

Eclarite and other Bi-minerals from the Jishakuyama ore deposit of the Akagane mine, Iwate Prefecture, Japan

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Abstract Eclarite occurs in hydrothermal quartz veins cutting quartz porphyry at the Jishakuyama orebody of the Akagane mine, Oshu City, Iwate Prefecture, Japan. It is mainly found as aggregates of lead-grey platy acicular crystals up to 1 mm long. Eclarite-bearing quartz veins include such Bi-minerals as bismuth, bismuthinite, ikonolite, joséite-A and joséite-B. They are in association with chalcopyrite, pyrrhotite, galena, sphalerite, pyrite, molybdenite, scheelite and gold. The secondary Bi-bearing minerals are cannonite and bismite. The representative chemical analyses of eclarite gave Bi 46.86; 46.50, Sb 2.85; 2.82, Pb 31.89; 31.96, Cu 1.05; 0.92, Fe 0.52; 0.61, S 17.08; 17.04, total 100.25; 99.85 wt.%. The empirical formulae are: $(\text{Cu}_{0.87}\text{Fe}_{0.49})_{\Sigma 1.36}\text{Pb}_{8.09}(\text{Bi}_{11.79}\text{Sb}_{1.23})_{\Sigma 13.02}\text{S}_{28}$ and $(\text{Cu}_{0.76}\text{Fe}_{0.57})_{\Sigma 1.33}\text{Pb}_{8.13}(\text{Bi}_{11.73}\text{Sb}_{1.22})_{\Sigma 12.95}\text{S}_{28}$ on the basis of S = 28, respectively. The unit cell parameters calculated from the single-crystal X-ray diffraction data are; $a = 4.030(4)$, $b = 22.71(9)$, $c = 54.66(7)$ Å, $V = 5002(22)$ Å³.

Key words: eclarite, Bi-minerals, Jishakuyama ore deposit, Akagane mine

Introduction

In May of 2014, S. H. and Y. S. collected much specimens including gold and some Bi-minerals at the dump of the Jishakuyama ore deposit of the Akagane mine, Iwate Prefecture. S. M. visited the localities in order to research the occurrence of minerals in September of 2014 and June of 2015, guided by them and collected specimens. During the mineralogical study, we have found eclarite among the specimens. Eclarite, $(\text{Cu}, \text{Fe})\text{Pb}_9\text{Bi}_{12}\text{S}_{28}$, is a rather rare sulfosalt mineral firstly recognized from Bärenbad, Austria (Paar *et al.*, 1983), and afterward Kupčík (1984), one of the authors for the original description, reported the crystal structure of eclarite. At the present time Slovakia (Pršek *et al.*, 2008) and other eight localities of eclarite are known in the world (Mindat.org database, 2016).

The present paper deals with eclarite as first occurrence in Japan, and discussion on the chem-

ical and crystallographic characters to comparison with original eclarite.

Occurrence

The Akagane mine and the surround ore mines have a long history. Tradition says that the mine started by the discovery of gold in twelfth century (the Oshu-Fujiwara age). After seventeenth century mainly copper and iron ores have been mined. Although the name of the Akagane mine changed to the Esashi mine in 1973 according to company convenience, we use the name of Akagane mine in this paper because Akagane is long-time popular and many scientific papers on geology, economic geology and mineralogy use Akagane (e.g., akaganeite is a mineral species name).

The Akagane mine is located at Esashi Ward, Oshu City, Iwate Prefecture, Japan (around 39°10'N, 141°21'E). In the surround of the Aka-

gane mine, are observed sedimentary rocks of Carboniferous, Permian and Cretaceous period, and their rocks were intruded by some igneous rocks in early Cretaceous period (gabbro, quartz porphyry, granodiorite, granite porphyry etc.) (e.g. Takahashi and Nambu, 2003; Ishiyama, 2005). The ore deposits are massive type mainly composed of magnetite, pyrrhotite and chalcopyrite formed in amphibole, epidote and garnet skarn, and Au-, Bi-, and W-bearing hydrothermal quartz veins in later stage. The main ore deposits were developed at ten areas of Akagane, Okura, Higashi, Sakae etc. In the Sakae ore deposit are observed barren high-temperature skarn formed along the contact zone between limestone and gabbro, and the skarn minerals include bicchulite, tilleyite, gehlenite, foshagite and dellaite (Bunno *et al.*, 1982; Shimazaki *et al.*, 2008). In this skarn valleriite and pentlandite are found (Muramatsu *et al.*, 1975). Akaganeite was discovered at an outcrop of the Marumori pyrrhotite deposit (Nambu, 1968). Besides them the occurrence of mackinawite and tochillinite was recognized (e.g. Muramatsu *et al.*, 1975; Takahashi and Nambu, 2003).

The studied materials were collected at the dump derived from 450m Level ore body in the Jishakuyama ore deposit. The hydrothermal quartz veins are under 20 cm in width and generally poor in ore minerals. The quartz veins at the Jishakuyama ore deposits are formed in quartz porphyry, and chalcopyrite, pyrrhotite, pyrite, gold, bismuth, bismuthinite and scheelite have been reported (e.g. Sumita *et al.*, 1975; Takenouchi, 1975). Except the above minerals we have recognized galena, sphalerite, molybdenite, ikonolite, joséite-A, joséite-B and eclarite, and also cannonite and bismite as Bi-secondary minerals.

Eclarite rarely occurs in the quartz vein as aggregates of platy acicular crystals less than 1 mm long. It is lead-grey in color and has distinct striation parallel to elongated direction ([100]) (Fig. 1). It is often partially replaced by ikonolite and minor bismuth (Fig. 2). Eclarite-bearing quartz veins also include small amounts of gold, scheelite, bismuth, joséite-A, joséite-B



Fig. 1. The aggregate of acicular eclarite crystals in quartz vein. Field view: approximately 3.6×4.5 mm.

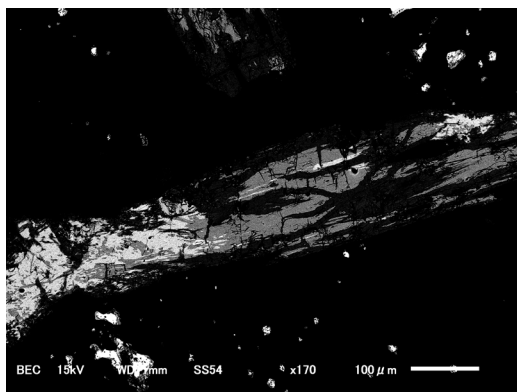


Fig. 2. Back-scattered electron image of eclarite (grey) and aggregates composed of ikonolite including minor bismuth (light) in quartz matrix (black).

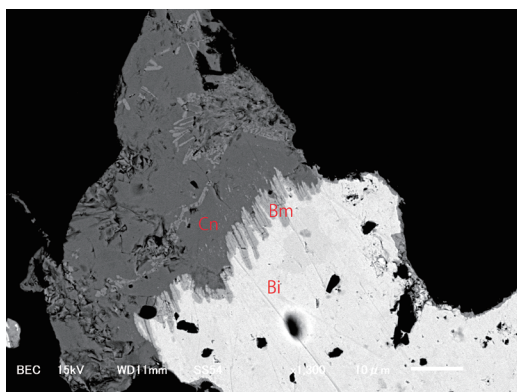


Fig. 3. Back-scattered electron image of bismuth (Bi), bismite (Bm) and cannonite (Cn). Field view: approximately $70 \times 95 \mu\text{m}$.

Table 1. List of X-ray powder diffraction peaks of eclarite from Jishakuyama measured by Gandolfi camera compared with data given by Paar *et al.* (1983).

Jisyakuyama (This study)			Barenbad (Paar <i>et al.</i> , 1983)	
d (Å)	I/I_0	hkl	d (Å)	I/I_0
4.81	4	0 4 6		
4.16	7	0 1 13		
4.08	6	0 5 6		
3.93	22	0 5 7	3.944	20
3.65	41	1 2 4, 1 1 6, 0 5 9	3.631	30
3.58	34	0 1 15, 0 6 5	3.576	10
3.50	48	1 2 6, 0 6 6, 0 5 10	3.488	40
3.42	73	1 1 8, 0 0 16, 1 2 7, 0 6 7, 1 3 5	3.414	100
3.32	25	1 3 6, 0 6 8		
3.25	44	1 0 10, 1 3 7, 1 2 9, 0 6 9	3.253	20
3.17	18	1 3 8	3.204	10
3.10	15	1 4 6		
3.01	80	1 5 0, 0 6 11, 1 5 1, 0 1 18, 1 5 2, 1 3 10	3.01	60
			2.993	20
2.90	91	0 6 12, 1 3 11, 1 4 9	2.893	70
2.82	22	1 0 14	2.813	5
2.75	100	1 6 1, 1 6 2, 1 4 11	2.742	40
			2.728	20
2.67	23	1 4 12	2.668	5
2.64	13	1 5 10		
2.61	10	1 6 7		
2.53	22	1 7 0	2.526	2
2.45	27	1 4 15	2.431	10
2.38	11	1 3 17		
2.31	51	1 8 2, 1 4 17	2.309	15
			2.297	15
2.27	24	1 4 17, 0 10 1, 1 5 16	2.26	5
2.22	20	1 2 20	2.211	5
2.18	14	1 5 17, 1 1 21		
2.14	45	0 7 19, 0 6 21, 1 9 0, 1 9 1	2.141	50
2.11	11	1 9 4	2.109	1
2.08	19	1 9 6, 0 6 22	2.074	5
2.04	58	1 6 18, 0 11 4, 1 7 16	2.037	45
2.02	21	2 0 0, 1 2 23, 0 6 23	2.014	80
1.994	23	1 9 10, 1 6 19	1.969	5
1.974	19	0 5 25		
1.961	22	1 10 4	1.961	5
1.943	9	1 7 18, 1 6 20		
1.919	13	0 5 26	1.907	10
1.869	9	1 0 26		
1.846	17	1 9 15	1.841	5
1.817	20	1 10 12	1.813	10
1.789	9	2 5 7	1.786	5
1.763	18	2 5 9, 1 3 27, 1 11 9	1.759	30
1.739	9	2 5 10	1.733	35
1.728	8	2 0 16		
1.713	10	0 0 32, 2 6 9	1.706	15
1.682	10	1 4 28	1.678	10

Table 2. Details of the sample, data collection, and structural refinement.

Temperature	293(2) K
Radiation	CuK α
Crystal size	0.05 $\times$ 0.03 $\times$ 0.02 mm
Space Group	<i>Pm</i> <i>cn</i> (#62 <i>Pnma</i>)
Unit cell dimensions	<i>a</i> = 4.030(4), <i>b</i> = 22.71(9), <i>c</i> = 54.66(7) Å
Volume	<i>V</i> = 5002(22) Å ³
<i>Z</i>	4
<i>F</i> (000)	8860
Absorption correction	Semi-empirical (psi-scan) method by North <i>et al.</i> (1968)
Diffractometer	Rigaku AFC-7
Voltage, Current	50 kV, 200 mA
2 θ max	150.01°
No. of Reflections Measured	9766
Independent reflections	5631 (<i>I</i> > 2 σ (<i>I</i>) = 2402, <i>R</i> _{int} = 0.2737, <i>R</i> _{sigma} = 0.2434)
Structure Solution	Superflip (Palatinus and Chapuis, 2007)
No. of parameters	225
Refinement	Full-matrix least-squares on <i>F</i> ²
Function Minimized	$\sum w(F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Residuals: <i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.1070
Residuals: <i>R</i> (All reflections)	0.2610
Residuals: <i>wR</i> 2 (All reflections)	0.3249
Goodness of Fit Indicator	1.279
Largest diff. peak and hole	8.416 e/Å ³ and -6.375 e/Å ³

and bismuthinite except such common minerals as arsenopyrite, pyrite, chalcopyrite, galena and sphalerite. The rim of bismuth is often replaced by bismite and/or cannonite (Fig. 3).

X-ray Crystallography

X-ray powder diffraction data of eclarite were obtained using a Gandolfi camera with a diameter of 114.6 mm and Ni-filtered CuK α radiation. The data were recorded on an imaging plate, and processed with a Fuji BAS-2500 bio-image analyser using a computer program written by Nakamura (1999). List of observed diffraction peaks is shown in Table 1.

Single-crystal X-ray diffraction data of eclarite were collected with a 4-circle diffractometer (Rigaku AFC-7) using CuK α radiation. The refined unit cell parameters are *a* = 4.030(4), *b* = 22.71(9), *c* = 54.66(7) Å, *V* = 5002(22) Å³. The initial structural model was solved by the SUPERFLIP program (Palatinus and Chapuis, 2007) based on the charge-flipping algorithm, and structural refinement was then performed using the SHELX-97 software (Sheldrick 2008). Details of data collection and refinement are

given in Table 2. The final reliability indices (*R*1 = 10.70% and *wR*2 = 32.49%) are relatively high and details of cation orderings or anisotropic atomic displacements of sulfur atoms could not be refined due to poor crystal quality of the sample. Nevertheless, the refined structural model is consistent with the one reported by Topa and Makovicky (2012) for eclarite from Felbertal, Austria. The refined atomic coordinates are listed in Table 3.

Chemical Composition

Chemical analyses for eclarite and the associated minerals were carried out with a JEOL JXA-8800M WDS electron microprobe analyzer (15 kV, 2 nA, beam diameter 2 μ m). The standard materials used were bismuthinite for Bi, galena for Pb, stibnite for Sb, chalcopyrite for Cu, pyrite for Fe, HgTe for Te, and bismuthinite for S, respectively. No other elements were observed in the EPMA analysis. Table 4 shows results for the chemical composition of the present eclarite and that from various localities including type locality (Paar *et al.*, 1983) for comparison. The representative empirical formulae (No. 4 and No. 14) of eclarite

Table 3. Refined atomic coordinates and displacement parameters ($\text{\AA}^2$) of eclarite.

Site	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$	Occ
Bi1	0.75	0.14838(17)	0.07029(7)	0.0262(9)	1
Bi2	0.75	0.33103(17)	0.06583(6)	0.0253(8)	1
Bi3	0.25	0.22291(19)	0.12565(7)	0.0325(10)	1
Bi4	0.25	0.40858(17)	0.12323(6)	0.0261(8)	1
Bi5	0.25	0.03612(17)	0.24511(7)	0.0291(9)	1
Bi6	0.25	0.37559(19)	0.25092(7)	0.0329(10)	1
Bi7	0.25	0.27979(18)	0.31600(7)	0.0293(9)	1
Bi8	0.75	0.44322(16)	0.31964(7)	0.0267(9)	1
BiM2	0.25	0.42136(18)	0.00591(7)	0.0303(9)	1
BiM3	0.75	0.32739(18)	0.37928(6)	0.0297(9)	1
BiM4	0.75	0.20490(17)	0.43777(6)	0.0268(9)	1
BiM5	0.25	0.36738(17)	0.44140(7)	0.0291(9)	1
Pb1	0.25	0.23465(19)	0.00819(8)	0.0345(10)	1
Pb2	0.75	0.0037(2)	0.11623(8)	0.0401(11)	1
Pb3	0.75	0.1179(2)	0.17935(8)	0.0358(10)	1
Pb4	0.75	0.3158(2)	0.18383(8)	0.0350(10)	1
Pb5	0.75	0.2069(2)	0.24980(7)	0.0349(10)	1
Pb6A/Bi6B	0.25	−0.0006(2)	0.32171(10)	0.0448(12)	1
Pb7A/Bi7B	0.25	0.1377(3)	0.36916(8)	0.0514(14)	1
Pb8A/Bi8B	0.25	0.0337(3)	0.42971(10)	0.0484(13)	1
Cu/Fe	0.75	0.1394(7)	0.3054(4)	0.042(5)	Cu0.5Fe0.5
Bi9	0.25	0.0441(2)	0.02632(9)	0.0334(18)	0.839(18)
Cu1	0.25	0.077(2)	0.0110(8)	0.045(15)	0.38(4)
Cu2	0.25	−0.007(4)	0.0481(14)	0.04(2)	0.22(5)
S1	0.75	0.1362(11)	0.0233(4)	0.023(5)	1
S2	0.75	0.3248(11)	0.0185(4)	0.024(5)	1
S3	0.25	0.0681(14)	0.0762(5)	0.043(7)	1
S4	0.25	0.2386(9)	0.0638(3)	0.015(4)	1
S5	0.25	0.4176(10)	0.0649(4)	0.018(4)	1
S6	0.75	0.1383(10)	0.1245(4)	0.022(5)	1
S7	0.75	0.3151(11)	0.1254(4)	0.024(5)	1
S8	0.75	0.4912(11)	0.1235(4)	0.023(5)	1
S9	0.25	0.0360(11)	0.1527(4)	0.024(5)	1
S10	0.25	0.2176(12)	0.1722(4)	0.030(5)	1
S11	0.25	0.4087(9)	0.1717(3)	0.011(4)	1
S12	0.25	0.1322(11)	0.2218(4)	0.029(5)	1
S13	0.25	0.2827(10)	0.2256(3)	0.018(4)	1
S14	0.75	0.4163(12)	0.2249(5)	0.032(6)	1
S15	0.75	0.0626(13)	0.2750(5)	0.037(6)	1
S16	0.25	0.1820(11)	0.2923(4)	0.025(5)	1
S17	0.75	0.3246(13)	0.2849(5)	0.035(6)	1
S18	0.25	0.4879(12)	0.2915(4)	0.031(6)	1
S19	0.75	0.0812(10)	0.3397(4)	0.021(5)	1
S20	0.75	0.2323(13)	0.3466(5)	0.035(6)	1
S21	0.25	0.3948(12)	0.3526(4)	0.031(5)	1
S22	0.75	0.1040(10)	0.4079(4)	0.021(5)	1
S23	0.25	0.2706(11)	0.4060(4)	0.023(5)	1
S24	0.75	0.4213(11)	0.4111(4)	0.028(5)	1
S25	0.75	0.0365(10)	0.4761(3)	0.017(4)	1
S26	0.25	0.1644(11)	0.4642(4)	0.023(5)	1
S27	0.75	0.3073(12)	0.4658(4)	0.031(5)	1
S28	0.25	0.4607(12)	0.4731(5)	0.032(6)	1

are $(\text{Cu}_{0.87}\text{Fe}_{0.49})_{\Sigma 1.36}\text{Pb}_{8.09}(\text{Bi}_{11.79}\text{Sb}_{1.23})_{\Sigma 13.02}\text{S}_{28}$ and $(\text{Cu}_{0.76}\text{Fe}_{0.57})_{\Sigma 1.33}\text{Pb}_{8.13}(\text{Bi}_{11.73}\text{Sb}_{1.22})_{\Sigma 12.95}\text{S}_{28}$ on the basis of $S = 28$, respectively.

The representative chemical compositions of

bismuth and ikonolite in association with eclarite are demonstrated in Table 5. Chemical analysis for cannonite were carried out using an INCA Oxford energy dispersive X-ray Spectrometer

Table 4. Chemical composition of eclarite from Jishakuyama and various localities.

	1	2	3	4	5	6	7	8
Bi	46.86	46.50	46.67	45.6	47.07	49.54	48.41	44.64
Sb	2.85	2.82	2.89	1.5	1.53	0.38	0.44	3.95
Pb	31.89	31.96	32.19	34.2	32.63	31.64	32.93	31.72
Cd	0	0	0	0	0.17	0.21	0.17	0
Cu	1.05	0.92	0.91	0.9	0.84	1.05	0.67	1.49
Ag	0	0	0	0.2	0.40	0.45	0.31	0.21
Fe	0.52	0.61	0.53	0.6	0.53	0.40	0.61	0.25
Te	0	0.00	0	0	0.02	0	0	0
S	17.08	17.04	16.89	17.2	17.10	16.78	16.88	17.54
Total	100.25	99.85	100.08	100.2	100.31	100.44	100.41	99.79
Bi	11.79	11.73	11.87	11.4	11.83	12.68	12.32	10.94
Sb	1.23	1.22	1.26	0.6	0.66	0.17	0.19	1.66
Σ	13.02	12.95	13.13	12.0	12.59	12.85	12.51	12.50
Pb	8.09	8.13	8.26	8.6	8.28	8.17	8.45	7.84
Cd					0.08	0.10	0.08	
Cu	0.87	0.76	0.76	0.7	0.69	0.88	0.56	1.20
Ag				0.1	0.19	0.22	0.15	0.10
Fe	0.49	0.57	0.51	0.6	0.50	0.46	0.58	0.23
Σ	1.36	1.33	1.27	1.4	1.46	1.66	1.37	1.43
S	28	28	28	28	28	28	28	28

1: No. 4 analysis (Jishakuyama) (this study)

2: No. 14 analysis (Jishakuyama) (this study)

3: average of 9 analyses (Jishakuyama) (this study)

4: Bärenbad (Paar *et al.*, 1983)

5: Bärenbad (average of 93 analyses) (Topa and Mackovicky, 2012)

6: Felbertal 1 (average of 35 analyses) (Topa and Mackovicky, 2012)

7: Felbertal 2 (average of 134 analyses) (Topa and Mackovicky, 2012)

8: Brezno-Hviezda (average of 10 analyses) (Pršek *et al.*, 2008)

Table 5. Chemical compositions of ikonolite and bismuth associated with eclarite from Jishakuyama.

	1	2
Bi	98.99	82.09
Sb	0.46	0
Pb	0	5.80
Cu	0	0.01
Fe	0.02	0
Te	0	1.73
S	0	9.60
Total	99.47	99.23
Bi	0.99	3.77
Sb	0.01	
Pb		0.27
Cu		0
Fe	0	
Te		0.13
S		2.87

1: bismuth

2: ikonolite (on the basis of S + Te = 3)

Table 6. Chemical composition of cannonite from Jishakuyama.

	1	2	3
Bi ₂ O ₃	83.02	82.38	84.07
SO ₃	13.92	14.69	14.18
H ₂ O*	3.06	2.93	2.75
Total	100	100	100
*: by difference			
	O = 7		
Bi	2.12	1.99	1.97
S	0.96	1.03	0.96
H	1.88	1.83	2.31

installed in JSM-6610SEM, because cannonite is easily damaged by beam of WDS electron microprobe analyzer (Table 6). The standard materials used were Bi for Bi and pyrite for S, respectively. No other elements were observed in the EPMA analysis.

Discussion

Although eclarite has vicinity to the minerals of tintinaite–kobellite series, the chemical composition is always Bi-rich and Sb-dominant member is not yet known. In Fig. 4, two chemical compositions of eclarite analyzed in this study (⑥, ⑦) are plotted in addition to the data reported by Paar *et al.* (1983) (①), Pršek *et al.* (2008) (⑤), and Topa and Makovicky (2012) (②, ③, ④), as the same plot as Figure 6 presented by Moëlo *et al.* (1995). We used the average data of Hviezda specimen published by Pršek *et al.* (2008) and of Bärenbad and Felbertal specimens

published by Topa and Makovicky (2012). The distribution of the plotted points does not occupy narrow range. In this time we could not decide the reason due to the problem of chemical analysis or the nature of eclarite itself.

On Sb content the present eclarite is also poor ($\text{Bi}/(\text{Bi} + \text{Sb}) \sim 0.90$). Although the chemical composition of kobellite rich in Bi resembles that of eclarite, it is considered that maximum of $\text{Bi}/(\text{Bi} + \text{Sb})$ of kobellite do not exceed 0.8 (Moëlo *et al.*, 1995).

Figures 5, 6, 7, 8 and 9 indicate diagrams of $(\text{Bi} + \text{Sb} - \text{Ag}) - (\text{Pb} + \text{Cd} + 2\text{Ag}) - (\text{Cu} + \text{Fe})$, Cu vs. Fe, Bi vs. Sb, $(\text{Bi} + \text{Sb})$ vs. Pb and $(\text{Bi} + \text{Sb} - \text{Ag})$ vs. $(\text{Pb} + \text{Cd} + 2\text{Ag})$, respectively. Figures 5 and 6 are same as Figure 2 and Figure 3 by Topa and Mackovicky (2012), respectively. In Figure 5, numbers 1, 2 and 3 are plotted under the hypothetical formulae (1: $\text{Fe}^{2+}\text{Pb}_9\text{Bi}_{12}\text{S}_{28}$, 2: $\text{Cu}^+\text{Pb}_8\text{Bi}_{13}\text{S}_{28}$, 3: $\text{Cu}^{+1.5}\text{Pb}_{7.75}\text{Bi}_{13}\text{S}_{28}$) proposed by Topa and Mackovicky (2012). They concluded that the general formula of eclarite is $\text{Cu}_{1.5n}\text{Fe}_{1-n}\text{Pb}_{9-1.25n}\text{Bi}_{12+n}\text{S}_{28}$ indicated on tie line from number 1 to number 3, because most results of EPMA analyses distribute near the tie line. The present analytical results are plotted near this tie line. Although the relationships of

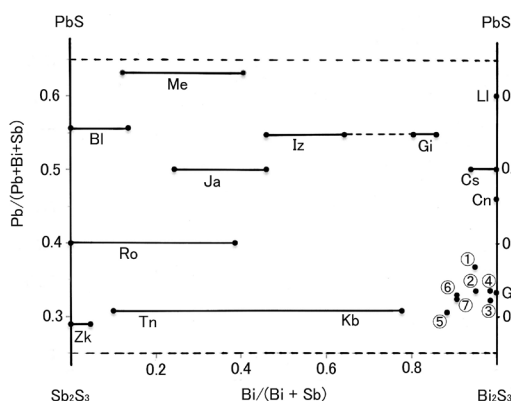


Fig. 4. PbS vs. Sb_2S_3 – Bi_2S_3 diagram. Fe, Cu and Ag are converted to Pb or Bi according to $\text{Fe} = 2\text{Cu}$, $\text{Cu} + \text{Pb} = \text{Bi}$, $\text{Bi} + \text{Ag} = 2\text{Pb}$ (Moëlo *et al.*, 1995). Me, meneghinite; BL, boulangierite; Ro, robinsonite; Zk, zinkenite; Iz, izoklakeite; Gi, giessenite; Ja, Jaskólskiite; Tn, tintinaite; Kb, kobellite; Li, lillianite; Cs, cosalite; Cn, cannizzarite; Gb, galenobismutite. ①, Bärenbad (Paar *et al.*, 1983); ②, Bärenbad (Topa and Makovicky, 2012); ③, Felbertal 1 (Topa and Makovicky, 2012); ④, Felbertal 2 (Topa and Makovicky, 2012); ⑤, Hviezda (Pršek *et al.*, 2008); ⑥, Jishakuyama No. 4 (this study); ⑦, Jishakuyama No. 14 (this study).

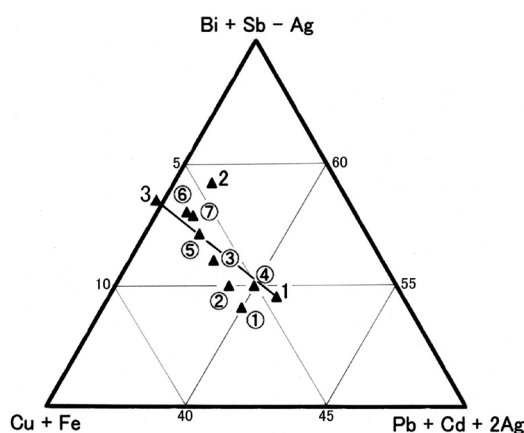


Fig. 5. $(\text{Bi} + \text{Sb} - \text{Ag}) - (\text{Pb} + \text{Cd} + 2\text{Ag}) - (\text{Cu} + \text{Fe})$ diagram (retouch in Fig. 2 reported by Topa and Makovicky, 2012). 1, $\text{Fe}^{2+}\text{Pb}_9\text{Bi}_{12}\text{S}_{28}$; 2, $\text{Cu}^+\text{Pb}_8\text{Bi}_{13}\text{S}_{28}$; 3, $\text{Cu}^{+1.5}\text{Pb}_{7.75}\text{Bi}_{13}\text{S}_{28}$. Circled numbers are same references as Fig. 4.

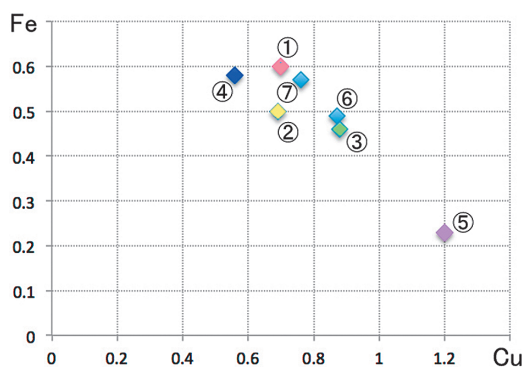


Fig. 6. Cu vs. Fe diagram. Cu and Fe are in inverse proportion. Scale numbers are per formula unit on the basis of S = 28. Data source are same as Fig. 4.



Fig. 7. Bi vs. Sb diagram. Bi and Sb are in inverse proportion. Scale and data source are ditto.

Cu vs. Fe, Bi vs. Sb, and (Bi + Sb) vs. Pb are distinctly in inverse proportion, the relationship of (Bi + Sb - Ag) vs. (Pb + Cd + 2Ag) is rather obscure.

The present eclarite is characterized in Bi-rich component comparing with known eclarite. The reason is considered that eclarite from Jishakuyama ore deposit crystallized under Bi-rich and Pb-poor condition, because the eclarite is in association with bismuth and ikunolite, and moreover no galena or Pb-bearing sulfosalts occur in this assemblage.

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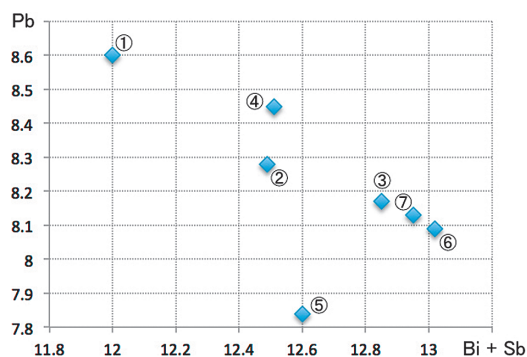


Fig. 8. (Bi + Sb) vs. Pb diagram. (Bi + Sb) and Pb are in inverse proportion except ⑤. Scale and data source are ditto.

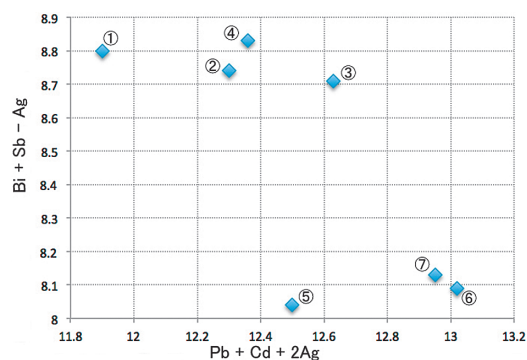


Fig. 9. (Bi + Sb - Ag) vs. (Pb + Cd + 2Ag) diagram. No distinct inverse correlation of (Bi + Sb - Ag) and (Pb + Cd + 2Ag) is observed. Scale and data source are ditto.

their help to study and collecting samples in field works.

References

- Bunno, M., Shimazaki, H. and Sato, K. (1982). Occurrence and genesis of bicchulite and tilleyite skarns at the Sakae adit, the Akagane mine, Iwate Prefecture. *Mining Geology*, **32**: 141–150. (In Japanese with English abstract)
- Ishiyama, D. (2005). World skarn deposits: Skarns of Japan. One Hundredth Anniversary Volume. In: Hedenquist, J. W., Thompson, J. F. H., Goldfarb, R. J. and Richards, J. P. (Eds.), Appendix, CD-ROM, Society of Economic Geology, Colorado, USA.

- Kupčík, V. (1984). Die Kristallstruktur des Minerals Eclarit, $(\text{Cu,Fe})\text{Pb}_9\text{Bi}_{12}\text{S}_{28}$. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **32**: 259–269.
- Moëlo, Y., Roger, G., Maurel-Palacim, D., Marcoux, E. and Laroussi, A. (1995). Chemistry of $\text{Pb}-(\text{Cu, Fe})-(\text{Sb, Bi})$ -sulfosalts from France and Portugal, and correlated substitutions in the Cu-poor part of the $\text{Pb}_2\text{S}_2\text{–Cu}_2\text{S–Sb}_2\text{S}_3\text{–Bi}_2\text{S}_3$ system. *Mineralogy and Petrology*, **53**: 229–250.
- Muramatsu, Y., Nambu, M. and Takeuchi, T. (1975). Valeriite and mackinawite from Akagane mine, Iwate Prefecture, Japan. *Journal of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists*, **70**: 236–244. (In Japanese with English abstract)
- Nakamuta, Y. (1999). Precise analysis of a very small mineral by an X-ray diffraction method. *Journal of the Mineralogical Society of Japan*, **28**: 117–121. (In Japanese with English abstract)
- Nambu, M. (1968). New mineral akaganeite, $\beta\text{-FeOOH}$, from Akagane mine, Iwate Prefecture, Japan. *Journal of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists*, **59**: 143–151. (In Japanese with English abstract)
- North, A. C. T., Phillips, D. C. and Mathews, F. S. (1968). A semi-empirical method of absorption correction. *Acta Crystallographica, Section A*, **24**: 351–359.
- Paar, W. H., Chen, T. T., Kupčík, V. and Hanke, K. (1983). Eclarit, $(\text{Cu, Fe})\text{Pb}_9\text{Bi}_{12}\text{S}_{28}$, ein neues Sulfosalz von Barenbad, Hollersbachtal, Salzburg, Österreich. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **32**: 103–110.
- Palatinus, L. and Chapuis G. (2007). SUPERFLIP—a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied Crystallography*, **40**: 786–790.
- Pršek, J., Ozdín, D. and Seikora, J. (2008). Eclarite and associated Bi sulfosalts from the Brezno-Hviezda occurrence (Nízke Tatry Mts., Slovak Republic). *Neues Jahrbuch für Mineralogie, Abhandlungen*, **185**: 117–130.
- Sheldrick, G. M. (2008). A short history of SHELX. *Acta Crystallographica, Section A*, **64**: 112–122.
- Shimazaki, H., Miyawaki, R., Yokoyama, K., Matsubara, S. and Bunno, M. (2008). Occurrence and new data of dellaite from the Akagane mine, Japan. *Journal of Mineralogical and Petrological Sciences*, **103**: 385–389.
- Sumita, M., Aisawa, K., Watanabe, K., Fujisawa, M., Kikuchi, T. and Chiba, K. (1975). Recent prospecting at the Akagane mine, Iwate Prefecture. *Mining Geology*, **25**: 93–107. (In Japanese with English abstract)
- Takahashi, I. and Nambu, M. (2003). Shin Iwateken Kozan Shi (New guide book of the mines in Iwate Prefecture). 307 pp. Tohoku University Press, Sendai. (In Japanese)
- Takenouchi, S. (1975). Fluid inclusion study of the Jishakuyama and Koganetsubo ore deposits and acidic igneous rocks at the Akagane mine, Iwate Prefecture. *Mining Geology*, **25**: 247–259. (In Japanese with English abstract)
- Topa, D. and Makovicky, E. (2012). Eclarite: new data and interpretations. *Canadian Mineralogist*, **50**: 371–386.