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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 Fe(Ni)S and $Fe_{1+x}S$, are both wrong and misleading. Statistical analyses of over 100 mackinawite compositions reported over the last 50 years show a mean composition of $Me_{1.0}S$ where Me = Fe + Co + Ni + 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 derive 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

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 2012a) 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, serpentinized ultrabasic rocks (e.g., Ashley 1975), meteorites (Ramdohr 1973), and even diamonds (Agrosì 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 $Fe_{0.96}Ni_{0.04}S$ (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 sufficient quantities mechanically for wet chemical analyses. Unfortunately, this was not entirely successful, and the result was subject to errors due to the inclusion of silicates and other metal sulfides in the separates. Even so, it appeared that the Outokumpu mackinawites were also nickelian with trace Co, giving compositions like $Fe_{0.92}Ni_{0.13}Co_{0.01}S$ and resulting in a non-stoichiometric formula $Me_{1.06}S$. In both cases, these early workers assumed that the S concentration was equivalent to 1.00 atoms per formula unit (apfu).

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

Table 1 gives examples of mackinawite compositions as defined by some current widespread—and otherwise authoritative—mineralogical databases. The only one that gives some clue to the actual compositions in the listing in the *Handbook of Mineralogy* (Anthony et al. 2003), which at least gives examples of Ni-, Co-, and Cu-bearing mackinawites even though the title gives a composition $(Fe,Ni)_{1+x}S$ (x = 0 to 0.11), which seems

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

Mackinawite composition	Source	
(Fe,Ni)$_{1+x}$S	Wikipedia[a]	
(Fe,Ni)$_9$S$_8$	Mindat.org[b]	
(Fe,Ni)S$_{0.9}$	Webmineral.com[c]	
(Fe,Ni)S$_{0.9}$	Dana's New Mineralogy	Gaines et al. (1997)
(Fe,Ni)$_{1+x}$S (x = 0 to 0.11)	Handbook of Mineralogy	Anthony et al. (2003)

[a] Wikipedia, The Free Encyclopedia, accessed November 26, 2022.
[b] Hudson Institute of Mineralogy, accessed December 10, 2022.
[c] Barthelmy, S.D., 2022, Mackinawite mineral data, Mineralogy Database, accessed January 11, 2023.

odd. Fe$_{1+x}$S may have been a nod to the other popular and equally misleading formula for mackinawite.

Kuovo et al. (1963) and Clark (1966) recommended that the composition of mackinawite should be presented as Me$_{1+x}$S. However, Babkine and Conquéré (1968) concluded that:

> L'établissement d'une formule telle que M$_{1+x}$ S (x = 0,05 à 0,07) paraît prématuré compte tenu du peu de précision des données analytiques. Il serait alors préférable de conserver pour la mackinawite la formule stoïchiométrique MS.[1]

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

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

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

However, the problem of the reported compositions of natural mackinawites remains. These compositions are almost exclusively for mackinawites occurring in higher temperature sulfide mineral associations. The mackinawites in these occurrences are fine-grained, and the mackinawites occur mainly as apparent exsolution or hydrothermal alteration products in chalcopyrite, pyrrhotite, and pentlandite. Because of their microscopic nature, their compositions are almost entirely determined by electron probe microanalysis (EPMA). Indeed, the identification of mackinawite and its distinction from valleriite [a complex mineral consisting of alternating Mg(OH)$_2$- and (Cu,Fe,)S-dominated layers] was one of the great triumphs of the early deployment of EPMA in mineralogy (Evans et al. 1964).

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)

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

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

The purpose of this paper is to present a statistical re-evaluation of published chemical analyses of natural mackinawites worldwide with a view to establishing the chemical composition of this mineral.

METHODS

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

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

materials by secondary fluorescence from the Cu-sample holder.

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

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

The parameters for including analyses in this study were that analytic totals should be available, and some reports were therefore not included. (e.g., Clark and Clark 1968). Some examples were omitted because S analyses were not reported (e.g., Vaughan 1969). Many of the reports were published in the last century before computerized manuscript preparation, electronic submission, and publication were universally available. Reported analyses in which transcription errors occurred (e.g., errors in analytical totals, transposition of numbers) were not included in this study. There is no a priori reason that separate mackinawite grains from the same deposit should show similar compositions, and the analyses are for individual grains, with no averaging of the composition of a group of analyses. An exception might be the cohesive group of mackinawite analyses reported by Spiridonov et al. (2008) from late veins in the Noril'sk ore field. The eight analyses, which are included in the listing in Online Materials[2] Table A1, show an average composition ($\bar{x}$) and standard deviation (σ) of $Fe_{1.05(0.01)}Ni_{0.07(0.01)}S$, but these are treated as separate analyses in this report.

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

RESULTS

Mackinawite compositions

The results are detailed in the Online Materials[2] Tables A1–A3 and Figure A1. The compositions of 103 mackinawites reported in the literature are listed in Online Materials[2] Table A1. The occurrences listed in Online Materials[2] Table A1 refer almost exclusively to mackinawites associated with magmatic or hydrothermal ore assemblages. There are very few published analyses of mackinawites in sediments. Bonev et al. (1989) listed two microprobe analyses of mackinawite from concretions from Black Sea sediments. Unfortunately, no totals were listed, but a small S-deficit in the element ratios was reported (0.05 apfu). Morin et al. (2016) reported that mackinawite nodules from the river Seine, France, have compositions approaching FeS as measured by energy dispersive methods. Berner (1962) originally noted that it proved impossible to separate mackinawite from sediments, and this has remained the situation to date. Indeed, it appears that the assumption that mackinawite is widely present in sediments may be mistaken (cf. Rickard and Morse 2005).

It is possible—and indeed probable—that the mackinawites associated with the high-temperature monosulfide solid solution or intermediate solid solution, which appear as anomalous pseudo-exsolution features in chalcopyrite, pentlandite, and pyrrhotite are the result of lower temperature reactions of late-stage convecting sulfidic solutions with the original exsolution products. There is, therefore, a continuum between the magmatic mackinawites and the hydrothermal mackinawites, typically exemplified by the association widely observed in the Kuroko ores of Japan. At the extreme lower end of this continuum are the mackinawites in the remarkable vein ores of the Moschellandsberg Hg deposits described by Krupp (1994). The mackinawites occurring in this association occur as distinct euhedral crystals up to 100 μm in size. These formed during late-stage activity in the hydrothermal system when the temperature reached as low as 50 °C. The average composition of the eight pure iron monosulfides is $Fe_{1.00}S$ with $\sigma = 0.01$ apfu. Two samples had trace Ni (<0.03 apfu), but the Me:S ratio is still unity.

Statistical analysis of the results

Online Materials[2] Table A1 lists 103 published mackinawite analyses that meet the analytic criteria mentioned above. As pointed out by Limpert et al. (2001) and Rickard (2019), most natural distributions follow log-normal distributions. This results from the multiplicative hypothesis of elementary errors, which states that if a random variation is the product of several random effects, a log-normal distribution must result (Heath 1967). The average of a log-normal distribution is the geometric mean ($\bar{x}^*$). The geometric mean composition of the 103 mackinawite analyses listed in Online Materials[2] Table A1 is $Me_{1.0}S$. This is similar to the arithmetic mean ($\bar{x}$), and the total data can conveniently be treated with the more familiar additive rather than multiplicative statistics.

The approximation to the normal distribution also suggests that the variables are random and not systematic. One area of potential systematic errors in these EPMA analyses is the uncertainties in the analyses of the lightest constituent, sulfur. The problem here, especially with early EPMA analyses, is that S is a relatively light element and that the standard often used was pyrite, which has both considerable variation from mackinawite and uncertainties in its composition (cf. Rickard 2021). To test this hypothesis, all total analytic errors are loaded onto the S analyses in Online Materials[2] Table A2 and the statistical parameters for the corrected data are compared with the original data in Table 4.

The results show that the variation in the individual metal concentrations, and therefore mackinawite formulas, is small but that the Me:S ratio condenses to 1.00 for both the arithmetic and geometric means. The 1σ error increases from 0.05 to 0.06 apfu. This suggests that there is a systematic error in the data but that its effect is small. Dispensing the total error across all the analyses, and not just S, does not, of course, change the results measurably.

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

TABLE 4. Evidence for systematic error in sulfur analyses

	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

Notes: Weight percentage (wt%) and Me: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 Online Materials[2] Tables A1 and A2. 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 ±].

The area where the use of geometric means and standard deviations becomes important is in the minor element analyses. Statistical parameters for the metal analyses in the data listed in Online Materials[2] Table A1 are summarized in Table 5. The arithmetic average of the reported Cu analyses is 1.00 wt% and 1σ is 1.27. However, a large number of samples (59 of the listed 103) have no reported Cu concentrations. This does not equate to zero wt% literally but merely means that the Cu contents of the samples were below the EPMA detection limits. The arithmetic average value ($\bar{x}$) for all the listed mackinawites, including those with Cu concentrations below the detection limit, is 0.45 wt% Cu, and the arithmetic standard deviation (σ) is 0.98. This means that the range of ca. 70% of the Cu values (±1σ) is –0.53 to 1.43 wt%. The negative value is obviously impossible, so the arithmetic average—which assumes a normal distribution—is invalid. The distribution is thus highly skewed, and the mean Cu value is better described by the multiplicative or geometric mean. The weakness of the geometric mean is that analytic totals of 0 cannot be included in the analysis. However, there is a work-around that avoids guessing the actual concentration, which relates the geometric means and standard deviations to their arithmetic counterparts (Rickard 2019). This suggests that the geometric mean value ($\bar{x}^*$) of the Cu analyses is 0.18 wt% and the geometric standard deviation (σ*) is 3.78. The range of Cu analyses then described by the 95% confidence interval [$\bar{x}^*\ {}^{\times}\!/\ (\sigma^*)^2$] is 0.01–2.64 wt%. The statistical parameters for the Cu distribution diverge considerably from those for Co and Ni (Table 5).

DISCUSSION

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

TABLE 5. Summary statistical parameters for mackinawite compositions for data listed in Online Materials[2] Table A1 (n = 103)

		wt% Cu	wt% Co	wt% Ni	wt% Fe
			Arithmetic		
Average	$\bar{x}$	0.45	3.11	2.67	57.39
St. dev.	σ	0.98	4.34	3.34	5.00
			Geometric		
Mean	$\bar{x}^*$	0.18	1.81	1.67	57.17
St.dev.	σ*	3.78	2.83	2.64	1.09
95% range		0.01–2.64	0.23–14.50	0.24–11.62	48.03–68.04

Notes: The range for a log normal distribution is $\bar{x}^*\ {}^{\times}\!/\ (\sigma^*)^2$ and includes around 95% of the data.

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

Cobaltian mackinawite

Cobaltian mackinawite is defined as mackinawite where Co is the dominant minor metal and where its concentration is >0.1 wt%. Clark (1970) reported 18.5 wt% Co in large mackinawite crystals (≤500 μm) from the Kilembe Cu-Co deposit, Uganda, but no further details have been presented. Otherwise the maximum amount of Co in these data is 12.68 wt% (0.19 apfu) in a mackinawite from the Shimokama deposit, Japan (Mariko 1988). This is a Kuroko-style volcanogenic massive sulfide deposit in Hokkaido and is a 13 Ma old equivalent of current deep ocean hydrothermal vent deposits. The mackinawite occurs as a herringbone replacement of chalcopyrite with cubanite and pyrrhotite (Bamba and Motoyoshi 1985). Bamba and Motoyoshi (1985) also listed two EPMA analyses of Co-rich mackinawites from the Shimokama mine but these seem to have been contaminated with Cu from the enclosing chalcopyrite, although one large grain which appears to be about 100 μm long and up to 20 μm wide may be the source of the virtually Cu-free analysis listed in Online Materials[2] Table A1.

Nickelian mackinawite

Nickelian mackinawite is defined as mackinawite, where Ni is the dominant minor metal and where its concentration is >0.1 wt%. As long ago as 1969, Ni-rich mackinawites were reported. For example, Vaughan (1969) reported 18.7 wt% Ni in a mackinawite from Vlakfontein, R.S.A. Unfortunately, there are no S analyses listed, and the totals are also missing. Papunen (1970) reported that mackinawite was locally the main Ni-bearing mineral in the Hitura Ni deposit, Finland. These early reports may have helped establish the mistaken view that mackinawite was an iron-nickel sulfide. The maximum amount of Ni in nickelian mackinawite in Online Materials[2] Table A1 is 22.7 wt% (Lorand 1989).

Cupriferous mackinawite

Cupriferous mackinawite is defined as mackinawite where Cu is the dominant minor metal and where its concentration is >0.1 wt%. The problem here is that cupriferous mackinawites are often reported from mackinawite inclusions within chalcopyrite. As noted above, with the older EPMA values a relatively large volume of the section may have been interrogated by the beam, and the analyses may include Cu from the enclosing chalcopyrite. Zôka et al. (1973) specifically addressed this problem and concluded that the EPMA analyses of 5 of their mackinawite samples (including one from the Mackinaw type locality) were unsafe since the reported Cu values were undoubtedly due to excitation of the enclosing chalcopyrite. The highest Cu contents reported for mackinawite are both from analyses of Zôka et al. (1973) and refer to mackinawites enclosed by chalcopyrite. These two analyses, from the Shimokama (8.80 wt%) and Kawayama (6–0.80 wt%) mines from the Japanese Kuroko deposits, are the only mackinawites listed as having Cu ≥0.1 apfu. Analyses of mackinawites from these deposits by Takeno (1965) and Mariko (1988) did not report similarly high Cu contents. It appears that Cu is not an abundant minor element in mackinawite.

Other minor elements in mackinawite

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

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

Small quantities of silver (0.02–0.07 wt%) were reported in two mackinawite samples for the Noril'sk ores in parkerite ($Ni_3Bi_2S_2$)-bearing veins by Spiridonov et al. (2008). The mineral association also includes native Ag, but the mackinawite seems mostly associated with chalcopyrite and magnetite. High concentrations of Ag (7.1 wt%) were also reported from energy-dispersive (EDS) analyses of mackinawite, associated with chalcopyrite and pyrrhotite from the Zona Basal shear zone gold deposit, SE Brazil (Alves et al. 2022) but no other information on the mackinawite composition was recorded.

Substitution vs. addition

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

$$(Fe_{1-x}M_x)S \text{ where } M = Cu + Co + Ni \text{ (substitute for Fe)} \quad (1)$$

$$FeM_xS \text{ where } M = Cu + Co + Ni \quad (2)$$

(added to mackinawite intercalated between the Fe-S sheets).

The data listed in Online Materials[2] Table A1 have been interrogated statistically, and the results are summarized in Figure 1 and Online Materials[2] Figure A1.

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

The question of whether the Cu analyses presented in the mackinawite analyses are real or a function of contamination of the mackinawite analyses through the EPMA exciting Cu from enclosing chalcopyrite is also examined in Figure 1. The regression coefficients and the slopes of the lines forced through $Fe_{1.00}S$ are very similar whether (Co+Ni) or (Co+Ni+Cu) are considered. However, the plot of Cu apfu vs. Fe apfu (Online Materials[2] Fig. A1a) is a pure scattergram. This suggests that Cu can substitute for Fe in mackinawite but that there is substantial analytical uncertainty in the Cu data, as discussed above. There is, furthermore, no correlation between (Co+Ni) and Cu.

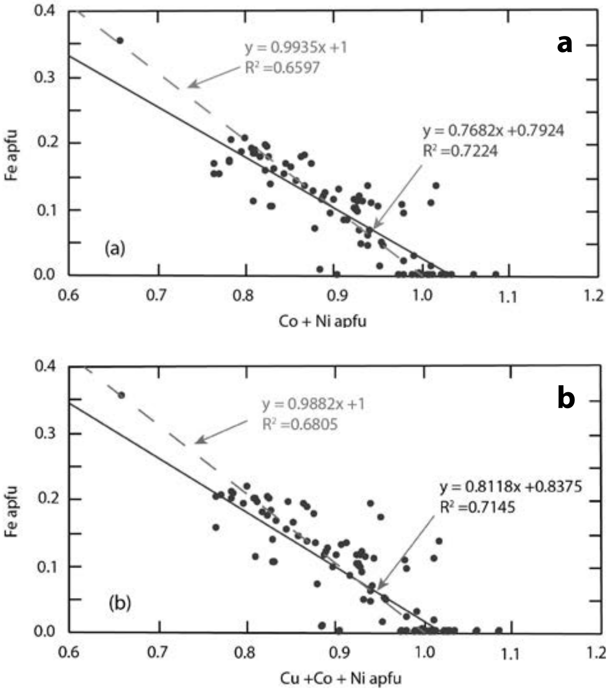

FIGURE 1. Plots of (**a**) Co+Ni (afpu) vs. Fe (apfu) and (**b**) Cu+Ni+Co (afpu) and vs. Fe (apfu). The solid lines and their equations and regression coefficients (R^2) are the best fit for the data; the dashed lines and their equations and regression coefficients (R^2) are for a best-fit line forced through $Fe_{1.00}S$. Error bars for the data are not shown.

The data in Online Materials[2] Table A3 also show that there is no significant correlation between the Co and Ni contents of mackinawite. However, the plot of Co vs. Ni (Online Materials[2] Fig. A1d) suggests a correlation between Co and Ni in cobaltian mackinawites with Co >0.01 apfu (>6.8 wt%) and Ni. Eighteen of the 103 reported mackinawites are Co-rich, and they reveal a regression coefficient for Co vs. Ni of 0.87 with a negative slope of the trend line of 3.4. If Co replaced Ni in the mackinawite structure on an atom for atom basis, then we might expect a slope approaching –1. The observed correlation between Co and Ni for these Co-rich mackinawites most probably reflects the composition of the solutions in which the mackinawite crystals grew combined with molecular effects of Co and Ni substituting for Fe the mackinawite structure. It might be an interesting area of research. Overall, however, the data suggest that cobaltian and nickelian mackinawites are essentially unrelated species: there are a similar number of nickelian mackinawites with no detectable Co.

IMPLICATIONS

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

Even simple, balanced chemical equations involving mackinawite are likely to be wrong if the composition of mackinawite is assumed to be non-stoichiometric. It is obvious, for example, that the composition $Fe_{1+x}S$ cannot be balanced electronically with normally charged Fe and S ions. By contrast, $Fe_{1-x}S$, the usual representation of pyrrhotite compositions, is readily electronically balanced with oxidized Fe^{3+} and S_n(-II) ions. The finding that mackinawite is stoichiometric has considerable implications in the thermodynamic modeling of geologic processes involving mackinawite as well as understanding the chemistry of several key industrial processes. This has been long realized by the compilers of the thermodynamic data sets used in popular geochemical modeling programs, such as Geochemist's Workbench, where the composition of mackinawite is listed in their thermodynamic database as stoichiometric FeS.

The result of this study that the composition of mackinawite in higher temperature associations is the same as that reported for synthetic ambient-temperature mackinawite—and thus, by extension, to sedimentary mackinawite—resolves an uncomfortable anomaly in the mineralogical and geochemical literature. It is obvious that, a priori, a mineral must have the same composition at low temperatures as at high temperatures—otherwise they are distinct phases.

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

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

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

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Endnotes:

[1] The establishment of a formula such as M$_{1+x}$ 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.

[2] Deposit item AM-24-38943. Online Materials are free to all readers. Go online, via the table of contents or article view, and find the tab or link for supplemental materials.