

NATURAL AND SYNTHETIC MENEHGINITE

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ABSTRACT

Meneghinite crystals from three Ontario localities range closely in composition about the ideal formula $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$. All exhibit the faint X-ray reflections given by Bottino crystals, which have been interpreted by Euler & Hellner (1960) as indicative of a multiple cell with $c = 24 \times 4.128 \text{ \AA}$. The reflections are not given by Jambor's (1975) synthetic Cu-free meneghinite which has a composition close to $\text{Pb}_{12.5}\text{Sb}_8\text{S}_{24}$. The apparent structural difference suggested by the chemistry of natural and synthetic Cu-free meneghinite can be reconciled by an expression based on Euler & Hellner's determination of the distribution of metal atoms in Bottino crystals, $4[M_x\text{Pb}_2(\text{Sb,Pb})_3\text{S}_6]$ in which M_x in $\text{Cu}_{1/2}$ (natural) and $\text{Pb}_{1/6}$ (synthetic). Presumably the faint reflections in natural meneghinite result from some ordering of Pb and Sb in the common metal positions. Thus, the solid solution field of Cu-bearing, stoichiometric meneghinite phases synthesized by Hoda & Chang (1975) is seen to develop an increasing vacancy rate in the Pb positions toward the Sb_2S_3 -rich end when compositions are cast in the format of the general expression given above. Presumably this accounts for the decrease in crystallinity across the field.

SOMMAIRE

Des cristaux de ménéghinite provenant de trois gîtes de l'Ontario sont très proches, en composition, de la formule idéale $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$. Ils montrent tous les réflexions X faibles qui caractérisent les cristaux de Bottino et qui, d'après Euler & Hellner (1960), indiquent une maille multiple, $c = 24 \times 4.128 \text{ \AA}$. Ces réflexions sont absentes sur les diagrammes que donne la ménéghinite synthétique dépourvue de cuivre (Jambor 1975) de composition approchant $\text{Pb}_{12.5}\text{Sb}_8\text{S}_{24}$. La différence structurale entre la ménéghinite naturelle et le produit de synthèse qu'implique la différence de chimisme s'explique par la distribution des atomes métalliques dans les cristaux de Bottino, suivant Euler & Hellner: $4[M_x\text{Pb}_2(\text{Sb,Pb})_3\text{S}_6]$, $M_x = \text{Cu}_{1/2}$ (minéral), $M_x = \text{Pb}_{1/6}$ (synthétique). Les réflexions faibles seraient dues à une certaine mise en ordre de Pb et Sb dans les trois positions à occupation mixte. Le

champ de solution solide des phases stoechiométriques à teneur en cuivre (synthétisées par Hoda & Chang 1975) montre que les lacunes dans les positions du plomb augmentent avec la proportion de Sb_2S_3 , lorsqu'on exprime la composition des phases selon la distribution ci-dessus. Ce serait là l'explication de la cristallinité décroissante observée d'un bout à l'autre du champ.

(Traduit par la Rédaction)

INTRODUCTION

The few published analyses of natural meneghinite all show small amounts of copper; at first, these were attributed to the presence of impurities. However, Berry & Moddle (1941) proposed the composition $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$; Euler & Hellner (1960) found that the composition derived from the determination of the structure of meneghinite from Bottino, Italy is in agreement with this formula. It has been suggested that the copper might be necessary to stabilize the structure. Despite this, the existence of Cu-free synthetic meneghinite is well established by powder X-ray data (Jambor 1975). Also, the unit-cell dimensions obtained by Wang (1977) on synthetic material are in close agreement with the subcell of natural meneghinite: Euler & Hellner (1960) report a 11.363, b 24.057, c 4.218 \AA for natural meneghinite, whereas Wang (1977) found a 11.36, b 23.98, c 4.10 \AA for the Cu-free synthetic material. Both Jambor and Wang found that synthetic meneghinite is nonstoichiometric; Wang proposed a metal-rich formula, $\text{Pb}_{8+x}\text{Sb}_8\text{S}_8$, in which $0 < x \leq 0.15$.

Euler & Hellner concluded that the true cell of Bottino meneghinite has a c period of $24 \times 4.128 \text{ \AA}$, giving the cell contents $24[\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}]$. The multiple nature of the period is revealed on oscillation photographs about the c (needle) axis as two sparsely populated, very faint layer lines between the zero line and the strong line that represents the 4.128 \AA sub-period. When the latter line is indexed as the

24th order, the faint lines index as the 11th and 13th orders. Thus the layer lines that register on oscillation photographs index as: zero (strong), 11th and 13th (very weak), 24th (strong), 35th and 37th (very weak), 48th (strong), *etc.* Very long exposures fail to develop any of the missing layer lines. Publications dealing with synthetic, Cu-free meneghinite do not refer to the faint layer lines.

This brief summary points up several unusual features in the description of meneghinite and suggests that the data for natural and synthetic meneghinite are not entirely in harmony. In view of the results of studies of synthetic material, the supposed ubiquitous presence of copper in the structure and the interpretation of the faint reflections on oscillation photographs are in need of confirmation. Also, the compositions of natural and synthetic meneghinite seem to be at variance. As most of the published data have been obtained on the fine prismatic crystals from Bottino, a study of material from other localities seemed in order; the several occurrences in Ontario, which have received little attention, were chosen for this purpose.

PRESENT STUDY

Our material consists of three specimens of natural meneghinite, intimately associated with boulangerite, and one of synthetic material (see footnotes to Table 1). The natural material exhibits a brilliant metallic lustre and subconchoidal fracture on fresh surfaces. It is generally massive but is infrequently truncated by crystal faces with reasonably sharp striations which proved to be parallel to the *c* axis. The striations served to make an approximate visual setting of fragments on the Weissenberg goniometer, but a precise setting with orientation oscillation photographs seldom could be achieved. The fragments almost invariably were found to be bundles of subparallel crystals. Single crystals could not be isolated by additional splitting. On Weissenberg films they give elongate reflections that are usually of little value for cell dimension determinations. We experienced the same difficulty with Jambor's synthetic meneghinite.

Despite the poor quality of the crystals, it was possible to obtain rotation photographs from well-chosen small fragments; these could be compared with similar photographs of Bottino crystals to make a positive identification of the crystals. In this way material was selected for microprobe analyses. Long-exposure oscillation photographs of the best fragments showed that the faint 11th and 13th order layer lines

are always present on Ontario meneghinite, suggesting that they are characteristic of all natural meneghinite. In contrast, similar work on Jambor's material did not reveal any additional layer lines; therefore, the true cell of his Cu-free, synthetic meneghinite has a *c* dimension of about 4.1 Å.

The new analyses (Table 1) were obtained on an ARL-EMX electron microprobe with a solid-state detector for energy-dispersive analysis. An examination of the energy spectra for each sample revealed the presence of only copper, lead, antimony and sulfur. X-ray intensity counts taken for these elements with wavelength-dispersive spectrometers over at least ten micro-areas on each sample indicated that the samples are homogeneous. As an additional test for the presence of iron, reported as occurring in trace amounts in all old analyses of meneghinite, counts of X rays emitted at the FeK α wavelength were collected over a number of micro-areas on each sample and compared with the counts obtained from a metallic iron standard. None of the samples seems to contain iron above the limits of detection of the microprobe (less than 0.05%).

The final quantitative values for the four elements were obtained with the wavelength-dispersive spectrometers using as standards synthetic galena (Pb), stibnite (Sb, S) and chalcocopyrite (Cu). Two separate sets of analyses were made for each sample; their averages are reported in Table 1.

The analyses of Ontario meneghinite range closely about the ideal composition, CuPb₁₃Sb₇S₂₄ proposed by Berry & Moddle. The analyses support the assumption that a small but nearly constant amount of copper is essential to the formation of meneghinite in nature. The composition of the Cu-free synthetic meneghinite is close to Pb_{12.5}Sb₈S₂₄.

The structure proposed by Euler & Hellner

TABLE 1. MICROPROBE ANALYSES* AND CATION PROPORTIONS OF MENEGHINITE

	Cu	Pb	Sb	S	Total	Cu ⁺	Pb	Sb
1	1.20	61.52	19.53	17.59	99.84	0.83	12.99	7.02
2	1.46	61.30	19.55	17.88	100.19	0.99	12.74	6.91
3	1.49	61.92	18.55	17.69	99.65	1.02	13.00	6.63
4	1.52	62.44	19.47	17.49	100.92	1.05	13.26	7.03
5	--	59.72	22.55	17.58	99.99	--	12.52	8.05

*In weight per cent.

+atomic proportions recalculated to S = 24.

1. Bottino, Italy (UT R45). 2. Anglesea Tp., Ont. (ROM M19743). 3. Perry Silver Mine, Marble Lake, Frontenac Co., Ont. (ROM M4094). 4. Marmora, Hastings Co., Ont. (ROM M4095). 5. Synthetic (Jambor 1975): average of 3 analyses.

Analysts: 1-4, E. Gasparrini. Data reduction effected with EMPADR VII (Rucklidge & Gasparrini 1969). 5, A. G. Plant (Jambor 1975).

for the subcell contains 6 metal positions, each with 4 equivalent sites. Of the 6 positions, Euler & Hellner found that 2 are fully occupied by Pb, 3 are fully occupied by Pb and Sb, and 1 is one-quarter filled by Cu. This distribution of atoms in the subcell can be expressed by the formula $4[\text{Cu}_{1/4}\text{Pb}_2(\text{Sb},\text{Pb})_3\text{S}_6]$, in which the ratio of Sb to Pb in the brackets is 7:5. A relation between the compositions of natural and synthetic meneghinite becomes apparent if the latter composition is expressed by a similar formula $4[\text{Pb}_{1/4}\text{Pb}_2(\text{Sb},\text{Pb})_3\text{S}_6]$, in which the Sb:Pb ratio in the brackets is 8:4. The portion $\text{Pb}_{1/4}$ represents the metal-excess part of the formula. In the absence of Cu, which is apparently necessary to stabilize the structure in nature, Pb fulfills this function in a Cu-free synthesis of the structure, although this results in a non-stoichiometric composition. The composition of the sub-cell of natural meneghinite and the cell of Cu-free synthetic meneghinite can be expressed by the general formula $4[M_x\text{Pb}_2(\text{Sb},\text{Pb})_3\text{S}_6]$, in which M_x is $\text{Cu}_{1/4}$ (natural) and $\text{Pb}_{1/4}$ (Cu-free synthetic).

The absence of the faint lines in synthetic meneghinite implies a less perfect ordering of the metal atoms in the structure. Presumably the sharing of atomic positions by Pb and Sb occurs on a more random basis.

THE CU-BEARING SYNTHETIC MENEHGINITE OF HODA & CHANG

Hoda & Chang (1975) synthesized Cu-bearing stoichiometric meneghinite at temperatures of 500°, 400° and 300° C using an evacuated glass-capsule technique. They identified the products of quenching by a powder X-ray diffraction method. Products judged to be homogeneous by observation in polished section were taken to have the compositions of the starting mixtures. Meneghinite was found to have an elongate $\text{PbS-Sb}_2\text{S}_3$ solid-solution region with the composition of natural meneghinite at the high-PbS end of the field. The extent of the field proved to be temperature-dependent, being considerably restricted at 300°.

Hoda & Chang observed that the X-ray diffraction patterns of various compositions synthesized by them at 500°C (Table 2) are identical (and identical with the pattern given by crystals from Bottino) except that the crystallinity, as revealed by the quality of the patterns, declined with decreasing PbS content. It is apparent from Table 2 that the compositions of the phases trend from the composition of natural meneghinite toward $\text{CuPbSb}_3\text{S}_6$. The composition of the final phase in the table, when cast in the

TABLE 2. PHASE COMPOSITIONS* AND CATION PROPORTIONS OF SYNTHETIC MENEHGINITE

Cu_2S	PbS	Sb_2S_3	Cu^\dagger	Pb	Sb
5.56	81.11	13.33	0.5	3.8	1.3
2.94	76.47	20.59	0.25	3.25	1.75
4.00	72.00	24.00	0.3	2.9	1.9
4.00	68.00	28.00	0.3	2.6	2.2
8.00	63.00	29.00	0.6	2.4	2.2
8.00	59.00	33.00	0.6	2.1	2.4
13.00	50.00	37.00	0.9	1.7	2.6
11.00	46.00	43.00	0.7	1.5	2.8

* in weight per cent (Hoda & Chang 1975). † atomic proportions recalculated to S = 6.

format of the general expression derived above, has the form $4[\text{Cu}_{0.7}\text{Pb}_{1.3}(\text{Sb}_{2.8}\text{Pb}_{0.2})\text{S}_6]$. The deteriorating crystallinity is evidently related to the increasing vacancy rate in the positions occupied by Pb in natural meneghinite. As the value of Pb in the formula falls from 2 to 1.3, the structure becomes increasingly unstable and, at 500°, is not able to exist with a smaller amount of Pb.

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