Joséite-A from Nagakuki, Hanawa-cho, Fukushima Prefecture, Japan

By

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Abstract   Average of three microprobe analyses of joseite A in diopside-grossular-quartz skarn from Nagakuki is: Bi 82.16, Pb 0.22, Te 10.56, S 6.52, Se 0.10, total 99.56%. The empirical formula calculated on the basis of total atoms$=7$ is $(Bi_{4.04}Pb_{0.01})_{\Sigma 4.05}$ $(Te_{0.85}S_{0.09}Se_{0.01})_{\Sigma 0.95}S_{2.00}$, which is placed between the ideal formulae of joseite-A (Bi_4TeS_2) and joséite-C $(Bi_{16}Te_3S_9)$, the natures of the latter being considered. The associated opaque minerals include native bismuth, bismuthinite, pyrrhotite, chalcopyrite, sphalerite, and minor native gold. The mineralogical implication of the association of three bismuth minerals is presented. The mineralogical differences between joséite-A and joséite-B are considered. The ideal formula of the latter, Bi_4Te_2S, is given as $2 Bi+Bi_2Te_2S$ (tetradymite), while the former has no mineral corresponding to tetradymite, though csiklovaite is to have the chemical formula $Bi_2Te(S, Se)_2$ where $S>Se$. The status of this mineral is also considered to conclude that the existence as a bismuth chalcogenide seems unlikely, unless any other constituent than bismuth and chalcogenides such as lead or silver partakes as the essential constituent.

Introduction

Joséite A is a member of trigonal bismuth chalcogenides with the general formula Bi: X$=4$: 3, where X signifies chalcogenides, together with ikunolite $(Bi_4(S, Se)_3)$, laitakarite (Bi_4Se_2S), joséite-B (Bi_4Te_2S), and pilsenite (Bi_4Te_3). All the members have a layer structure composed of hexagonally packed Bi, Te, or $(S+Se)$ atoms, where S and Se behave similarily in ikunolite (KATO, 1959). Their cell parameters range: $a=$ 4.15 to 4.45 Å and $c=39.2$ to 41.0 Å, respectively. The above 4: 3 ratio is not fixed but fluctuates about 4: 3 through the substitutions among them, and the range of substitution of Bi for Te is most prominent (ZAV'YALOV & BEGIZOV, 1983). GODOVIKOV et al. (1970, 1971 a) created joséite-C with the ideal chemical formula $Bi_{16}Te_3S_9$, but the status of this mineral has not been created yet. Although the X-ray powder pattern of joséite-C seems to exclude any trigonal cell derivable from those fitting to the existing bismuth chalcogenides with Bi: X$=4$: 3, the formula might be considered as a

terminal member to express a compositional variation of joséite-A towards a sulphur-rich composition after taking the chemical composition of the present material into consideration. On the opposite side of compositional variation is joséite-B (Bi_4Te_2S), which is considered to be mineralogically discrete from joséite-A due to the lack of material with the intermediate composition (ZAV'YALOV & BEGIZOV, 1983). The status of joséite-B is also considered here and the substantial difference between the two is found. That is, the chemical formula of joséite-B is expressed as an intermediate of two stable mineral phases, native bismuth (Bi) and tetradymite (Bi_2Te_2S), whereas that of joséite-A has no partner corresponding to tetradymite, or Bi_2TeS_2, which is neither mineralogically (GODOVIKOV et al., 1971 b) nor synthetically (GLATZ, 1967) known, although a formula partially substituted by Se has been assigned to an inadequately described mineral csiklovaite (KOCH, 1948).

In Japan, the first occurrence of joséite-A is documented from Narabigaoka, Kyoto (OKAMOTO et al., 1980), where it occurs in wolframite-quartz vein with native gold. Also, at about 45 km northeast of Nagakuki, joséite-A is found in heyrovskýite-bearing lead ore from the skarn ore deposit of the Yakuki mine, Fukushima Prefecture (SHIMIZU et al., 1993).

Occurrence

The examined materials were all obtained in a dump of skarn developed between dolomitic limestone and granitic intrusive at Nagakuki, Hanawa-cho, Higashi-Shira-kawa-gun, Fukushima Prefecture, Japan (approx. N 36°52′, E 140°33.5′). The present dump was constituted at the occasion to reconstruct a river flowage along which the original dump was located. No rock exposure is found around the point, however, the other skarn composed of rather non-dolomitic association including scheelite is exposed together with marble at about 500 m south of the point.

The rocks found in the present dump include two kinds of schistose granite, coarse-grained granite, hornfelses, a schistose hornfels, amphibolite, marble, and a fragment of quartz vein besides skarns. The constituting minerals of the skarns are grossular, diopside, quartz, calcite, and tremolite in the order of abundance. Among them, the first three form aggregates with variable ratio. Grossular is reddish brown to yellowish brown in colour and granular, forming aggregates with minor quartz and calcite. The individual grains are dodecahedral and the maximum dimension exceeds 20 mm across. The grains with well developed forms are exclusively found as inclusions in coarser-grained aggregates of quartz, which is clear, whereas fine-grained one is turbid, and the former involves interstices surrounded by partially developed idiomorphs. Tremolite forms light yellowish grey aggregates with minor quartz, where the maximum length of the fiber reaches 1 cm. Since the aggregates of tremolite are found separately from the other skarns, the relation to the other skarn minerals was not still observable. A small amount of talc is detected in the tremolite aggregate after the X-ray powder study, though not visibly realized.

Fig. 1.   Joséite-A (grey white) and bismuthinite (grey) in diopside-quartz skarn.   Minor grains
of native bismuth (white) are involved within the grains of the former.   Bar-like outline in
the larger grain and drop-like in the smaller one in the bottom.   One polar.   Field view
appr. 0.3×0.4 mm.

Joséite-A is exclusively found within coarse-grained aggregates of quartz grains in diopside-quartz skarns with or without grossular.   It occurs as tablets or tiny grains with bismuthinite and bismuth.   The maximum dimension reaches 4 mm across. Under the ore microscope, joséite-A has an indefinite outline against quartz and is in direct contact with native bismuth very frequently (Fig. 1).   Among skarn minerals a preferential co-existence with diopside is realized.   The other opaque minerals identified under the ore microscope are pyrrhotite, chalcopyrite, and sphalerite.   Also, a piece of diopside-quartz skarn with a partially developed void of quartz is found to include an extremely small grain of native gold.

Chemical Analyses

The microprobe analyses of joséite-A, bismuthinite, and native bismuth were made.   In Table 1, those of the first and second ones are given.   The third one was 100% Bi.

The analyses of joséite-A gave a slightly hlgher (Bi+Pb) and (S+Se) contents and lower Te content as compared with the ideal Bi_4TeS_2.   Among available chemical analyses of joséite-A in the literatures, the material from Magadan, Russia (ZAV'YALOV & BEGIZOV, 1983) has similar figures to those of the present one as compared in Table 1.   As readily noticed, all the chemical analyses of the present joséite-A have Bi and S-rich and Te-poor tendency towards the ideal formula of joséite-C, $Bi_{16}Te_3S_9$.   However, the given chemical analyses of this mineral are not always conformable with this ideal formula.   All the original analyses of this mineral approach to $Bi_7(Te, S)_5$ where

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Table 1.   Chemical analyses of joséite-A (1∼6) and bismuthinite (7∼11).

	1	2	3	4	5	6	7	8	9	10	11
Weight percentages:											
Cu									0.04	0.01	
Ag								0.02	0.01	0.01	
Pb	0.47	0.13	0.06	0.22	1.8				0.08	0.03	
Bi	81.77	82.05	82.26	82.16	81.2	81.34	80.95	81.75	81.12	81.27	81.29
Te	10.54	10.48	10.66	10.56	10.7	12.42					
Se	0.12	0.11	0.08	0.10	0.5		0.09	0.19	0.15	0.14	
S	6.54	6.55	6.48	6.52	6.1	6.24	18.58	18.76	18.70	18.68	18.71
Total	99.43	99.33	99.93	99.56	100.3	100.00	99.62	100.72	100.10	100.14	100.00

1∼3 Joséite-A. Nagakuki. The present study.
4   Ditto. Nagakuki. Average of analyses 1, 2, and 3.
5   Ditto. Magadan. After ZAV'YALOV and BEGIZOV (1983).
6   Theoretical Bi_4TeS_2.
7∼9 Bismuthinite. Nagakuki. The present study.
10 Ditto. Nagakuki. Average of analyses 7, 8, and 9.
11 Theoretical Bi_2S_3.

Empirical formulae:
   (bases of calculation: Joséite-A, total atoms=7; bismuthinite, total atoms=5)
4   $(Bi_{4.04}Pb_{0.01})_{\Sigma 4.05}(Te_{0.85}S_{0.09}Se_{0.01})_{\Sigma 0.95}S_{2.00}$
5   $(Bi_{4.01}Pb_{0.09})_{\Sigma 4.10}(Te_{0.87}Se_{0.07})_{\Sigma 0.94}S_{1.97}$
10 $Bi_{2.00}(S_{2.99}Se_{0.01})_{\Sigma 3.00}$

Re-calculated empirical formulae:
   (bases of calculation: total atoms=28 in conformity with the ideal formula of joséite-C,
   $Bi_{16}Te_3S_9$) (Compare with $Bi_{16}Te_4S_8$, that of joséite-A on the same basis)
4' $(Bi_{16.15}Pb_{0.04})_{\Sigma 16.19}Te_{3.40}(S_{3.35}Se_{0.05})_{\Sigma 8.40}$
5' $(Bi_{16.06}Pb_{0.36})_{\Sigma 16.42}Te_{3.47}(S_{7.86}Se_{0.26})_{\Sigma 8.12}$

Te: S about 1: 3.   If the original ideal formula of joséite-C is taken into considera-
tion, it is to mark a kind of terminal member to account for the compositional varia-
tion of joséite-A in the present one.   However, if the real compositions of joséite-C
are subjected to re-examination, the mineral are not to be classed with joséite-A and
joséite-B.

The chemical analysis of bismuthinite is very close to the ideal composition if
minor Se is added to S.

X-ray Powder Study

A hand-picked material including unremovable quartz, diopside, native bismuth
and bismuthinite was subjected to X-ray powder diffractometer study.   After the
elimination of diffractions due to these phases, the remainder corresponds well with
that of joséite-A from Glacier Gulch, Canada (ZAV'YALOV & BEGIZOV, 1983), one of

Table 2. X-ray powder patterns of joséite-A.

| 1		2			1		2		
I	d	I	d	hkl	I	d	I	d	hkl
		2	6.65	006	20	1.823			
30	4.41	25	4.440	009	10	1.787			
10	3.64	10	3.633	102	30	1.752	3	1.750	207, 10.20
30	3.33			105, 00.12	30	1.658	4	1.658	00.24, 11.15
100	3.10	100	3.095	017	20	1.623			01.22
10	2.71	5	2.706	01.10	10	1.566			10.23
10	2.65			00.15	30	1.545	10*	1.544	02.14
20	2.59	10	2.574	10.11	20	1.532			11.18
80	2.25	10	2.253	10.14	10	1.461			01.25
20	2.21			00.18	10	1.447			02.17
30	2.13	15	2.124	110	40	1.415	5	1.416	01.26
30	2.06	3	2.063	01.16					
30	1.973	10	1.976	10.17					
10	1.915			119	$a_0=4.250$Å		$a_0=4.248$Å		
30	1.894	3	1.897	00.21	$c_0=39.82$Å		$c_0=39.84$Å		

1. Joséite-A. Glacier Gulch, British Columbia, Canada. After ZAV'YALOV and BEGIZOV (1983).

2. Joséite-A. Nagakuki. The present study. Cu/Ni radiation. Diffractometer method.
   *: Intensity enhanced due to overlapped diffraction of quartz.

the most compositionally ideal joséite-A (Table 2). The unit cell parameters of the present material are calculated as $a=4.248$ from (110) and $c=39.84$ Å from (000.21), respectively. These are very well coincident with those of the material from Magadan, $a=4.248$ and $c=39.86$ Å (ZAV'YALOV & BEGIZOV, 1983) (No. 5 in Table 1) and those of the material from Glacier Gulch, $a=4.250$, $c=39.82$ Å (ZAV'YALOV & BEGIZOV, 1983) (No. 1 in Table 2). The former has the chemical composition closest to the present material among available chemical analyses of joséite-A.

The status of joséite-C is also considered from the X-ray powder pattern (GODOVIKOV et al., 1971 a). The trial indexing by the author could not find any proper trigonal cell, despite repeated calculation using many probable trigonal cells. But the smaller d-values of probably corresponding diffractions with joséite-A suggest the smaller values of cell parameters if satisfactorily derived.

Consideration of the Relation to the Other Trigonal Bismuth Chalcogenides of Similar Compositions

The relation of joséite-A to joséite-B is considered after the reference to their ideal formulae, Bi_4TeS_2 and Bi_4Te_2S, respectively. The relation of joséite-A to joséite-C is uncertain as previously stated. Suppose the following chemical equation:

$$Bi_2Te_2S \quad + \quad 2\,Bi \quad = \quad Bi_4Te_2S$$
Tetradymite   Native bismuth   Joseite-B
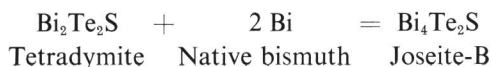
The formation of joséite-B means the right side to be more stable under the condition of formation, unless the handling of these minerals after the reference to their ideal formulae is proved to be incorrect.   It is certain that some textbooks enumerate native bismuth as one of the associated minerals of tetradymite (ANTHONY *et al.*, 1990), although the textbook of RAMDOHR (1980) does not refer to the co-existence.   While, if joséite-A is placed instead of joséite-B, this equation can be by no means constructed on account of absence of a phase Bi_2TeS_2.   In this respect, the statii of them are not equivalent.   The chemical formula of this phase is interpreted as follows:

$$2\,Bi_2TeS_2 = \underset{\text{Tetradymite}}{Bi_2Te_2S} + \underset{\text{Bismuthinite}}{Bi_2S_3}$$
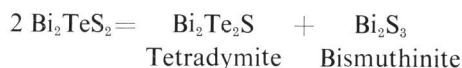
Therefore, the following equation can be derived to constitute joséite-A.

$$\underset{\text{Tetradymite}}{Bi_2Te_2S} + \underset{\text{Native bismuth}}{4\,Bi} + \underset{\text{Bismuthinite}}{Bi_2S_3} = \underset{\text{Joséite-A}}{2\,Bi_4TeS_2}$$

The association of tetradymite with bismuthinite is observed at Sannotake, Fukuoka Prefecture, Japan (KATO & SAKURAI, 1962).   The synthetic work of the binary system Bi_2S_3-Bi_2Te_3 proves the co-existence of Bi_2S_3 with Bi_2Te_2S (GLATZ. 1967).   This indicates that in the pure ternary system Bi-Te-S co-existence of tetradymite with bismuthinite is likely although the application to any natural cases will be limited, since the role of selenium is still uncertain in relation to the stability of the concerned phases, although this does not always lead to the survival of an inadequately described mineral csiklovaite to which an ideal formula $Bi_2Te(S, Se)_2$ is assigned (KOCH, 1948).   Even if the role of selenium is confirmed to be identical with that of sulphur, it is still necessary to consider the roles of silver and lead, which are very frequent accessoric components in trigonal bismuth chalcogenides, especially richer in bismuth than $2:3$ chalcogenides.   Though substantially not verified yet, it is still probable that these elements are capable of stabilizing such compounds with the above chemical formula.

The association of native bismuth, joséite-A, and bismuthinite is quite common. The existence of the association of native bismuth and bismuthinite may relate with the absence of tellurium at the occasion of the formation of this association unless temperature is significant on the formation of joséite-A.

If the sulphur fugacity is subjected to consider, the observed association could be stable under the condition of higher sulphur fugacity, the composition of joséite-A would be indiscernibly dragged onto the sulphur-rich side as seen in the described case.   If further extention of this idea is permitted, the association of native bismuth with joséite-A is to have its previous step, that of native bismuth with joséite-B from which the change of associations to reflect increasing sulphur fugacity.

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