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SOME NEW OBSERVATIONS
ON MACKINAWITE AND VALLERIITE

RIASSUNTO. — Vengono resi noti i risultati di un ciclo di ricerche effettuate sulla mackinawite e sulla valleriite di campioni tipici provenienti, per la mackinawite, da Balangero (Piemonte), Rammelsberg (Harz), Kaveltorp (Svezia), Salamina (Argentina), Matooster (Transvaal), Laxia tou Mavrou (Limasol, Cipro), Hellenic Mining (Cipro); per la valleriite, da Kaveltorp, Balangero, Laxia tou Mavrou, Hellenic Mining, Loolekop (Transvaal), Mavro (Eretria, Grecia), Saxberget (Svezia), White Horse (Yukon). Di questa discussa coppia di minerali sono state definite le caratteristiche ottiche, la paragenesi ed il chimismo.

Caratteristiche ottiche: nella quasi totalità dei casi la mackinawite si distingue chiaramente dalla valleriite. All'osservazione in luce riflessa la mackinawite presenta, nella posizione di minimo assorbimento, un potere di riflessione nettamente più elevato (quantitativamente $42,1 \pm 2\%$) di quello della valleriite ($17 \pm 1,5\%$). Il colore di riflessione corrispondente è bianco-rosa crema, più chiaro del colore della pirrotina nella medesima posizione. In condizioni analoghe la valleriite presenta un colore di riflessione bruno-giallo crema. A nicols non esattamente incrociati la mackinawite mostra, nella posizione diagonale più chiara, un colore bianco con tonalità giallo limone brillante, più chiaro del colore della valleriite nella medesima posizione (giallo bruno aranciato); nella posizione più scura, la mackinawite presenta un colore verdazzurro acquamarina (diagnostico). La durezza di levigatura della mackinawite è superiore a quella della calcopirite e simile a quella della pentlandite, mentre la valleriite presenta durezza di levigatura nettamente inferiore.

Paragenesi: la mackinawite e la valleriite si rinvencono in quantità rilevanti soprattutto associate a calcopirite, pirrotina, cubanite, pentlandite, blenda e magnetite. Se entrambe fanno parte della stessa associazione paragenetica, la macki-

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nawite appare di formazione più precoce, originatasi sia per smistamento (ad es. in calcopirite) sia per sostituzione (di calcopirite e di altri minerali). La valleriite è chiaramente un minerale di sostituzione tardiva, lungo cavità, fratture e direzioni cristallografiche degli altri costituenti ad essa associati, essenzialmente magnetite, calcopirite e pirrotina (Loolekop, Transvaal; White Horse, Yukon; Laxia tou Mavrou, Cipro).

Chimismo: per quanto riguarda la composizione chimica, la valleriite si distingue dalla mackinawite per la presenza di notevoli quantità di Cu e di idrossidi quali $Mg(OH)_2$, $Fe(OH)_2$ e $Al(OH)_3$. La composizione della mackinawite varia fra $(Fe, Ni, Co, Cu)_{1-x}S$ e $(Fe, Ni, Co, Cu)_{1+x}S$. Non è sicuramente accertabile — tutte le analisi sono state effettuate con la sonda elettronica — se la variabilità della formula dipenda realmente dalla natura non esattamente stechiometrica del minerale, oppure da un possibile errore analitico. Nell'eventualità della prima ipotesi, la variabilità può essere ascritta sia ad un eccesso di Fe, Ni, Co, Cu sia ad un difetto di S. Tuttavia, in base ai dati analitici sino ad oggi disponibili, nessuna delle due ipotesi sembra trovare sicura conferma. I dati sperimentali mostrano invece un rapporto di interdipendenza fra il contenuto in Ni, Co e Cu e la temperatura di formazione: Ni e Co sembrano aumentare con l'aumentare della temperatura di formazione. La valleriite ha formula generale $(Cu Fe S_2) \cdot n [Mg, Ca, Fe, Ni, Mn (OH)_2] \cdot m [Al (OH)_3]$, dove n varia da 1,14 a 2,33 ed m da 0 a 0,50. La formula $[Cu Fe S_2]^+ \cdot 1,56 [Mg_{0,68} Al_{0,32}(OH)_2]^-$ proposta da EVANS & ALLMANN (1967) e ALLMANN (1971) non coincide con i risultati analitici finora disponibili.

ZUSAMMENFASSUNG. — An Hand der Literatur wird die historische Entwicklung der Erforschung der Minerale Mackinawit und Valleriit beschrieben.

Eingehend neu untersucht wurden die Mackinawit-Vorkommen von Balangero/Piedmont, Rammelsberg/Harz, Salamanca/Argentinien, Matooster/Transvaal, Hellenic Mining/Zypern sowie die Valleriit-Vorkommen von Eretria/Griechenland, Loolekop/Schweden, Balangero/Piedmont und Hellenic Mining/Zypern.

Behandelt werden die optische Charakteristik, die Mineralparagenesen und die genetische Interpretierung, sowie das Problem des Mackinawits als geologisches Thermometer. Insbesondere diskutiert wird die chemische Zusammensetzung. Bekannte Analyseergebnisse werden mit neuen eigenen Mikrosonde-Analysen in Vergleich gesetzt und diskutiert.

Die allgemeine Formel für Mackinawit schwankt demnach von:



Valleriit hat die allgemeine Formel:



wobei n von 1,14 bis 2,33 und m von 0 bis 0,50 variieren kann.

History.

Mackinawite.

Mackinawite was first discovered in the platinum-bearing nickeliferous-pyrrhotitic basic and ultrabasic rocks of the Bushveld Complex (Transvaal) by SCHNEIDERHÖHN (1929 b). SCHNEIDERHÖHN having spectrographically determined large quantities of Fe and Ni, and moderate quantities of Co, called the mineral « unknown Ni-Fe mineral » (Tab. I).

After RAMDOHR (1925, 1928) and SCHNEIDERHÖHN (1929 a, b) and until 1963/64 (see Tab. I) mackinawite in ore deposits was referred to as « valleriite ». Examples of such deposits include those listed in Table I, as well as Kaveltorp, Sweden (ÖDMAN, 1933), Mount Isa, Australia (GRONDIJS & SCHOUTEN, 1937), Keban-Maden, Turkey (MAUCHER, 1938), Boliden, Sweden (ÖDMAN, 1941), Sudbury, Canada (HAWLEY, 1962), Aba Suwajel, Egypt (EL GORESY, 1964) and Noril'sk and Monchegorsk, Siberia (GENKIN, 1971).

BIRKS et al. (1959) unequivocally demonstrated through electron microprobe analyses of a « copper-iron mineral (mackinawite) » that an iron sulfide mineral — (Fe, Cu)S —, other than valleriite, occurred within the chalcopyrite of the Mackinaw Mine ores.

BERNER (1962) synthesized mackinawite by immersing reagent grade metallic iron wire in saturated H₂S-solution at 25°C and atmospheric pressure; however, based on X-diffraction studies, he gave it the name « tetragonal iron sulfide ».

In 1963 KOUVO et al. described mackinawite from several Finnish ore bodies (see Table I), but also gave it the name tetragonal iron sulfide based on X-ray diffraction studies and wet-chemical, X-ray fluorescence and electron microprobe analyses.

EVANS et al. (1964) named the mineral mackinawite after the type-locality Mackinaw Mine, Snohomish County, Washington.

Valleriite.

Valleriite was first described from Nya Kopparberg, Sweden and analyzed by BLOMSTRAND (1870, cited by HINTZE, C.). PETRÉN (1898, cited by SCHEIBE, R., 1899) discredited the mineral valleriite as a mixture of covellite, pyrrhotite, spinel, hydrotalcite, siderite and limonite.

RAMDOHR & ÖDMAN (1932) revived the name valleriite and, disregarding the presence of aluminium, magnesium (sodium and potassium

oxides?) in the total chemical analyses, assigned it the formula $\text{Cu}_2\text{Fe}_4\text{S}_7$. HILLER (1939) provided the first X-ray diffraction data for valleriite and assigned it the formulas $\text{Cu}_2\text{Fe}_4\text{S}_7$ and $\text{Cu}_3\text{Fe}_4\text{S}_7$. EVANS et al. (1962) provided the first unit cell data on valleriite. EVANS et al. (1964) provided additional X-ray powder diffraction and unit cell data; however, the link of magnesium and aluminium hydroxides with valleriite as an integral part of the valleriite structure was still discredited as corresponding to a foreign mineral phase and the mineral assigned the formulas CuFe_2S_4 , Cu_2FeS_4 and $\text{Cu}_2\text{Fe}_2\text{S}_4$. In 1967, EVANS & ALLMANN for the first time established that magnesium and aluminium hydroxides are an integral part of the valleriite structure and that the structure of valleriite consists of an unusual interleaving of brucite-like layers of $[(\text{Mg}, \text{Al})(\text{OH})_2]$ composition and sulfide layers of $[\text{Fe}, \text{Cu}]_2\text{S}_2$ composition and assigned it the formula $[(\text{Fe}_{1.03}\text{Cu}_{0.97})\text{S}_2] \cdot 1.526 [\text{Mg}_{0.68}\text{Al}_{0.32}(\text{OH})_2]$.

Formation of Mackinawite and Valleriite.

Mackinawite.

The formation of mackinawite has been explained as follows:

I - *by exsolution.*

a) in chalcopyrite (in part oriented) (SCHNEIDERHÖHN, 1929 b; HAWLEY, 1962; EL GORESY, 1964; ANTUN et al., 1966; SCHIDLowski & OTTEMANN, 1966; RAO & RAO, 1968; OMENETTO, 1969; SARKAR, 1971);

b) from chalcopyrite (Fe-rich chalcopyrite) (MILTON & MILTON, 1958; KOUVO et al., 1963; CLARK, 1966 b; RENSBERG & LIEBENBERG, 1967; RAO & RAO, 1968; SARKAR, 1971);

c) from chalcopyrrhotite in chalcopyrite exsolution bodies within sphalerite (OGNIBEN & OMENETTO, 1964);

d) in pentlandite (in part oriented) (SCHNEIDERHÖHN, 1929 b; PANAGOS & RAMDOHR, 1965; RAMDOHR, 1969);

e) from pentlandite (Ni-and Co-pentlandite) (KOUVO et al., 1963; RENSBERG & LIEBENBERG, 1967);

f) from pyrrhotite (CLARK, 1966 b);

g) from cubanite (KOUVO et al., 1963; CLARK, 1966 b);

h) from complex Fe-Cu sulfide solid solution (BUERGER, 1935);

i) from other Cu-Fe or Fe-Ni minerals (CLARK, 1966 b).

II - *by replacement.*

a) of chalcopyrite (in part oriented) (SCHOLTZ, 1936; CLARK, 1966 b; RAO & RAO, 1968; GENKIN, 1971);

b) of pentlandite (SCHOLTZ, 1936; CHAMBERLAIN & DELABIO, 1965; CLARK, 1967; VAUGHAN, 1969; PAPUNEN, 1970; GENKIN, 1971);

c) of intermediate pyrrhotite (CLARK, 1966 b);

d) of cubanite (in part oriented) (EL GORESY, 1964; CHAMBERLAIN & DELABIO, 1965; CLARK, 1966 b; OMENETTO, 1969);

e) of troilite (late-stage troilite) (CLARK, 1966 a; b; CLARK & CLARK, 1968);

f) of millerite (SARKAR, 1971);

g) of other Cu-Fe or Ni-Fe minerals (CLARK, 1966 b);

h) of olivine (pseudomorphism) (GENKIN, 1971).

III - *primary crystallization.*

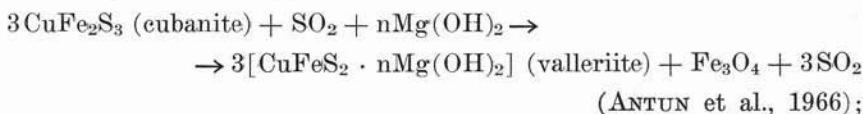
KOUVO et al. (1963) report the presence of single idiomorphic mackinawite crystals on the walls of open tension cracks at Outokumpu, Finland to which they assign a primary origin.

Valleriite.

Valleriite is generally considered to form through the *replacement* of:

a) pyrrhotite (ÖDMAN, 1933; ANTUN et al., 1966; RAMDOHR, 1969), sometimes in connection with the conversion of pyrrhotite to a pyrite-marcasite-carbonate assemblage (probably «intermediate products»-carbonate) during carbonate metasomatism (RAO & RAO, 1968);

b) cubanite (ÖDMAN, 1933; RAMDOHR, 1969; GENKIN, 1971) sometimes in connection with dynamometamorphism:



c) chalcopyrite (ÖDMAN, 1933; SCHOLTZ, 1936; ANTUN et al., 1966);

d) pentlandite (ÖDMAN, 1933; SCHOLTZ, 1936; RAMDOHR, 1969);

e) mackinawite (ANTUN et al., 1966);

f) magnetite (in part oriented and in part pseudomorphic) (CHAMBERLAIN & DELABIO, 1965; RAMDOHR, 1969; GENKIN, 1971);

g) serpentine (CHAMBERLAIN & DELABIO, 1965; RAMDOHR, 1969; PAPUNEN, 1970) and apparently chlorite (ANTUN et al., 1966).

Mackinawite, valleriite and serpentinization.

A number of authors, a.o. ÖDMAN (1933), SCHOLTZ (1936), KORICH (1964), CHAMBERLAIN & DELABIO (1965), PANAGOS & RAMDOHR (1965), ANTUN et al. (1966), RAMDOHR (1967), CLARK (1967, 1969), CLARK & CLARK (1968), PAPUNEN (1970) and GENKIN (1971) relate the formation of mackinawite to the serpentinization (early, intermediate and late stage serpentinization) of the host-rock. According to SCHOLTZ (1936, p. 170) «... [the] distribution [of mackinawite] ⁽¹⁾ within the silicates of the sparsely mineralized ore is apparently closely associated with the degree of serpentinization». Serpentinization apparently enhances the formation of mackinawite through:

1. - The release of Ni, Fe, and Co through the breakdown, i.e., the conversion of primary Ni-bearing spinel to magnetite and the breakdown of olivine, and the release of Ni, Fe, Co, and Cu through the breakdown of primary sulfides (SCHOLTZ, 1936; CHAMBERLAIN & DELABIO, 1965; CLARK, 1967; RAMDOHR, 1967; CLARK & CLARK, 1968; PAPUNEN, 1970; GENKIN, 1971);

2. - The release of S through the breakdown of pyrite, reduction of pentlandite (to metallic iron) by hydrogen released during the serpentinization ($\text{FeS} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{S}$) and the breakdown of other Cu-Fe or Fe-Ni minerals (coupled with the release of Fe, Ni, Co and Cu) (RAMDOHR, 1967; CLARK & CLARK, 1968; CLARK, 1969; PAPUNEN, 1970).

Both processes are purported to be hydrothermal autometamorphic in character (SCHOLTZ, 1936; PANAGOS & RAMDOHR, 1965; GENKIN, 1971); according to GENKIN (1971) alkaline solutions play a role.

The formation of mackinawite is purportedly nucleated by the released Ni and Co; according to CLARK & CLARK (1968, p. 265): «In the great majority of natural occurrences... mackinawite has probably crystallized owing to its status as the only iron sulfide which

⁽¹⁾ Authors' insertions.

can accept considerable Ni (> 1 weight per cent) [and Co] into solid solution at low temperatures (50°C and below)...». The formation of mackinawite apparently requires more or less strongly reducing conditions and the presence of sulfur (with S-fugacities lower than those leading to the formation of troilite) (CHAMBERLAIN & DELABIO, 1965; CLARK & CLARK, 1968; CLARK, 1969).

As with mackinawite, the formation of valleriite may also be closely linked to serpentinization (intermediate and late stage serpentinization) of the host rock (ÖDMAN, 1933; PANAGOS & RAMDOHR, 1965; PAPUNEN, 1970; GENKIN, 1971). According to PANAGOS & RAMDOHR (1965) and PAPUNEN (1970) syn- or post-tectonic processes in the course of serpentinization play a definite role in its formation and its distribution; according to the latter author valleriite at Hitura, Finland apparently prefers tectonically disturbed parts of the serpentine host rock.

Chemistry.

Mackinawite.

Existing electron microprobe analyses of natural mackinawite show a general composition ranging from $(\text{Fe, Ni, Co, Cu})_{0.994}\text{S}$ to $(\text{Fe, Ni, Co, Cu})_{1.068}\text{S}$; our analyses provide a range of composition ranging from $(\text{Fe, Ni, Co, Cu})_{0.921}\text{S}$ for mackinawite from Balangero, Italy to $(\text{Fe, Ni, Co, Cu})_{1.025}\text{S}$ for mackinawite from Matooster, Transvaal (Table III). BERNER (1962, 1964) synthesized mackinawite with a range in composition from $\text{Fe}_{1.04}\text{S}$ to $\text{Fe}_{1.07}\text{S}$. Today, it is still debated whether the general formula for mackinawite should read $(\text{Fe, Ni, Co, Cu})_{1+x}\text{S}$ as first advocated by CLARK (1966/a and /b) or $(\text{Fe, Ni, Co, Cu})\text{S}$ as advocated by BERNER (1962, 1964), EVANS et al. (1962, 1964), TAKENO (1965), EVANS & ALLMANN (1967), and SPRINGER (1968). The first assumption would entail the implication that mackinawite and FeS (troilite) are not strictly polymorphs (CLARK, 1966 a, b; CLARK & CLARK, 1968); the second one, that mackinawite is a tetragonal polymorph of FeS (troilite) (EVANS & ALLMANN, 1967; SPRINGER & SCHACHER-KORN, 1967, cited by CLARK & CLARK, 1968). The range in composition, particularly, however, the variation in total metal content depicted in the microprobe analyses (Table III) suggests a degree of non-stoichiometry which may or may not be real (VAUGHAN, 1969). BERNER (1962), e.g., reported a metal to sulfur ratio for synthesized mackinawite of $\text{Fe}^{++} : \text{S} = 1.02 \pm 0.02$, but attributed the small ex-

cess of Fe to oxidation. Recently, TAYLOR & FINGER (1971) attempted to resolve the question of the non-stoichiometry of mackinawite by suggesting that deviations from stoichiometry in mackinawite may be accounted for by sulfur deficiency rather than a metal surplus and proposed the general formula FeS_{1-x} .

RAMDOHR (1967, p. 243) indicated the possibility of a sulfur deficient structure for mackinawite by writing: « It is... surprising to see that some layer lattice sulfides, such as mackinawite instead of pyrrhotite (which represents a small decrease in S-content), and valeriite... occur... in the above [serpentinized alpine peridotite] environment ».

KULLERUD (1967) indicates that mackinawite may not be a phase in the pure Fe-S system, implying that in order for mackinawite to crystallize, the presence of small quantities of Ni and/or Co in the mackinawite structure are required. This implication is refuted by the work of BERNER (1962, 1964) and the analytical results of CLARK & CLARK (1968) (See Table III). According to CLARK (1966 b, p. 335) «... it is evident that Ni, Co, (and Cu) are not essential constituents of naturally occurring mackinawite ».

CLARK & CLARK (1968) tentatively placed mackinawite in the Fe-S system with a stability field between 51,53 atomic % Fe and at temperatures below $135 \pm 5^\circ\text{C}$ at less than 1 atm. If one, however, takes the data of BERNER (1962, 1964), this field would have to be extended down to 50,98 atomic % and up to 51,69 atomic % Fe. At any rate, this tentative T-X plot is based on the general formula Fe_{1+x}S , i.e., on a cation: anion ratio consistently greater than unity. The available analytical data (Table III) do not conclusively support this formula, and therefore cannot support this T-X plot. Furthermore, the transformation temperature data of mackinawite determined by CLARK (1966 b) and used in this T-X plot as well as those determined by KOUVO et al. (1963), TAKENO (1965), PAPUNEN (1970), GENKIN (1971), and SARKAR (1971) actually do not reflect the upper stability limit of pure mackinawite, but instead reflect the breakdown of mackinawite in mackinawite-pyrrhotite-troilite (CLARK, 1966 b), mackinawite-chalcopyrite-cubanite (-sphalerite), mackinawite-chalcopyrite-pyrrhotite (-sphalerite), mackinawite-chalcopyrite-pyrrhotite-sphalerite, mackinawite-chalcopyrite (all TAKENO, 1965), and other mackinawite-sulfide assemblages (L. A. TAYLOR, person. communication) (see also « Mackinawite as a geologic thermometer »).

Valleriite.

Table IV shows the chemical composition of valleriite from various localities. The values for Mg, Fe, Ca, Ni, Mn, and Al obtained from the literature, where they are reported as oxides, were recalculated using the procedure outlined by EVANS & ALLMANN (1968). Magnesium, iron, calcium, nickel, manganese and cobalt were calculated as hydroxides from the brucite-group, i.e., as $\text{Mg}(\text{OH})_2 = \text{brucite}$, $\text{Fe}(\text{OH})_2$, $\text{Ca}(\text{OH})_2 = \text{portlandite}$, $\text{Ni}(\text{OH})_2$, $\text{Mn}(\text{OH})_2 = \text{pyrochroite}$, and $\text{Co}(\text{OH})_2$ (STRUNZ, 1970).

For iron this may appear at first to be somewhat questionable. EVANS & ALLMANN (1968) were the first to suggest that Fe^{+3} may substitute for Mg^{+2} in the brucite layer. SPRINGER (1968) was the first to suggest that Fe^{+3} enters the hydroxide sublattice as $\text{FeO}(\text{OH})$ or $\text{Fe}(\text{OH})_3$ replacing the Al^{+3} . In both cases the suggestions were made assuming that the overall composition for valleriite is $[\text{FeCuS}_2] \cdot 1.526[\text{Mg, Al, Fe}(\text{OH})_2]$, and that Al^{+3} can substitute for Mg^{+2} . Both assumptions, however, are questionable. EVANS & ALLMANN (1968) after making the following assertion (p. 87): « It is well known that trivalent aluminum ions cannot replace divalent magnesium ions in the brucite crystal structure to any appreciable extent », then go on to propose that « atom-for-atom substitution of Al^{+3} for Mg^{+2} in the $\text{Mg}(\text{OH})_2$ layer [brucite layer] can readily take place if the [resulting] excess positive charge is compensated by interleaving other layers [sulfide layers] with negative charge ». ALLMANN (1971) shows this mechanism of compensation in his valleriite formula $\sim [\text{Mg}_2\text{Al}(\text{OH})_6]^+ \cdot [(\text{Fe, Cu})_4\text{S}_4]^-$. A survey of all the valleriite analyses (see Table IV), however, shows that both formulas as proposed by EVANS & ALLMANN (1968) and ALLMANN (1971) are inconsistent with the range of composition found for valleriite, and are applicable only in those special cases where an atomic ratio of 2Mg : 1 Al is given, as for example at Kaveltorp. In most analyses, however, Al is only present in quantities insufficient to make the substitution mechanism feasible or is totally absent (see Plates 1 & 8 and Table IV). Whether Fe enters the hydroxide sublattice in the trivalent or divalent state is also still open to question. HARRIS et al. (1970) reported the occurrence of a « valleriite-type » mineral from Noril'sk, Siberia in which only Fe makes up the entire

hydroxide sublattice as $\text{Fe}(\text{OH})_2$. Indeed, the entrance of iron as Fe^{+2} into the hydroxide sublattice would actually conform more closely to the concept of EVANS & ALLMANN (1968) — according to which this sublattice is brucitic in composition — and to the crystal-chemical data of STRUNZ (1970).

Again in conformance with the crystal-chemical data of STRUNZ (1970), we chose to enter Al^{+3} in the valleriite structure as $\text{Al}(\text{OH})_3$, i.e., as gibbsite-bayerite, and Al was calculated accordingly.

Accepting that iron enters the valleriite structure as Fe^{++} and aluminium as Al^{+3} , the chemical analyses of valleriite (Table IV) indicate a general composition $[\text{CuFeS}_2] \cdot n [\text{Mg, Ca, Fe, Ni, Co, Mn}(\text{OH})_2] \cdot m [\text{Al}(\text{OH})_3]$, where $n = 1,14$ to $2,33$ ⁽²⁾ and $m = 0,00$ to $0,50$. The range in valleriite composition and the large number of cations which can enter the hydroxide sublattice indicated by the above formula clearly illustrates that a rigid formula cannot be applied to this mineral (compare also p. 291, Nb in valleriite).

Optical properties.

Mackinawite.

Table I shows the optical properties of mackinawite. Mackinawite under reflected light, in air, has a pale creamy pinkish-white (like pyrrhotite, but paler) (lightest position) to a light creamy gray with a light lila-pinkish tint (mauve gray) colour (like sphalerite, but lighter) (darkest position). Under oil immersion the colours remain essentially the same, and are only slightly darker from a bright pale creamy pink with a lila tint (much lighter than pyrrhotite) (lightest position) to a creamy gray with a pink-lila tint (much lighter than sphalerite) (darkest position). Its bireflectance is generally high, the reflectivity changing from about $42,1 \pm 2\%$ ($\sim R_E$) to $26,4 \pm 3\%$ ($\sim R_0$). The mineral is very highly anisotropic. In air, under reflected light, and with Nicols \pm , its colours range from a bright pale whitish yellow (more whitish than valleriite) to a light greenish blue (almost aquamarine). Under oil immersion the colours change from a bright whitish yellow (very pale lemon yellow) to greenish blue (almost aquamarine). The

⁽²⁾ The value $n = 0,89$ reported by BLOMSTRAND (1870, etc.) and RAMDOHR & ÖDMAN (1932) is not considered because of the reported presence of K_2O and Na_2O .

colour change, under Nicols \pm , from a bright pale whitish yellow to a light greenish blue is characteristic for mackinawite only, providing a diagnostic criterium to differentiate it optically from valleriite (CHAMBERLAIN & DELABIO, 1965). Also, in its brightest position, with the Nicols \pm , mackinawite has a lemon yellow tint; valleriite has a brownish-orange tint. The hardness of mackinawite is \cong pentlandite, \geq pyrrhotite, and $>$ chalcopyrite. Undulatory extinction is common.

Valleriite.

Table II shows the optical properties of valleriite. Valleriite under reflected light, in air, varies in colour. This variability is particularly prevalent at Laxia tou Mavrou and Hellenic Mining, Cyprus. Generally, the colour changes from a creamy gray (darker than sphalerite) to a yellow-brown or brown-yellow (lightest position). Under oil immersion the colour varies considerably. Valleriite is highly anisotropic, its reflectivity ranging from $17 \pm 1,5\%$ ($\sim R_E$) to $12,5 \pm 1,5\%$ ($\sim R_O$). Its bireflectance is very high, the colours changing from a bright whitish yellow to a pale bluish green, in air and with the Nicols \pm . Under oil immersion the colour ranges from a bright whitish yellow to a dark blackish-bluish gray (similar to sphalerite). Its hardness is $<$ chalcopyrite and \ll pyrrhotite. Undulatory extinction is frequent.

Ore microscopic observations.

SALAMANCA (ARGENTINA).

The paragenesis consists essentially of pyrrhotite, cubanite, chalcopyrite and sphalerite. The pyrrhotite contains small grains of pentlandite and occurs predominantly as large plates; subordinately as small grains along the cubanite/pentlandite borders and as spindles in cubanite. Sometimes the pyrrhotite shows deformation patterns and subsequent recrystallization (Fig. 1 *a*). The cubanite occurs as spindles and also as flame-like bodies associated with mackinawite in chalcopyrite. Traces of valleriite along the borders chalcopyrite-gangue are also present. Fractured, elongated crystals of a gangue mineral show cementation of the fractures by chalcopyrite, mackinawite, valleriite and sphalerite. One small flake of molybdenite was observed in pyrrhotite.

Mackinawite is very abundant and shows the following distribution:

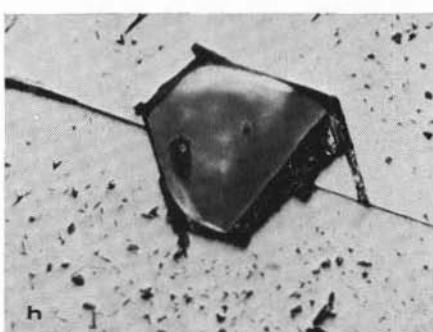
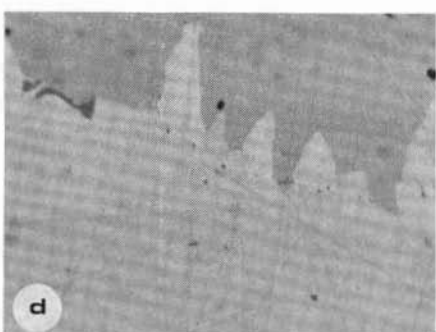
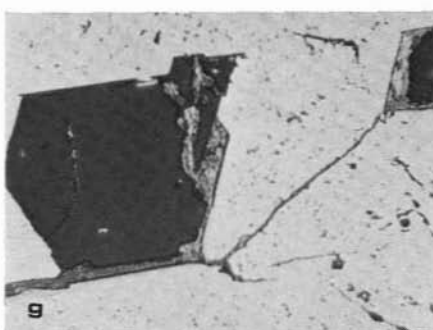
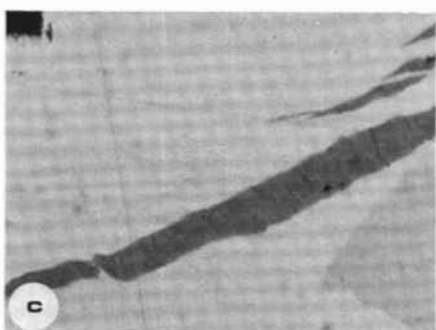
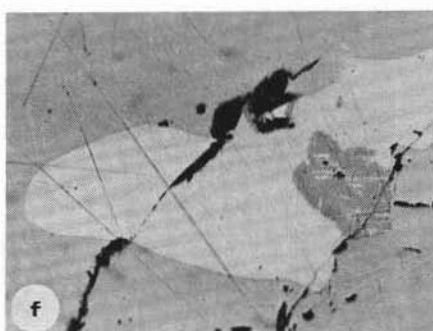
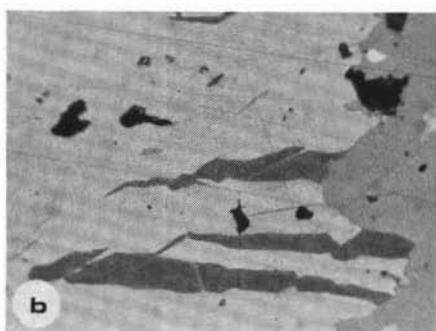
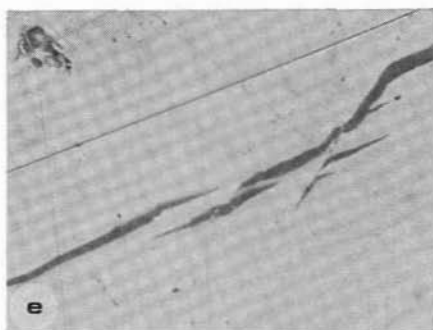
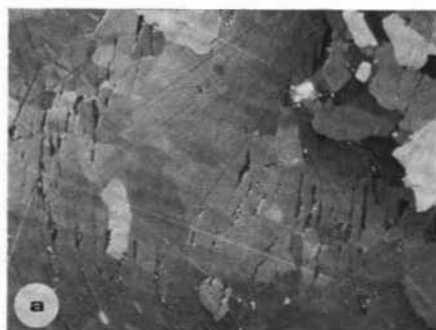
- in chalcopyrite, along the border pyrrhotite-chalcopyrite (Fig. 1 *b*);
- in chalcopyrite, along the border cubanite-chalcopyrite (Fig. 1 *c*);
- in cubanite, along the border cubanite-chalcopyrite (Fig. 1 *d*);
- in chalcopyrite exsolved (?) in sphalerite;
- as spindles in chalcopyrite (Fig. 1 *e*).

LAXIA TOU MAVROU AND HELLENIC MINING, CYPRUS.

The paragenesis of these two localities has been described in detail by ANTUN et al. (1966). At Laxia tou Mavrou it includes predominantly (in order of decreasing frequency) pyrrhotite, chalcopyrite, cubanite, mackinawite, pentlandite, and valleriite, with bravoite, chrome-spinel, oregonite, magnetite, maucherite?, limonite, gold, and graphite in subordinate quantities; gangue minerals include serpentine, talc?, and ankerite. At Hellenic Mining the paragenesis consists again predominantly of cubanite, valleriite, chalcopyrite, pyrrhotite, pentlandite, and mackinawite (in order of decreasing frequency), with «chromite», magnetite, oregonite, maucherite, linnaeite (i.e., violarite), a Co-Ni-ar-

Fig. 1.

- a) Deformed and partly recrystallized pyrrhotite. Right upper corner: chalcopyrite. Salamanca, Argentina. Nicols \pm , oil immersion, 180 \times .
- b) Mackinawite (dark) ending against pyrrhotite (gray) in chalcopyrite (light gray). Some pentlandite (white) in pyrrhotite. Black: holes. Salamanca, Argentina. Parallel Nicols, oil immersion, 635 \times .
- c) Mackinawite (dark) ending against cubanite (gray) in chalcopyrite (light gray). Salamanca, Argentina. Parallel Nicols, oil immersion, 480 \times .
- d) Mackinawite (very light gray) in cubanite (gray) at the border with chalcopyrite (light gray). Salamanca, Argentina. Parallel Nicols, oil immersion, 480 \times .
- e) Mackinawite spindles (dark) in chalcopyrite (light). Salamanca, Argentina. Parallel Nicols, oil immersion, 480 \times .
- f) Chalcopyrite (almost white) and chalcopyrrhotite (gray, with chalcopyrite inclusions) in pyrrhotite (light gray). Matooster, Transvaal. Parallel Nicols, oil immersion, 200 \times .
- g) Vallerite replacing spinel in magnetite. Dark gray: spinel; white with pores: magnetite; white to grayish white around spinel crystals: valleriite (see also Plate 4). Loolekop, Transvaal. Parallel Nicols, oil immersion, 180 \times .
- h) Valleriite (dark) replacing baddeleyite (dark gray, showing internal reflections) in magnetite (white). Loolekop, Transvaal. Parallel Nicols, oil immersion, 575 \times .



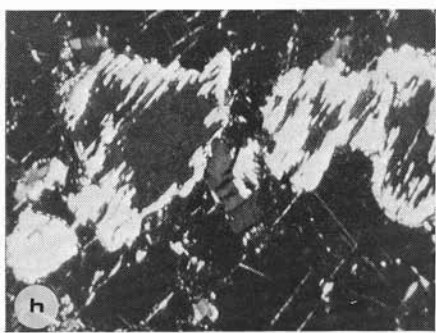
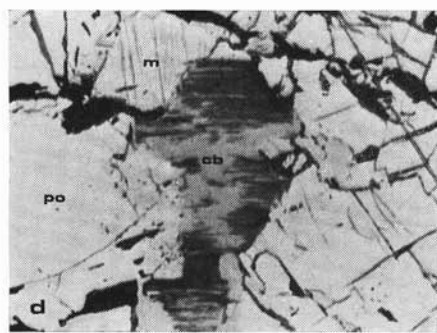
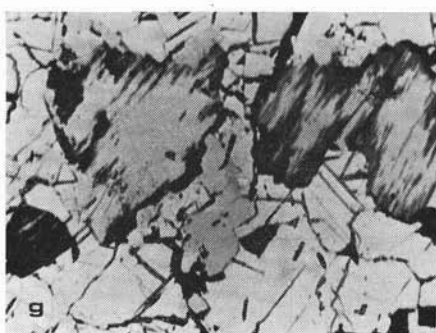
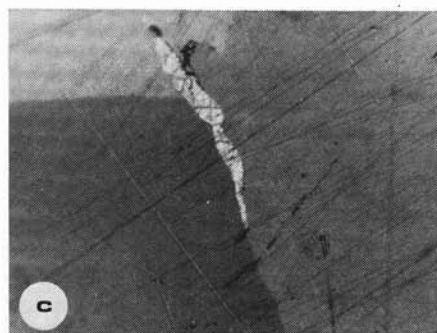
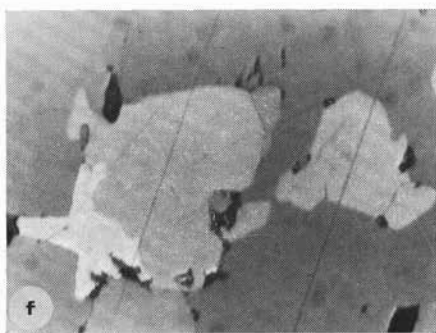
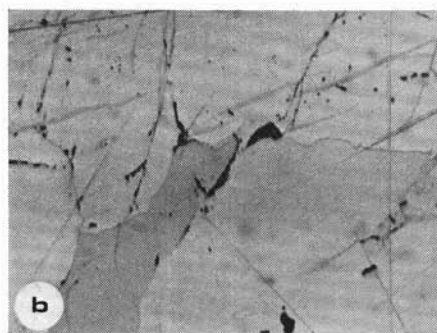
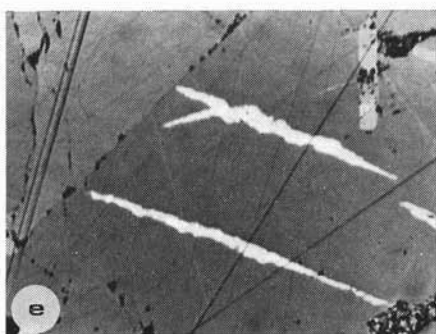
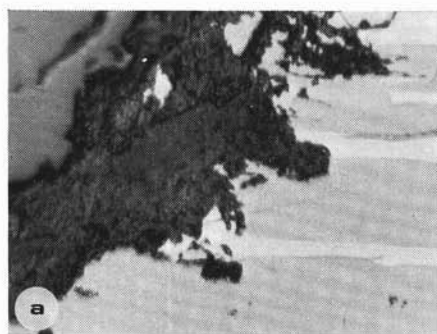
senide, a Co-arsenide, sphalerite, niccolite, gersdorffite, ilmenite, gold, gold-cuprite, rutile, molybdenite, millerite, heazlewoodite, two platinoid minerals, bornite, chalcocite, pyrite, and covellite in subordinate quantities; gangue minerals include serpentine, chlorite, calcite, lievrite, and saponite or talc.

The ores in both localities show considerable deformation, resulting in the cataclasis of pyrrhotite, chalcopyrite (along the cubanite lamellae), pentlandite, oregonite, and niccolite; the development of pressure lamellae in pyrrhotite and mackinawite, of undulatory extinction in pyrrhotite and cubanite, and of the pseudocleavage of pyrrhotite // (0001), and the partial recrystallization of pyrrhotite.

At Laxia tou Mavrou, mackinawite occurs predominantly within the chalcopyrite and pentlandite. At Hellenic Mining, the mackinawite occurs in cubanite as an exsolution product (Fig. 2 *e*), in chalcopyrite as an exsolution product // (001), in pentlandite as a decomposition product with the basal plate // (001, 010, 100) (Fig. 3 *e*), and in pyrrhotite along the border pyrrhotite/pentlandite (Fig. 2 *f*).

Fig. 2.

- a*) Mackinawite spindles (medium gray) along chalcopyrite (white gray) - cubanite (light gray) grain boundaries, and valleriite (dark gray) replacing cubanite, chalcopyrite and magnetite (medium gray). Kaveltorp, Sweden. Parallel Nicols, oil immersion, 430 \times .
- b*) Pyrrhotite (gray, showing pleochroism) and cubanite (white gray) with spindles of pyrrhotite. Kaveltorp, Sweden. Parallel Nicols, oil immersion, 635 \times .
- c*) Mackinawite spindle (white gray) between two cubanite grains (medium and dark gray); light gray: chalcopyrite. Kaveltorp, Sweden. Nicols \pm , oil immersion, 200 \times .
- d*) Valleriite (dark) in cubanite (*cb*), mackinawite (*m*) in chalcopyrite, pyrrhotite (*po*) and gangue veins (black). Hellenic Mining, Cyprus. Parallel Nicols, oil immersion, 260 \times .
- e*) Mackinawite spindles in cubanite, lath of chalcopyrite, some valleriite. Hellenic Mining, Cyprus. Nicols \pm , oil immersion, 285 \times .
- f*) Pentlandite grains (light medium gray), one with mackinawite (white gray) in pyrrhotite (medium gray). Hellenic Mining, Cyprus. Nicols \pm , oil immersion, 285 \times .
- g*) Valleriite (dark gray) replacing cubanite (light gray) from grain boundary, in chalcopyrite matrix. Some pyrrhotite and mackinawite are also present. Hellenic Mining, Cyprus. Parallel Nicols, oil immersion, 260 \times .
- h*) Idem, Nicols \pm , oil immersion.



Valleriite occurs at Laxia tou Mavrou in the following manner:

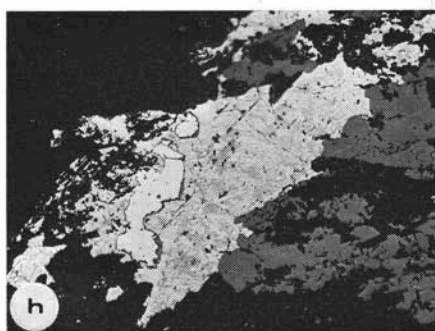
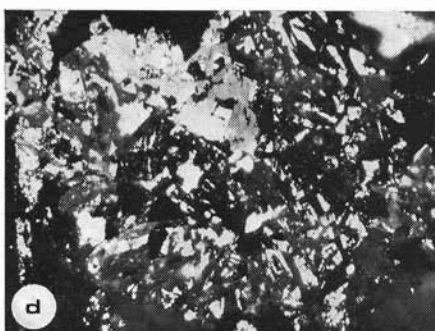
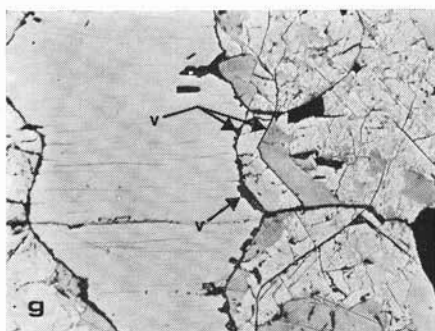
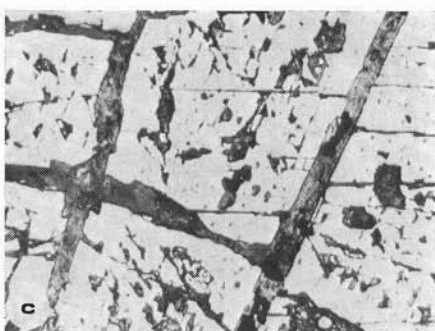
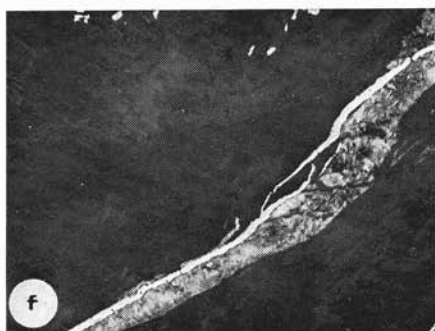
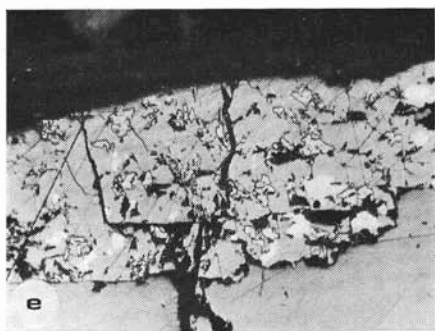
1. in chalcopyrite within fractures, in part oriented with (0001) // (111) of chalcopyrite;
2. in chalcopyrite replacing lamellar cubanite, oriented with (0001) // (111);
3. in chalcopyrite, along the border with FeS, CuFeS₂, chromite, magnetite, and gangue minerals;
4. in cubanite, replacing it selectively along the border;
5. in pyrrhotite, within fractures \perp (0001) with the (0001) of valleriite // to the (0001) of pyrrhotite;
6. in magnetite within fractures, similar to that found at Loolekop, Transvaal and White Horse, Yukon;
7. along sulfide grain boundaries embedded in serpentine.

At Hellenic Mining, valleriite occurs as follows:

1. in chalcopyrite as an exsolution product // (111) of chalcopyrite;
2. in chalcopyrite replacing lamellar cubanite;
3. in chalcopyrite through non-oriented replacement;
4. in pyrrhotite within fractures and through non-oriented edgewise (rim) replacement;

Fig. 3.

- a) Pyrrhotite decomposing into «intermediate products» + magnetite; at the boundary pyrrhotite-gangue (black), some valleriite (gray), sphalerite (*s*) and chalcopyrite (white). Saxberget, Sweden. Parallel Nicols, oil immersion, 200 \times .
- b) Valleriite replacing chalcopyrite (white) at the border chalcopyrite-gangue (black). Some sphalerite (distinct gray) is present. Saxberget, Sweden. Parallel Nicols, oil immersion, 200 \times .
- c) Valleriite (gray) in fractures and holes in magnetite (white gray). White Horse, Yukon. Parallel Nicols, oil immersion, 180 \times .
- d) Valleriite (very white or black in the center) replacing dolomitic gangue (see also Plate 9). White Horse, Yukon. + Nicols, oil immersion, 180 \times .
- e) Pentlandite with mackinawite inclusions (like Balangero) // (001)[?], in a pyrrhotite-gangue matrix. Hellenic Mining, Cyprus. Nicols \pm , oil immersion, 200 \times .
- f) Valleriite veinlet (gray) with chalcopyrite (white) in the serpentine matrix. Balangero, Piedmont. Parallel Nicols, 170 \times .
- g) Pyrrhotite (whitish gray), pentlandite (white) and mackinawite (gray). Some valleriite (*v*). Balangero, Piedmont. Parallel Nicols, 250 \times .
- h) Magnetite (dark gray), pentlandite (light gray) and mackinawite (gray), native Ni-Fe (white). Some valleriite is also present. Black: gangue. Balangero, Piedmont. Parallel Nicols, 95 \times .



5. in pyrrhotite through replacement of chalcopyrite lamellae;
6. in cubanite through oriented replacement along the grain boundaries, in part through decomposition and oxidation ($\text{CuFeS}_2 + \text{Fe}_3\text{O}_4 + \text{valleriite}$);
7. in pentlandite within fractures (pseudocleavage) // (111);
8. replacing mackinawite.

LITTLE CHIEF ORE BODY, NEW IMPERIAL MINE, WHITE HORSE, YUKON.

The paragenesis consists essentially of magnetite, valleriite, bornite, chalcocite and wittichenite. Valleriite occurs predominantly in fractures within the magnetite (Fig. 3 *c*). Its form of occurrence and optical properties are similar to those of Loolekop. Frequently it also replaces the gangue minerals (Fig. 3 *d* and Plate 9).

RAMMELSBERG, HARZ, WEST GERMANY.

The paragenesis consists of sphalerite, galena, pyrite, chalcopyrite, marcasite, pyrrhotite, magnetite, tetrahedrite, bournonite, jamesonite, boulangerite, and barite. Less common are: arsenopyrite, nat. bismuth, bismuthinite, linnaeite, nat. gold, gudmundite, cubanite, molybdenite, kobellite, electrum, freibergite, mackinawite, and wolframite. The most common gangue minerals include quartz, calcite, and dolomite.

The mackinawite is closely associated with chalcopyrite and pyrrhotite. It is frequently idiomorphic to subidiomorphic and often shows twinning (Fig. 4). Apparently its formation resulted largely through primary crystallization; little or none resulted through the replacement of other sulfides.

MATOOSTER (TRANSVAAL).

The mineralization at Matooster is liquid-magmatic to pegmatitic according to RAMDOHR (1969). The observed paragenesis includes principally pyrrhotite, pentlandite and chalcopyrite. The pyrrhotite contains numerous flame-like exsolution bodies of pentlandite, and

Fig. 4. — Mackinawite (twinned, yellowish white and brown), kobellite (blue-gray), pyrite (gray) in chalcopyrite matrix. Rammelsberg, Goslar/Harz. + Nicols, oil immersion, 910 ×.

Figs. 5 and 6. — Mackinawite (yellowish white and blue) and valleriite (bluish-greenish gray and creamy yellow) in chalcopyrite + pyrrhotite matrix. Hellenic Mining, Cyprus. Nicols ±, oil immersion, 665 ×.



Fig. 4.

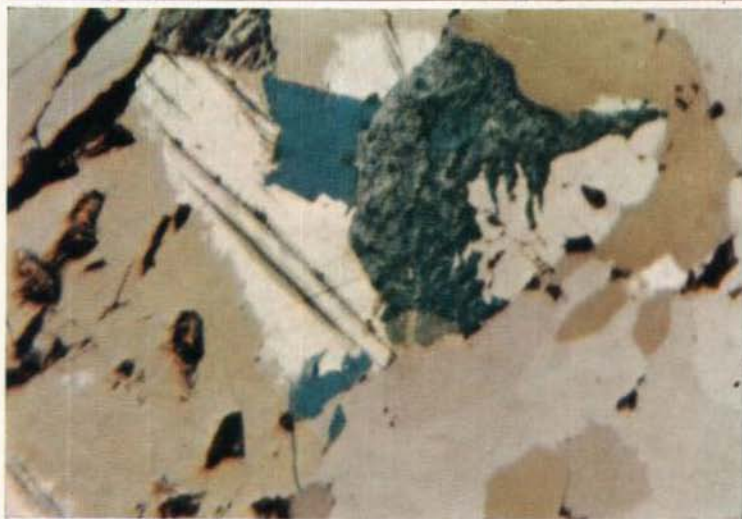


Fig. 5.



Fig. 6.

shows rim alteration into « intermediate products ». Single large grains of pentlandite show alteration to bravoite. Chalcopyrrhotite with oriented inclusions of chalcopyrite was also observed (Fig. 1 *f*). The mackinawite observed here occurs only in chalcopyrite, in part along the borders chalcopyrite/pentlandite. Traces of valleriite are also observed.

LOOLEKOP (PALABORA, TRANSVAAL).

Valleriite occurs predominantly in fractures within the magnetite. It also replaces gangue minerals, such as spinel (Fig. 1 *g*) and baddeleyite (Fig. 1 *h*).

ERETRIA (GREECE).

The paragenesis consists essentially of chromite, spinel, magnetite and valleriite. Small relicts of magnetite, pentlandite and chalcopyrite occur within the valleriite. The valleriite occurs in association with magnetite and a flaky gangue mineral.

KAVELTORP (SWEDEN).

The ore deposit of Kaveltorp belongs to the pyrite-chalcopyrite group and is weakly metamorphosed according to RAMDOHR (1969). The observed paragenesis includes mainly cubanite, valleriite, magnetite, chalcopyrite, sphalerite and pyrrhotite. Valleriite is very abundant and apparently replaces chalcopyrite (Fig. 2 *a*), cubanite, sphalerite and magnetite. The valleriite occurs mainly around gangue mineral grains, frequently rhythmic and in common association with a flaky gangue mineral. Magnetite occurs as large subrounded grains and as relicts within the valleriite. Pyrrhotite is observable subordinately as spindles in cubanite near the border cubanite/pyrrhotite (Fig. 2 *b*). Mackinawite was also observed and occurs 1) in chalcopyrite along the boundary cubanite-chalcopyrite and between recrystallized cubanite grains (Fig. 2 *c*) and 2) as spindles in chalcopyrite. Some digenite and covellite were found as alteration products in the valleriite-chalcopyrite assemblage.

SAXBERGET (SWEDEN).

The paragenesis includes principally sphalerite, chalcopyrite, pyrrhotite, valleriite, magnetite and galena. The pyrrhotite shows alteration in pyrite and « alteration products », plus magnetite (Fig. 3 *a*).

Chalcopyrite frequently occurs as rims along the boundaries sphalerite-pyrrhotite. Sphalerite is often present as spindles in the chalcopyrite. Valleriite apparently replaces chalcopyrite (Fig. 3 *b*) and pyrrhotite; occasionally it occurs together with magnetite in rims along the sphalerite-gangue or chalcopyrite-gangue boundaries.

BALANGERO (PIEDMONT, ITALY).

The paragenesis includes predominantly magnetite, pentlandite, mackinawite and valleriite. The magnetite is disseminated in patches and nebulitic masses within the serpentine matrix. The pentlandite occurs commonly associated with mackinawite and minor amounts of pyrrhotite and valleriite (Fig. 3 *g*). Two varieties of pentlandite are present, one of which appears to be more yellowish in colour than the other variety under reflected light. According to ZUCCHETTI (1968) this more yellowish pentlandite is a cobalt-rich variety. The mackinawite occurs as irregular patches and fine intergrowths frequently oriented along the crystallographic directions (111) of the pentlandite.

The valleriite forms very small veinlets, on the order of 0,05 mm in thickness, in part associated with chalcopyrite along the rims of the veinlets (Fig. 3 *f*). Valleriite is also present in minor amounts in the pentlandite-mackinawite-pyrrhotite assemblage (Fig. 3 *g*), where native nickel-iron is also present (Fig. 3 *h* and Plate 10). Plate 10 shows a series of scanning pictures, substantiating the presence of Ni, Fe, Co and a trace of Cu in the native Ni-Fe assemblage.

Mackinawite as a Geologic Thermometer.

ÖDMAN (1933) stated that the association and textural relationship of mackinawite with cubanite (mackinawite ends abruptly against cubanite) points to a temperature of formation below 450°C.

SCHOLTZ (1936, p. 172) concluded the following with regard to the formation temperature of mackinawite: « it appears to have developed in the interval which elapsed between the segregation of lamellar cubanite (450°C) and the precipitation of minerals like niccolite, bornite and chalcocite ».

RENSBURG & LIEBENBERG (1967) favor the origin of mackinawite through exsolution from pentlandite and chalcopyrite below 580°C.

RAO & RAO (1968) observed that mackinawite exsolved later than exsolved orthorhombic cubanite and therefore must have exsolved at a temperature much lower than 213°C (KULLERUD, 1967).

CLARK (1969) through analogy with a chromian tetragonal iron sulfide (Cr to Fe atomic ratio = 0,6 to 1,1) formed through the corrosion of chromium steel by hot H₂S at a temperature of 375°C intimates a formation temperature of chromian mackinawite well below 375°C.

TAKENO (1965) first attempted the use of mackinawite as a geologic thermometer by relating the compositional variation to the transformation temperature of mackinawite in mackinawite-sulfide assemblages (henceforth referred to as the «transformation temperature of mackinawite» ⁽³⁾ - see p. 289) determined in heating experiments. In contrast to later authors — who rely on the variation in the Ni, Co (and Cu) content — he chose to relate the transformation of mackinawite to its Fe-content (in wt. %), i.e., to the Fe-S ratio in its inner structure.

CLARK (1966 a, b) was the first to relate the transformation temperature of mackinawite to the Ni, Co (and Cu) content, i.e., to the Fe-Ni+Co(+Cu) ratio.

Heating experiments carried out by KOUVO et al. (1963), TAKENO (1965), CLARK (1966 a, b), PAPUNEN (1970), GENKIN (1971), and SARKAR (1971) revealed an upper stability limit for mackinawite or transformation temperature ranging from $\sim 135^{\circ} \pm 5^{\circ}\text{C}$ to $\sim 250^{\circ} \pm 50^{\circ}\text{C}$ (see Table V).

Fig. 7 shows the relationship of the transformation temperature of mackinawite to both the Fe(+Cr) content (in atomic %) and the Ni + Co(+Cu) content (in atomic %) based on the data provided in Table V. In contrast to TAKENO (1965) who used weight %, we chose atomic % as it 1) more clearly relates the role played by all of the cations in the mackinawite composition and structure, 2) automatically adjusts all analyses to 100 atomic %, and 3) allows us to directly plot Fe(+Cr) and Ni + Co(+Cu) against temperature on the same graph; the problem of the non-stoichiometry is reflected in the graph.

⁽³⁾ In the literature the terms breakdown temperature and (upper) stability limit are also used.

Recalculating the cation weight % to atomic % provided some difficulty with the mackinawite analyses from Kôtori, Kawayama, and Muskox as the published analyses only provided information on the cation fraction. The analyses for Komori and Muskox were recalculated

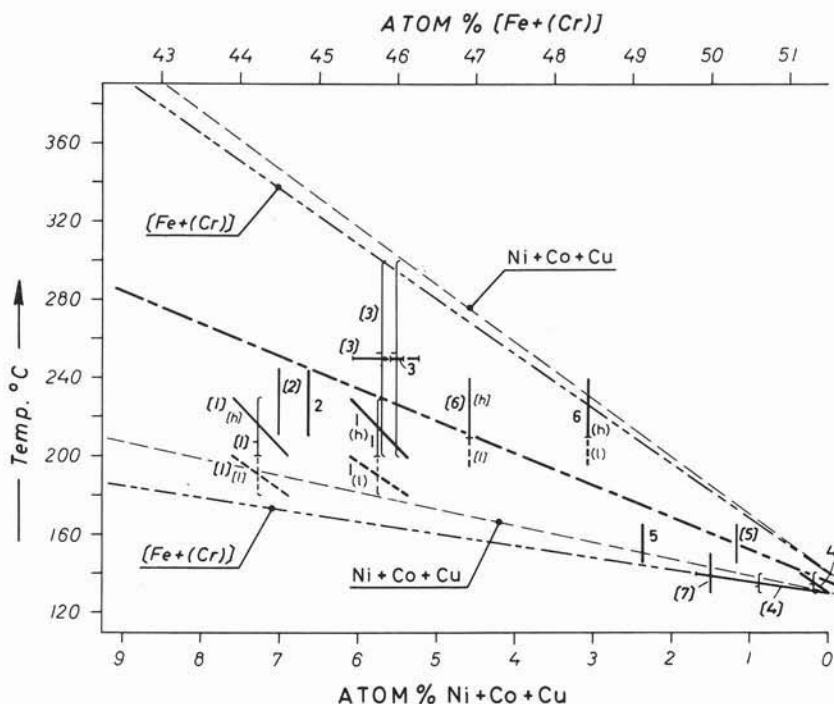


Fig. 7. — Tentative curve showing the relationship between determined transformation temperatures and the Ni + Co + Cu and Fe + (Cr) content of mackinawite in mackinawite-sulfide assemblages.

accepting a cation-anion ratio of 1:1 (TAKENO, 1965; CHAMBERLAIN & DELABIO, 1965). The analysis for Kawayama was recalculated accepting 1) that Ni, Co, and Cu are absent or that the content of these cations is negligible (TAKENO, 1965; CLARK, 1966 b), 2) a 58 weight % Fe-fraction (TAKENO, 1965, Fig. 8) and 3) a Fe-S ratio of 1:1. The plotting of the transformation temperatures of the various mackinawites from Kôtori and Kawayama (Japan), Outokumpu, Hitura, and Ylöjärvi

(Finland), Machinaw (Washington, U.S.A.), and MuskoX (Canada) against the atomic % of both Ni+Co(+Cu) and (Fe+Cr) reveals that the upper stability limit of mackinawite increases markedly with increasing substitution of Fe(+Cr) by Ni, Co (and Cu), e.g. from $\sim 135^\circ \pm 5^\circ\text{C}$ at $\sim 51,5$ atomic % Fe(+Cr) and zero (0) atomic % Ni + Co + Cu to $\sim 285^\circ \pm 100^\circ\text{C}$ at $\sim 42,5$ atomic % Fe(+Cr) and ~ 9 atomic % Ni + Co + Cu.

Although the quantity of Ni, Co, and Cu that can enter into solid solution increases in general with increasing temperature, this quantity is to some extent also determined by the availability of those elements as well as by other physico-chemical conditions (CLARK, 1966 b, 1967, 1969). TAYLOR (person. commun.), e.g., reports a decrease in the transformation temperature of mackinawite within mackinawite-sulfide assemblages with increasing S-fugacities during heating experiments.

TAKENO (1965) intimated that the range of mackinawite transformation temperatures for each locality, listed in Table V, is indicative of a dependency of the transformation temperature on the duration of the heating. This, in turn, may indicate that the lower transformation temperatures obtained from Fig. 7 are more realistic geologically because of the time factor involved.

With transformation, the mackinawite in the assemblage is apparently converted to hexagonal pyrrhotite and troilite (KOUVO et al., 1963; TAKENO, 1965; CLARK, 1966 b; GENKIN, 1971; SARKAR, 1971).

The transformation temperature of Valleriite.

According to TAKENO (1965), the transformation temperature of valleriite is $\geq 500^\circ\text{C}$; upon transformation, the valleriite is converted to a phase the X-ray powder-diffraction patterns of which show some identity with those of β -chalcopyrite.

YUND & KULLERUD (1966) place the transformation temperature of valleriite at $\geq 450^\circ\text{C}$, the transformation resulting in its conversion to chalcopyrite, water and one or more Mg, Al-bearing phases.

IISHI et al. (1970) placed the transformation temperature of valleriite at somewhere between 600° and 650°C .

PLATES 1-5.

Microprobe Scanning Pictures

1. - Saxberget, Sweden - Valleriite replacing chalcopyrite in serpentine. The sample current (S.C.) picture clearly shows the fabric of the valleriite oriented with the long direction \perp to the surface of the chalcopyrite. The scanning pictures show the presence of Mg and Si along with Cu, Fe and S. The replacement boundary is very irregular. 14 μ / #
2. - Balangero, Piedmont - Valleriite veinlet in silicate matrix. Besides Fe, Cu and S, the scanning pictures show the presence of Ni, Mg, Al and a trace of Cr. At the bottom right corner the valleriite is bordered by a veinlet of chalcopyrite. 12 μ / #
3. - Balangero, Piedmont - The top left picture shows the disposition of the mackinawite and associated minerals. Ni shows a strongly differentiated distribution, whereas Co appears not to have been affected by any mobilization. Cu shows a very irregular distribution with mobilization along fractures. 18 μ / #
4. - Loolekop, Transvaal - Valleriite replacing an idiomorphic spinel crystal (in part observable in Fig. 1g) in magnetite. The S.C. picture shows that the replacement occurs in part along the imperfect cleavage direction (111) of the spinel. The valleriite contains Fe, Cu, S, Mg and Al; the latter two were derived from the breakdown of the spinel. 12 μ / #
5. - Loolekop, Transvaal - Valleriite replacing spinel in a magnetite matrix. The scanning pictures again reveal a replacement in part along the imperfect cleavage direction (111); the replacement front is irregular. The scanning pictures for Ca, Nb and O point the presence of a calcium niobate inclusion. 13 μ / #

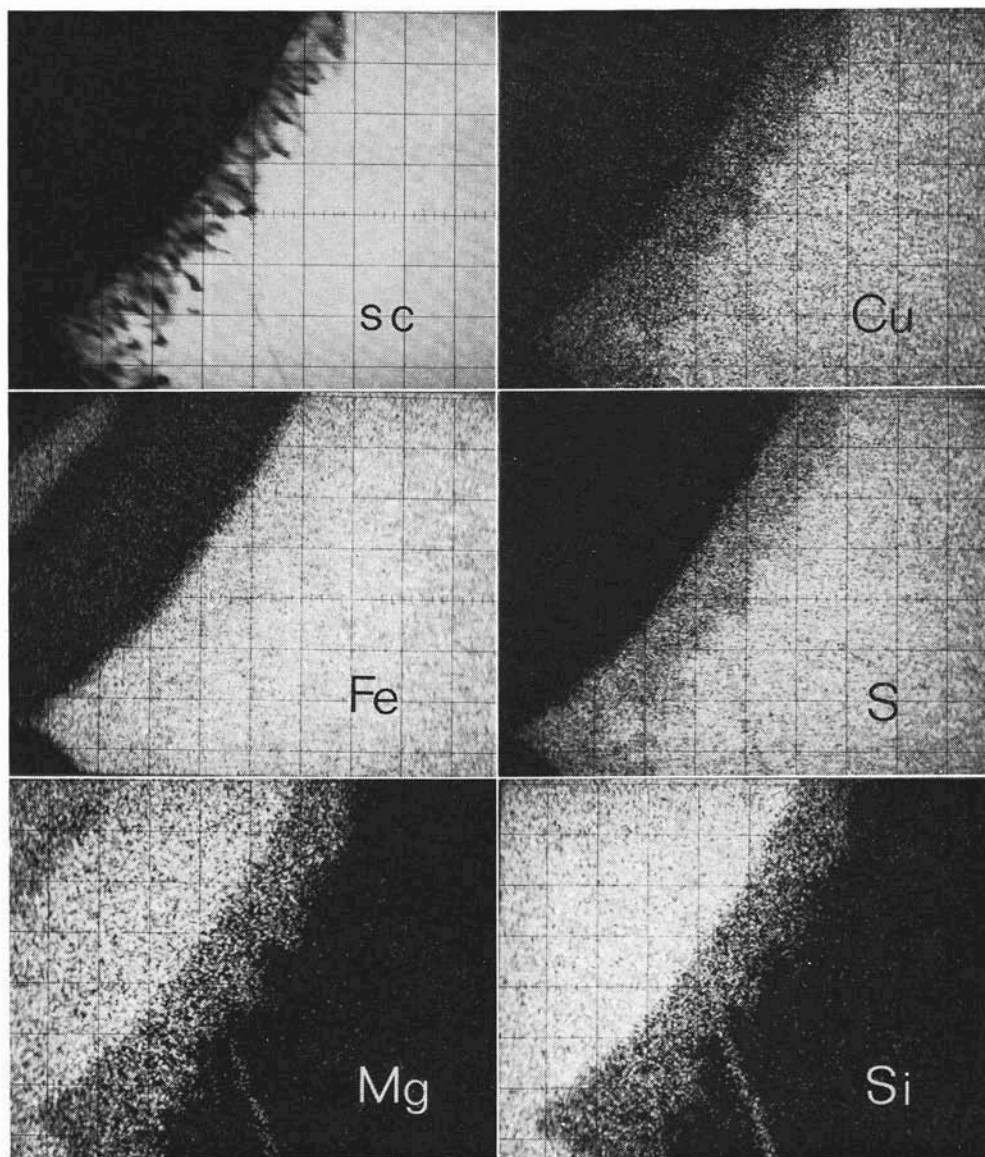


PLATE 1.

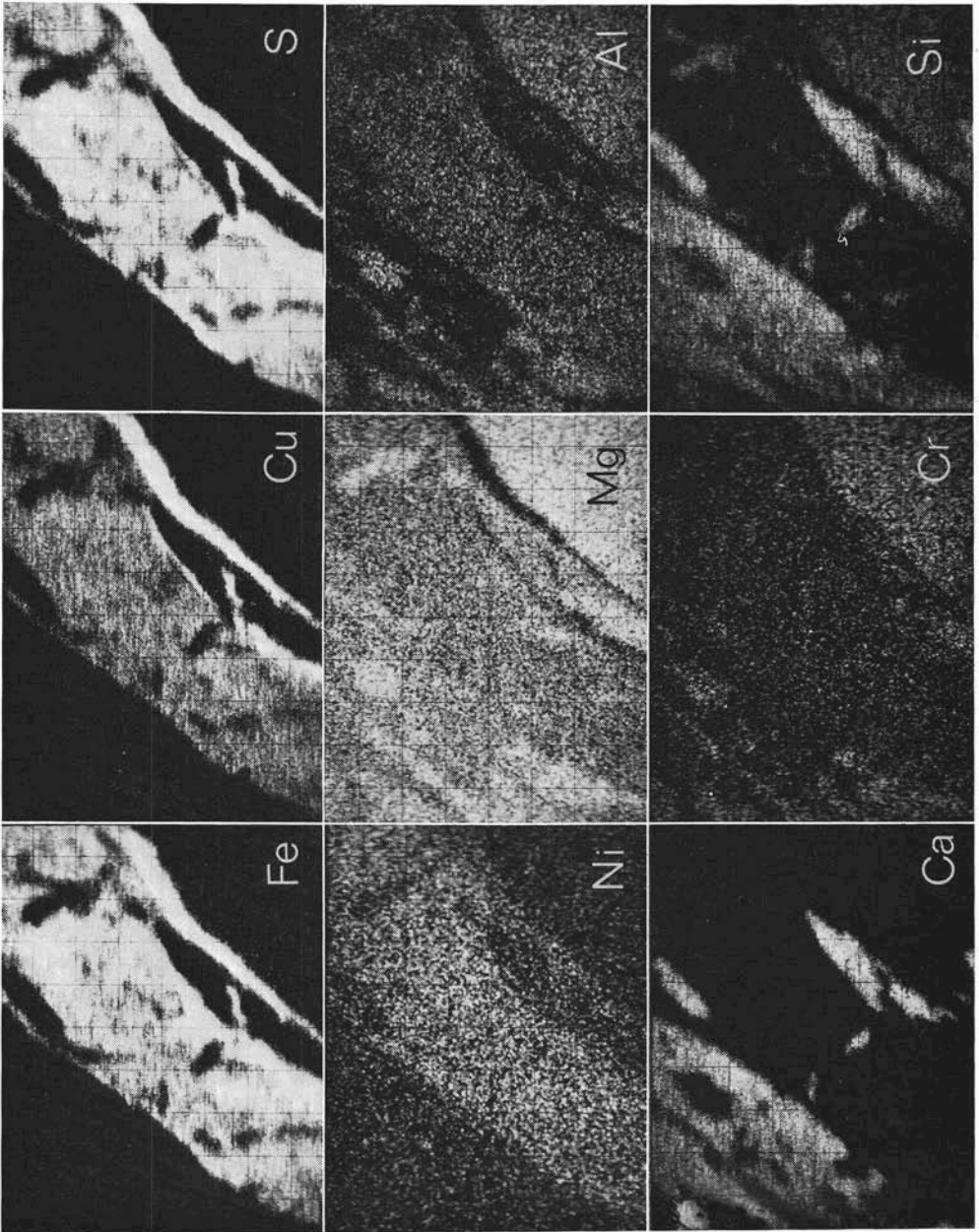


PLATE 2.

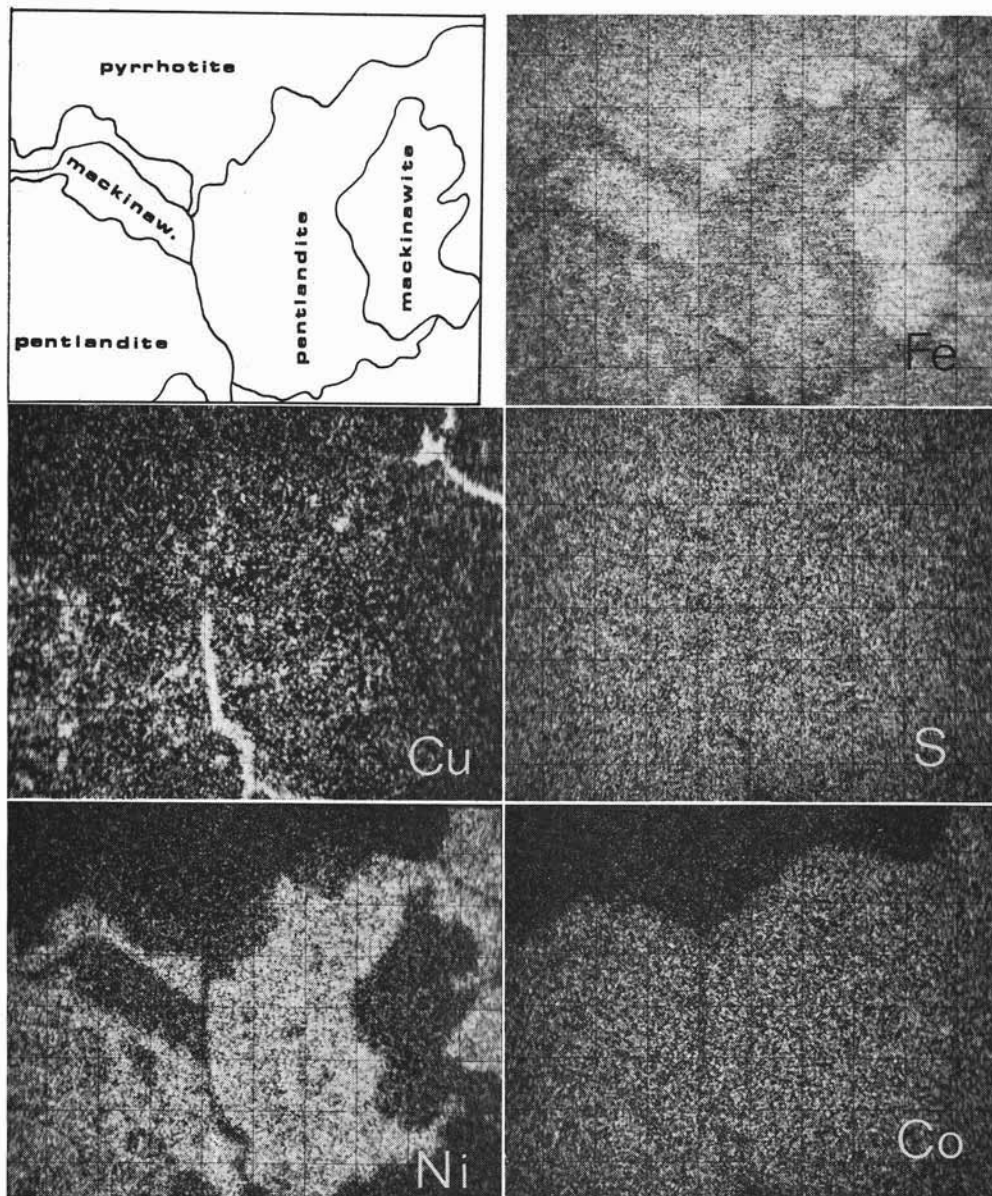


PLATE 3.

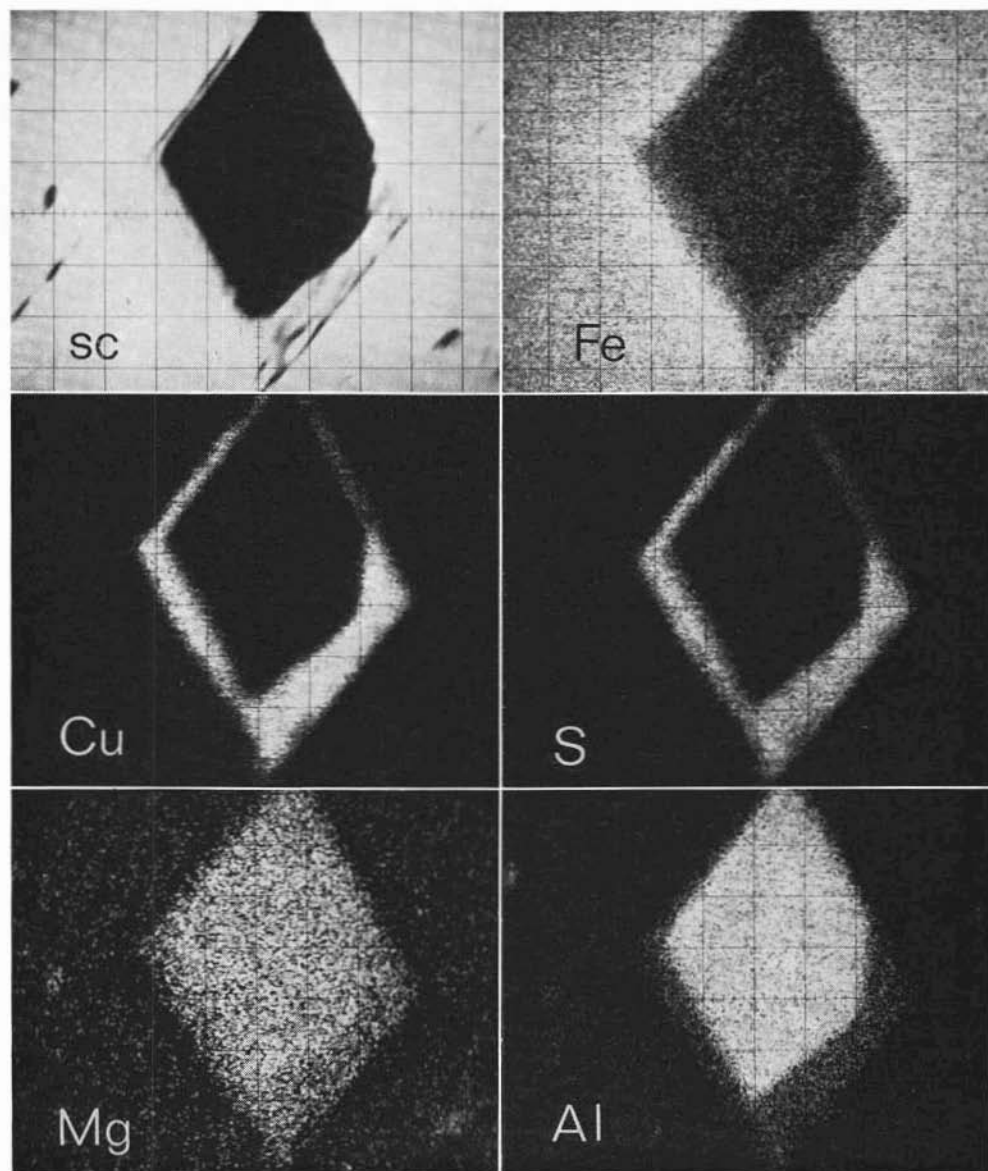


PLATE 4.

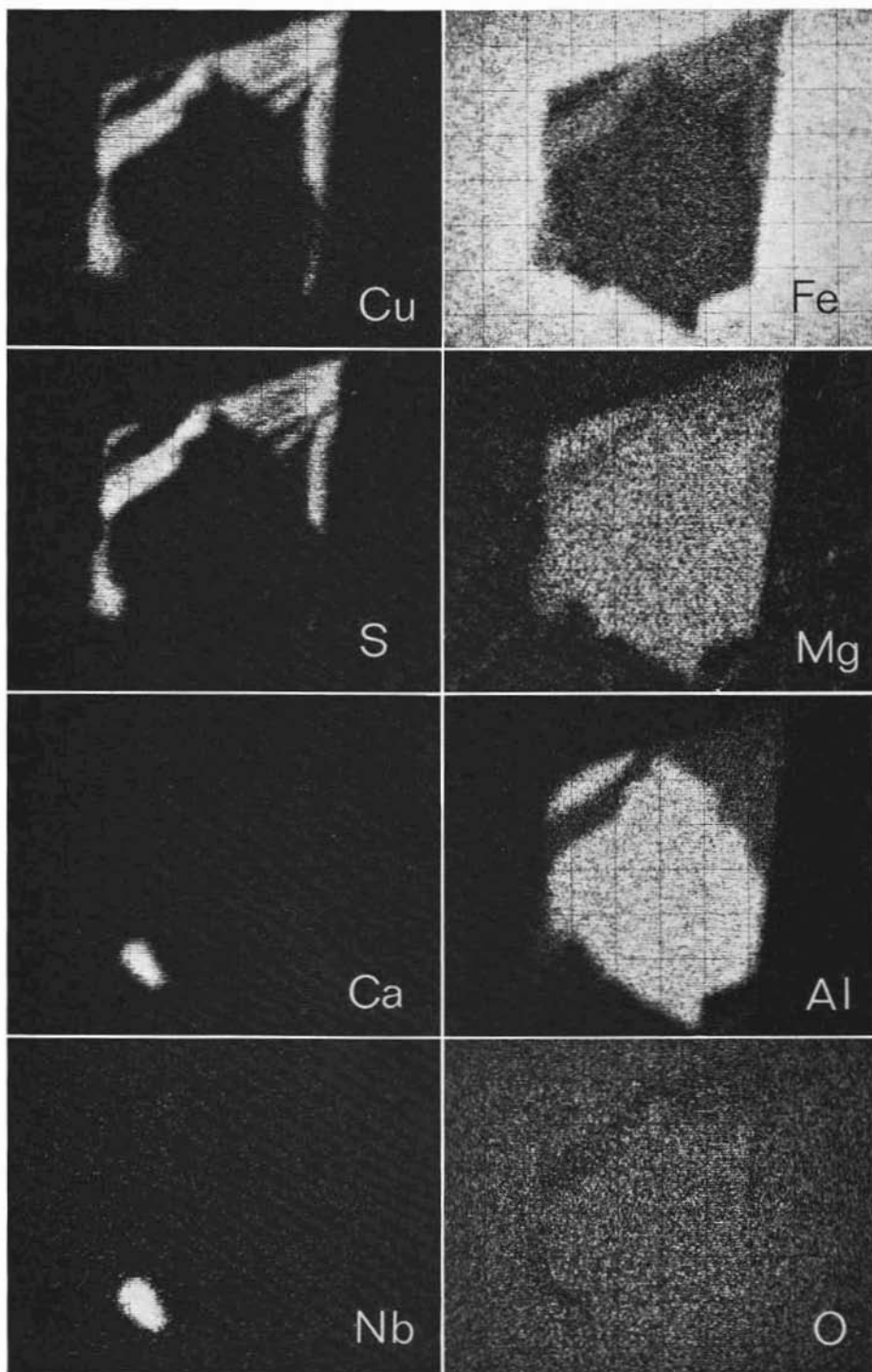


PLATE 5.

PLATES 6-10.

Microprobe Scanning Pictures

6. - Loolekop, Transvaal - Valleriite apparently replacing an idiomorphic baddeleyite crystal in a magnetite matrix (compare Fig. 1 h). The original idiomorphic outline of the baddeleyite can best be seen in the scanning picture for Fe. The baddeleyite contains Zr, Nb, Fe and Hf. The valleriite contains Cu, Fe, S, Mg, Al and most interestingly Nb. 8 μ /#
7. - Hellenic Mining, Cyprus, Section 10601 (Prof. Ramdohr's collection) - Valleriite in a sulfide matrix, predominantly cubanite and chalcopyrite. The scanning picture for Ca best reveals the location of the valleriite. The valleriite is an Fe-rich variety inhomogeneous in composition, with abundant Ca and little Ni, Co and Mg. 19 μ /#
8. - Hellenic Mining, Cyprus, Section 10601 - Valleriite replacing cubanite and mackinawite in chalcopyrite. The scanning picture for Ca clearly locates the valleriite; those for Ni and Co locate the mackinawite. Again the valleriite shows an inhomogeneous chemical composition like in Plate 7. The mackinawite shows a high Ni and Co-content, and a trace of Cu. The Cu-free area is pyrrhotite. 20 μ /#
9. - White Horse, Yukon - Valleriite in dolomitic matrix (see Ca, Mg²⁺ and C-scanning pictures). The S.C. picture locates the valleriite. Besides Cu, Fe and S, the valleriite contains only Mg and no Ca at all. The scanning picture for «C» shows more «C» than actually present, because the sample was coated with carbon to make it more conductive. 16 μ /#
10. - Balangero, Piedmont - Scanning pictures of the native Ni-Fe (compare Fig. 3 h). 25 μ /#

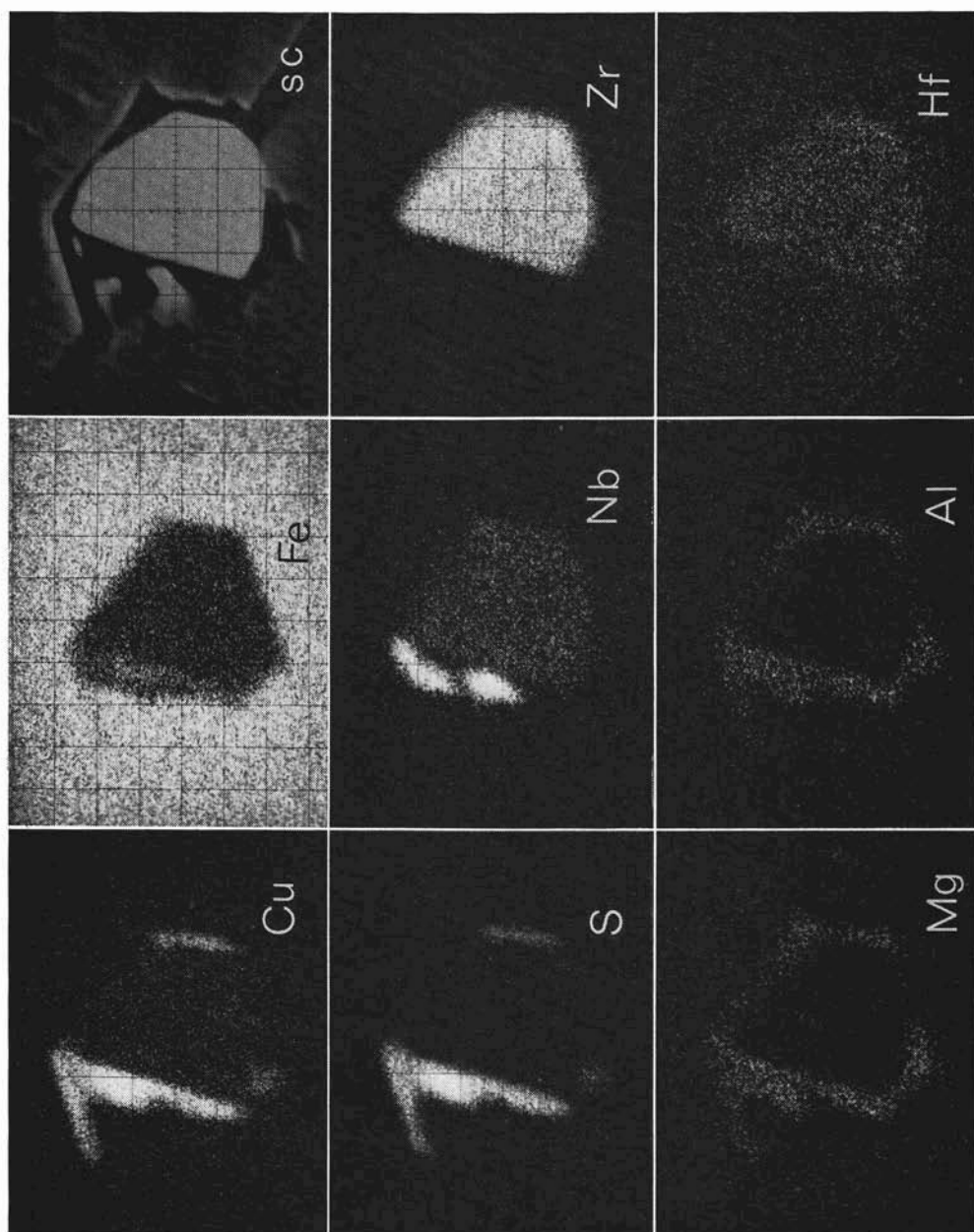


PLATE 6.

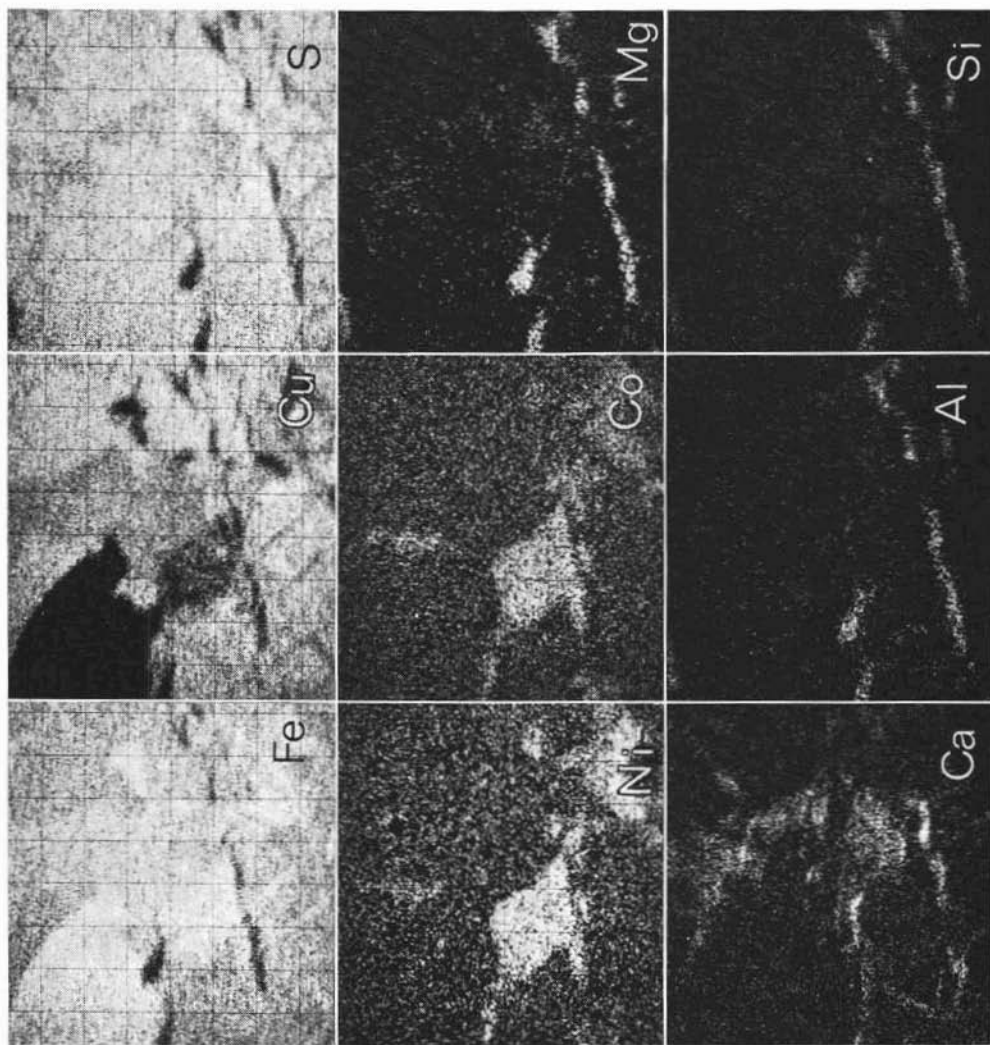


PLATE 7.

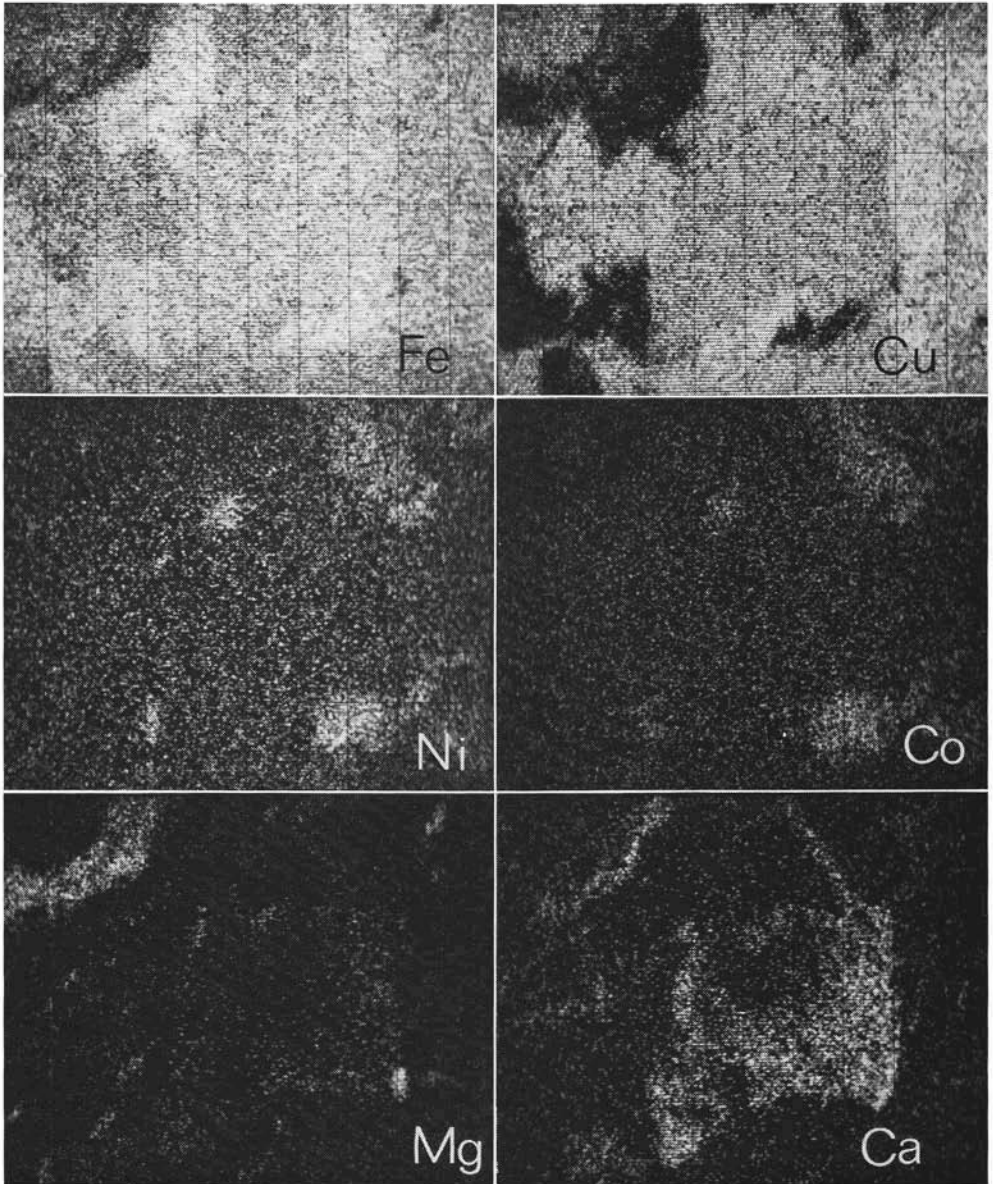


PLATE 8.

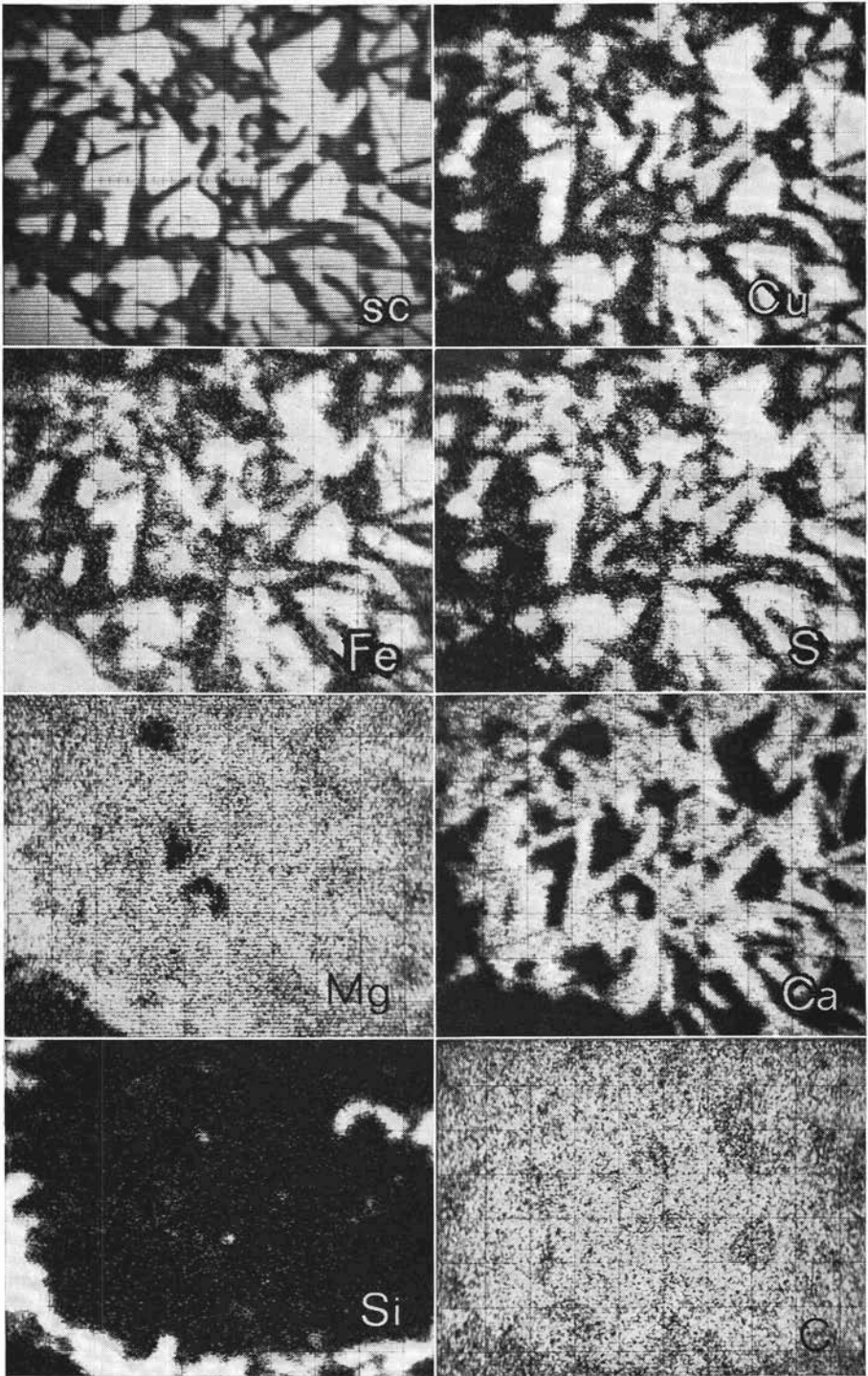


PLATE 9.

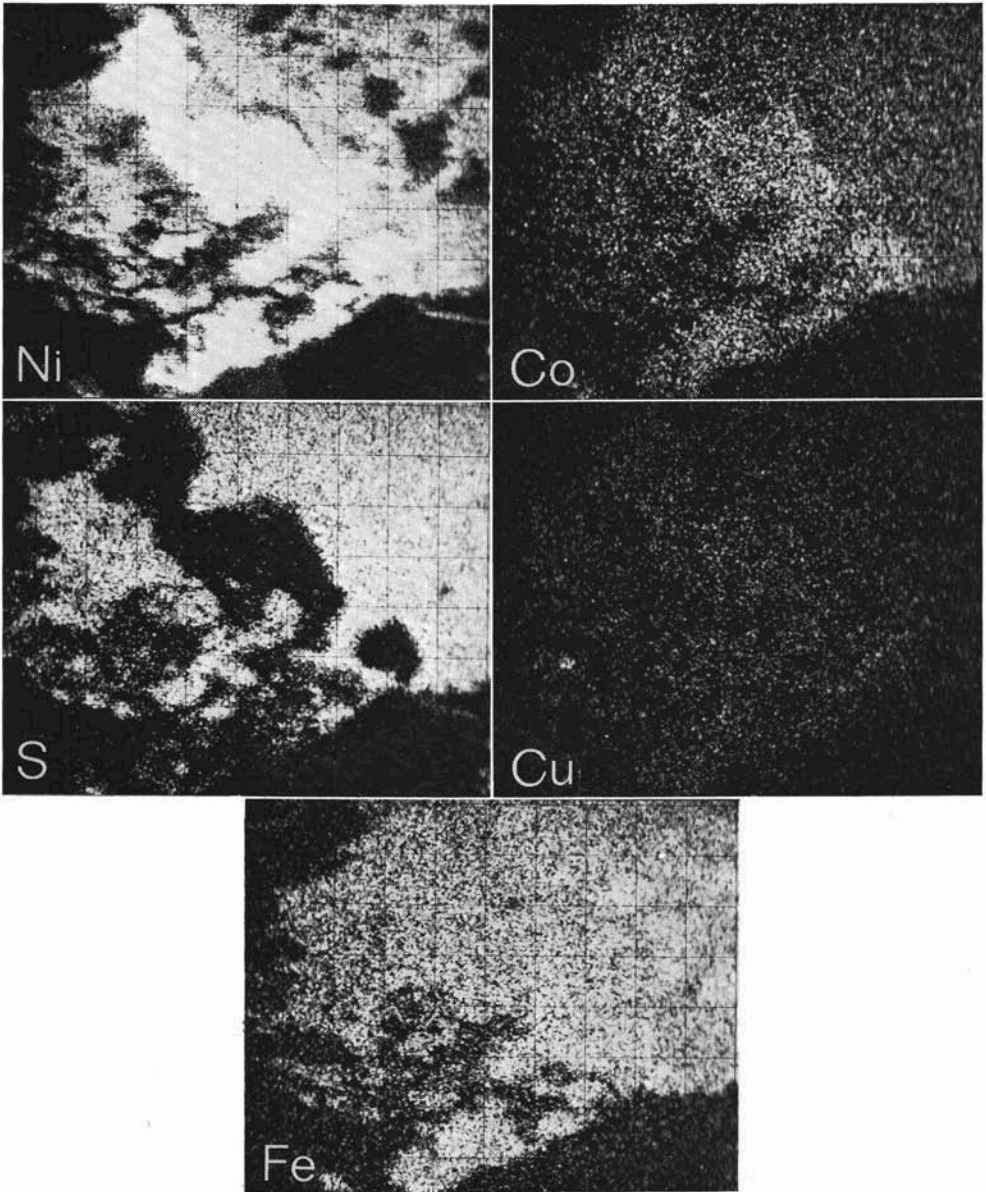


PLATE 10.

TABLE I. — *Optical Properties of Mackinawite.*

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|--|---|---|---------------------------------------|---------------------------------------|---------------------------|--|
| Sulitjelma, Norway | — | very high; in air: like pyrrhotite; normal there-to, under oil imm.: like sphalerite | high | — | RAMDOHR (1925) | «Ein noch nicht bestimmbares Mineral im Kupferkies» ⁽¹⁾ |
| England: East Lovell, Cornwall; Norway: Sulitjelma, Wadda- gaisa, Skardalen (Kaafjord), Bergs Mine (Kåfjord, Hindoen), Björkäsen (Ofotenfjord); Sweden: Kaveltorp, Tunaberg, Atvidaberg; South-Africa: Vlakfontein (Rustenburg-Distr., Transvaal), Witwatersrand; SW-Africa: Otjozongati, Gorob | — | high (> graphite) | — | — | RAMDOHR (1928) | «? Erz im Kupferkies» ⁽²⁾ |
| Bushveld, Transvaal | air imm. oil, $\eta = 1,515$ green 37% 25% orange 33 23 red 33 23 | exceptionally high: bright yellow with rosa tint to dull dark gray (somewhat like sphaleri- te; darker than chromi- te); under oil imm.: black in one direction | extremely high: pure white to dark | \cong pentlandite > chalcopyrite | SCHNEIDERHÖHN (1929 a) | « unbekanntes Ni-Fe-Erz » ⁽³⁾ |

⁽¹⁾ « an as yet undefined mineral in chalcopyrite ».

⁽²⁾ « ? ore-mineral in chalcopyrite ».

⁽³⁾ « unknown Ni-Fe-ore-mineral ».

(cont. Table I)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|---|--------------------------|--|---|----------------------------------|------------------------|--|
| Merensky Reef, Rustenburger-Distr., Bushveld, Transvaal | — | extremely high: rosa yellow | very high | — | SCHNEIDERHÖHN (1929 b) | « unbekanntes Ni-Fe-Mineral » ⁽⁴⁾ |
| Orange County, Vermont Copper District | — | strong: pale yellow with rosa tint (\cong pyrrhotite) to dull gray, somewhat bluish | bright | \cong graphite | BUERGER (1935) | « valleriite » |
| East Griqualand & Pondoland, South-Africa | orange filter 18% to 42% | strong: bright pinkish cream to gray; bright yellow to gray (with bluish tint) | extreme, intense; + Nicols: bright cream to dark mottled steel gray; + Nicols — 5°: bright pinkish cream to blue gray | < chalcopyrite | SCHOLTZ (1936) | « valleriite » |
| Mackinaw Mine, Shonomish County, Washington | — | extraordinarily strong | extraordinarily strong | — | MILTON & MILTON (1958) | « valleriite » |
| Sudbury, Canada | — | strong: pale yellow (lighter and brighter than surrounding chalcopyrite) to mauvish gray (distinctly darker than pyrrhotite); bright yellow to blue gray | — | — | HAWLEY (1962) | « valleriite » |
| Outokumpu, Ylöjärvi, Varislahti & Möhko, Ilomantsi, Finland | — | very strong; in air: gray to reddish | very strong; in air: gray to reddish (undulatory extinction common) | > pyrrhotite < Co-pentlandite | KOUVO et al. (1963) | « tetragonal iron sulfide » |

(4) « unknown Ni-Fe-mineral ».

(cont. Table I)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|--|---|---|---|---|-------------------------------|-------------------|
| Gadoni, Italy | — | very high; in air: pale yellow to brown; under oil imm.: pale pink-yellow to dark brown | very high; in air: white pearly gray to peanut yellow; under oil imm.: bright lemon yellow in one position | > chalcopyrite | OGNIBEN & OMENETTO (1964) | « valleriite » |
| — | — | very strong: pale pink to pinkish gray | extreme | — | EVANS et al. (1964) | mackinawite |
| Kawayama Mine, Japan | — | under oil imm.: pale yellowish pink (very little more pinkish than chalcopyrite) to creamy gray (more brownish than sphalerite) | very strong; under oil imm.: brilliant yellow through bluish gray to dark gray | >> chalcopyrite & cubanite; slightly < pyrrhotite | TAKENO (1965) | mackinawite |
| Outokumpu, Finland | — | very strong; in air: gray to reddish | very strong | > pyrrhotite; < Co-pentlandite | — | — |
| Muskox Intrusion, Canada | — | moderate to high: pink to gray | high; grayish white to dark gray | — | — | — |
| Muskox Intrusion, Canada | not measured, but in the same range as pyrrhotite | moderate to high: pink (pinkish gray) to gray | high, but decreasing with time after polishing; under completely crossed nicols: grayish white to dark gray; under incompletely crossed nicols: bluish white to Sienna brown (diagnostic) | Vickers hardness (VHN) (50 gram load): 58; fair polishing hardness, always with scratches | CHAMBERLAIN & DELABIO (1965) | mackinawite |
| Witwatersrand, South-Africa | — | high: pinkish white to gray | graphite-like | ≅ chalcopyrite | SCHIDLOWSKI & OTTEMANN (1966) | mackinawite |
| Laxia tou Mavrou & Hellonic Mining, Cyprus | for O: >>> valleriite; for E: ≅ valleriite | — | — | — | ANTUN et al. (1966) | mackinawite |

(cont. Table I)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|--|---|--|---|---|------------------------------|---------------------------|
| Ylöjärvi, Finland | > valleriite | — | strong in air and under oil imm.; + Nic. —: bluish white to brown | VHN (50 gram load): 52 ± 3 | CLARK (1966 b) | mackinawite |
| Lizard, Cornwall | \equiv pyrrhotite | strong: pink to gray | marked: bluish white to dark gray | \equiv pyrrhotite | CLARK (1967) | mackinawite |
| Bushveld, Insizwa & Loolekop, South-Africa | > valleriite; optic sign = neg.; sign of phase differ. = strongly pos. | moderate to high: light to pink gray | high: white to black (with aid of a Nakamura plate and with + Nicols) | — | RENSBURG & LIEBENBERG (1967) | mackinawite |
| Kolihan, Rajasthan, India | lightest position: > chalcopyrite darkest position: < pyrrhotite | high: creamy brown to gray | strong; + Nicols —: Sienna brown to dark grayish blue | < chalcopyrite & pyrrhotite; takes good polish | RAO & RAO (1968) | mackinawite |
| Mina do Abessedo, Vinhais, Portugal | > valleriite; 37,3% to 40,2% at 589 nm. | moderate: brownish tint (in air & under oil imm.) in one direction | violent; + Nic.: gray-white to dark gray; + Nic. — 1 to 2°: bluish white to brown | > valleriite | CLARK (1969) | « chromian mackinawite » |
| Vlaktefontein, Transvaal | Vlaktefontein: $33,8 \pm 11,1\%$ at 589 nm. (Outokumpu: $37,7 \pm 5,7\%$ at 589 nm.) | very strong; in air: brownish cream to brown gray; under oil imm.: greenish cream to dark gray brown Vlaktefontein: $22,2\%$ at 589 nm. (Outokumpu: $\sim 11-12\%$ at 589 nm.) | creams to dark grays | VHN: 94-181 (Vlaktefontein) | VAUGHAN (1969) | « nickelian mackinawite » |
| Singhbhum, India | $19-41 \pm 0,5\%$ at 530 nm. (Photocell, carborundum standard, Leitz green filter) | intense: grayish-pink to pinkish-gray | — | \ll pyrrhotite > chalcopyrite takes good polish | SARKAR (1971) | mackinawite |

(cont. Table I)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|----------------------------|--|---|---|---------------------|------------------|-------------------|
| Balangero, Piedmont, Italy | lightest position: $40.5 \pm 0.3\%$ (^o) darkest position: $29.1 \pm 0.2\%$ both in air at 546 nm; green filter | moderate; in air: creamy yellow white with light lila-grayish tint (like pyrrhotite, but paler) to light creamy gray with light lila tint; under oil imm.: the same colours as in air, but darker (in one position much lighter than pyrrhotite under oil imm.) | very high; in air: bright (^o) whitish yellow to light bluish-green; under oil imm.: bright (^o) whitish-yellow to green blue; both air & oil: + Nicols — | \cong pentlandite | This publication | mackinawite |
| Kaveltorp, Sweden | — | high; in air: light pale pink to light bluish-gray (lighter than sphalerite); under oil imm.: bright pale pink to light drab gray (much lighter than sphalerite under oil imm.) | very high; in air: bright whitish yellow (more whitish than vallerite) to light greenish-blue (almost aquamarine); under oil imm.: bright pale yellow to pale greenish blue (almost aquamarine); both air & oil: + Nicols — | > chalcopyrite | | |
| Salamanca, Argentina | lightest position: $42.4 \pm 0.4\%$ (^o) darkest position: $27.1 \pm 0.4\%$ both in air at 546 nm; green filter | high; in air: very pale creamy whitish pink (lighter than pyrrhotite) to creamy gray with pinkish tint; under oil imm.: pale creamy pink with a very light lila tint to creamy gray with pink-lila tint | very high; in air: bright whitish yellow to light greenish blue (undulatory extinction); under oil imm.: bright white-yellow to greenish blue; both air & oil: + Nicols — (weak undulatory extinction) | | | |

(^o) determined with the Leitz MPV; standard: $\text{SrTiO}_3\text{R}_V = 17.5\%$.

(^o) bright = luminescent.

(cont. Table I)

| Locality | Reflectivity | Anisotropy | Bireflectance | Hardness | Author | Mineral Name Used |
|-----------------------------------|---|--|---|--------------------|--------|-------------------|
| Matooster, Transvaal | — | high; in air: very pale creamy lila-pink to creamy light gray with lila tint; under oil imm.: light creamy pinkish lila to creamy gray with lila tint | very high; in air: bright whitish yellow to greenish blue (aquamarine); under oil imm.: bright whitish yellow to greenish blue; both air & oil: + Nicols — | | | |
| Laxia tou Mavrou, Limasol, Cyprus | — | high; in air: pale pinkish white (lighter than pyrrhotite) to very light lila pinkish gray; under oil imm.: very pale pinkish white (much lighter than pyrrhotite) to creamy gray with pinkish lila tint | very high; in air: bright pale lemon-yellowish white to blue with greenish tint (with Nicols completely crossed: bright lemon-yellowish white → greenish bluish gray → greenish blue → blue with greenish tint → greenish bluish gray with lila tint, etc.); under oil imm.: bright white with very pale lemon yellow tint to blue with greenish tint; both air & oil: + Nicols — | | | |
| Hellenic Mining, Cyprus | lightest position: $42,0 \pm 2,1\%$ ($^{\circ}$) darkest position: $24,5 \pm 1,1\%$ both in air at 546 nm.; green filter | high; in air: pale pinkish white (slightly lighter than pyrrhotite) to very pale bluish gray | very high; in air: greenish blue to bright lemon-yellow white (much whiter than valleriite) | \cong pyrrhotite | | |

TABLE II. — *Optical Properties of Valleriite.*

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|--|---|---|---|---|------------------------------|-------------------|
| Nya Kopparberg †, Sweden | — | in air: bright yellow (colour tone between chalcopyrite and pyrrhotite) to (bluish) gray with bluish tone | white to bluish gray or white to yellow | — | RAMDOHR & ÖDMAN (1932) | valleriite |
| — | — | pale yellow to deep creamy brown | extreme | — | EVANS et al. (1964) | valleriite |
| Mavro, Eretria, Greece | — | very clear; dirty orange yellow white to blue gray | very strong | — | PANAGOS & RAMDOHR (1965) | valleriite |
| Muskox Intrusion, Canada | not measured, but very low, in the same range as graphite | extreme under high power: creamy (dull) bronze to purple | extreme: white to bronze, remaining much the same only less intense under incompletely crossed nicols | VHN (50 g. load): 30; very poor polishing hardness, showing semimatte surface despite all efforts to polish | CHAMBERLAIN & DELABIO (1965) | valleriite |
| «Laxia tou Mavrou (L.M.)» and «Hellenic Mining (H.M.)», Cyprus | L.M.: reflectivity and colour vary considerably | L. M.: < mackinawite and graphite; under oil imm.: O: light gray brown to darker gray rosa violet; E: bluish gray to dark gray. H.M.: oil imm.: O: brown-brown red towards yellow or violet; E: much darker: gray to bluish towards ink blue | — | — | ANTUN et al. (1966) | valleriite |

(cont. Table II)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|-----------------------------|--|---|---|-------------------------------------|------------------------------|-------------------------|
| — | — | — | very light bronze to gray bronze | — | RENSBURG & LIEBENBERG (1967) | valleriite |
| Kolihan, Rajasthan, India | lightest position: ~ 30% darkest position: ~ 10% | strong: brownish gray to dark gray | strong | very soft; seldom takes good polish | RAO & RAO (1968) | valleriite |
| Noril'sk, W-Siberia, Russia | — | moderate: light gray to dark bluish gray (with distinct bluish colour in contrast to magnetite) | distinct: light yellow to reddish purple | — | HARRIS et al. (1970) | valleriite-type mineral |
| Balangero, Piedmont, Italy | — | high; in air: brownish tan to gray (almost like the serpentine gangue); under oil imm.: light tan colour to light dirty gray | very high; in air: bright ⁽¹⁾ bronze yellow to bluish gray white; under oil imm.: bright bronze yellow to pencil lead colour (highly undulatory extinction; slight bluish tinge) | — | This publication | valleriite |
| Kaveltorp, Sweden | lightest position: $16.5 \pm 1\%$ ⁽²⁾ darkest position: $11.5 \pm 0.5\%$ both in air at 546 nm; green filter | high; in air: creamy gray (less bluish and darker than the adjoining sphalerite) to yellowish-beige brown; under oil imm.: pencil lead colour to beige yellowish brown (a shade darker than in air) | very high; in air: bright ⁽¹⁾ whitish yellow to very light bluish green; under oil imm.: bright whitish yellow to almost black; undulatory extinction | < chalcopyrite | | |

⁽¹⁾ bright = luminescent.

⁽²⁾ determined with the Leitz MPV; standard: SrTiO₃ — $R_{V_L} = 17.5\%$.

(cont. Table II)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|------------------------|---|--|--|----------|--------|-------------------|
| Loolekop, Transvaal | — | high; in air: creamy white gray (little grayer than magnetite) to pale brownish honey yellow; under oil imm.: creamy gray (clearly darker than magnetite) to brownish honey yellow | very high; in air: bright whitish honey yellow to pale bluish gray-white; under oil imm.: bright whitish honey yellow to very dark gray with bluish tint; highly undulatory extinction | | | |
| Mavro, Eretria, Greece | lightest position: $17 \pm 1.5\%$ (?) darkest position: $13.5 \pm 0.5\%$ both in air at 546 nm; green filter | high; in air: light brownish orange yellow (lighter in colour and more yellowish than valleriite from Saxberget and Kaveltorp) to very light bluish gray; under oil imm.: very light beige yellow to light blue gray | very high; in air: bright yellow with brownish tint (like tiger eyes; more yellow than valleriite from Saxberget and Kaveltorp) to very light blue gray; under oil imm.: bright whitish beige yellow to light bluish gray; undulatory extinction | | | |
| Saxberget, Sweden | — | high; in air: dark gray (darker than sphalerite) to beige or brownish yellow; under oil imm.: dirty brownish beige to very dark blackish or drab brown | very high; in air: bright pale whitish yellow to very pale bluish green; under oil imm.: bright pale dirty whitish yellow to dark blackish gray (similar to sphalerite under oil immersion) | | | |

(cont. Table II)

| Locality | Reflectivity | Bireflectance | Anisotropy | Hardness | Author | Mineral Name Used |
|--|--------------|--|---|--------------|--------|-------------------|
| Laxia tou Mavrou, Limasol, Cyprus | — | high; in air: lila-pinkish olive-brown (much darker than cubanite) to bluish gray; under oil imm.: lila-pinkish olive-brown (much darker than cubanite) to dark gray | very high; in air: bright whitish yellow to pale blue-greenish white; under oil imm.: bright whitish yellow with orange tint to bluish white-gray | | | |
| | | — | — | | | |
| | | high; in air: creamy yellowish brownish gray with orange pink tint to light bluish gray; under oil imm.: pale creamy brownish gray with pink (rosa) tint (darker than pyrrhotite) to dark brownish blue-gray | very high; in air: bright whitish yellow to yellowish greenish white with grayish tint (a bit lighter than pyrrhotite); under oil imm.: bright whitish yellow to yellowish bluish greenish gray | ≪ pyrrhotite | | |
| | | — | — | | | |
| Hellenic Mining, Cyprus | — | high; in air: creamy bluish grayish white to creamy yellowish brownish white; under oil imm.: dirty dark whitish gray with bluish tint to pale yellow brown | very high; in air: very pale yellowish bluish greenish white to bright whitish yellow; under oil imm.: bright whitish yellow to yellowish bluish gray white | | | |
| Little Chief Ore-body, New Imperial Mine, White Horse, Yukon | — | high; in air: creamy pale brownish yellow to creamy bluish gray; under oil imm.: mauve blackish gray to very light yellow brown | very high; in air: bright whitish yellow with brownish tint to bluish greenish whitish gray; under oil imm.: bright whitish yellow to bluish greenish whitish gray; undulatory extinction | | | |

TABLE III. — *Mackinawite Composition* (in weight %).

| Locality | Fe | Ni | Co | Cu | Cr | S | Total | Author | M/S Ratio |
|---|------------------|--------------------|----------------|----------------|--------|------------------|--------|-------------------------------|----------------|
| Mackinaw Mine, Snohomish Co., Washington | 51-58 | — | — | < 5 | — | — | — | BIRKS et al. (1959) | — |
| Outokumpu, Finland | 55,94 | 8,26 | 0,42 | 0,09 | — | 35,29 | 100,00 | KOUVO et al. (1963) | 1,046 1,056 |
| Serpentinite | 56,35 | 8,17 | 0,37 | 0,05 | — | 35,06 | 100,00 | | |
| Idiomorphic Crystals w/magnetite & cubanite | 58,9±2 60,0±2 | 0,5±0,2 — | 0,2 — | < 0,1 — | — — | — — | — — | — | 1,050 |
| In chalcopyrite & cubanite | 55,1±2 53,1±2 | 5,0±0,3 5,4±0,3 | < 0,2 < 0,2 | < 0,5 < 0,5 | — — | — — | — — | | |
| Replacing Co-pentlandite | — | 1,9±0,2 | 10,7±1 | — | — | — | — | | |
| Ylöjärvi, Finland | 63,2±2 | 0,2 | 0,2 | < 0,1 | — | — | — | — | 1,050 |
| In chalcopyrite | 64,7±2 | 0,2 | 0,2 | < 0,1 | — | — | — | | |
| Gadoni, Italy | 59,36 | — | — | 0,34 & 1,66 | — | 36,38 | — | OGNIBEN & OMENETTO (1964) | — |
| Mackinaw Mine, Snohomish Co., Washington | 63±5 | 3,1±0,5 | — | — | — | 34±4 | — | EVANS et al. (1964) | 1,000 |
| Muskox Intrusion, Canada | 55±5 | 2,3±1 | 1,5±1 | — | — | — | — | CHAMBERLAIN & DELABIO (1965) | — |
| Kōmori, Japan | 52,1 | 5,6 | 1,0~2,0 | — | — | — | — | TAKENO (1965) | — |
| Witwatersrand, South-Africa | Scanning Picture | 9,46 | 0,65 | — | — | Scanning Picture | — | SCHIDLOWSKI & OTTEMANN (1966) | — |

(cont. Table III)

| Locality | Fe | Ni | Co | Cu | Cr | S | Total | Author | M/S Ratio |
|---|---------|----------|---------|-----|---------|---------|--------|----------------------|-----------|
| Ylöjärvi, Finland | — | 0,2 | 0,2 | — | — | — | — | CLARK (1966 a, b) | — |
| Lizard, Cornwall | — | ~7-9 | 0,1-0,8 | — | 0,1-0,8 | — | — | CLARK (1967) | — |
| Ylöjärvi, Finland | 64,82 | — | — | — | — | 35,18 | 100,00 | CLARK & CLARK (1968) | 1,058 |
| | 64,80 | — | — | — | — | 35,20 | 100,00 | | 1,057 |
| | 64,95 | — | — | — | — | 35,05 | 100,00 | | 1,064 |
| | 64,91 | — | — | — | — | 35,09 | 100,00 | | 1,062 |
| Outokumpu, Finland | 52,7 | 1,9 | 7,6 | 0,4 | — | 35,7 | 98,3 | SPRINGER (1968) | 0,998 |
| Driekop, Bushveld, South-Africa | 56,8 | 4,5 | 1,2 | — | — | 35,5 | 98,0 | | 1,006 |
| Frood Mine, Sudbury, Canada | 52,4 | 7,6 | — | 1,3 | — | 35,2 | 96,5 | | 0,994 |
| Palabora, South-Africa | 55,2 | 6,3 | 0,1 | 0,4 | — | 34,7 | 96,7 | | 1,023 |
| Kaveltorp, Sweden | 58,8 | 2,1 | 1,9 | 1,0 | — | 35,6 | 99,4 | | 1,026 |
| Vlakfontein, Transvaal, South-Africa | 38,1 | 18,7 | 3,3 | — | — | — | — | VAUGHAN (1969) | — |
| Outokumpu, Finland | 52,1 | 1,8 | 5,9 | — | — | — | — | | — |
| Mina do Abessedo, Vinhais, Portugal | Present | ~0,5-1,3 | — | — | ~7-9±1 | Present | — | CLARK (1969) | ~1,0-1,1 |

(cont. Table III)

| Locality | Fe | Ni | Co | Cu | Cr | S | Total | Author | M/S Ratio |
|---------------------------------------|-------|------|------|------|----|-------|--------|------------------------|--------------------------------------|
| Hitura, Finland | 57,6 | 6,66 | 0,56 | — | — | 35,8 | 100,6 | PAPUNEN (1970) | 1,049 |
| | 57,4 | 6,82 | 0,50 | 0,04 | — | 35,0 | 99,8 | | 1,056 |
| | 57,6 | 6,64 | 0,40 | 0,03 | — | 34,6 | 99,3 | | 1,068 |
| Outokumpu, Finland | 60,29 | 5,63 | 0,99 | — | — | 33,21 | 100,12 | TAYLOR & FINGER (1971) | 1,151 (0,869 after refinement) |
| Singhbhum, India | 54,74 | 7,99 | 0,30 | 0,57 | — | 35,63 | 99,23 | SARKAR (1971) | 1,019 |
| | 54,35 | 8,07 | 0,41 | 0,69 | — | 35,76 | 99,28 | | 1,012 |
| Balangero, Piedmont, Italy | 57,6 | 2,7 | 1,3 | 0,3 | — | 35,9 | 97,8 | This publication | 0,921 |
| Rammelsberg, Harz, West-Germany | 62,43 | 0,02 | 0,08 | 0,88 | — | 36,23 | 99,64 | | 1,003 |
| | 62,69 | — | 0,10 | 0,70 | — | 36,07 | 99,56 | | 1,009 |
| Salamanca, Argentina | 53,58 | 2,38 | 7,60 | 0,77 | — | 36,19 | 100,52 | | 1,009 |
| | 53,36 | 1,78 | 8,07 | 0,75 | — | 36,48 | 100,44 | | 0,997 |
| Matooster, Transvaal, South-Africa | 57,01 | 6,91 | 0,16 | 1,09 | — | 36,25 | 101,42 | | 1,025 |
| | 56,59 | 7,14 | 0,28 | 1,18 | — | 36,27 | 101,46 | | 1,024 |
| Hellenic Mining, Cyprus | 57,5 | 0,6 | 5,5 | 0,1 | — | 36,6 | 100,3 | | 0,994 |
| | 57,9 | 0,8 | 4,8 | 0,3 | — | 36,7 | 100,5 | | 0,993 |
| | 59,1 | 1,5 | 2,7 | 0,4 | — | 36,3 | 100,0 | | 1,003 |

TABLE IV.
Vallerite Composition (in weight %).

| Locality | Cu | Fe | S | Al | Mg | Ca | OH | Ni | Mn | Insol. | Total | Author | Formula |
|---------------------------------------|------------|------------|------------|-------------------------------|------------------|----------------|-----------------------------------|-------|----------------|--------|---------------------------------|---|---|
| Aurora Mine, Nya Kopparberg, Sweden | 17,77 | 26,34 | 22,54 | 2,73 (5,16) ⁽¹⁾ | 6,34 (10,51) | 0,18 (0,25) | 15,82 | — | — | — | 91,72 ⁽⁵⁾ [87,35] | BLOMSTRAND (1870; cited by HINTZE, 1904) ⁽⁶⁾ | [Cu _{0,80} Fe _{1,20} S ₂] · 0,89 [Mg _{0,83} Ca _{0,01} Fe _{0,15} (OH) ₂] · 0,29 [Al(OH) ₃] |
| Nya Kopparberg, Sweden | 17,77 | 26,34 | 22,54 | 2,73 (5,16) | 6,34 (10,51) | 0,18 (0,25) | 15,82 ((10,77)) ⁽²⁾ | — | — | — | 91,72 ⁽⁵⁾ [94,24] | RAMDOHR & ÖDMAN (1932) ⁽⁶⁾ | Same as above |
| | 14,32 | 24,03 | 24,96 | 3,46 (6,54) | 11,61 (19,25) | — | 22,78 | — | — | 2,81 | 104,02 [91,96] | | [Cu _{0,69-x} Fe _{1,31-y} S ₂] · 1,23 [Mg(OH) ₂] · 0,33 [Al(OH) ₃] |
| Aurora Mine, Nya Kopparberg, Sweden | 18,67 | 21,47 | 22,31 | 3,22 (6,09) | 10,78 (17,87) | 0,66 (0,93) | 21,78 ((12,16)) | — | 0,08 (0,10) | 1,75 | 100,72 [101,34] | HILLER (1939) ⁽⁶⁾ | [Cu _{0,87-x} Fe _{1,13-y} S ₂] · 1,33 [Mg _{0,961} Ca _{0,036} Mn _{0,003} (OH) ₂] · 0,34 [Al(OH) ₃] |
| Kaveltorp, Sweden | 17,6 | 21,2 | 21,4 | 4,29 (8,1) | 9,77 (16,2) | 1,21 (1,7) | 22,81 ((12,2)) | — | — | 1,8 | 100,08 [100,2] | EVANS et al. (1964) | [Cu _{0,84-x} Fe _{1,16-y} S ₂] · 1,30 [Mg _{0,93} Ca _{0,07} (OH) ₂] · 0,48 [Al(OH) ₃] |
| Loolekop, South-Africa | 19,8 | 20,0 | 21,6 | 4,50 (8,5) | 9,65 (16,0) | 0,93 (1,3) | 22,80 ((10,8)) | — | — | 3,3 | 102,58 [101,3] | | [Cu _{0,93-x} Fe _{1,07-y} S ₂] · 1,25 [Mg _{0,94} Ca _{0,06} (OH) ₂] · 0,50 [Al(OH) ₃] |
| Kaveltorp, Sweden | 18,6 | 29,5 | 23,3 | — | 11,5 (19,07) | — | 19,30 | — | — | — | 102,20 [102,2] | SPRINGER (1968) | [Cu _{0,81} Fe _{1,19} S ₂] · 1,56 [Mg _{0,83} Fe _{0,17} (OH) ₂] |
| Palabora, South-Africa Carbonatite | 22,0 | 21,0 | 23,4 | 4,2 (7,94) | 10,1 (16,75) | — | 22,07 | — | — | — | 102,77 [100,2] | | [Cu _{0,96} Fe _{1,04} S ₂] · 1,14 [Mg(OH) ₂] · 0,43 [Al(OH) ₃] |
| Phoscorite | 21,6 | 30,9 | 22,2 | 0,1 (0,19) | 9,4 (15,59) | — | 20,13 | — | — | — | 104,33 [104,2] | | [Cu _{0,98} Fe _{1,02} S ₂] · 1,69 [Mg _{0,67} Fe _{0,33} (OH) ₂] · 0,01 [Al(OH) ₃] |
| | 21,0 | 27,4 | 22,4 | 0,4 (0,76) | 10,7 (17,74) | — | 19,89 | — | — | — | 101,79 [100,4] | | [Cu _{0,95} Fe _{1,05} S ₂] · 1,61 [Mg _{0,78} Fe _{0,22} (OH) ₂] · 0,02 [Al(OH) ₃] |
| | 23,4 | 24,3 | 22,6 | 1,4 (2,65) | 10,7 (17,74) | — | 20,98 | — | — | — | 103,38 [102,4] | | [Cu _{1,05} Fe _{0,95} S ₂] · 1,53 [Mg _{0,82} Fe _{0,18} (OH) ₂] · 0,15 [Al(OH) ₃] |
| Eretria, Greece | 16,32 | 30,55 | 21,32 | 3,13 (5,91) | 6,89 (11,42) | — | 20,29 ((10,20)) | — | — | — | 98,50 [95,72] | PANAGOS (1967) | [Cu _{0,77} Fe _{1,23} S ₂] · 1,27 [Mg _{0,67} Fe _{0,33} (OH) ₂] · 0,35 [Al(OH) ₃] |
| Hitura, Finland | 17,5 | 29,0 | 23,0 | n.d. ⁽³⁾ | n.d. | — | — | 0,23 | — | — | — | PAPUNEN (1970) ⁽⁴⁾ | |
| Noril'sk, Western Siberia | 20,0 ± 0,5 | 43,8 ± 0,5 | 20,3 ± 0,5 | — | — | — | 15,85 | — | — | — | 99,95 [84,1 ± 4] | HARRIS et al. (1970) | [Cu _{0,99} Fe _{1,01} S ₂] · 1,47 [Fe(OH) ₂] |
| Eretria, Greece | 20,31 | 30,18 | 21,80 | 3,91 | 6,07 | — | 22,07 | 0,10 | — | — | 104,44 | This publication | [Cu _{0,94} Fe _{1,06} S ₂] · 1,27 [Mg _{0,733} Fe _{0,265} Ni _{0,02} (OH) ₂] · 0,43 [Al(OH) ₃] |
| Loolekop, South-Africa | 20,16 | 21,20 | 21,33 | 3,64 | 11,42 | — | 23,99 | 0,08 | — | — | 101,82 | | [Cu _{0,95} Fe _{1,05} S ₂] · 1,51 [Mg _{0,934} Fe _{0,063} Ni _{0,003} (OH) ₂] · 0,41 [Al(OH) ₃] |
| Kaveltorp, Sweden | 16,75 | 30,68 | 22,13 | — | 11,21 | — | 19,89 | 0,05 | — | — | 100,71 | | [Cu _{0,76} Fe _{1,24} S ₂] · 1,69 [Mg _{0,788} Fe _{0,210} Ni _{0,002} (OH) ₂] |
| Balangero, Piedmont, Italy | 13,9 | 26,7 | 19,6 | 1,07 | 15,13 | 0,11 | 26,20 | trace | — | — | 102,71 | | [Cu _{0,72} Fe _{1,28} S ₂] · 2,33 [Mg _{0,876} Ca _{0,004} Fe _{0,120} (OH) ₂] · 0,06 [Al(OH) ₃] |
| Hellenic Mining, Cyprus | 15,9 | 30,0 | 21,0 | — | 9,00 | — | 18,62 | 0,08 | 0,27 | — | 104,00 ⁽⁷⁾ | | [Cu _{0,77} Fe _{1,23} S ₂] · 1,67 [Mg _{0,551} Fe _{0,437} Mn _{0,007} Ni _{0,002} Co _{0,003} (OH) ₂] |

⁽¹⁾ Number in brackets indicates the oxide reported in the literature.

⁽²⁾ Number in double brackets indicates OH as H₂O reported in the literature.

⁽³⁾ n.d. indicates not determined.

⁽⁴⁾ PAPUNEN reports 0,01 wt. % Co.

⁽⁵⁾ BLOMSTRAND and RAMDOHR & ÖDMAN reported 0,28 wt. % K₂O and 0,62 wt. % Na₂O.

⁽⁶⁾ Indicates wet-chemical analysis.

⁽⁷⁾ 0,13 wt. % Co was detected.

TABLE V. — Transformation Temperatures of Mackinawite in Mackinawite-Sulfide Assemblages.

| | Locality | Ni (atom. %) | Co (atom. %) | Cu (atom. %) | Ni+Co+Cu (atom. %) | Fe (atom. %) | Transformation Temperature in °C | | Author |
|------------------|---------------------------------|----------------------|----------------------|-------------------|-----------------------|-------------------------|-------------------------------------|---------------|---|
| | | | | | | | lower limit | upper limit | |
| 1 ⁽¹⁾ | Kômorî, Japan | 4,56 4,49 | 0,81 1,60 | — — | 5,37 6,09 | 44,62 43,91 | 180°C ~ 200°C | 200°C ~ 230°C | TAKENO (1965) |
| 2 | Outokumpu, Finland | 6,25 | 0,32 | 0,06 | 6,63 | 44,49 | 210°C | to 245°C | KOUVO et al. (1963) |
| 3 | Hitura, Finland | 4,99 5,18 5,07 | 0,42 0,38 0,30 | — 0,03 0,02 | 5,41 5,59 5,49 | 45,42 45,79 46,23 | 250°C ± 50°C | | PAPUNEN (1970) |
| 4 | Ylöjärvi, Finland | 0,15 (max.) | 0,15 (max.) | 0,07 (max.) | 0,37 (max.) | 49,81 51,44 | ~130°C | to 140°C | KOUVO et al. (1963) CLARK (1966 a, b) CLARK & CLARK (1968) |
| 5 | Mackinaw Mine, Wash., U.S.A. | 2,36 | — | — | 2,36 | 50,34 | 145°C | to 165°C | EVANS et al. (1964) TAKENO (1965) |
| 6 | Muskox, Canada | 1,87 | 1,21 | — | 3,06 | 46,92 | 210°C | 240°C | CHAMBERLAIN & DELABIO (1965) TAKENO (1965) |
| 7 | Kawayama, Japan | — | — | — | — | ~50,00 | 130°C | to 150°C | TAKENO (1965) |
| 8 ⁽²⁾ | Singhbhum, India | 6,07 6,13 | 0,23 0,31 | 0,40 0,49 | 6,70 6,93 | 43,76 43,37 | 220°C | to 225°C | SARKAR (1971) |

(¹) The numbers coincide with those used in Fig. 7.

(²) Not included in Fig. 7.

Genetic interpretation.

It is evident from the relatively low transformation temperatures of mackinawite and its paragenetic relationship to cubanite (Figs. 1 *c*, 2 *a*, 2 *c*) as well as from the paragenetic relationship of valleriite to cubanite and mackinawite, that both mackinawite and valleriite are relatively low temperature minerals. At Laxia tou Mavrou and Hellenic Mining, Cyprus, valleriite on the one hand replaces cubanite, and is replaced by cubanite on the other hand; this points to formation temperatures of $\sim 250^{\circ}\text{C}$ (ANTUN *et al.*, 1966) (using Fig. 7, a temperature of $\sim 190^{\circ}\text{C}$ to 240°C was obtained). At the same two localities valleriite subordinately replaces mackinawite; here mackinawite apparently formed before valleriite. GENKIN (1971), however, reports the coexistence of mackinawite with valleriite at Noril'sk and Monchegorsk in which valleriite apparently formed before mackinawite; there, mackinawite rims border valleriite pseudomorphs after magnetite.

In this study, mackinawite was observed to have formed as follows:

1. predominantly through exsolution (at least in part connected with recrystallization) within chalcopyrite and cubanite, e.g., Salamanca, Argentina; Matooster, Transvaal, and Laxia tou Mavrou and Hellenic Mining, Cyprus (Figs. 1 *e* and 2 *e*);
2. through replacement of chalcopyrite and pentlandite, e.g., Balanero, Italy, and Hellenic Mining, Cyprus (Fig. 3 *g* & 3 *e* and Plate 3);
3. through primary crystallization (⁴), e.g., Rammelsberg, Germany (Fig. 4).

Valleriite was observed to have formed thus:

1. predominantly through replacement (rim) of chalcopyrite, cubanite, magnetite, sphalerite, pyrrhotite and mackinawite, e.g., Saxberget, Sweden; Kaveltorp, Sweden, and Laxia tou Mavrou and Hellenic Mining, Cyprus (Figs. 2 *d*, 2 *e*, 2 *g*, 2 *h*, 3 *b* and Plates 1 & 8);

(⁴) One may differentiate here between syngenetic primary crystallization which apparently accounts for the euhedral mackinawite at Rammelsberg, Germany and epigenetic primary crystallization which accounts for the idiomorphic mackinawite crystals deposited in open tension cracks at Outokumpu (Kouvo, 1963).

2. through replacement of the following gangue minerals:
 - a) spinel and baddeleyite, e.g., Loolekop, Transvaal (Figs. 1 *h* & 1 *g* and Plates 4, 5 & 6);
 - b) serpentine, e.g., Kaveltorp, Sweden; Laxia tou Mavrou and Hellenic Mining, Cyprus, and Balangero, Italy (Fig. 3 *f* and Plate 2);
 - c) chlorite, e.g., Laxia tou Mavrou and Hellenic Mining, Cyprus;
 - d) dolomitic gangue mineral, e.g., White Horse, Yukon (Fig. 3 *d* and Plate 9) (here, the simultaneous crystallization of dolomite and valleriite offers another genetic explanation);
3. through deposition in fracture zones, e.g., Loolekop, Transvaal; Eretria, Greece; Laxia tou Mavrou and Hellenic Mining, Cyprus, and White Horse, Yukon (Fig. 3 *c*).

Valleriite typically occurs along fractures, (pseudo) cleavage planes, and along the grain boundaries of the minerals it replaces, whereas mackinawite occurs almost always within a sulfide groundmass, frequently along the cleavage directions of the sulfides it replaces and along the grain boundaries between adjoining (and apparently recrystallized) sulfide minerals (Fig. 2 *c*). The mode of occurrence of both minerals points to a connection of their genesis with tectonic and recrystallization, i. e. dynamometamorphic processes. Serpentinization can play a role.

Particularly interesting are some of the observations made in connection with the prevailing physico-chemical conditions and the replacement mechanism connected with the replacement origin of valleriite.

The apparent replacement of baddeleyite (ZrO_2) by valleriite (Plate 6 & Fig. 8) indicates that the formation of valleriite may be connected with alkaline hydrothermal solutions; GENKIN (1971) already pointed out the role of alkaline autometamorphic hydrothermal solutions in the formation of valleriite. The mobilization of Nb from the baddeleyite into the valleriite supports this interpretation; microprobe analysis (simultaneous point-scan for Nb and S) proved the coexistence of Nb and S. Microprobe analysis showed, furthermore, that the valleriite contains ~16 wt. % Nb; the baddeleyite was shown to contain ~0,8 wt. % Nb. Plate 6 reveals that Nb^{+5} (ionic radius = 0,70 Å) probably substitutes for Cu^{+2} (ionic radius = 0,72 Å) and Fe^{+2} (ionic radius 0,74 Å) in the valleriite structure. If this observation is correct, it signifies the possibility of a wide range valency exchange.

Regarding the replacement mechanism, Plate 2 shows the replacement of serpentine by valleriite in which Mg, Al and Ni were apparently derived from the breakdown of the serpentine (Ni is present only in traces in the valleriite; compare the analysis for Balangero, Table IV). Plates 4 and 5 show that in the replacement of spinel ($MgO \cdot Al_2O_3$) by valleriite the Mg and Al are derived from the spinel and that in addition to the solutions having been alkaline hydrothermal, they must have been Cu- and S-bearing. In contrast thereto is the observation shown in Plate 1, where Cu and S were mobilized away from the replaced chalcopyrite in connection with substitution by Mg and Si (~ 8 wt. % Si). Plates 4 and 5 show furthermore, that the replacement of the spinel by valleriite proceeds along the pseudocleavage planes of the spinel. Plate 5 also shows that, in this case, no Nb was mobilized for incorporation into valleriite; instead Nb is bound to Ca, perhaps as a calcium niobate. Plates 1 and 8 show that valleriite need not necessarily contain Al^{+3} in its hydroxide lattice. Plate 8 also shows, that with an Al-bearing mineral nearby, physico-chemical conditions were not favorable for the mobilization of the Al from this mineral into the valleriite during its formation.

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