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Observations on Tetragonal (Fe, Ni, Co)$_{1+x}$S, Mackinawite

By

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ABSTRACT: In this paper the writers have discussed the stability of mackinawite, the importance of the cation : anion ratio in its structure on the basis of the analytical data, and the relation of the α-transformation of hexagonal FeS$_x$ to the transformation temperatures of natural mackinawites.

Mackinawite has long been confused with valleriite because of resemblance in their optical properties until the works of MILTON and MILTON (1958), KOUVO and VUO-RELAINEN (1959), KOUVO et al. (1963), FUJIKI (1963) and EVANS et al. (1962, 1964) were made public. The mineral from many of copper and nickel deposits all over the world has thus so far often been mis-named valleriite but is in recent papers (FU-JIKI, 1963; OGNIBEN and OMINETTO, 1964; TAKENO, 1965; CHAMBERLAIN and DELA-BIO, 1965; CLARK, 1965 and 1966 etc.) identified with mackinawite associated very intimately with Cu–Fe–S minerals such as cubanite, chalcopyrite and pyrrhotite.

The fact is that there have been little discussions in the literature concerning the stability of mackinawite and its relation to that of valleriite investigated by BORCHERT (1934) and MERWIN and LOMBARD (1937). The paragenesis of mackinawites is considered indicative of relatively low-temperature formation (cf. CHAMBERLAIN and DELABIO, 1965; CLARK, 1966a). The tetragonal Fe$_{1+x}$S phase has been synthesized in aqueous solutions at the ordinary state of temperatures and pressures by BERNER (1962 and 1964), and has been identified with mackinawite by MILTON (1966) on the basis of the close agreement in their x–ray powder data.

Mackinawite is unquestionably unstable above about 250°C (TAKENO, 1965; CLARK, 1966; and SARDISCO et al., 1967) while true valleriite is stable, at least, below about 500°C (TAKENO, 1965; YUND and KULLERUD, 1966). Moreover, these two minerals are clearly distinguishable from each other in their structures since mackinawite is in a close connection with hexagonal FeS$_x$ and valleriite with tetragonal CuFeS$_2$. However, there remain several problems in this field:

1) It is known that natural mackinawite has a widely variable upper limit of stability and has marked variation in composition. Are these factors related to each other or not?

2) Through what processes has the crystal habit of natural mackinawite (only minute crystals from few to some dozen microns) been derived?

3) Is there any relation of stability between the tetragonal $Fe_{1+x}S$ (mackinawite) and the hexagonal FeS_x (pyrrhotite group) with near stoichiometric composition?

4) In what form may nickel or cobalt be contained in the structure of the mineral? Is the crystal structure ordered or not in state?

5) Is the mineral formed in aqueous solution (MEYER's "kansite" and BERNER's "tetragonal FeS") identical with natural mackinawite?

All of these problems still remain to be solved systematically. In a previous paper concerning the decomposition of mackinawite from a number of localities on heating in vacuo at the temperatures between 130° and 245°C, S. TAKENO tentatively suggested that the upper stability limit of the tetragonal iron sulfide depends on the iron content but not directly on the degree of substitution of iron by nickel and cobalt. These facts imply that the tetragonal phase is stable with a wide range of cation:anion ratio with deviation from stoichiometric FeS.

On the other hand, A.H. CLARK considered on the basis of the available analytical data and his preliminary experiments that the above conclusions are not acceptable. Then the two authors examined the results respectively and CLARK's suggestion has accepted to be legimate. Details of the examinations for transformations of natural mackinawite have already been described by CLARK (1966b) as follows:

Only three analyses of natural mackinawite include sulfur determinations and are therefore potentially suitable for calculation of the $Fe+Ni+Co:S$ atomic ratios. The published data are certainly too few to permit confident estimation of the compositional range shown by natural mackinawites, but would agree with BERNER's view (1964) that the available evidence suggests that "tetragonal FeS" has a cation:anion ratio consistently greater than unity. In view of uncertainty of the analytical data for the Mackinaw mackinawite, it may be suggested that mackinawite has a composition in the range $M_{1.04}S \sim M_{1.07}S$. This surely signifies that mackinawite and troilite, which shows no appreciable deviation from stoichiometric FeS in natural assemblages, are not dimorphous with each other in the strict sense.

TABLE 1. SELECTED ANALYSES OF MACKINAWITE (CLARK, 1966 b)

Sample locality and description	Fe	Ni	Co	S	$Fe+Ni+Co:S$
	(in weight per cent)				
Outokumpu, Finland (1)	56.00	8.28	0.42	35.29	1.046 : 1
Outokumpu, Finland (1)	56.37	8.18	0.37	35.08	1.056 : 1
Mackinaw, Wash. (2)	63±5	3.1±5	—	34±4	1.114 : 1 (av.)
Synthetic (3)					1.04 : 1
					1.045 : 1
					1.07 : 1

Refs.: (1) Kouvo et al., 1963 (p. 517); chemical analysis, analytical precision poor.
(2) Evans et al., 1964 (p. D66); electron microprobe analyses, cation:anion ratio is average.
(3) Berner, 1964 (p. 297); chemical analyses.

If the variation in the cation : anion ratio of mackinawite is in fact as limited as suggested, then the iron : sulfur ratios of this mineral would chiefly reflect the degree of substitution of iron by nickel and/or cobalt. The available data related to the breakdown temperatures of mackinawites with various contents of nickel and cobalt are given in Table 2. Taking into account uncertainty of the minor element determinations, heterogeneity of the specimens, and the gradational or indistinct breakdown characteristics observed at least in one of the specimens, these data may be interpreted as indicating that the upper stability limit of mackinawite is strongly influenced by the nickel and cobalt contents (that is, with the Fe : Ni + Co ratio) and rises markedly with increasing substitution of iron by these elements.

A temperature of $135 \pm 5°C$ has been proposed (CLARK, 1966a) for the stability limit of essentially pure $Fe_{1+x}S$, on the basis of the data obtained from heating experiments of mackinawites intergrown with troilite, intermediate hexagonal pyrrhotite ($Fe_{0.912}S$), monoclinic pyrrhotite, and chlorite and quartz in the Ylöjärvi deposit. This temperature closely approximates to that for the α-transformation of stoichiometric hexagonal FeS ($139 \pm 2°C$) (Moh and Kullerud, 1964).

The available observations on the stability and composition of natural mackinawite appear to suggest that in the Fe–S system tetragonal $Fe_{1+x}S$ occupies a narrow, perhaps vertical field in the composition range $30.9_8 \sim 51.6_9$ atomic per cent iron at the temperatures below $135°C$. Mackinawite and troilite can improbably exist as continuous solid solution but should coexist stably as independent phases.

TABLE 2. NICKEL AND COBALT CONTENTS AND BREAKDOWN TEMPERATURES OF MACKINAWITES (CLARK, 1966 b)

Sample locality		Ni	Co	Ni+Co	Breakdown temperatures (°C)	
		(in weight per cent)			Lower limit	Upper limit
Ylöjärvi, Finland	(1)	0.2	0.2	0.4	130	140
Kawayama, Japan	(2)	n.d.	n.d.	—	130	147
Mackinaw, Wash.	(2)	3.1±0.5	—	3.1	145	165
Muskox, Canada	(2)	2.3±1	1.5±1	3.8	195	210
Komori, Japan	(2)	5.6	1.0~2.0	6.6~7.6	130	200–230
Outokumpu, Finland	(3)	3.28	0.42	8.7	210	245

Refs.. on annealing studies: (1) CLARK (1966 a)
(2) TAKENO (1965 b)
(3) Kouvo et al. (1963); specimen heated in air.

The paragenetic relations of mackinawite with the pyrrhotite group have been studied by CLARK (1966a). In the Ylöjärvi deposit nickel- and cobalt-poor mackinawites are found associated with pyrrhotites of (a) monoclinic, (b) monoclinic + hexagonal, and (c) intermediate hexagonal habits and (d) stoichiometric composition. These assemblages are also confirmed in the case of the nickel- and cobalt-free mackinawite from the Kawayama mine except that of (d). Although the paragenesis of the mine ral in the Ylöjärvi ores are suggestive of late-stage, most of the textural associations

are not indicative of the restricted range of temperature. CLARK (1966a) concluded that mackinawite might have been formed after the mutual exsolution of troilite and intermediate pyrrhotite and the local diffusion of the hexagonal phases to form the coarser intergrowths. Formation of mackinawite through exsolution from the original pyrrhotite solid solutions cannot be entirely discounted in the Ylöjärvi, Kawayama and Mackinaw ores.

In the Ylöjärvi ores, exsolution of troilite and iron-deficient hexagonal pyrrhotite from initially homogeneous pyrrhotite solid solutions is assumed to have taken place at temperatures below $\sim$140°C. The approximate upper stability limit of $\sim$130° – $\sim$140°C tentatively proposed by CLARK for the nickel-free mackinawite coincides with the temperature of the α-transformation for stoichiometric hexagonal FeS and is in very good agreement with the breakdown temperaures of the Kawayama mackinawite. In contrast, clearly separated tetragonal $M_{1.046}S$ from the Outokumpu mine (KOUVO et al., 1963) apparently broke down at 200° – $\sim$210°C.

The mechanism of α-transformaton is interpreted in relation to magnetism by HIRAHARA and MURAKAMI (1958) and HIHARA (1960) as follows:

At the temperature of α-transformation, the sign of anisotropy energy and the constant of molecular field alter. The axis of magnetizability is disposed along the c-axis below T_α but in the c-plane above T_α, while the lattice constant c contracts abruptly or c/a decreases from 1.69 down to 1.66 for $FeS_{1.00}$. This transition is of the first order and corresponds to the transformation from the superlattice structure with a = 5.968 and c = 11.74Å below T_α to the hexagonal NiAs structure above T_α, causing the change of exchange interaction and decrease in the values of the constant for the molecular field among the sublattice. On cooling, the change in the sign of anisotropy energy and that in the constant of the molecular field are separate and the former is recognizable below the room temperature in the case of x > 1.04 (x in FeS_x) while the latter combined with the transformation of the crystal structure decreases gradually but is still preserved at about 100°C.

In the light of the mechanism described above, it is difficult to interprete reasonably the relation between α-transformation and the transformation of natural mackinawite, because we have no knowledges at present about the influence of Ni and Co on the transformation of hexagonal FeS_x, the precise composition of mackinawite and the variation of the lattice constant c of the mineral. If, as has already been suggested, the upper stability limit for Ni and Co-free mackinawite at ca. 135°C is correct, it is probable that the transformation lies "horizontally" at this temperature in the region with Fe content more than that in stoichiometric FeS (50.9$_8$~51.9$_6$ atomic per cent iron) (mackinawite + troilite region). As is evident in Table 2, the breakdown temperatures increase with increasing content of Ni and Co. If the lattice constant c of the tetragonal $Fe_{1+x}S$ varies with the content of these minor elements, the intimate relation between the α-transformations of hexagonal FeS_x and that of tetragonal $Fe_{1+x}S$ will be accountably explained.

On the other hand, aqueous conditions are considered necessary for synthesis of

TABLE 3. COMPARISION OF "KANSITE", "TETRAGONAL FeS" AND "MACKINAWITE"

	Kansite	Tetragonal FeS	Mackinawite
References	MEYER *et al.*, 1958	BERNER, 1962, 1964	EVANS *et al.*, 1964
Formula	Fe$_9$S$_8$	FeS	FeS
Crystallography	Face centered cubic Fm3m a = 10.1Å	Tetragonal P4/nmm a=3.679±0.002Å c=5.047±0.002Å	Tetragonal P4/nmm a=3.673±0.001Å c=5.035±0.001Å
Color	Black	Black	Pale pink to pinkish grey
Density	3.13	4.29 (calc.)	4.30 (calc.)
Optical	—	—	Strongly anisotropic

X-ray powder data:

dÅ	I	hkl	dÅ (meas)	I (obs)	hkl	dÅ (calc)	I (obs)	hkl
5.05	M	200	5.04	10	001	5.03	100	001
2.99	M	311	2.97	8	101	2.97	80	101
			2.60	2	110	2.60	20	110
2.32	S	331	2.31	8	111	2.305	80	111
			1.839	6	200	1.835	60	200
1.80	S	440	1.811	8	112	1.805	80	112
1.73	M	531	1.728	6	201	1.723	60	201
			1.681	2	003	1.677	20	003
1.54	VW	533	1.564	4	211	1.564	40	211
			1.530	2	103	1.527	20	103
1.42	W	711 551	1.412	3	113	1.410	30	113
1.31	M	731 553	1.300	5	220	1.298	50	220
1.26	M	800	1.261	5	004	1.258	50	004
			1.241	3	203	1.239	30	203
			1.192	1	301	1.190	10	104
			1.176	2	213	1.174	20	213
1.14	W	840	1.134	5	311	1.133	50	114
			1.056	8	312	1.055	80	312

mackinawite with considerable duration of time. It seems that the precise relations between mackinawite and troilite in terrestrial assemblage are still obscure. The marked difference in the environments of formation has been stressed by CLARK (1966a), and it is possible that, under suitable conditions of temperature and of vapor pressure of sulfur, the development of mackinawite may be more stimulated than that of troilite with the appreciable presence of nickel and cobalt.

MILTON (1966) concluded merely on the basis of the x–ray diffraction data that the tetragonal FeS synthesized in aqueous solution (*cf.* MEYER *et al.*, 1958; GRECO and WRIGHT, 1962; SARDISCO *et al.*, 1962, 1963 and 1965; and BERNER, 1964) is quite identical with natural mackinawite. This form of synthesized "FeS" may be distinguished from the natural phase because of the difference recognized in the stability relation at the normal temperature and atmospheric pressure.

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