

## A SECOND OCCURRENCE OF FALKMANITE: PINNACLES MINE, BROKEN HILL, NEW SOUTH WALES

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### ABSTRACT

A Pb-Sb sulfosalt in galena-rich ore from the Pinnacles lead-zinc deposit (Broken Hill, Australia) has been identified as falkmanite, a formerly discredited mineral, recently rehabilitated on material from the original Bavarian locality. Electron-microprobe analysis indicates the composition  $Pb_{5.35}Sb_{3.65}As_{0.04}S_{10.92}$ . The crystals are monoclinic, with cell dimensions:  $a$  21.547(6),  $b$  23.475(9),  $c$  8.090(1) Å,  $\beta$  100.75(3)°,  $V$  4020 Å<sup>3</sup>. Maximum reflectance values at  $\lambda = 420, 546, 589,$  and  $650$  nm, are 43.9, 42.9, 41.7, 39.3 in air and 27.7, 26.4, 25.3, 23.0 in oil, respectively. The microindentation hardness (VHN<sub>100</sub>) ranges from 128 to 176 (average 144). The falkmanite forms part of a complex assemblage of sulfosalts, which developed below 650°C during retrograde alteration of the ore. It is probably a low-temperature form of the Cu-free meneghinite composition, with an ordered superstructure, formed by the alteration of Cu-bearing meneghinite solid-solution. This is only the second verified occurrence of falkmanite. This species has probably been confused with boulangerite in other sulfosalt assemblages and is likely to be more common in nature than previously realized.

**Keywords:** lead-antimony sulfosalt, falkmanite, reflectance, microhardness, X-ray data, microprobe analysis, retrograde metamorphism, Pinnacles mine, Broken Hill, Australia.

### SOMMAIRE

On a identifié la falkmanite dans le minerai riche en galène, du gîte Pb-Zn de Pinnacles (Broken Hill, Australie). Cette espèce jadis discréditée a été réhabilitée sur des spécimens provenant du gîte original bavarois. L'analyse du matériau de Broken Hill donne la composition  $Pb_{5.35}Sb_{3.65}As_{0.04}S_{10.92}$ . Les cristaux, monocliniques, ont la maille  $a$  21.547(6),  $b$  23.475(9),  $c$  8.090(1) Å,  $\beta$  100.75(3)°,  $V$  4020 Å<sup>3</sup>. Les valeurs maxima de la réflectance, 43.9, 42.9, 41.7, 39.3 dans l'air et 27.7, 26.4, 25.3, 23.0 dans l'huile, se présentent à  $\lambda = 420, 546, 589,$  et  $650$  nm, respectivement. La dureté microindentation (VHN<sub>100</sub>) varie de 128 à 176 (moyenne 144). La falkmanite fait partie d'un assemblage complexe de sulfosels; elle s'est formée sous 650°C, au cours d'une altération rétrograde du minerai. C'est probablement une forme de ménéghinite à surstructure ordonnée, où le Cu ferait défaut, formée à basse température par altération d'une solution solide de ménéghinite (de cuivre). Notre trouvaille de falkmanite est la seconde qui soit authentifiée. On a probablement confondu cette espèce avec la boulangerite dans d'autres assemblages de

sulfosels; elle est vraisemblablement plus répandue dans la nature qu'on ne l'a pensé précédemment.

(Traduit par la Rédaction)

**Mots-clés:** sulfosel de plomb et d'antimoine, falkmanite, réflectance, dureté, données de rayons X, analyse à la microsonde, métamorphisme rétrograde, mine Pinnacles, Broken Hill, Australie.

### INTRODUCTION

The mineral falkmanite has had a chequered history since it was first proposed as a separate species by Ramdohr & Ödman (1940). These authors described the mineral in samples from the Bayerland mine, Bavaria and from Boliden, Sweden and derived the formula  $Pb_5Sb_3S_6$  from the results of chemical analyses of inhomogeneous material, after correction for admixed bournonite and arsenopyrite. They found the X-ray-diffraction pattern to be very similar to that of boulangerite, but with some additional reflections and differences in intensity for identical lines. The optical properties differed sufficiently from those of boulangerite to suggest a different mineral.

Robinson (1948) re-examined type specimens of falkmanite after he was unable to synthesize the mineral in experiments in the system Pb-Sb-S. He found the X-ray powder pattern and cell dimensions for unanalyzed material to be indistinguishable from those of boulangerite. He ascribed the higher lead content in chemical data reported by Ramdohr & Ödman (1940) to galena impurities and concluded that falkmanite should be discredited as an individual mineral species. After this, falkmanite was generally considered a discredited mineral (Chudoba 1960, Strunz 1966), although some texts persisted in describing it, and several studies reported new occurrences but without conclusive evidence (e.g., Ramdohr 1955, Hiller 1955, Knauer & Richter 1968).

Recently Mozgova *et al.* (1983) were able to prove that falkmanite, as described by Ramdohr & Ödman (1940), does indeed exist in material from the Bayerland mine. These authors also proposed that falkmanite should be considered a member of a boulangerite series and that the composition limit of greater than 74.2 mole% PbS be used to separate falkmanite

from the other members of this series (plumosite, <70.2 mole% and boulangerite 70.2–74.2 mole%).

In the course of a study of Ag-bearing minerals from the Pinnacles mine near Broken Hill, the present author discovered a boulangerite-like mineral that has the composition, X-ray-diffraction pattern and other properties of falkmanite. Data from this occurrence confirm the existence of the falkmanite composition in nature and provide additional information on the properties and paragenesis of this mineral. This is the first documented occurrence of falkmanite from the Broken Hill area and from Australia.

#### OCCURRENCE

The Pinnacles lead–zinc sulfide deposit lies 16 km southwest of Broken Hill and appears to be a metamorphosed exhalative deposit similar to the main Broken Hill lode, though much smaller and probably formed at a different stratigraphic level (Barnes 1980). The deposit occurs in high-grade metamorphic rocks (mainly gneisses of granulite-facies grade; Hewins 1975, Phillips & Wall 1981) and consists of a lead-rich lode overlain and underlain by weakly developed zinc lodes. Most of the small production at the mine (200,000 tonnes) has been from the lead lode which, in addition to galena and minor sphalerite, contains a range of accessory Pb–Sb sulfosalts and Ag-bearing minerals (Stillwell 1926,

1953, Ramdohr 1950, Lawrence 1968, McQueen 1984). In 1984, a near-surface extension to the lead lode was located and is being worked from a small open-pit. Galena-rich ore from this location has higher-than-average silver values and was found to contain minor freibergite  $\text{Cu}_{4.5}\text{Ag}_{6.5}(\text{FeZn})_2\text{Sb}_{4.5}\text{S}_{13}$ , pyrrargyrite  $\text{Ag}_3\text{SbS}_3$ , trace famatinite  $\text{Cu}_3\text{SbS}_4$ , and falkmanite.

Falkmanite occurs as irregular and subhedral, prismatic grains (<1.2 mm long) within galena. It is intimately associated with irregular intergrowths and veins of minor pyrrargyrite as well as small grains (<0.05 mm) of famatinite. The ore sample containing falkmanite has undergone some incipient oxidation and shows narrow zones and patches of anglesite along fractures in galena and around the margins of other mineral inclusions (Fig. 1). Where galena is unaltered, falkmanite and pyrrargyrite show mutual boundaries with galena. Famatinite (identified from optical properties and microprobe analysis) generally occurs around the edges of falkmanite grains and is intergrown with fine-grained galena or anglesite after galena. Associated gangue minerals are quartz, spessartine garnet, calcite and gahnite. Freibergite occurs as small inclusions in galena from the same part of the lead lode but is not present in the sample containing falkmanite. Boulangerite, meneghinite, bournonite and jamesonite, which are more common sulfosalts in the Pinnacles ores (Ramdohr 1950, McQueen 1984), are also absent in this sample.

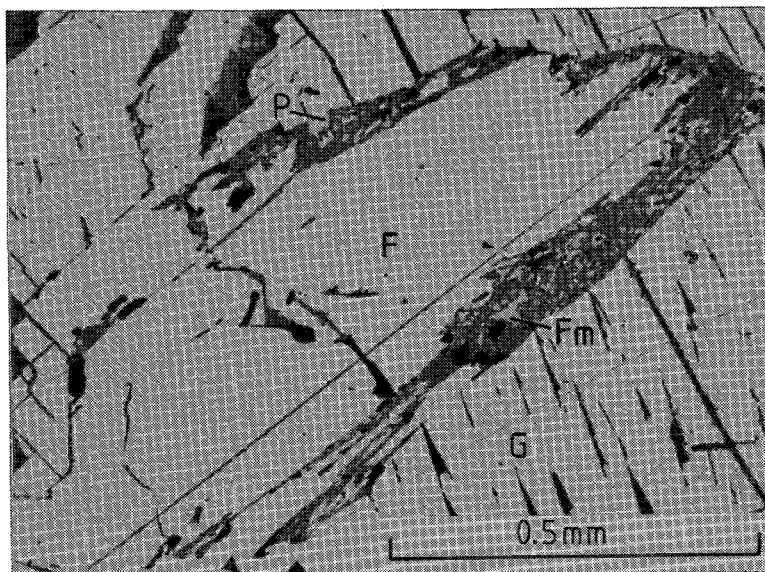


FIG. 1. Prismatic grain of falkmanite (F) in galena (G) with small irregular grains of famatinite (Fm) and pyrrargyrite (P). Dark grey area is anglesite after galena. Grain 1, sample Pn 24, plane-polarized light. Reflectivity, microhardness, X-ray diffraction and compositional data were obtained from this grain.

## COMPOSITIONAL DATA

Falkmanite was initially detected by its compositional difference from boulangerite and meneghinite. An analysis (Table 1) was obtained using a Cameca

TABLE 1. CHEMICAL COMPOSITION OF FALKMANITE

wt. %	1	S	2	S
Pb	58.15	0.28	58.32	0.36
Sb	23.31	0.16	23.43	0.11
As	0.17	0.01	0.16	0.03
S	18.32	0.16	18.47	0.04
TOTAL	99.95		100.38	

Formulae			
Pb	5.35		5.35
Sb	3.65		3.65
As	0.04		0.04
S	10.90		10.94

1. Average of 4 spot analyses, grain 1 (sample Pn24).  
 2. Average of 3 spot analyses, grain 2 (sample Pn24).  
 Data obtained using a Cameca Camebax microbeam microprobe.  
 ZAF data reduction (N. Ware). S = standard deviation.  
 Ag, Cu and Fe were also sought but are below detection.  
 Detection limits: S 0.03%; As, Cu, Fe, Sb 0.05%;  
 Ag 0.06%; Pb 0.12%.

electron microprobe with Ag, As, Cu, Sb, troilite and galena as standards. The beam current was 39 nA with an accelerating voltage of 20 kV. The  $L\alpha$  line was used for As analysis to avoid overlap with the  $PbL\beta$  peak. Two separate grains gave a composition close to that found by Mozgova *et al.* (1983) in their re-investigation of type material from the Bayerland mine. This composition is also very close to the ideal formula of  $Pb_{5.4}Sb_{3.6}S_{11}$  (Table 1, Mozgova *et al.* 1983). Silver, Cu and Fe are below detection, but both grains contain trace, detectable As (0.16 wt. %). The mean Pb/Sb ratio (1.47) is significantly different from that of boulangerite (1.28) and meneghinite (1.88) from the same deposit (McQueen 1984).

## MINERAL PROPERTIES

Falkmanite from the Pinnacles deposit is distinctly bireflectant in prismatic section, varying from white with a yellowish green tint against galena to white with a darker bluish green tint. It shows strong anisotropism from blue grey to olive grey and near-parallel extinction. Reflectance values for a grain showing maximum observable bireflectance (Fig. 1) are:  $R_1$  38.1, 37.2, 36.3, 34.7;  $R_2$  43.9, 42.9, 41.7, 39.3 (in air for  $\lambda = 420, 546, 589$  and 650 nm, respectively) and  $R_1$  22.1, 21.2, 20.6, 19.0;  $R_2$  27.7, 26.4, 25.3, 23.0 (corresponding data in oil). Dispersion curves and specifications are given in Figure 2.  $R_2$  values (in air) correspond closely to those of Mozgova *et al.* (1983); however, values of  $R_1$  are higher, suggesting that sections exhibiting minimum reflectivity were not present in the two mounts studied.

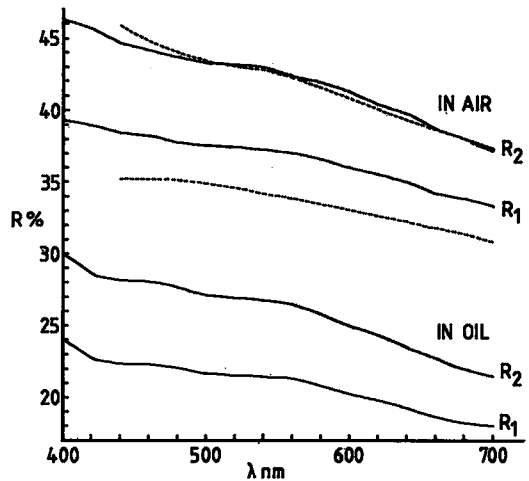


FIG. 2. Dispersion curves of reflectance in air and oil for falkmanite from the Pinnacles mine. Measurements were made on a Zeiss MPM 03 microscope photometer, WC standard (Zeiss 036), Zeiss oil (518C) at 23°C with continuous filter monochromator (b type Veirl Z160),  $\Delta\lambda = 15-18$  nm, aperture 2  $\mu$ m, 40/.85 objective. Measurements were reproducible to within  $\pm 0.3$  percentage units. Dashed curves are  $R_1$  and  $R_2$  data for falkmanite from the Bayerland mine (Mozgova *et al.* 1983).

Mozgova *et al.* (1983) did not report the reflectivity in oil.

Falkmanite shows good cleavage parallel to grain length in prismatic sections. Polishing hardness is slightly less than for galena and greater than for pyrargyrite. Microindentation hardness was determined using a Leitz Miniload hardness tester. The Vickers hardness number ( $VNH_{100}$ ) ranges from 128 to 176 (average 144) for 26 indentations on 5 separate grains. Indentations are square to slightly elongate parallel to cleavage. On prismatic grains, indentation edges are typically convex normal to the grain length and concave parallel to this direction. Cleavage and simple shell-fractures are common (*cf.* Mozgova *et al.* 1983). The Vickers hardness values compare closely with values of 169–186 for meneghinite and 147–174 for boulangerite from the Pinnacles deposit.

## X-RAY DATA

X-ray-diffraction data were obtained from one of the falkmanite grains analyzed by electron microprobe. The powder pattern is similar to that obtained by Mozgova *et al.* (1983) and close to the pattern of boulangerite (*cf.* Robinson 1948, Mozgova & Bortnikov 1980). It was possible to determine some additional  $d$  values (Table 2). Indexing of the pow-

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR FALKMANITE

hkl	$d_{obs}(\text{\AA})$	$d_{calc}(\text{\AA})$	I	hkl	$d_{obs}(\text{\AA})$	$d_{calc}(\text{\AA})$	I
430	4.39	4.385	<1	2101	2.18	2.180	<1
331	4.13	4.121	<1	971	2.14	2.140	1
411	4.01	4.008	2	173	2.04	2.040	4
530	3.74	3.738	10	1050	1.93	1.930	1
540	3.43	3.434	<1	093	1.86	1.859	5
170	3.31	3.314	1	383	1.83	1.830	<1
630	3.22	3.217	3	1070	1.79	1.790	<1
242	3.02	3.022	5	5102	1.76	1.761	<1
342	2.82	2.820	8		1.73		<1
062	2.79	2.789	2	843	1.65	1.649	<1
740	2.70	2.697	<1	205	1.53	1.530	<1
190	2.59	2.590	<1		1.47		<1
532	2.53	2.534	<1	684	1.41	1.410	<1
670	2.43	2.431	1	864	1.37	1.370	<1
481	2.38	2.381	2	385	1.33	1.330	<1
372	2.32	2.322	1	485	1.30	1.300	<1
282	2.25	2.252	1	1054	1.28	1.279	<1
590	2.22	2.222	<1				

114.6 mm Gandolfi camera calibrated with Si standard,  $\text{CuK}\alpha$  Ni filtered radiation, 7 hr exposure, 20 mA 40kV, intensities estimated visually, hkl values calculated to  $\text{Sin}^2\theta$  tolerance of  $5 \times 10^{-4}$ .

der pattern and refinement of the cell dimensions assuming a monoclinic structure gave  $a$  21.547(6),  $b$  23.475(9),  $c$  8.090(1) Å,  $\beta$  100.75(3)° and  $V$  4020 Å<sup>3</sup>. These values are essentially identical to the cell parameters of boulangerite and falkmanite (Berry 1940, Mozgova *et al.* 1983).

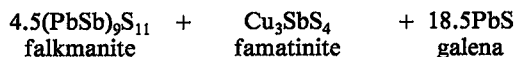
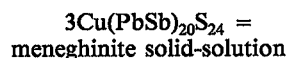
#### PARAGENESIS AND DISCUSSION

The falkmanite at the Pinnacles deposit appears to be part of an Sb-sulfosalt assemblage developed during complex retrograde metamorphism of the ores. Mineralogical and textural relationships in other parts of the deposit indicate that a number of sulfosalts and associated decomposition-phases have formed during retrograde alteration at temperatures below 650°C (McQueen 1984). Some of these relationships can be explained in terms of experimental phase-equilibria for temperatures above 300°C. For example, symplectitic intergrowths of boulangerite and galena around meneghinite appear to have formed by the breakdown of a high-temperature phase (phase II of Salanci 1979) or by the separation of meneghinite solid-solution into meneghinite and a Cu-free meneghinite (Jambor 1975, Wang 1977), with breakdown of the latter phase to galena and phase II, and ultimately to galena and boulangerite (*cf.* Salanci 1979).

Relationships within the Pb-Sb sulfosalts below 300°C are not fully understood and appear to be complicated by nonstoichiometric compositions and development of a number of solid-solution series with more-or-less ordered members. These include a meneghinite homologous series showing orthorhombic symmetry and containing natural Cu-bearing meneghinite, synthetic Cu-free meneghinite and synthetic  $\text{Pb}_2\text{Sb}_2\text{S}_5$  (Mozgova *et al.* 1983,

Makovicky & Nørrestam 1985) and a boulangerite solid-solution series with falkmanite, boulangerite, plumosite and  $\text{Pb}_4\text{Sb}_6\text{S}_{13}$  (Mozgova *et al.* 1983). Falkmanite and boulangerite appear to be ordered compounds showing monoclinic symmetry but different degrees and types of ordering (Mozgova *et al.* 1983, E. Makovicky, pers. comm.). Falkmanite is compositionally similar to Cu-free meneghinite and may represent the structurally stable form of this composition at lower temperatures. Copper-free meneghinite has not been recorded in nature; a small amount of Cu is considered essential to stabilize the meneghinite structure to a low temperature (Hoda & Chang 1975, Jambor 1975, Hicks & Nuffield 1978). Falkmanite has apparently not been produced experimentally but could conceivably form by the structural transformation of Cu-free meneghinite or by the removal of Cu from low-temperature meneghinite solid-solution.

In the Pinnacles occurrence, intergrowths of minor famatinite and galena around the margin of falkmanite grains suggest thermal breakdown, or fluid-assisted alteration of a Cu-bearing phase such as meneghinite. A schematic reaction for this alteration could be:



This is essentially an equal-volume reaction and closely approximates the observed proportions of falkmanite and intergrown famatinite and galena. It is also possible that minor pyrargyrite was involved in this breakdown, accounting for small amounts of Cu, Sb, S and possibly Ag derived from the meneghinite solid-solution.

As falkmanite has very similar physical properties and crystal structure to the other members of the boulangerite series and can only be effectively detected using compositional distinctions, it is likely that this phase has been overlooked in other sulfosalt assemblages and may be more common in nature than previously realized.

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## REFERENCES

- BARNES, R.G. (1980): Types of mineralization in the Broken Hill Block and their relationship to stratigraphy. *New South Wales Geol. Surv. Rec.* **20**(1), 33-70.
- BERRY, L.G. (1940): Studies of mineral sulphosalts. III. Boulangerite and "epiboulangerite". *Univ. Toronto Studies, Geol. Ser.* **44**, 5-19.
- CHUDOBA, K.F. (1960): *Handbuch des Mineralogie, Erzüngungsband II. Neue Mineralien und Neue Mineralnamen*. Walter de Gruyter, Berlin.
- HEWINS, R.H. (1975): Pyroxene geothermometry of some granulite facies rocks. *Contr. Mineral. Petrology* **50**, 205-209.
- HICKS, W.D. & NUFFIELD, E.W. (1978): Natural and synthetic meneghinite. *Can. Mineral.* **16**, 393-395.
- HILLER, J.E. (1955): Über den Falkmanit und seine Unterscheidung von Boulangerit. *Neues Jahrb. Mineral. Monatsh.*, 1-10.
- HODA, S.N. & CHANG, L.L.Y. (1975): Phase relations in the pseudo-ternary system  $PbS-Cu_2S-Sb_2S_3$  and the synthesis of meneghinite. *Can. Mineral.* **13**, 388-393.
- JAMBOR, J.L. (1975): Synthetic copper-free meneghinite. *Geol. Surv. Can. Pap.* **75-1B**, 71-72.
- KNAUER, E. & RICHTER, P. (1968): Neue Beobachtungen zur Erzmineralführung der Gold-Quarz-Gänge bei Brandholz im Fichtelgebirge. *Neues Jahrb. Mineral. Monatsh.*, 463-471.
- LAWRENCE, L.J. (1968): The minerals of the Broken Hill district. In *Broken Hill Mines - 1968* (M. Radmanovich & J.T. Woodcock, eds.). *Austral. Inst. Mining Metall.*, 103-136.
- MCQUEEN, K.G. (1984): Meneghinite, boulangerite and associated minerals from the Pinnacles mine, Broken Hill, New South Wales. *Neues Jahrb. Mineral. Monatsh.*, 323-336.
- MAKOVICKY, E. & NØRRESTAM, R. (1985): The crystal structure of jaskolskiite  $Cu_xPb_{2+x}(Sb,Bi)_{2-x}S_5$  ( $x \approx 0.2$ ), a member of the meneghinite homologous series. *Z. Krist.* **171**, 179-194.
- MOZGOVA, N.N. & BORTNIKOV, N.S. (1980): On non-stoichiometry of the acicular lead sulphantimonites. In *Geochimiya Mineralogiya, Nauka, Moscow*, 126-138 (in Russ.).
- \_\_\_\_\_, \_\_\_\_\_, TSEPIN, A.I., BORODAIEV, YU. S., VRUBLEVSKAYA, S.V., VYALSOV, L.N., KUZMINA, O.V. & SIVTSOV, A.V. (1983): Falkmanite,  $Pb_{5.4}Sb_{3.6}S_{11}$ , new data and relationship with sulphantimonites of lead (re-examination of type material from Bayerland mine, Bavaria). *Neues Jahrb. Mineral. Abh.* **147**, 80-98.
- PHILLIPS, G.N. & WALL V.J. (1981): Evaluation of prograde regional metamorphic conditions: their implications for the heat source and water activity during metamorphism in the Willyama Complex, Broken Hill, Australia. *Bull. Minéral.* **104**, 801-810.
- RAMDOHR, P. (1950): Die Lagerstätte von Broken Hill in New South Wales im Lichte der neuen geologischen Erkenntnisse und erzmikroskopischer Untersuchungen. *Heidelb. Beitr. Mineral. Petrog.* **2**, 291-333.
- \_\_\_\_\_. (1955): *Die Erzminerale und ihre Verwachsungen*. Akademie-Verlag, Berlin.
- \_\_\_\_\_. & ÖDMAN, O. (1940): Falkmanit, ein neues Bleispiessglanz erz, und sein Verkommen, besonders in Boliden und Grube Bayerland. *Neues Jahrb. Mineral. Abt. A.* **75**, 315-350.
- ROBINSON, S.C. (1948): The identity of falkmanite and yenerite with boulangerite. *Amer. Mineral.* **33**, 716-723.
- SALANCI, B. (1979): Beiträge zum System  $PbS-Sb_2S_3$  in Beziehung zu natürlichen Blei-Antimon-Sulfomineralien. *Neues Jahrb. Mineral. Abh.* **135**, 315-326.
- STILLWELL, F.L. (1926): Observations on the mineral constitution of the Broken Hill lode. *Proc. Austral. Inst. Mining Metall.* **64**, 97-172.
- \_\_\_\_\_. (1953): Mineralogy of the Broken Hill lode. In *Geology of Australian Ore Deposits* (A.B. Edwards, ed.). *Austral. Inst. Mining Metall.*, 601-626.
- STRUNZ, H. (1966): *Mineralogische Tabellen*. Akademische Verlagsgesellschaft Geest and Portig, Leipzig.
- WANG, N. (1977): Synthesis and crystal data of a Cu-free "meneghinite". *Can. Mineral.* **15**, 115-116.

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