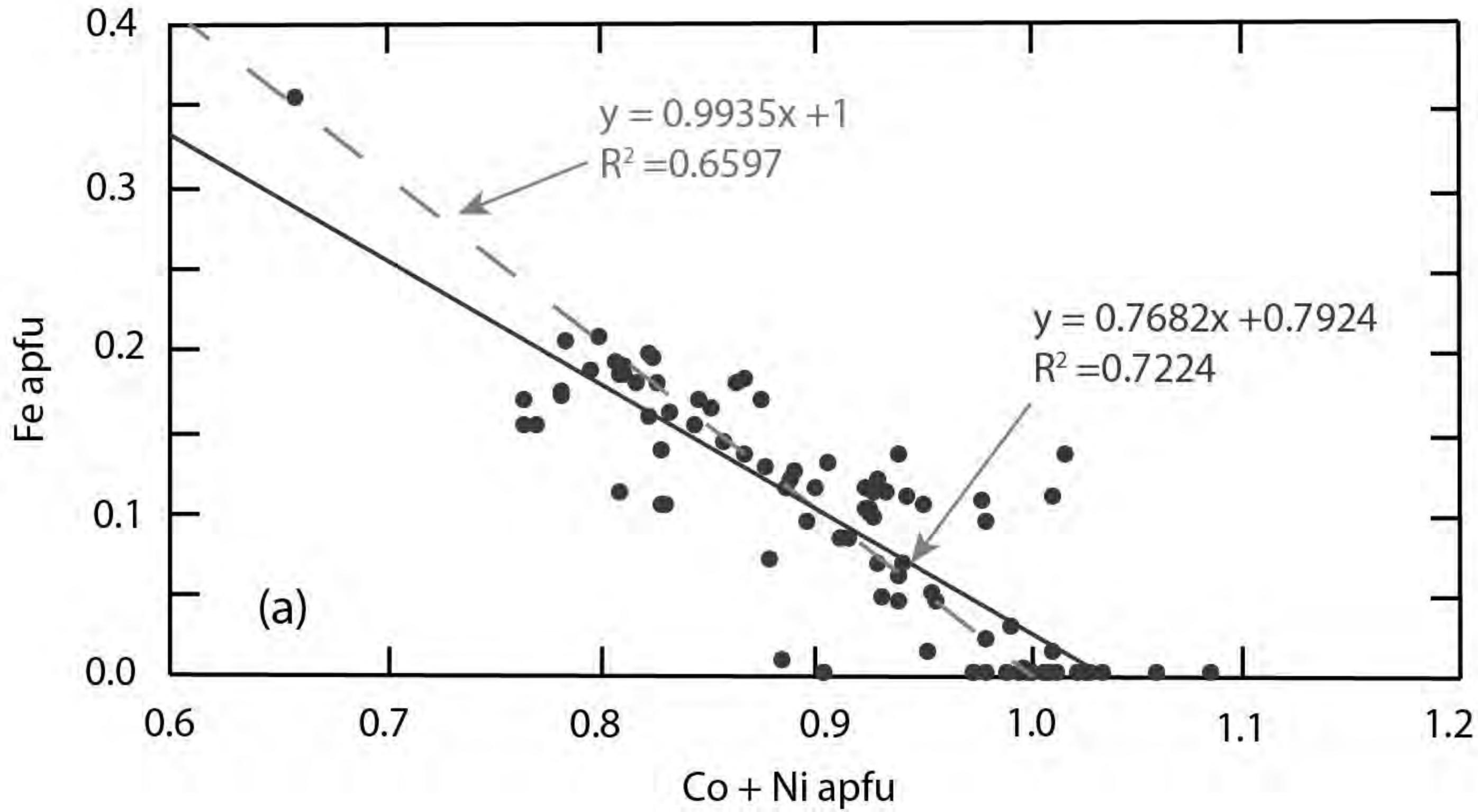


Figure 1(b)

