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Research Article

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Review on Mackinawite and Valleriite: Formulae, Localities, Associations and Intergrowths of the Minerals, Mode of Formation and Optical Features in Reflected Light

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Abstract

Investigations of the two minerals concern their chemical compositions and formulae, their intergrowths with other minerals, typical minerals that occur in association with them, their mode of formation within defined types of ore deposits/occurrences and finally also their optical characteristics under reflected light. Mackinawite was observed at 16 localities distributed all over the world from which more than 50 polished sections were available and more than 70 analyses were carried out. Valleriite was found at six localities. Microscopic work was based on more than 40 polished sections and more than 30 analyses.

In the literature, mackinawite is reported as a metal excess phase with the formula $(Fe, Ni)_{1+x}S$ and ($x \le 0.07$). Deduced from analyses of this study, mackinawite has a wider compositional range and the formula: $(Fe, Ni, Co)_{1-x}S$ to $(Fe, Ni, Co)_{1+y}$ S, where x=0.00–0.10 and y=0.00–0.10. Therefore, mackinawite may not only occur as a metal excess phase, but also as a metal deficiency one. The high-temperature (max. about 500°C) mineral mackinawite occurs in various types of sulphidic deposits, and is characteristically accompanied with chalcopyrite, pyrrhotite, sometimes pentlandite, pyrite, sphalerite and cubanite and occurs often in oriented intergrowth within chalcopyrite which is always twinned due to inversion. At lower temperature, mackinawite was also formed by the replacement of chalcopyrite (not twinned) and rarely by that of pentlandite and linneite.

The formula of valleriite is $(Fe, Cu)_2S_2 \bullet 1.5 [(Mg, Al)_1(OH)_2]$. The analyses of this study show, that valleriite has a wider compositional range and the proposed formula is: $(Fe, Cu)_2S_2 \bullet [(Mg, Fe)_1(OH)_2] \bullet y [Al(OH)_3]$ with x=1.20 – 2.10 and y=0 – 0.50. Identical with the latter formula, namely that Al and vacancies are constituents of the OH-layer, the formula inverts to: $(Fe, Cu)_2S_2 \bullet [(Mg^{2+}, Fe^{2+}, Al^{3+}_y, \square_{y/2})_1(OH)_2]$ where x=1.24–2.25 and y=0.00–0.26.

Valleriite, formed under mesothermal up to low katathermal conditions, is always a newly-formed mineral. It occurs together with chromite and/or magnetite, mostly along their cracks and fissures, in ultramafic rocks that are serpentinized, but only in the presence of chalcopyrite. Valleriite was also observed as replacer of chalcopyrite. Valleriite decomposes under high-grade metamorphic conditions (e. g. in Outokumpu, Finland).

Keywords: 70 Mackinawite analyses; 16 localities; 30 valleriite analyses; Six localities; New formulae; Mineral-associations; Mineral-intergrowths; Characteristic features in reflected light

Introduction

During their history, only a few minerals may have created so much confusion as scientific investigations about the two minerals mackinawite and valleriite. Up to the end of the 60th years of the last century, mackinawite and valleriite were considered as minerals which could not be clearly differentiated from each other. This was in particular emphasized by Ramdohr [1] in his book "The ore minerals and their intergrowths", where he stated, that the optical properties of the two minerals often intersect to such a degree so that they are barely distinguishable.

Blomstrand [2] was the first who discovered valleriite from Kopparberg/Sweden. However, Petrén [3] called this mineral in question and defined it as a mixture of covellite, pyrrhotite, spinel, talc, siderite and limonite. Neglecting Mg and Al of their analytical data, Ramdohr and Ödman [4] postulated for valleriite a composition of $Cu_2Fe_4S_7$. Deduced from X-ray data, Hiller [5] mentioned two formulae, namely $Cu_2Fe_4S_7$, but also $Cu_3Fe_4S_7$. Later, Evans et al [6]. determined the lattice-constants of valleriite. Because these authors (at that time) could not imagine that Mg and Al are constituents of sulphidic minerals, they proposed compositions of $CuFe_2S_4$, Cu_2FeS_4 and $Cu_2Fe_2S_4$. In corporation with Allmann, an expert on the field of sheet silicates, Evans and Allmann [7] determined the crystal structure of valleriite to consist of alternate layers of two kinds: a newly-discovered layer of composition $[Fe_{1.07}Cu_{0.93}S_2]$ and a brucite layer of composition $[Mg_{0.68}Al_{0.32}(OH)_2]$.

Mackinawite was discovered by Schneiderhöhn [8] as unknown Fe-Ni-sulphide of the Bushveld Complex of South Africa. From that time on up to the year 1959, mackinawite was found in various other deposits, but was wrongly described as valleriite (e.g. Ödman[9], Grondijs and Schouten [10], Maucher [11] and Ödman [12]. However, in the Mackinaw Mine, Snohomish County, Washington/USA, an optical similar mineral was discovered, having a composition not identical with valleriite [13]. Berner [14] synthesized mackinawite by giving metallic iron into a H_2S-saturated solution. He characterized this product as tetragonal Fe-sulphide. This mineral, attributed as tetragonal Fe-sulphide, was found by Kuovo et al. [15] in various Finnish deposits. Finally, it were Evans et al. [6] which characterised this Fe-sulphide as the new mineral mackinawite from the type-deposit of Mackinaw.

Methods

Analytical technique

The electron microprobe analyses were carried out at the Geochemical Department, Centre of Geosciences of the Georg-August-University of Göttingen with an ARL-SEMQ-II equipped with six spectrometers and four different crystals (LiF, PET, ADP, TAP). It was operated at 15 kV accelerating voltage and a 15nA current on brass. As standards were used: “Kuki” (= chalcopyrite) for Fe, Cu and S, “Mill” (= millerite) for Ni, “Cobi” (= cobaltite) for Co and “Kaer” (= kaersutite) for Ca, Mg and Al.

The analyzed positions were carefully selected under the microscope and nearly only restricted to grains which were large enough to represent data of only single phases. Using too small grains (restricted to mackinawite), the neighbouring mineral was also analyzed and based on these results, corrections were undertaken. The detailed calculation procedures of mackinawite and valleriite can be obtained from the author.

Origin, Mineral Associations and Analyses of Mackinawite and Valleriite

Mackinawite

The investigated samples originated from 16 localities distributed all over the world. From each locality, at least three samples were available and in total 71 analyses were carried out. Material of the following localities was used:

Olympias/Greece: The Pb-Zn deposit contains mainly pyrite, but also galena, sphalerite and rarely graphite. Sphalerite contains inclusions of twinned chalcopyrite which carries inclusions of myrmekitic mackinawite. The composition of mackinawite is uniform (Table 1, Columns I - III).

Sjögruvan, Grythyttan, Västmanland/Sweden: Main minerals of the deposit are hematite, hausmannite and braunite. However, the investigated polished sections consist of sulphides only. These are pyrrhotite, pyrite and subordinate twinned chalcopyrite which contains cubanite lamellae and tiny needle-like crystals of mackinawite which is Co-bearing and homogeneously composed (Table 1, columns VI and VII).

Tibschi/Nigeria: The sulphide mineralization occurs in the so-called “Younger Granites” of the Jos Plateau/Nigeria [16]. The following ore minerals were detected: sphalerite, twinned chalcopyrite, stannite, cassiterite, pyrrhotite, mackinawite, covellite, galena, matildite and native Bi. Myrmekites of homogeneously composed mackinawite (Table 2, columns I - III) are restricted to exsolutions of chalcopyrite from sphalerite.

Panasqueira/Portugal: The deposit is a tin-tungsten deposit associated with collisional granites. Observed minerals are: sphalerite, chalcopyrite, pyrrhotite, cubanite, mackinawite, arsenopyrite, native Bi, pyrite, wolframite and stannite. Sphalerite contains inclusion of pyrrhotite and twinned chalcopyrite. The latter contains oriented intergrown inclusions of star-like sphalerite, cubanite lamellae and flame- like and elongated mackinawite which is homogeneously composed (Figure 1; Table 2, columns VI – VIII).

	Olympias/Greece					**Sjögruvan /Sweden**			
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
A: Analytical data in weight percent (wt. %)									
Fe	60.78	61.11	60.77	60.89	30.02	55.57	55.23	55.40	40.39
Co	-	-	-	-	-	7.23	7.19	7.21	-
Cu	-	-	-	-	33.28	-	-	-	23.28
S	38.52	38.72	38.49	38.58	34.41	38.32	38.14	38.23	35.54
Σ	**99.30**	**99.83**	**99.26**	**99.47**	**97.71**	**101.12**	**100.56**	**100.84**	**99.21**
B: Atoms per formula unit (apfu)									
Fe	-	-	-	0.906	1.013	-	-	0.832	1.990
Co	-	-	-	-	-	-	-	0.104	-
Cu	-	-	-	-	0.987	-	-	-	1.010
Σ	**-**	**-**	**-**	**0.906**	**2.000**	**-**	**-**	**0.936**	**3.000**
S	**-**	**-**	**-**	**1.000**	**2.000**	**-**	**-**	**1.000**	**3.000**

Table 1: Mackinawite analyses of Olympias/Greece and Sjögruvan/Sweden (columns I – III; VI and VI), averaged analyses (IV and VIII) and analyses of chalcopyrite (column V) and cubanite (column IX). A: analytical data in wt. % and B: in apfu.

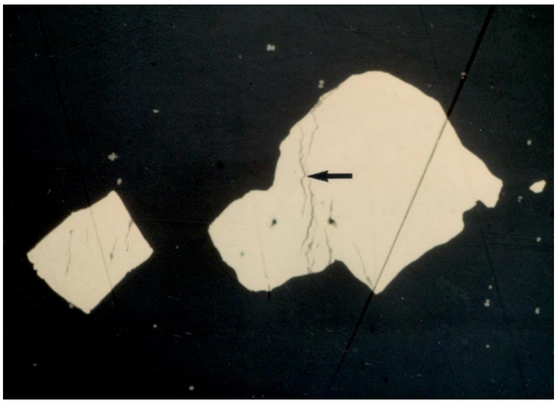

Figure 1: Sphalerite contains chalcopyrite inclusions which themselves contain flame-like developed (arrow) mackinawite. Reflected light, oil immersion objective, longer edge 450 µ. – Panasqueira/Portugal.

Monte Frerone, Bergamascian Alps /Northern Italy: The hill Frerone (2673 m) lies at the southern border of the Tertiary Adamello Pluton.

The hill consists of folded limestones that are horizontally and vertically intersected by gangue rocks consisting of lamprophyre and aplite [17]. The samples were collected from a vertical arranged lamprophyre. Apart from chromite, pyrrhotite (partially replaced by pyrite), and untwinned chalcopyrite (partially replaced by mackinawite; Figure 2) occur. The latter is Ni-bearing and homogeneously composed (Table 2, Columns X and XI).

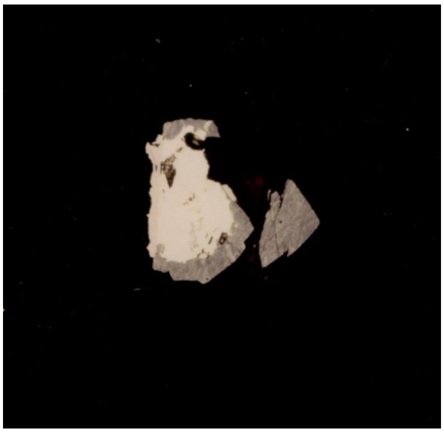

Figure 2: Two chalcopyrite crystals in a lamprophyric groundmass. The small crystal is completely, the bigger along the rim, replaced by mackinawite. Reflected light, oil immersion objective, longer edge 450 µ. – Mte. Frerone/Italy

Owyhee County, Idaho/USA: Within the pegmatite, the following ore minerals were detected: twinned chalcopyrite, pyrrhotite, sphalerite, pyrite, native Bi, bismutinite and mackinawite. Mackinawite occurs in the form of abundant tiny and needle-like crystals homogeneously distributed within chalcopyrite or along grain boundaries between chalcopyrite and pyrrhotite. Mackinawite is Ni-bearing and inhomogeneously composed (Table 3, Columns I - II).

Outokumpu/Finland: The Cu-Co-Zn-Ni deposit is related to submarine volcanism and lies in Eastern Finland within the Archian Basement. Predominating minerals are twinned chalcopyrite, pyrrhotite and pyrite. Chalcopyrite contains inclusions of sphalerite, cubanite and mackinawite (Figure 3 and 4). Pyrrhotite, partially replaced by pyrite, carries inclusions of pentlandite. Mackinawite may also occur in the form of replacements of chalcopyrite and pentlandite. In homogeneously composed mackinawite is Co- and Ni-bearing (Table 3, columns IV – IX).

Domokos/Greece: The podiform chromite deposit consists of two mineralizations which are either sulphide- or oxide-dominated. The sulphide dominated mineralization is of submarine-exhalative origin and consists of pyrrhotite which contains inclusions of twinned chalcopyrite and pentlandite which may be partially replaced by homogeneously composed mackinawite which is Ni- and Co-bearing (Table 4, columns I and II).

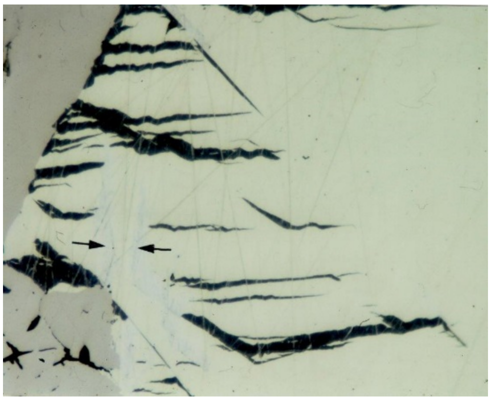

Figure 3: Pyrrhotite (brownish) and chalcopyrite (yellow and slightly brighter than pyrrhotite). The latter contains flame-like inclusions of mackinawite mostly in the dark cutting position. The brightest cutting position is arrowed. Reflected light, oil immersion objective, longer edge 450 µ. – Outokumpu/Finland

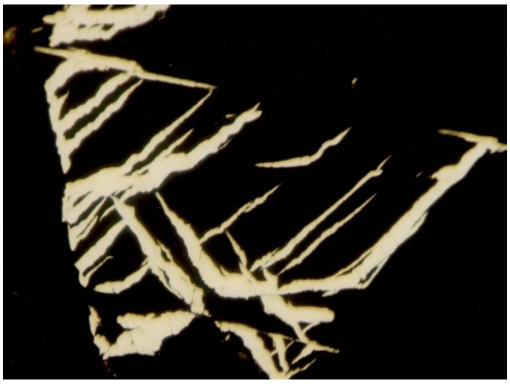

Figure 4: Identical with A/3. Note the luminous appearance of mackinawite which occurs in the bright 45°-degree position. Reflected light, crossed polars, oil immersion objective, longer edge 450 µ. – Outokumpu/Finland

	Tibschi/Nigeria					Panasqueira/Portugal				Frerone/Italia		
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
A: Analytical data in weight percent (wt. %)												
Fe	62.44	62.13	62.37	62.31	29.48	62.80	62.53	62.59	62.64	56.88	57.01	56.95
Ni	-	-	-	-	-	-	-	-	-	5.99	5.92	5.96
Cu	-	-	-	-	33.14	-	-	-	-	-	-	-

S	36.77	36.33	36.75	36.62	34.97	36.41	36.77	36.87	36.68	36.09	36.17	36.13
Σ	**99.21**	**98.46**	**99.12**	**98.93**	**97.59**	**99.21**	**99.30**	**99.46**	**99.32**	**98.96**	**99.10**	**99.04**
B: Atoms per formula unit (apfu)												
Fe	-	-	-	0.977	1.010	-	-	-	0.980	-	-	0.905
Ni	-	-	-	-	-	-	-	-	-	-	-	0.090
Cu	-	-	-	-	0.990	-	-	-	-	-	-	-
Σ	**-**	-	-	**0.977**	**2.000**	-	-	-	**0.980**	-	-	0.995
S	**-**	-	-	**1.000**	**2.000**	-	-	-	**1.000**	-	-	**1.000**

Table 2: Mackinawite analyses of Tibshi/Nigeria, Panasqueira/Portugal and Mte. Frerone/Italy (I – III; VI – VIII; X and XI), averaged analyses (IV; IX; and XII) and one analysis of chalcopyrite (column V). A: analytical data in wt. % and B: in apfu.

	Owyhee County/USA			**Outokumpu/Finland**						
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**
A: Analytical data in weight percent (wt. %)										
Fe	57.89	58.79	31.04	53.96	56.02	53.58	51.82	53.40	52.42	30.32
Co	-	-	-	5.45	2.66	6.83	10.14	8.30	8.89	-
Ni	5.43	4.38	-	2.27	2.05	2.39	1.67	1.77	1.89	-
Cu	-	-	33.32	-	-	-	-	-	-	34.27
S	36.25	35.84	34.97	38.22	36.49	37.02	36.33	36.21	35.94	34.96
Σ	**99.57**	**99.01**	**99.33**	**99.90**	**97.22**	**99.82**	**99.96**	**99.68**	**99.14**	**99.54**
B: Atoms per formula unit (apfu)										
Fe	0.917	0.942	1.030	0.811	0.881	0.831	0.819	0.847	0.837	1.019
Co	-	-	-	0.078	0.040	0.101	0.153	0.126	0.136	-
Ni	0.082	0.067	-	0.032	0.031	0.035	0.025	0.027	0.029	-
Cu	-	-	0.970	-	-	-	-	-	-	0.981
Σ	**0.999**	**1.009**	**2.000**	**0.921**	**0.952**	**0.967**	**0.997**	**1.000**	**1.002**	**2.000**
S	**1.000**	**1.000**	**2.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**2.000**

Table 3: Mackinawite analyses of Owyhee County/USA and Outokumpu/Finland (I and II; IV – IX) and analyses of chalcopyrite (columns III; and X). A: analytical data in wt. % and B: in apfu.

Domokos/Greece				**Hagendorf/Germany**				**Otterstope/Australia**			
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
A: Analytical data in weight percent (wt. %)											
Fe	55.61	55.62	55.62	63.79	63.96	63.74	63.83	56.10	55.74	55.88	33.39
Co	3.34	3.37	3.36	-	-	-	-	0.42	0.54	0.48	0.45
Ni	4.20	4.42	4.31	-	-	-	-	8.05	7.64	7.85	33.10

Cu	-	-	-	-	-	-	-	-	-	-	-
S	35.91	35.89	35.90	36.26	36.20	36.23	36.23	35.49	35.89	35.69	32.10
Σ	**99.06**	**99.30**	**99.19**	**100.05**	**100.16**	**99.97**	**100.06**	**99.97**	**99.81**	**99.90**	**99.04**
B: Atoms per formula unit (apfu)											
Fe	-	-	0.889	-	-	-	1.012	-	-	0.900	4.601
Co	-	-	0.051	-	-	-	-	-	-	0.007	0.059
Ni	-	-	0.066	-	-	-	-	-	-	0.120	4.340
Cu	-	-	-	-	-	-	-	-	-	-	-
Σ	-	-	**1.006**	-	-	-	**1.012**	-	-	**1.027**	**9.000**
S	-	-	**1.000**	-	-	-	**1.000**	-	-	**1.000**	**8.000**

Table 4: Mackinawite analyses of Domokos/Greece, Hagendorf/Germany and Otterstope/ Australia (columns I and II; IV – VI; and VIII and IX), averaged analyses (III; VII; and X) and one analyses of pentlandite (column XI). A: analytical data in wt. % and B: in apfu.

Hagendorf/Oberpfalz (Bavaria), Germany: The pegmatite contains apart from many other minerals, in particular phosphates. Sulphides may also occur. Within the chalcopyrite-paragenesis [18], the following minerals were detected: twinned chalcopyrite, pyrrhotite, pyrite, cubanite, mackinawite, sphalerite and stannite. Newly-formed pyrite, replacing pyrrhotite and chalcopyrite, contains often relics of chalcopyrite and pyrrhotite. The chalcopyrite remnants have tiny stannite- and star-like sphalerite inclusions, lamellae of cubanite and myrmekites of mackinawite (Figure 5) which is homogeneously composed (Table 4, columns IV - VI).

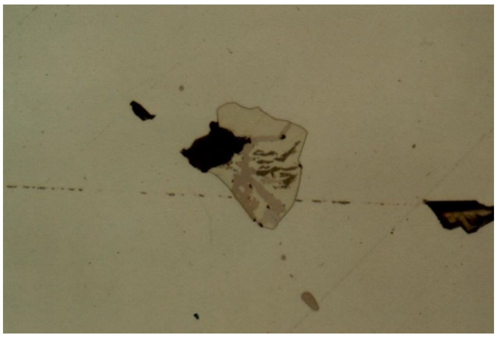

Figure 5: Remnants of chalcopyrite (yellow) and pyrrhotite (brownish) in pyrite formed by pyritization of the first two minerals. Chalcopyrite contains newly-formed myrmekites of mackinawite (dark-grey). Quarz is black. Reflected light, oil immersion objective, longer edge 450 µ. – Hagendorf-South/ Germany

Otterstope, Kambalda/Australia: Otterstope belongs to the Kambalda nickel deposits located within Archean greenstone belts of the Yilgarn block. The following ore minerals were recognized: pyrrhotite, pentlandite, chalcopyrite, pyrite, cubanite, mackinawite, molybdenite, native Bi, bismuthinite and chromite. Pentlandite (= groundmass) is closely intergrown with pyrite, pyrrhotite, cubanite, twinned chalcopyrite, rarely molybdenite and chromite. Mackinawite replaces pentlandite and chalcopyrite. Mackinawite is Ni- and Co-bearing and homogeneously composed (Table 4, columns VIII and IX).

Figure 6: Tiny mackinawite crystals arranged in the form of strings of pearls in chalcopyrite. Note the twinning of the host chalcopyrite and the fact that all the mackinawite crystals reveal the same brightness and therefore the same cutting position. Reflected light, oil immersion objective, longer edge 450 µ. – Broken Hill/Australia

Vihanti/Central Finland: The Zn-Cu mine of Vihanti is the most important volcanogenic massive sulphide deposit of Finland. Minerals are: chalcopyrite, pyrrhotite, sphalerite arsenopyrite, breithauptite, mackinawite and cubanite. Twinned chalcopyrite, the main mineral, is closely intergrown with pyrrhotite, minor sphalerite. Chalcopyrite contains inclusions of star-like shaped sphalerite, lamellae of cubanite and flame-like lamellae of mackinawite which is homogeneously composed and Ni-bearing (Table 5, columns I – III).

Singbhum/India: The deposit belongs to the massive sulphide type in high-grade metamorphic terranes. Detected minerals are: twinned chalcopyrite, cubanite, mackinawite, sphalerite and bornite. Chalcopyrite, the main mineral, contains inclusions of cubanite and elongated, twin-like mackinawite which is either Co- and Ni-bearing (Table 5, columns VI and VII) or Co-bearing (columns IX and X).

Broken Hill, NSW/Australia: Broken Hill belongs to the massive sulphide deposits occurring in high-grade metamorphic terranes. The following ore minerals were detected: sphalerite, galena, twinned chalcopyrite, pyrrhotite, stannite, pyrite, mackinawite and magnetite. Chalcopyrite is the host of tiny mackinawite crystals. These are arranged in the form of strings of pearls along two directions (Figure 6). Mackinawite is uniform composed and Ni-bearing (Table 6, columns I - II).

Rajpura-Dariba, Rajasthan/India: The ore body of the Precambrian Pb-Zn-Cu sulphidic deposit was overprinted under high-grade metamorphic conditions. Ore minerals are: twinned chalcopyrite, arsenopyrite, cubanite, pyrrhotite, mackinawite, fahlore, sphalerite and pyrite. Chalcopyrite forms the groundmass. Within small domains, tiny xenomorphic aggregates of mackinawite occur which are homogeneously composed (Table 6, columns IV - VI).

Vihanti/Finland						Shingbhum/India					
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
A: Analytical data in weight percent (wt. %)											
Fe	57.80	57.91	57.54	57.75	31.04	54.13	54.69	54.41	57.32	57.28	57.30
Co	-	-	-	-	-	6.05	5.53	5.79	-	-	-
Ni	6.39	6.23	6.48	6.37	-	3.34	3.40	3.37	6.63	6.57	6.60
Cu	-	-	-	-	33.32	-	-	-	-	-	-
S	35.78	35.77	35.36	35.64	34.97	36.16	36.13	36.15	35.56	35.47	35.52
Σ	**99.97**	**99.91**	**99.38**	**99.76**	**99.33**	**99.68**	**99.75**	**99.72**	**99.51**	**99.32**	**99.42**
B: Atoms per formula unit (apfu)											
Fe	-	-	-	0.930	1.005	-	-	0.864	-	-	0.926
Co	-	-	-	-	-	-	-	0.088	-	-	-
Ni	-	-	-	0.098	-	-	-	0.051	-	-	0.102
C u	-	-	-	-	0.095	-	-	-	-	-	-
Σ	-	-	-	**1.028**	**2.000**	-	-	**1.003**	-	-	**1.028**
S	-	-	-	**1.000**	**2.000**	-	-	**1.000**	-	-	**1.000**

Table 5: Mackinawite analyses of Vihanti/Finland and Shingbhum/India (columns I – III; VI and VII, and IX and X), averaged analyses (III; VIII, and XI) and one analyses of chalcopyrite (column V). A: analytical data in wt. % and B: in apfu.

Broken Hill/Australia			Rajpura-Dariba/India				
	I	II	III	IV	V	VI	VII
A: Analytical data in weight percent (wt. %)							
Fe	60.92	61.02	60.97	63.77	63.70	63.67	63.71
Ni	3.28	3.21	3.25	-	-	-	-
S	35.60	37.57	35.59	35.71	35.32	35.70	35.58
Σ	**99.80**	**99.80**	**99.81**	**99.48**	**99.02**	**99.37**	**99.29**
B: Atoms per formula unit (apfu)							
Fe	-	-	0.984	-	-	-	1.047
Ni	-	-	0.050	-	-	-	-
Σ	-	-	**1.034**	-	-	-	**1.047**

S	-	-	**1.000**	-	-	-	**1.000**

Table 6: Mackinawite analyses of Broken Hill/Australia and Rajpura-Dariba/India (columns I and II; IV – VI) and averaged analyses (III; and VII). A: analytical data in wt. % and B: in apfu.

Rustenburg, Transvaal/South Africa: The platinum mine belongs to the Bushveld Complex. The investigated material originates from the top of the Critical Zone known as Merensky Reef. Apart from chromite, main minerals are chalcopyrite, pyrrhotite and pentlandite. Mackinawite occurs in the form of worm-like to flame-like inclusions in twinned chalcopyrite or as replacement product of chalcopyrite, pentlandite (Figure 7 and 8) and linneite. Mackinawite is inhomogeneously composed: Ni-bearing (Table 7, columns I and II) and Ni- + Co-bearing (columns IV and V).

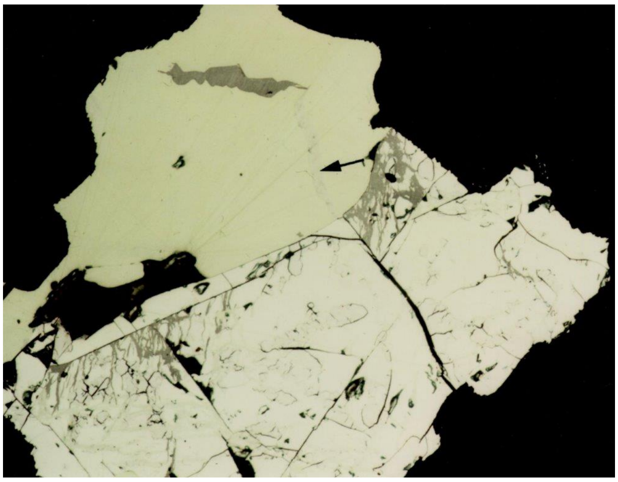

Figure 7: Chalcopyrite (yellow) and pentlandite (nearly white and slightly brighter) which both are partially replaced by mackinawite. Mackinawite in chalcopyrite occurs in the dark and in the bright cutting position (arrowed). In pentlandite, mackinawite forms net-like replacement-structures. Reflected light, oil immersion objective, longer edge 450 µ. – Rustenburg/South Africa

Zungeru, Birnin Gwari schist belt/Nigeria: The occurrence of Zungeru lies in the Birnin Gwari schist belt of North-Western Nigeria [19]. In the area of Zungeru, some authors [21] described a major shear zone marked by discontinuous ridges of mylonitized and silicified rocks and lenses of quartz veins (= so-called “Zungeru mylonites”). Metallic minerals are pyrite, pyrrhotite, twinned chalcopyrite, magnetite, mackinawite and cubanite. Pyrite, the main ore mineral, contains some chalcopyrite remnants which itself may contain inclusions of pyrrhotite, magnetite, cubanite and myrmekitic mackinawite (Figure 9) which is inhomogeneously composed (Table 7, columns VIII – X).

Valleriite

The investigated samples originated from 6 world-wide distributed localities. From Palabora and Gole Gohar about 30 samples were available and from the other localities, at least always more than two. 32 analyses were carried out, from which 17 were used in this paper only, because various results are either nearly identical or the total of the analyses is too low caused by the bad polishing behaviour of valleriite. Material of the following localities was used:

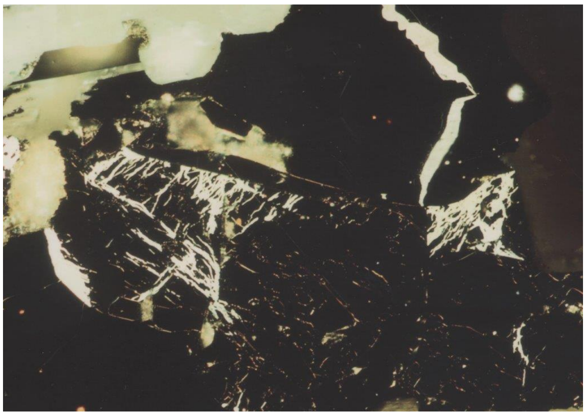

Figure 8: Identical with B/1. Obvious is the bright luminous cutting position of mackinawite. Reflected light, crossed polars, oilimmersion objective, longer edge 450 µ. – Rustenburg/South Africa

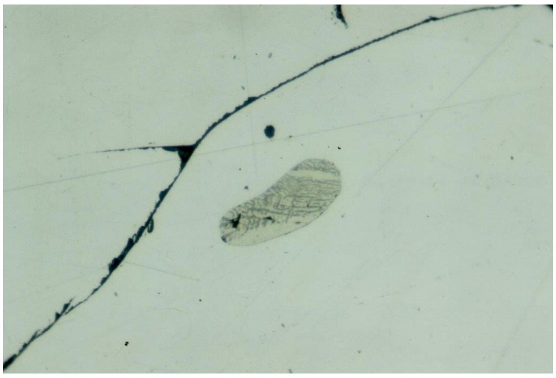

Figure 9: Chalcopyrite remnant in newly formed pyrite replacing chalcopyrite. Chalcopyrite contains mymekites of mackinawite. Reflected light, oil immersion objective, longer edge 450 µ. Zungeru/Nigeria

Palabora, Transvaal/South Africa: The Proterozoic igneous complex lies in the Archaean of north-eastern Transvaal which is intruded in its central part by various phases of carbonatite containing disseminated copper. These mineralizations were investigated. Clefty magnetite, containing spinel exsolutions, forms the groundmass. Predominantly within the clefts, mostly fine-grained fibrous aggregates of valleriite occur (Figure 10), but also coarse-grained and polysynthetic twinned crystals can be observed (Figure 11). Chalcopyrite is often replaced by valleriite. The composition of valleriite is inhomogeneous (Table 8, columns I – VI).

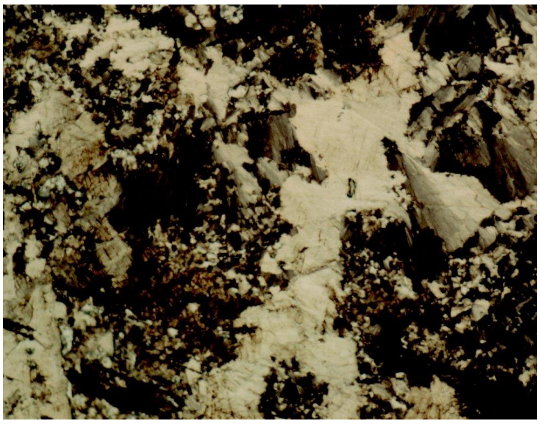

Figure 10: Aggregate consisting of mostly radiating arranged valleriite crystals. Reflected light, oil immersion objective, longer edge 450 µ. – Palabora/South Africa

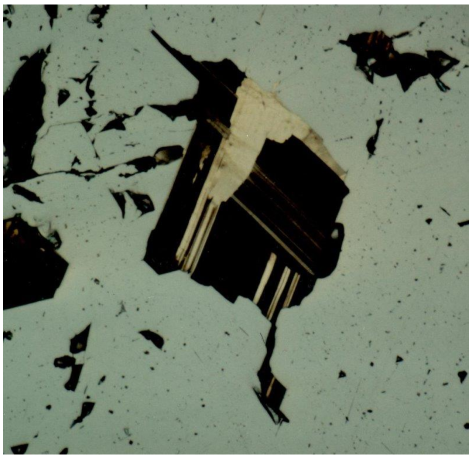

Figure 11: Parquet-like, polysynthetic twinning of valleriite caused by translation. The crystal which is embedded in magnetite shows a cutting position in which the brightes and lowest reflecting positions occur together. Reflected light, oil immersion objective, longer edge 450 µ. – Palabora

Centovalli, Tessin/Italy: Located in the eastern part of the Tessin, the Centovalli Valley forms the border between the northern (represented predominantly by the so-called Bündner Schists, ophiolites and partially also of flysch) and southern part (consisting of mafic to ultramafic plutonites) of the Alps. The sample originates from the Italian part of the valley close to the border to Switzerland. Ore minerals are chromite, valleriite, magnetite, pentlandite and graphite. Chromite, replaced along grain boundaries by magnetite and spinell, is mechanically broken. Along the cracks and small fissures, valleriite was newly-formed. The chemical composition is shown in Table 8 (columns VII – IX).

Figure 12: Valleriite in various cutting positions (brown to black) intimately intergrown with lensoidal-shaped magnetite (grey) embedded in pyrrhotite. Reflected light, oil immersion objective, longer edge 450 µ. – Domokos/Greece

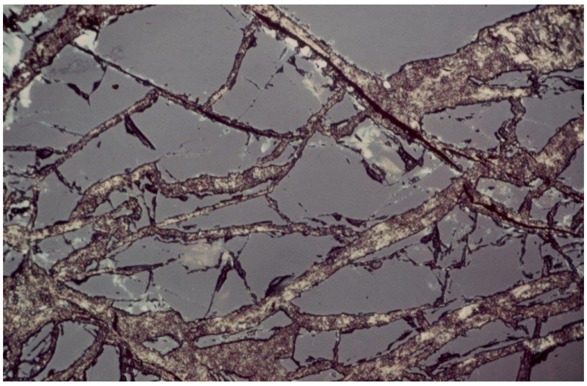

Figure 13: Valleriite occurring along cracks and fissures of magnetite (grey). Reflected light, oil immersion objective, longer edge 450 µ. – Domoskos/Greece

Hitura/Finland: The Hitura nickel mine belongs to a zone which contains a considerable number of Finnish sulphide deposits, the bedrocks of which consist mainly of Precambrian migmatites, black schists and ultamafic rocks including serpentinite. Minerals are chromite, but also pyrite, magnetite and valleriite. Pyrite is the host of net-like arranged magnetite containing valleriite inclusions. The composition of valleriite is summarized in Table 9, columns I – III.

Domokos/Greece: The locality was already described under mackinawite. The oxide-dominated mineralization contains valleriite which is included in pyrrhotite (Figure 12) and more abundant along cracks and fissures in magnetite (Figure 13). In Table 9 (columns IV – VI) the analyses are summarized.

Gole Gohar/Iran: The iron deposit lies in the Province of Kerman and belongs to the Sanandaj-Sirjan Zone and is hosted by ultramfic rocks [21,22]. The ore mineralization contains magnetite, pyrrhotite which contains flame-like exsolutions of pentlandite, pyrite, chalcopyrite, valleriite and brucite. Dominating mineral is magnetite which may contain inclusions of valleriite (Figure 14). Valleriite may also occur as replacer of chalcopyrite (Figure 15). The composition of valleriite is summarized in Table 9 (columns VII and VIII).

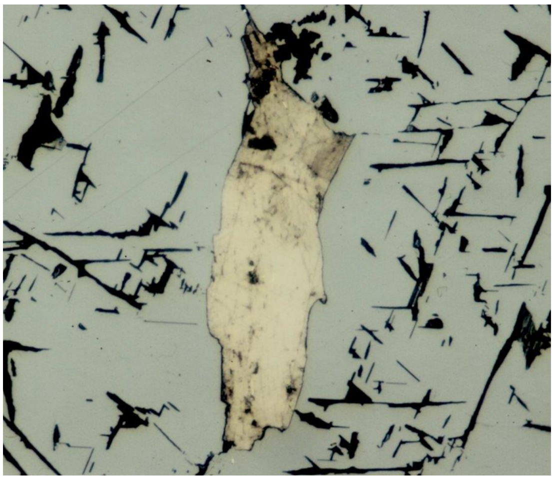

Figure 14: Valleriite in the bright cutting position included in magnetite which contains oriented arranged (parallel to [111]-magnetite) brucite-lamellae. Reflected light, oil immersion objective, longer edge 450 µ. – Gole Gohar/Iran

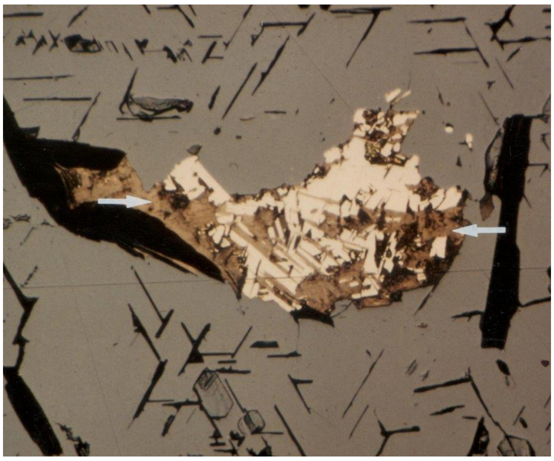

Figure 15: Chalcopyrite replaced by valleriite in magnetite which contains brucite-lamellae arranged along [111]-magnetite. Reflected light, oil immersion objective, longer edge 450 µ. – Gole Gohar/Iran

Outokumpu/Finland: Within the Outokumpu deposit, which was already described, abundant valleriite is distributed within chromite-rich and serpentinized ultramafic rocks. Other minerals are magnetite and subordinate pyrite which replaces pyrrhotite. Valleriite occurs in relatively big, platy crystals. As a sign of their decomposition, they are optical inhomogeneous (Figure 16). The analytical data are summarized in Table 10.

Figure 16: Metamorphically decomposed valleriite in a silicate groundmass (black). Spot-like distributed and concentrated along the rim of the original valleriite crystal, magnetite occurs (brightest mineral). Reflected light, oil immersion objective, longer edge 450 µ. – Outokumpu/Finland

Discussion

Mackinawite

According to Evans et al. [6] mackinawite has the formula (Fe, Ni)$_{1+x}$S (with $x \leq 0.07$), is tetragonal, has the space group P4$_2$/m and the lattice constants of a=3.68 and c=5.03 Å with Z=2. Refining the structure, Lennie et al. [23] presented new data, namely a=3.67 Å and the space group P4/nmm. The structure of mackinawite possesses a layer similar to that found in PbO (litharge with the same space group) with Fe and S occupying the sites of O and Pb, respectively, in litharge. Explained in terms of a distorted cubic close-packed arrangement of S atoms, the structure contains slightly distorted tetrahedron formed by S-atoms, whereas Fe fills the tetrahedral interstices which occur in the centre [23,24]. The FeS4 tetrahedra share edges and thus, form sheets of tetrahedra that are stacked normal to the c-axis. These sheets are hold together by weak van der Waals forces [25].

	Rustenburg/South Africa							**Zungeru/Nigeria**			
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
A: Analytical data in weight percent (wt. %)											
Fe	55.92	56.92	56.42	57.29	56.43	56.86	47.74	63.47	63.60	66.08	30.51

Co	-	-	-	0.31	0.51	0.41	0.74	-	-	-	-
Ni	7.37	7.60	7.49	6.65	6.75	6.70	15.15	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-	-	33.58
S	35.61	35.08	35.35	34.82	34.98	34.90	40.61	36.54	35.56	34.93	34.56
Σ	**98.90**	**99.60**	**99.26**	**99.07**	**98.67**	**98.87**	**99.24**	**100.01**	**99.16**	**101.01**	**98.65**
B: Atoms per formula unit (apfu)											
Fe	-	-	0.916	-	-	0.936	2.216	0.997	1.027	1.098	1.017
Co	-	-	-	-	-	0.006	0.037	-	-	-	-
Ni	-	-	0.116	-	-	0.105	0.747	-	-	-	-
Cu	-	-		-	-	-	-	-	-	-	0.983
Σ	-	-	**1.032**	-	-	**1.047**	**3.000**	**0.997**	**1.027**	**1.098**	**2.000**
S	-	-	**1.000**	-	-	**1.000**	**4.000**	**1.000**	**1.000**	**1.000**	**2.000**

Table 7: Mackinawite analyses of Rustenburg/SA and Zungeru/Nigeria (columns I and II and IV and V; VIII – X) and averaged analyses (III and VI) and analyses of linneite (column VII) and chalcopyrite (column XI). A: analytical data in wt. % and B: in apfu.

	Phalabora/South Africa						**Centovalli/Italia**		
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
A: Analytical data in weight percent (wt. %)									
Fe_{total}	20.12	20.57	27.41	19.05	21.48	18.97	30.43	30.90	30.19
Cu	20.48	20.69	21.52	21.18	22.51	24.36	17.10	17.43	17.54
S	21.80	22.35	23.54	21.18	21.54	21.15	23.30	22.43	21.67
Mg	9.85	10.45	8.91	10.98	10.79	10.87	8.53	8.63	9.06
Al	4.72	4.32	0.51	4.21	1.74	2.88	1.94	0.89	1.16
Σ_1	76.97	78.38	81.89	76.60	78.06	78.23	81.30	80.28	79.82
B_1: Atomic percent (at. %)									
Fe_{total}	**1.060**	**1.066**	**1.337**	**1.032**	**1.145**	**1.030**	**1.500**	**1.582**	**1.600**
B_2: Atoms per formula unit (apfu)									
Fe_I	1.052	1.066	1.077	0.991	0.946	0.838	1.259	1.216	1.183
Cu	0.948	0.934	0.923	1.009	1.054	1.162	0.741	0.784	0.817
Σ_1	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
S	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
(1) Fe_{II}	0.008	-	0.260	0.041	0.199	0.192	0.241	0.366	0.417
(2) Mg	1.192	1.233	0.998	1.367	1.321	1.356	0.966	1.015	1.103
Σ_2	**1.200**	**1.233**	**1.258**	**1.408**	**1.520**	**1.548**	**1.207**	**1.381**	**1.520**
Fe_{II}	0.007	-	0.207	0.029	0.131	0.124	0.200	0.265	0.274
Mg	0.993	1.000	0.793	0.971	0.869	0.876	0.800	0.735	0.726

Σ_3	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**
(3) Al	**0.515**	**0.459**	**0.052**	**0.472**	**0.192**	**0.324**	**0.198**	**0.094**	**0.127**
$OH_{(1)}$	0.016	-	0.520	0.082	0.398	0.384	0.482	0.732	0.834
$OH_{(2)}$	2.384	2.466	1.996	2.734	2.642	2.712	1.932	2.030	2.206
$OH_{(3)}$	1.545	1.378	0.156	1.416	0.576	0.972	0.594	0.282	0.381
Σ_4	**3.945**	**3.844**	**2.672**	**4.232**	**3.616**	**4.068**	**3.008**	**3.044**	**3.421**
C: Calculated data in weight percent (wt. %)									
Fe_I	19.97	20.57	22.08	18.29	17.75	15.43	26.54	23.75	22.32
Cu	20.48	20.69	21.52	21.18	22.51	24.36	17.10	17.43	17.54
S	21.80	22.35	23.54	21.18	21.54	21.15	23.30	22.43	21.67
Fe_{II}	0.15	-	5.33	0.76	3.73	3.54	4.89	7.15	7.87
Mg	9.85	10.45	8.91	10.98	10.79	10.87	8.53	8.63	9.06
Al	4.72	4.32	0.51	4.21	1.74	2.88	1.94	0.89	1.16
OH	22.80	22.78	16.67	23.76	20.65	22.81	18.58	18.10	19.65
Σ_2	**99.77**	**101.16**	**98.56**	**100.26**	**98.71**	**101.04**	**99.88**	**98.38**	**99.27**

Table 8: Valleriite analyses of Palabora/SA and Centovalli/Italy. A: analytical data including the analytical total (= Σ_1) in wt. %. B1: Fe_{total} in atom %. B_2: sulfidic layer: Fe_I + Cu (= Σ_1) and S; brucitic layer: amount of (1) Fe_{II} + (2) Mg in relation to the sulfidic layer [= x (= Σ_2) in the formula], ratio of Fe_{II} + Mg on the basis that their total is = 1.000 (=Σ_3), amount of (3) Al (= y of the formula) and the total of (OH=Σ_4) calculated from $Fe_{II}(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$ (all data in apfu). C: data of A. including the distribution of Fe_{total} into Fe_I + Fe_{II} and the calculated OH-amount by transformation of Σ_4 (= mol. %) into wt. % (Σ_{1+2+3}:OH) including the calculated total (=Σ_2).

	Hitura/Finland			**Domokos/Greece**			**Gole Gohar**	
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
A: Analytical data in weight percent (wt. %)								
Fe_{total}	37.64	37.21	39.58	36.85	34.80	31.36	21.10	25.15
Cu	8.50	8.23	9.04	16.53	16.04	17.76	22.05	21.87
S	24.76	25.29	21.78	22.21	20.33	21.20	19.85	19.89
Mg	10.74	12.24	9.48	6.54	5.70	9.32	11.48	10.46
Al	-	-	-	-	-	0.27	2.13	0.11
Σ_1	**81.64**	**82.97**	**79.90**	**82.13**	**76.87**	**79.91**	**76.61**	**77.49**
B_1: Atomic percent (at. %)								
Fe_{total}	1.746	1.690	2.087	1.905	1.941	1.699	1.220	1.453
B_2: Atoms per formula unit (apfu)								
Fe_I	1.653	1.672	1.581	1.249	1.229	1.155	0.879	0.990
Cu	0.347	0.328	0.419	0.751	0.771	0.845	1.121	1.110
Σ_1	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
S	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**

(1) Fe_{II}	0.093	0.018	0.506	0.656	0.712	0.544	0.341	0.563
(2) Mg	1.144	1.277	1.148	0.777	0.726	1.159	1.525	1.387
Σ_2	**1.237**	**1.295**	**1.654**	**1.433**	**1.438**	**1.703**	**1.866**	**1.950**
Fe_{II}	0.075	0.014	0.306	0.458	0.495	0.319	0.183	0.289
Mg	0.925	0.986	0.694	0.542	0.505	0.681	0.817	0.711
Σ_3	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**
(3) Al	-	-	-	-	-	0.030	0.255	0.013
OH_1	0.186	0.036	1.012	1.312	1.424	1.088	0.682	1.126
OH_2	2.288	2.554	2.296	1.554	1.452	2.318	3.050	2.774
OH_3	-	-	-	-	-	0.090	0.765	0.039
Σ_4	**2.474**	**2.590**	**3.308**	**2.866**	**2.876**	**3.496**	**4.497**	**3.939**
C: Calculated analytical data in weight percent (wt. %)								
Fe_I	35.63	36.81	29.98	24.16	22.27	21.56	15.20	15.41
Cu	8.50	8.23	9.04	16.53	16.04	17.76	22.05	21.87
S	24.76	25.29	21.78	22.21	20.33	21.20	19.85	19.89
FeII	2.01	0.40	9.60	12.69	13.53	10.04	5.90	9.75
Mg	10.74	12.24	9.48	6.54	5.70	9.32	11.48	10.46
Al	-	-	-	-	-	0.27	2.13	0.11
OH	16.24	17.12	19.10	16.88	16.65	19.65	23.69	20.77
Σ_2	**97.88**	**100.09**	**98.98**	**99.01**	**98.06**	**99.56**	**100.30**	**98.26**

Table 9: Valleriite analyses of Hitura/Finland, Domokos/Greece and Gole Gohar/Iran. A: analytical data including the analytical total (= Σ_1) in wt. %. B_1: Fe_{total} in atom %. B_2: sulfidic layer: Fe_I + Cu (= Σ_1) and S; brucitic layer: amount of (1) Fe_{II} + (2) Mg in relation to the sulfidic layer [= x (= Σ_2) in the formula], ratio of Fe_{II} + Mg on the basis that their total is = 1.000 (=Σ_3), amount of (3) Al (= y of the formula) and the total of (OH=Σ_4) calculated from $Fe_{II}(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$ (all data in apfu). C: data of A. including the distribution of Fe_{total} into Fe_I + Fe_{II} and the calculated OH-amount by transformation of Σ_4 (= mol. %) into wt. % (Σ_{1+2+3}:OH) including the calculated total (=Σ_2).

	Outokumpu/Finland				
	I	**II**	**III**	**IV**	**V**
Analytical data in weight percent (wt. %)					
Fe	39.09	39.20	35.50	36.61	38.08
Ni	1.21	-	1.17	0.68	1.17
Cu	8.96	12.14	7.76	8.44	8.37
S	12.81	7.60	14.51	15.10	8.86
Mg	5.35	3.76	4.65	5.09	3.86
Σ	**67.42**	**62.70**	**63.59**	**65.92**	**60.55**

Table 10: Analytical data (in wt. %) of valleriite from Outokumpu/Finland.

The calculated data of the mackinawite analyses into apfu are summarized under B of the Tables 1-7. In cases that mackinawite is homogeneously composed, only the averaged analyses were used for calculation. The apfu-data reveal two characteristic features:

Apart from compositions consisting of Fe and S only (Olympias, Tibschi, Panasqueira, Hagendorf, Rajpura-Dariba and Zungeru), others contain additional Ni (Frerone, Owyhee County, Vihanti, Shingbhum, Broken Hill and Rustenburg) or Co (Sjögruvan) or both Ni and Co (Outokumpu, Domokos, Otterstope, Shingbhum and Rustenburg); and

1. The metal concentration of Fe + Ni + Co in apfu varies around 1.
2. The lowest values (<1) were observed in Olympias (0.906 apfu), Sjögruvan (0.936), Outokumpu (0.921 – 0.967) and Tibschi (0.977).
3. Some values are lying close to ± 1. These are those of Panasqueira (0.980), Frerone (0.995), Owyhee County (0.999 – 1.009), Outokumpu (0.997 – 1.002), Zungeru (0.997), Shingbhum (1.003) and Domokos (1.006).
4. The highest values (>1) were detected at Hagendorf (1.012), Otterstope (1.027), Vihanti and Shingbhum (1.028), Broken Hill

(1.034), Rajpura-Dariba (1.047), Rustenburg (1.032 – 1.047) and Zungeru (1.027 and 1.098)

Locality	**Mackinawite**
Olympias	$Fe_{0.906}\ S_{1.000}$
Sjögruvan	$(Fe_{0.832}\ Co_{0.104})_{0.936}\ S_{1.000}$
Tibschi	$Fe_{0.977}\ S_{1.000}$
Panasqueira	$Fe_{0.980}\ S_{1.000}$
Frerone	$(Fe_{0.909}\ Ni_{0.091})_{0.995}\ S_{1.000}$
Owyhee County	$(Fe_{0.917}\ Ni_{0.082})_{0.999}\ S_{1.000}$;$(Fe_{0.942}\ Ni_{0.067})_{1.009}\ S_{1.000}$
Outokumpu	$(Fe_{0.811}\ Co_{0.078}\ Ni_{0.032})_{0.921}\ S_{1.000}$; $(Fe_{0.881}\ Co_{0.040}\ Ni_{0.031})_{0.952}\ S_{1.000}$; $(Fe_{0.831}\ Co_{0.101}\ Ni_{0.035})_{0.967}\ S_{1.000}$; $(Fe_{0.819}\ Co_{0.153}\ Ni_{0.025})_{0.997}\ S_{1.000}$; $(Fe_{0.847}\ Co_{0.126}\ Ni_{0.027})_{1.000}\ S_{1.000}$; $(Fe_{0.837}\ Co_{0.136}\ Ni_{0.029})_{1.002}\ S_{1.000}$
Domokos	$(Fe_{0.889}\ Co_{0.051}\ Ni_{0.066})_{1.006}\ S_{1.000}$
Hagendorf	$Fe_{1.012}\ S_{1.000}$
Otterstope	$(Fe_{0.900}\ Co_{0.007}\ Ni_{0.120})_{1.027}\ S_{1.000}$
Vihanti	$(Fe_{0.930}\ Ni_{0.098})_{1.028}\ S_{1.000}$
Shingbhum	$(Fe_{0.864}\ Co_{0.088}\ Ni_{0.051})_{1.003}\ S_{1.000}$; $(Fe_{0.926}\ Ni_{0.102})_{1.028}\ S_{1.000}$
Broken Hill	$(Fe_{0.984}\ Ni_{0.050})_{1.034}\ S_{1.000}$
Rajpura-Dariba	$Fe_{1.047}\ S_{1.000}$
Rustenburg	$(Fe_{0.916}\ Ni_{0.116})_{1.032}\ S_{1.000}$; $(Fe_{0.936}\ Co_{0.006}\ Ni_{0.105})_{1.047}\ S_{1.000}$
Zungeru	$Fe_{0.997}\ S_{1.000}$; $Fe_{1.027}\ S_{1.000}$; $Fe_{1.098}\ S_{1.000}$

Table 11: Formulae of mackinawite resulting from B. of the Tabs. 1 – 7 arranged with increasing metal concentration (= Fe + Ni + Co).

All calculated formulae are presented in Table 11. Deduced from this table, the resulting general formula is as follows: $(Fe, Ni, Co)_{1-x}S$ to $(Fe, Ni, Co)_{1+y}S$ with $x=0.00 - 0.10$ and $y=0.00 - 0.10$ showing that mackinawite may have the already known excess of the metal content shown on the right side of the formula. This excess can be explained by additional Fe-positions or a deficiency on the S-positions in the mackinawite structure. This interpretation agrees which considerations about mackinawite which has been reported as a metal excess phase [26] as well as a sulphur deficient phase [24]. The left side of the formula, illustrating a deficiency of the metals, was till now unknown. The deficiency is relatively easily explainable. In the mackinawite structure, some Fe-positions within the S-tetrahedra are not occupied. Nearly identical with the results of this paper, Schot et al. [27] postulated a formula of $(Fe, Ni, Co, Cu)_{1-x}S$ to $(Fe, Ni, Co, Cu)_{1+x}S$ in which their metal-content provides a range between 0.921 and 1.025.

In the literature, mackinawite is known to occur under various conditions, namely:

1. In meteorites (iron and carbonaceous chondrites);
2. In reducing environments such as river bottom muds and marine sediments as a result of the transformation of iron and sulphate (in solution) in the presence of sulphate-reducing bacteria;
3. As a major corrosion product when iron alloys are corroded by sulphate-reducing bacteria
4. As important metastable phases [28] due to its role as precursor to the formation of pyrite in sedimentary and hydrothermal systems;
5. In ultramafic rocks during serpentinization;
6. From hydrothermal activity in association with chalcopyrite, cubanite, pentlandite, pyrrhotite and sphalerite.

The formation of mackinawite, mentioned under the points 5 and 6 is of interest for this paper. However, ultramafic rocks and their serpentinization create just this environment under which valleriite, but not mackinawite generates. The points 2 to 4 were only mentioned for completeness, because these have no significance for this paper or are doubtful (e.g. the author has never observed the formation of pyrite under hydrothermal conditions from pre-existing mackinawite). It may be of note that mackinawite, synthesized under low temperature conditions reflecting the environments mentioned under the points 2 to 4, led to badly crystalline material [29] which is inferred to deviate structurally from well-crystalline mackinawite treated in this study.

According to this paper, the occurrence of mackinawite is connected with granites, pegmatites, high-grade metamorphic sediments and ultrabasic rocks (Domokos, Otterstope, Outokumpu and Rustenburg). Summarising the mode of formation of mackinawite, the following five variations occur which always resulted from hydrothermal conditions:

1. Most wide-spread is the formation of mackinawite which occurs in oriented intergrowth with chalcopyrite in the form of needle-like (Sjögruvan, Owyhee County), flame-like (Vihanti, Rustenburg) and elongated twin-like (Shingbhum) inclusions. Mackinawite may also occur in the form of tiny crystals (Owyhee County, Rustenburg) which may form an arrangement which resembles strings of pearls (Broken Hill). Mackinawite inclusions in chalcopyrite are nearly always associated with oriented lamellae of cubanite and rarely with star-like tiny exsolutions of sphalerite (e. g. Panasqueira).
2. Exsolved from sphalerite, chalcopyrite contains small sub-exsolution bodies of myrmekite-like (Olympias, Tibschi) or flame-like mackinawite (Panasqueira).
3. In various of the investigated occurrences chalcopyrite is replaced by pyrite, sometimes incompletely which led to chalcopyrite remnants in newly-formed pyrite. These remnants often contain myrmekitic mackinawite and also cubanite and star-like sphalerite (Hagendorf) or cubanite alone (Zungeru).
4. Mackinawite occurs along grain boundaries between chalcopyrite and pyrrhotite (Owyhee County).
5. Mackinawite is the result of the replacement of precursor minerals. These are: a) Chalcopyrite (Mte. Frerone, Outokumpu, Otterstope, Rustenburg). b) Pentlandite (Otterstope, Rustenburg, Domokos). C) Linneite replacing pentlandite is replaced by net-like arranged mackinawite (Rustenburg).

The formulae of chalcopyrite, cubanite, pentlandite and linneite occurring either as precursor or as associated mineral, are summarized in Table 12.

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Apart from the Italian occurrence Mte. Frerone, it was observed that chalcopyrite is twinned showing oleander-leaf like polysynthetic twinning (Figure 17). Twinning results from the fact that chalcopyrite, formed at high temperature (higher than 550°C), has a cubic structure in which Fe and Cu are statistically distributed and thus, has the formula of $(Fe,Cu)_2S_2$. With decreasing temperature, chalcopyrite inverts into the tetragonal modification in which Cu and Fe are in ordered arrangement with the formula of $FeCuS_2$. The inversion is accompanied with the formation of twins. The temperature of inversion decreases in the presence of $CuFeS_2$ – ZnS solid solutions (which were often observed in this study) to a temperature of about 500°C [30].

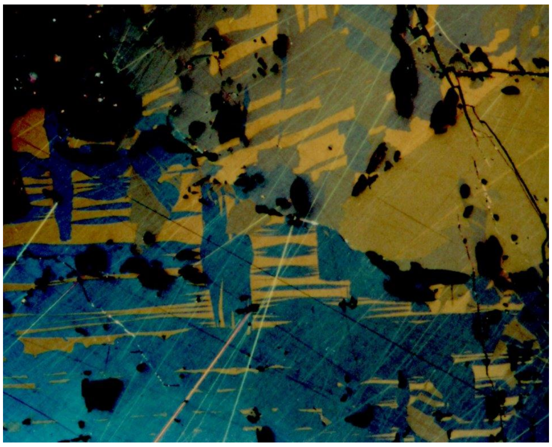

Figure 17: Chalcopyrite with polysynthetic arranged oleander leaf-like twins. The blue colour tint is attributed to the used objective which has a metal improved surface. Reflected light, oil immersion objective, crossed polars, longer edge 450 µ. – Hagendorf-South/ Germany

This temperature is the upper limit for the formation of mackinawite, insofar as it occurs in oriented intergrowth with twinned chalcopyrite. Some of the chalcopyrite crystals that host mackinawite in oriented intergrowth were also analysed. The calculated formulae are summarized in Table 12 showing that Fe is always greater than 1 and varies between 1.005 and 1.030. It is inferred that unexsolved high-temperature chalcopyrite had originally a distinctly higher Fe-concentration in relation to Cu. It is also inferred that the removal of Fe from primary Fe-rich chalcopyrite or the tendency to convert into the ordered and ideal $FeCuS_2$-composition, was initiated by the formation of the iron-sulphide mineral mackinawite.

Valleriite

Valleriite consists of two parallel arranged trigonal layers (S- and OH- or brucite-layer) and has the ideal formula (Fe, Cu)S • 0.75 [(Mg, Al, Fe)$(OH)_2$]. The S-layer (space group: $R\bar{3}m$) has lattice constants of a=3.79 and c=34.10 Å with Z=3 and the OH-layer (space group $P\bar{3}m1$) those of a=3.07 and c=11.37 Å with Z=2 [31]. The formula and the lattice constants are attributed from the data of Evans and Allmann [7] who established firstly the formula of valleriite with $(Fe_{1.07}\ Cu_{0.93})_{2.000}S_2 \bullet 1.526\ [(Mg_{0.68}\ Al_{0.32})_{1.000}(OH)_2]$. In the relevant literature other formulae are published: 2(Fe, Cu)S • 3[(Mg, Fe)$(OH)_2$] [32], $(Fe, Cu)_2S_2$ • [(Mg, Fe)$(OH)_2$] [33], 4(Fe, Cu)S • 3[(Mg, Al)$(OH)_2$] (Mineral data publishing) and $(Fe^{2+}, Cu)_4(Mg, Al)_3S_4(OH, O)_6$ (mindat.org).

Locality	Chalcopyrite
Olympias Tibschi Owyhee County Outokumpu Zungeru Vihanti	$(Fe_{1.013}\ Cu_{0.987})_{2.000}S_{2.000}$
	$(Fe_{1.010}\ Cu_{0.990})_{2.000}S_{2.000}$
	$(Fe_{1.030}\ Cu_{0.970})_{2.000}S_{2.000}$
	$(Fe_{1.019}\ Cu_{0.981})_{2.000}S_{2.000}$
	$(Fe_{1.017}\ Cu_{0.983})_{2.000}S_{2.000}$
	$(Fe_{1.005}\ Cu_{0.095})_{2.000}S_{2.000}$
Sjögruvan	**Cubanite**
	$Cu_{1.010}\ Fe_{1.990}S_{3.000}$
Otterstope	**Pentlandite**
	$(Fe_{4.601}\ Ni_{4.340}\ Co_{0.059})_{9.000}S_{8.000}$
Rustenburg	**Linneite**
	$(Fe_{2.216}\ Ni_{0.747}\ Co_{0.037})_{3.000}S_{4.000}$

Table 12: Formulae of chalcopyrite, cubanite, pentlandite and linneite resulting from B. of the Tables 1-5 and 7.

The data of the valleriite analyses, summarized in Tables 8 and 9, reveal that the data of the Outokumpu analyses (Table 10) differ distinctly from the other analyses. Supporting the microscopic observation of the valleriite decay at Outokumpu, the data of Table 10 could not be transformed into valleriite or valleriite-related formulae,

The calculated analytical data are summarized in Tables 8 and 9. The resulting general valleriite formula is: $(Fe, Cu)_2S_2$ • x [(Mg, Fe)$_1(OH)_2$] • y [Al$(OH)_3$] with x=1.20 - 2.10 and y=0 - 0.50. The results of the presented formula clearly demonstrate that the ratio between the S- and brucite-layer is not constant as it varies in a relatively wide range. In respect of the proposed formula, a paper must be mentioned, comparable to mackinawite, which obviously did not make its way into the relevant literature. This concerns the paper of Schot et al. [27] which proposed the following formula: $CuFeS_2$ • n [(Mg, Ca, Fe, Ni, Co, Mn)$_1(OH)_2$] • m [Al$(OH)_3$] with n=1.14 - 2.33 and m=0 - 0.50. These authors obviously inferred, that Al$(OH)_3$ forms a third layer (= gibbsite-layer) within the valleriite structure.

Writing the formula of this study in the sense of Evans and Allmann [7] by substitution of Mg by Al, it transforms into $(Fe, Cu)_2S_2$ • x [$(Mg^{2+}, Fe^{2+}, Al^{3+})(OH)_2$] with x=1.20 - 2.12. However, this substitution is not supported by the calculation of the analyses, because in that case, the amount of OH became too low, and as a consequence, also the analytical total. This can be deduced from Tables 8 and 9 under B2, where the Al: OH-ratio was calculated with 1: 3 [= Al$(OH)_3$]. However, in the Evans-formula, the ratio of Al: OH is 1: 2 and therefore, the OH-layer has to be positively charged [= Al$(OH)_2]^+$. In their discussion, Evans and Allmann [7] argued that valleriite belongs to the well-established group of minerals, where the positively charged brucite-layers are interleaved by negatively charged layers of another kind. However, their argumentation cannot be applied to valleriite, because the sulphide-layer is electroneutral. However, their assumption may be correct, if the Al-substitution is limited to only small quantities. This was not observed in this study. In order to eliminate this problem, the following exchange is proposed: $Mg_3(OH)_6=(Al_2\square_1)_3(OH)_6$ (□ = vacancy) and therefore the introduction of vacancies into the brucite-layer. Based on this interpretation, the analytical data of B_2 were newly calculated (Tables 13 and 14) and the corresponding formulae were summarized in Table 15. The newly deduced general formula is:

$(Fe, Cu)_2S_2 \bullet x\,[(Mg^{2+}, Fe^{2+}, Al^{3+}{}_y, \square_{y/2})(OH)_2]$ where x=1.24 – 2.25 and y=0.00 – 0.26.

	Palabora/South Africa						Centovalli/Italia		
	I	II	III	IV	V	VI	VII	VIII	IX
B_3: Atoms per formula unit (apfu)									
Fe_{II}	0.008	-	0.260	0.041	0.199	0.192	0.241	0.366	0.417
Mg	1.192	1.233	0.998	1.367	1.321	1.356	0.966	1.015	1.103
Al	0.515	0.459	0.052	0.472	0.192	0.324	0.198	0.094	0.127
□	0.258	0.230	0.026	0.236	0.096	0.162	0.099	0.047	0.064
Σ_1	**1.973**	**1.922**	**1.336**	**2.116**	**1.808**	**2.034**	**1.504**	**1.522**	**1.711**
Fe_{II}	0.004	-	0.195	0.019	0.110	0.124	0.160	0.240	0.244
Mg	0.604	0.641	0.747	0.646	0.731	0.876	0.642	0.667	0.645
Al	0.261	0.239	0.039	0.223	0.106	0.324	0.132	0.062	0.074
□	0.131	0.120	0.019	0.112	0.053	0.162	0.066	0.031	0.037
Σ_2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Table 13: Apfu-data of Phalabora and Centovalli calculated from the analytical data of Tab. 8 A and B_2 and based on the assumption that Al is part of the OH-layer. 1. Determination of the amount of Fe_{II} + Mg + Al + □ in relation to the sulfidic layer (= Σ_1=x of the formula) and 2. Determination of the ratio of Fe_{II} + Mg + Al + □ on the basis that their total is=1.000 (= Σ_2).

	Hitura/Finland			Domokos/Greece			Gole Gohar	
	I	II	III	IV	V	VI	VII	VIII
B_3: Atoms per formula unit (apfu)								
Fe_{II}	0.093	0.018	0.506	0.656	0.712	0.544	0.341	0.563
Mg	1.144	1.277	1.148	0.777	0.726	1.159	1.525	1.387
Al	-	-	-	-	-	0.030	0.255	0.013
□	-	-	-	-	-	0.015	0.128	0.007
Σ_1	1.237	1.295	1.654	1.433	1.438	1.748	2.249	1.970
Fe_{II}	0.075	0.014	0.306	0.458	0.505	0.311	0.152	0.286
Mg	0.925	0.986	0.694	0.542	0.495	0.663	0.678	0.704
Al	-	-	-	-	-	0.017	0.113	0.007
□	-	-	-	-	-	0.009	0.057	0.003
Σ_2	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**

Table 14: Apfu-data of Hitura, Domokos and Gole Gohar calculated from the analytical data of Table 9 A abd B_2 and based on the assumption that Al is part of the OH-layer. The arrangement of the data is identical to Table 13.

Locality	**Tab.8 and 13**	**Valleriite**
Palabora	I	$(Cu_{0.948}Fe_{1.052})_{2.000}S_{2.000} \bullet 1.973\ [(Mg_{0.604}Fe_{0.004}Al_{0.261}\square_{0.131})_1(OH)_2]$
	II	$(Cu_{0.934}Fe_{1.066})_{2.000}S_{2.000} \bullet 1.922\ [(Mg_{0.641}Al_{0.239}\square_{0.120})_1(OH)_2]$
	III	$(Cu_{0.923}Fe_{1.077})2.000S_{2.000} \bullet 1.336\ [(Mg_{0.747}Fe_{0.195}Al_{0.039}\square_{0.019})_1(OH)_2]$
	IV	$(Cu_{1.009}Fe_{0.991})_{2.000}S_{2.000} \bullet 2.116\ [(Mg_{0.646}Fe_{0.019}Al_{0.223}\square_{0.112})_1(OH)_2]$
	V	$(Cu_{1.054}Fe_{0.946})_{2.000}S_{2.000} \bullet 1.808\ [(Mg_{0.731}Fe_{0.110}Al_{0.106}\square_{0.053})_1(OH)_2]$
	VI	$(Cu_{1.162}Fe_{0.838})_{2.000}S_{2.000} \bullet 2.034\ [(Mg_{0.667}Fe_{0.094}Al_{0.159}\square_{0.080})_1(OH)_2]$
Centovalli	VII	$(Cu_{0.741}Fe_{1.259})_{2.000}S_{2.000} \bullet 1.504\ [(Mg_{0.642}Fe_{0.160}Al_{0.132}\square_{0.066})_1(OH)_2]$
	VIII	$(Cu_{0.784}Fe_{1.216})_{2.000}S_{2.000} \bullet 1.522\ [(Mg_{0.667}Fe_{0.240}Al_{0.062}\square_{0.031})_1(OH)_2]$
	IX	$(Cu_{0.817}Fe_{1.183})_{2.000}S_{2.000} \bullet 1.711\ [(Mg_{0.645}Fe_{0.244}Al_{0.074}\square_{0.037})_1(OH)_2]$
Hitura	Tab. 9 and 14	
	I	$(Cu_{0.347}Fe_{1.653})_{2.000}S_{2.000} \bullet 1.237\ [(Mg_{0.925}Fe_{0.075})_2(OH)_2]$
	II	$(Cu_{0.328}Fe_{1.672})_{2.000}S_{2.000} \bullet 1.295\ [Mg_{0.986}Fe_{0.014}(OH)_2]$
	III	$(Cu_{0.419}Fe_{1.581})_{2.000}S_{2.000} \bullet 1.654\ [Mg_{0.694}Fe_{0.306}(OH)_2]$
Domokos	IV	$(Cu_{0.751}Fe_{1.249})_{2.000}S_{2.000} \bullet 1.433\ [Mg_{0.542}Fe_{0.458}(OH)_2]$
	V	$(Cu_{0.771}Fe_{1.229})_{2.000}S_{2.000} \bullet 1.438\ [Mg_{0.505}Fe_{0.495}(OH)_2]$
	VI	$(Cu_{0.845}Fe_{1.155})_{2.000}S_{2.000} \bullet 1.748\ [(Mg_{0.663}Fe_{0.311}Al_{0.017}\square_{0.009})_1(OH)_2]$
Gole Gohar	VII	$(Cu_{1.121}Fe_{0.879})_{2.000}S_{2.000} \bullet 2.249\ [(Mg_{0.678}Fe_{0.152}Al_{0.113}\square_{0.057})_1(OH)_2]$
	VIII	$(Cu_{1.110}Fe_{0.990})_{2.000}S_{2.000} \bullet 1.970\ [(Mg_{0.704}Fe_{0.286}Al_{0.007}\square_{0.003})_1(OH)_2]$

Table 15: Formulae of valleriite resulting from the Tabs. 13 and 14 based on the proposed formula in which Al is part of the OH-layer.

Among the two formulae discussed in this paper, the vacancy-bearing version should be preferred. Otherwise it must be postulated, that valleriite is a three-layer mineral (sulphide-, brucite- and gibbsite-layer) and that Evans and Allmann [7] disregarded existing gibbsite during their structural investigations.

According to this study, valleriite is a product of secondary hydrothermal conditions (ranging from mesothermal to low katathermal) and occurs within deposits/occurrences that are, apart from the carbonatite deposit of Palabora, always associated with more or less serpentinized ultramafic rocks. Valleriite is the youngest mineral in the association and restricted to mineral associations that are dominated by chromite and/or magnetite, but only in the presence of chalcopyrite.

Under high-grade metamorphic conditions, valleriite is not stable and decomposes e.g. in Outokumpu (Figure 16). Thermal decomposition studies of valleriite carried out in an inert atmosphere by Iglesias et al. [34] show that the dehydroxylation of the brucite layers starts at about 350°C, followed by the lattice breakdown. At 450°C, valleriite disappears completely and new phases appear. In an oxidizing atmosphere, the same authors observed between 250°C and 650°C a long lasting oxidation process which obviously masked the valleriite breakdown.

Optical features of mackinawite and valleriite

Mackinawite and valleriite belong, similar to graphite, to those minerals which are characterized by striking optical features. Mackinawite is strongly bireflecting showing a reflectivity in the range between 44% and 37% (18% and 6%) corresponding with uncoloured effects from pure white to light grey (grey to dark grey) (in brackets: data in oil). Identical data for valleriite are: 21% and 11% (10% and 3%) corresponding with coloured effects from light crème-yellow to grey (dark crème-yellow to dark grey). Valleriite reveals therefore strong reflection pleochroism. Under crossed polars, strong anisotric effects become obvious. The extinction positions of mackinawite and valleriite are black in air and oil (in valleriite darker). The 45° position (brightest position) is pure white in air and oil for mackinawite and yellowish for valleriite.

These data reveal that confusion between mackinawite and valleriite during microscopic observations should normally be excluded, in particular in cases when the two minerals occur together (Figure 18). However, it should be noted that valleriite and graphite are not easily distinguishable from one another e. g. valleriite of Gole Gohar/Iran was wrongly identified as graphite by Mücke and Golestaneh [21] because the colour, the reflectivity in the bright position and the anisotropic effects in the 45° position of the two minerals are similar. Under crossed polars, the extinction position, often not clearly visible due to undulatory extinction, is darker in graphite, especially in air.

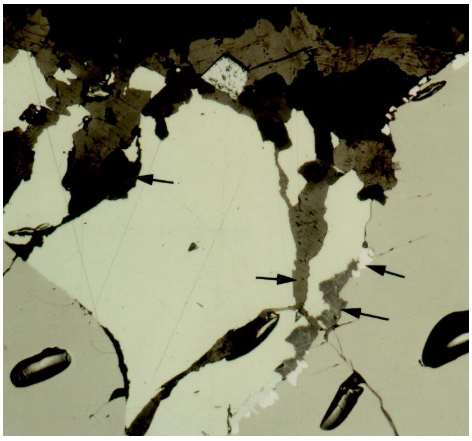

Figure 18: Valleriite replaces chalcopyrite (yellow) and mackinawite occurs along the grain boundary between chalcopyrite and pyrrhotite (brownish and slightly darker than chalcopyrite). Note the arrows within chalcopyrite: on the left side, valleriite in the dark cutting position and on the right side, in the bright cutting position of valleriite. The two arrows (on the extreme left side) within pyrrhotite mark the bright and the dark cutting positions of mackinawite. Note that the dark cutting position of mackinawite (grey) is similar to that of the bright cutting position of valleriite (grey with a brownish tint). Reflected light, oil immersion objective, longer edge 450 µ. – Kovdor/Russia

Under particular circumstances, the macroscopic recognition of valleriite may be possible. Mackinawite, on the other hand, can only be observed in reflected light. Also by the support of a pocket-lens, mackinawite is always by far too small as to be recognized.

Acknowledgement

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