

Re-study of Semseyite from the Chichibu Mine, Saitama Prefecture, Japan

Akira Kato¹, Masaaki Shimizu², and Yoshio Okada³

¹Department of Geology, National Science Museum,
3–23–1 Hyakunincho, Shinjuku-ku, Tokyo, 169 Japan

²Department of Petrology and Mineral Deposits,
University Museum, University of Tokyo,
7–3–1 Hongo, Bunkyo-ku, Tokyo, 113 Japan

³2–19–7 Shimo-Shakujii, Nerima-ku, Tokyo, 177 Japan

Abstract Semseyite from the contact metasomatic ore deposits of the Chichibu mine, Saitama Prefecture, Japan, previously identified after the X-ray powder and optical studies, is analysed by microprobe. The ranges and average (parenthesized) of 23 analyses are: Pb 51.29–53.09 (52.24), Sn 0.12–0.21 (0.17), Cd 0.03–0.14 (0.10), Ag 0.00–0.12 (0.07), Fe 0.00–0.05 (0.02), Zn 0.00–0.08 (0.01), Mn 0.00–0.04 (0.01), Cu 0.00–0.03 (0.01), Sb 27.39–28.37 (27.99), Bi 0.00–0.22 (0.09), S 19.77–20.09% (19.92%), and the total of the average is 100.58%. The calculated S content is 19.26%, giving the total 99.92%. The empirical formula calculated on the basis of the latter figure of S=21 is: $(\text{Pb}_{8.81}\text{Sn}_{0.05}\text{Cd}_{0.03}\text{Fe}_{0.01}\text{Ag}_{0.01}\text{Zn}_{0.01}\text{Mn}_{0.01}\text{Cu}_{0.01})_{\Sigma 8.94}(\text{Sb}_{8.03}\text{Bi}_{0.01})_{\Sigma 8.04}\text{S}_{21}$ ($\text{S}_{21.71}$ if uncorrected), where Sn is handled as divalent. Neither discrete Sn nor Bi mineral has been found not only in the associated minerals but also in the whole ore deposits. Semseyite coats galena grains, which is the unique direct associate, and the galena perches on coarse-grained pyrite forming hollow hemisphere aggregates with an iron-rich sphalerite. Minor associates are chalcopyrite, tetrahedrite, bournonite, arsenopyrite, quartz, and hedenbergite. No boulangerite is found therein despite its compositionally intermediary nature between galena and semseyite and its occurrence in the other part of the same orebody. An interval of sulphide formation seems to have existed between galena and semseyite, which was preferentially precipitated on galena at the latest stage of sulphide formation, or under lower temperature conditions, where many other Pb-Sb sulphosalts have been synthesized. Some of them are structurally out of the fülöppite-semseyite homologous series despite their chemical compositions between the members thereof.

Key words: semseyite, chemical composition, Chichibu mine.

Introduction

The described semseyite from the Daikoku orebody of the contact metasomatic ore deposits of the Chichibu mine, Saitama Prefecture, Japan (Uetani *et al.*, 1966) (NSM-M21104) is now subjected to the microprobe analysis and mineralogical consideration. The former proved the compositional proximity to the ideal $\text{Pb}_9\text{Sb}_8\text{S}_{21}$ and

the overall presence of Sn, Cd and Bi as the quantitatively measurable minor constituents. The latter informed the unique occurrence in ore deposits of contact metasomatic origin and the simpler association after the comparison with some semseyite descriptions including the subsequent occurrence in Japan (Ishiyama *et al.*, 1990), where some other sulphosalts and complex sulphides are found in a hydrothermal vein alike to the cases of the other semseyite occurrences. The present semseyite was deposited exclusively on galena grains after a break in the process of sulphide formation, where the composition of parental fluid must have favoured the formation preferentially to such commoner Pb-Sb sulphosalt like boulangerite, which has the intermediate composition between galena and semseyite.

Occurrence

The ore deposits of the Chichibu mine are located in the western part of Saitama Prefecture, where limestone beds are intruded by a later granite body, producing some orebodies (Miyazawa *et al.*, 1957) including the Daikoku orebody, from which the examined material comes (Uetani *et al.*, 1966). They had been worked for Cu, Pb, Zn, Au and Ag but now mined out completely. In the ore deposits are various kinds ore and skarn minerals including the new mineral hydroxyllestadite (Harada *et al.*, 1971).

Semseyite occurs as radially aggregated silvery lead grey blades of a millimeter long involving galena grains which perch on pyrite grains aggregated to form hollow hemisphere of about 10 cm across, the perching of the galena grains being exclusively on the inside (Uetani *et al.*, 1966). Although the mode of occurrence of this hemisphere could not be observed in underground, it is said that the aggregates of various size was found in recrystallized limestone. The material of the present time was taken from another pyrite aggregate collected in the same time as the previously examined material, the allotted number being same, NSM-M21104. Under the ore microscope, semseyite occurs exclusively on galena with a zig-zag boundary composed of near linear traces (Fig. 1). Also, the accumulation of semseyite blades is observed on galena (Fig. 2). Galena forms cubes or its aggregates on the pyrite aggregates forming hemisphere. It is pure without any inclusion except for minor chalcopyrite. Sphalerite grains appear to consist of two microscopically discriminated portions, rather round subgrains with fewer chalcopyrite dots and the interstitial portions including abundant chalcopyrite dots. Pyrite is coarse in grain size and aggregated with linear boundaries any interstitial materials. Tetrahedrite and bournonite encountered in the previous examination (Uetani *et al.*, 1966) were not found.

Chemical Analyses

The results of some microprobe analyses are given in Table 1. The empirical for-

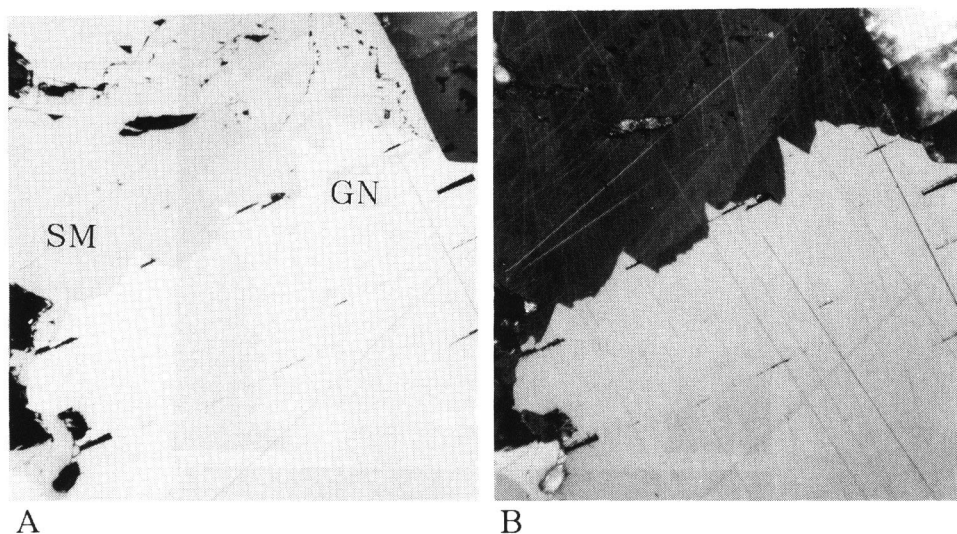


Fig. 1. Photomicrograph of semseyite (SM) on galena (GN) grains from the Daikoku orebody, the Chichibu mine, Japan, indicating the grain boundaries. A: in plane polarized light; B: with crossed polars, both in air. Lateral field view 0.23 mm.

mula derived from the average demonstrates a slight excess of Sb and concomitant deficiency of Pb, where Sn is tentatively handled as divalent. No systematic variation of the constituents was found in relation to the analysed points in the examined grains. The quantitative fluctuations of Pb and Sb onto the both sides of the ideal formula are also seen in the results of semseyite analyses in a single locality (Bevins *et al.*, 1990). In their work, two different specimens were analysed in different institutions, giving the wider range of compositional variation than the present case.

Also, the chemical formula of semseyite has been supported from the structural standpoints after Mozgova and Borodaev (1972), who created a homologous series with the general formula $Pb_{3+2n}Sb_8S_{15+2n}$, the members being fülöppite ($n=0$), plagionite ($n=1$), heteromorphite ($n=2$), and semseyite ($n=3$). Therefore, no excess of sulphur is expected beyond the theoretical figure referring to the most probable valency states of Pb and Sb, divalent and trivalent, respectively. The handling of Sn needs consideration as to the preference of the valency state, divalent or tetravalent. The general tendency in the deficiency of Pb and the groupable cations with it, Sn is considered to be divalent due to the ability to substitute Pb. If the tetravalent state is taken, it is to be amalgamated with Sb. This is to enhance the excess nature of Sb in proportion to Pb etc., although it tends to lessen the difference between the obtained and calculated S figures. Cd and minor Bi are added to Pb and Sb, respectively. Sn and Cd are the first minor constituents seen in semseyite. In all analyses, Cd is lower than Sn in quantity.

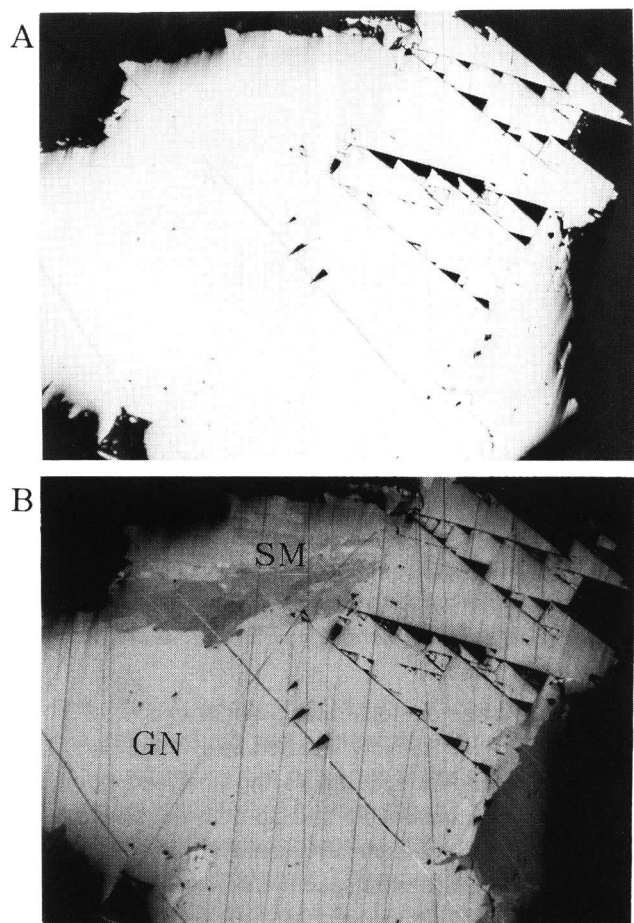


Fig. 2. Photomicrograph of semseyite (SM) on galena (GN) grains from the Daikoku orebody, the Chichibu mine, Japan, indicating the accumulation of blades of semseyite (SM) on galena (GN). A: in plane polarized light; B: with crossed polars, both in oil. Lateral field view 0.78 mm.

The derivation of empirical formula needed the correction of S contents. If the obtained figures are strictly calculated into empirical formulae on a tentative basis of $S=21$, it invites notable deficiency of Pb etc. as well as Sb in many cases. The employed manner of calculation was taken due to the judgement that the formulae should be balanced after the selection of most reasonable valency states of constituents, unless structurally proved unreasonable, such as the existence of excess sulphur.

Chemical analyses of semseyite are reported recently from the Bwlch Mine, Wales (Bevins *et al.*, 1988). They are obtained on two materials using different in-

Table 1. Chemical analyses of semseyite from the Daikoku orebody, Chichibu mine, Saitama Prefecture. (S* is for the calculated figure. See text.)

WEIGHT PERCENTAGES							
	Range	1.	2.	3.	4.	5.	6.
Pb	51.29–53.09	52.24	52.89	51.29	51.71	51.73	53.10
Sn	0.12– 0.21	0.17	0.12	0.14	0.22	0.18	
Cd	0.03– 0.14	0.10	0.06	0.09	0.14	0.10	
Ag	0.00– 0.12	0.07	0.02	0.08	—	0.09	
Fe	0.00– 0.05	0.02	0.01	0.04	0.05	0.04	
Zn	0.00– 0.08	0.01	—	0.01	—	—	
Mn	0.00– 0.04	0.01	0.01	—	—	0.03	
Cu	0.00– 0.03	0.01	0.02	—	—	—	
Sb	27.39–28.37	27.99	27.39	28.35	27.78	28.25	27.73
Bi	0.00– 0.22	0.09	—	0.05	0.13	0.22	
S	19.77–20.09	19.92	19.84	20.09	20.00	19.80	19.17
S*		19.26	19.09	19.25	19.13	19.34	
sum		100.58	100.39	100.14	100.03	100.43	100.00
sum*		99.92	99.64	99.30	99.16	99.97	

1. Average of 23 analyses.
2. The most Pb-rich analysis.
3. The most Sb-rich analysis.
4. The most Cd-and Sn-rich analysis.
5. The most Bi-rich analysis.
6. Theoretical figure.

EMPIRICAL FORMULAE (calculated on the basis of S*=21)

1. $(\text{Pb}_{8.81}\text{Sn}_{0.05}\text{Cd}_{0.03}\text{Fe}_{0.01}\text{Ag}_{0.01}\text{Zn}_{0.01}\text{Mn}_{0.01}\text{Cu}_{0.01})_{\Sigma 8.94}(\text{Sb}_{8.03}\text{Bi}_{0.01})_{\Sigma 8.04}\text{S}_{21}$
2. $(\text{Pb}_{9.00}\text{Sn}_{0.04}\text{Cd}_{0.03}\text{Fe}_{0.01}\text{Ag}_{0.01}\text{Mn}_{0.01}\text{Cu}_{0.01})_{\Sigma 9.11}\text{Sb}_{7.94}\text{S}_{21}$
3. $(\text{Pb}_{8.66}\text{Sn}_{0.04}\text{Cd}_{0.03}\text{Fe}_{0.02}\text{Ag}_{0.02}\text{Zn}_{0.01})_{\Sigma 8.78}(\text{Sb}_{8.15}\text{Bi}_{0.01})_{\Sigma 8.16}\text{S}_{21}$
4. $(\text{Pb}_{8.78}\text{Sn}_{0.07}\text{Cd}_{0.04}\text{Fe}_{0.03})_{\Sigma 8.92}(\text{Sb}_{8.03}\text{Bi}_{0.02})_{\Sigma 8.05}\text{S}_{21}$
5. $(\text{Pb}_{8.69}\text{Sn}_{0.05}\text{Cd}_{0.03}\text{Ag}_{0.03}\text{Fe}_{0.02}\text{Mn}_{0.02})_{\Sigma 8.84}(\text{Sb}_{8.08}\text{Bi}_{0.03})_{\Sigma 8.10}\text{S}_{21}$
6. $\text{Pb}_9\text{Sb}_8\text{S}_{21}$

struments of different institutions. The results indicate the fluctuation of S contents to be both of excess and deficient, suggesting the calculation of S contents to be significant. That the theoretical formula requires such a larger number of S as 21 for the basis of formula calculation leads to the exaggeration of deviation from stoichiometry than in the cases of simpler formula with smaller number of sulphur. More significant deviation is seen in semseyite from the Hayakawa ore deposit, Hokkaido (Ishiyama *et al.*, 1990), where the tendency is the same as the present one, i.e., Pb deficiency and Sb excess as compared with the theoretical values, although their optical study

favours the identification.

Consideration

The most implicative point to be considered is the simplicity of the content of associated minerals. All the available informations on semseyite associations, which come from hydrothermal veins, present mineralogical complexities, which consist of at least two factors. One is the larger number of elements besides Pb and Sb, and the other is that of sulphosalt species belonging to $\text{PbS-Sb}_2\text{S}_3$ system. The example of the former is the Hayakawa deposit, Hokkaido, Japan (Ishiyama *et al.*, 1990), where semseyite is found as inclusions within tetrahedrite grains. The other associated minerals are pyrite, galena, chalcopyrite, sphalerite, tetrahedrite, tennantite, enargite, arsenosulvanite, kesterite, bournonite, hessite, tetradymite, aikinite, and electrum. Twelve elements are involved in them as their essential constituents. In the association semseyite is the unique sulphosalt belonging to the binary system $\text{PbS-Sb}_2\text{S}_3$. The latter example is seen in the Bwlch Mine, Deganwy, Wales (Bevins *et al.*, 1988), where the associated minerals with semseyite are described as zinckenite, jamesonite, plagionite, robinsonite(?), and boulangerite(?). All the species are involved within the binary system $\text{PbS-Sb}_2\text{S}_3$, except for jamesonite. The cause inviting the complexity of sulphosalts is given on the material from Cougnasses, France (Moëlo & Lévy, 1976), who ascribed the variation to the gradual increase of Pb/Sb ratio in the hydrothermal solution that formed the ore deposit.

It is very likely that the present semseyite is the last product among the precipitated sulphides in a closed system under a lower temperature condition, formed after the precipitation of galena grains. The surrounding condition was inappropriate to produce any other Pb-Sb sulphosalts compositionally placed between galena and semseyite. Also, it is probable that the other elements concentrated within the hollow pyrite aggregates might have forbidden the formation of the other Pb-Sb sulphosalts.

In the present case, it is likely that the concentration of some elements must have taken place at the final stage of sulphide precipitation, or the formation of the hemisphere of pyrite aggregate, although the mechanism of such an unusual form of the aggregate remains unsolved. The absence of any other sulphosalts in the $\text{PbS-Sb}_2\text{S}_3$ system or the actual impoverishment of any sulphide except for Pb and Sb with a suitable ratio suggests the preferential precipitation of semseyite in favour of the other Pb-Sb sulphosalts. The most important factor forbidding the formation of boulangerite is considered to be the lower temperature condition. Hoda and Chang (1975) obtained synthetic semseyite at the temperature of 300°C for 300 days, at which the synthetic analogue of boulangerite was also obtained, but above this temperature semseyite was not synthesized.

Semseyite belongs to the semseyite-fülöppite homologous series (Mozgova & Borodaev, 1972) with the general formula $\text{Pb}_{3+2n}\text{Sb}_8\text{S}_{15+2n}$, and the known con-

stituents are fülöppite ($n=0$), plagionite ($n=1$), heteromorphite ($n=2$), and semseyite ($n=3$). But, if non-integer n is taken, there appears zinkenite ($\text{Pb}_9\text{Sb}_{22}\text{S}_{42} = \text{Pb}_{3.273}\text{Sb}_8\text{S}_{15.273}$; $n=0.137$), robinsonite ($\text{Pb}_4\text{Sb}_6\text{S}_{13} = \text{Pb}_{5.333}\text{Sb}_8\text{S}_{17.333}$; $n=1.167$), and launayite ($\text{Pb}_{22}\text{Sb}_{26}\text{S}_{61} = \text{Pb}_{6.769}\text{Sb}_8\text{S}_{18.769}$; $n=1.884$). All of them are devoid of crystallographically common points in the unit cell dimensions of the members of the homologous series. Namely, the constituents of this homologous series are compositionally peculiar and those fulfilling the relation $n=0, 1, 2$, and 3 (or integers) in the above general formula are qualified to have the homologous relation. If the chemical composition of fülöppite is taken as the starting point of consideration and examine the natures of appearing phases with respect to the increasing n number including subdecimal ones, the order of sequence is: fülöppite, zinkenite, plagionite, robinsonite, launayite, heteromorphite, and semseyite, where the second, fourth, and fifth members are out of the homologous series. The relation $n=\text{integer}$ in the general formula is fully implicative. It is to form a crystallographically discontinuous homologous series and the members sandwich a few crystallographically dissimilar phases, if the compositional variations of members are followed along one direction. Although there are many homologous series, such an example seems to be unique.

Most of phases out of this homologous relation are synthesized in dry experiments, whereas the members of homologous series except semseyite could not be synthesized in a dry system but in hydrothermal one including Cl under lower temperatures (Bortnikov, *et al.*, 1978). This evidence favours the appearance of a number of Pb-Sb sulphosalts in the associated minerals of semseyite in hydrothermal veins.

Another point needing consideration is the existence of minor Sn in the mineral. This implies two points of note. One is the concentration of Sn at the final stage of sulphide formation in such an aggregate with an apparent absence of any discrete Sn mineral. If the mineralogical natures of the associated minerals are referred to, the most probable manner of existence of Sn is as minute inclusions of stannite in chalcopyrite. But the associated chalcopyrite is at all free from such inclusions. The other is the capability of semseyite to admit the participation of minor Sn in place of Pb probably under a reducing condition provided that Sn is really in the divalent state. To date no discrete Sn mineral has been found not only in the ore deposit but also in the adjacent area. Thus, this is an example of occurrence of Sn in an area apparently impoverished in this element.

References

- Bevins, R. E., D. H. M. Alderton, & J. M. Horák, 1988. Lead-antimony mineralization at Bwlch Mine, Deganwy, Wales. *Miner. Mag.*, **52**: 391–394.
- Bortnikov, N. S., I. Yu. Nekrasov, & N. N. Mozgova, 1978. Phase equilibrium of the system Fe-Pb-HCl-Sb-S in temperatures 400–500°C. *Doklady Akad. Nauk SSSR*, **239**: 420–423. (In Russian)
- Harada, K., K. Nagashima, K. Nakao, & A. Kato, 1971. Hydroxyllellestadite, a new apatite from Chichibu Mine, Saitama Prefecture, Japan. *Amer. Miner.*, **56**: 1507–1518.

- Hoda, S. N. & L. L. Y. Chang, 1975. Phase relations in the pseudoternary system $\text{PbS-Cu}_2\text{S-Sb}_2\text{S}_3$ and the synthesis of meneghinite. *Canad. Miner.*, **13**: 388–393.
- Ishiyama, D., H. Matsueda, & O. Matsubaya, 1990. Copper-lead-zinc mineralization at the Hayakawa and Shakako deposits, Jokoku-Katsuraoka mining area, southwestern Hokkaido, Japan. *Jour. Miner. Petro. Econ. Geol.*, **85**: 341–353.
- Moëlo, Y. & Cl. Lévy, 1976. L'indice à sulfoantimoniures de plomb des Cougnasses (commune d'Orpierre, Haute-Alpes). Partie II: étude paragénétique. *Bull. minér.*, **99**: 38–49.
- Mozgova, N. N. & Yu. S. Borodaev, 1972. Homologous series of semseyite and fülöppite. *Zapiski Vses. Miner. Obshch.*, **101**: 299–312. (In Russian)
- Uetani, K., A. Kato, & Y. Okada, 1966. Occurrence of semseyite from the Chichibu Mine, Saitama Prefecture, Japan. *Bull. Nat. Sci. Mus. Tokyo*, **9**: 431–436.