

Munakataite, a new mineral from the Kato mine, Fukuoka, Japan

Satoshi MATSUBARA*, Takaaki MOURI**, Ritsuro MIYAWAKI*,
Kazumi YOKOYAMA* and Masae NAKAHARA***

*Department of Geology and Paleontology, National Museum of Nature and Science,
3-23-1 Hyakunin-cho, Shinjuku, Tokyo 169-0073, Japan

**Kagawa Prefectural Waterworks Office, 6-1 Tenjinmae,
Takamatsu, Kagawa 760-0018, Japan

***Kagawa Prefectural Industrial Technology Center, 587-1 Gotou-cho,
Takamatsu, Kagawa 761-8031, Japan

Munakataite, $\text{Pb}_2\text{Cu}_2(\text{Se}^{4+}\text{O}_3)(\text{SO}_4)(\text{OH})_4$, occurs as a thin coating on a fracture in a quartz vein containing Cu-Zn-Pb-Ag-Au ore minerals in the Kato mine, Munakata City, Fukuoka Prefecture, Japan. It is monoclinic with the space group $P2_1/m$ and lattice parameters $a = 9.766(8)$, $b = 5.666(5)$, $c = 9.291(10)$ Å, $\beta = 102.40(8)^\circ$, $V = 502.1(8)$ Å³, and $Z = 2$. An electron microprobe analysis gave the empirical formula as $\text{Pb}_{2.03}(\text{Cu}_{1.94}\text{Ca}_{0.01})_{\Sigma 1.95}(\text{Se}^{4+}\text{O}_3)_{1.00}(\text{SO}_4)_{1.02}(\text{OH})_{3.92}$ on the basis of $\text{Pb} + \text{Cu} + \text{Ca} + \text{Se} + \text{S} = 6$ apfu and the calculated (OH) with a charge balance. Munakataite is a member of the linarite-chenite group, and it is the first selenite mineral in Japan, corresponding to a (SO₄)-dominant analogue of schmiederite. The mineral occurs as light-bluish aggregates composed of minute fibrous crystals up to 30 µm long. The calculated density is 5.526 g/cm³, and Mohs hardness is less than 2.

Keywords: Munakataite, New mineral, Selenite, Kato mine

INTRODUCTION

During a mineralogical investigation of secondary minerals in the Kato mine, Fukuoka Prefecture, Japan, we recognized a light-blue mineral resembling linarite in a cavity of a quartz vein. A qualitative analysis of this mineral indicated that it contains a considerable amount of Se. A powder X-ray diffraction study indicated that its diffraction pattern is similar to the diffraction patterns of linarite and schmiederite.

Although schmiederite appeared as schmeiderite in Hey's Index published in 1963, Mitchell (1980) corrected the name to schmiederite after the German geographer, Oskar Schmieder; the mineral was initially named by Juan A. Olsacher. Schmiederite was found in the Condor mine, La Rioja, Argentina; however, a description of the mineral has not yet been published. In 1987, Sarp and Burri reported the chemical formula and mineralogical properties of the Condor mine material. Moreover, Effen-

berger (1987) described the crystal structure of the synthetic material and discussed its relationship to linarite. From these studies, schmiederite has been described as a lead-copper hydrous selenite-selenate mineral, $\text{Pb}_2\text{Cu}_2(\text{OH})_4(\text{SeO}_4)(\text{SeO}_3)$, having the same space group as linarite and double unit cells ($2 \times c$) of linarite.

In order to determine the detailed chemical composition of the material from the Kato mine, we performed electron microprobe analyses. The results showed that S is also a major constituent of the mineral, besides Pb, Cu, and Se. Moreover, the FT-IR spectrum confirmed that Se and S are separated into a selenite group, $(\text{Se}^{4+}\text{O}_3)^{2-}$, and a sulfate group, $(\text{S}^{6+}\text{O}_4)^{2-}$, respectively. Consequently, we considered the mineral to be a (SO₄)-dominant analogue of schmiederite. It is a member of the linarite-chenite group (Strunz and Nickel, 2001). The mineral name is for the city in which the Kato mine is located, Munakata. The mineral and the name have been approved by the IMA, CNMNC, #2007–012. This type material is deposited at the National Museum of Nature and Science, Tokyo, Japan (NSM-M28982).

OCCURRENCE

Munakataite occurs as a thin coating on a fracture in a quartz vein containing Cu-Zn-Pb-Ag-Au ore minerals at a dump in the Kato mine, Munakata City, Fukuoka Prefecture, Japan (33°49'N, 130°33'E). It exists in the form of aggregates composed of minute fibrous crystals with a length of up to 30 μm (Fig. 1). The hydrothermal ore veins develop into a tertiary porphyritic andesite. The Kato mine was operated as a branch of the Munakata gold mine during the Edo period (19th century); however, the mine was closed in 1958. The main ore minerals are electrum, chalcopyrite, sphalerite, and galena including hessite and sylvanite as minor constituents (Ueno et al., 1990). Although Matsukuma (1955) reported the occurrence of aguilarite through an optical study, he corrected it to hessite after performing an EPMA analysis (Ueno et al., 1990).

The secondary minerals such as cerussite, anglesite, linarite, pyromorphite, malachite, and brochantite are abundant. Munakataite occurs with malachite or with no other mineral on a tiny fracture of quartz. Its appearance is very similar to that of linarite; however, it is extremely rare.

PHYSICAL AND OPTICAL PROPERTIES

Munakataite is light blue in color with bluish white streaks. It is transparent with vitreous luster and pearly on cleavage surface. No fluorescence is observed. Munakataite is very soft, and its Mohs hardness is less than 2. Tenacity is brittle but fracture is not observed. Cleavage is perfect or distinct in one direction, // *b*. Although the density cannot be measured because of its small grain size, it is calculated to be 5.526 g/cm^3 by using an empirical formula.

Its optical properties also cannot be measured because of its small grain size. The minimum value of *n* (589 nm) is greater than 1.800, and the average value of *n* calculated from Gladstone-Dale constants and the density is 1.891 (Mandarino, 1976). It shows parallel extinction and positive elongation, and pleochroism is weak (colorless to very faint blue).

IR ABSORPTION SPECTRA

Infrared absorption spectra of the mineral were obtained using an FT-IR microspectrometer (JEOL JIR6000) with ATR and KBr methods for the region from 400 to 4000 cm^{-1} . The spectrum of munakataite (the main bands are underlined) exhibits absorption bands at 3400 cm^{-1} , 1100 cm^{-1} , 600 cm^{-1} , 790 cm^{-1} , 720 cm^{-1} , 440 cm^{-1} , 540 cm^{-1} ,

470 cm^{-1} , and 490 cm^{-1} (Fig. 2). In order to examine the characteristic bands of (SO_4), (SO_3), (SeO_4), and (SeO_3) groups, we used the following reference reagents in the FT-IR measurements: Na_2SO_4 , Na_2SO_3 , Na_2SeO_4 , and Na_2SeO_3 . The spectra of the four reagents exhibit absorption bands as follows: Na_2SO_4 , at 600 (medium) and 1100 (strong) cm^{-1} ; Na_2SO_3 , at 500 (weak) and 960 (strong) cm^{-1} ; Na_2SeO_4 , at 420 (strong) and 820 (medium) cm^{-1} ; and Na_2SeO_3 , at 440 (medium), 720 (strong), and 790 (weak) cm^{-1} . These data indicate that the absorption bands at 600 and 1100 cm^{-1} are due to the presence of the (SO_4) group, and those at 440, 720, and 790 cm^{-1} are due to the presence of the (SeO_3) group. The characteristic bands of the (SO_3) group at 960 cm^{-1} and those of the (SeO_4) group at 420 cm^{-1} are absent. The absorption band at 3400 cm^{-1} can be assigned to the (OH) group.

X-RAY CRYSTALLOGRAPHY

The powder X-ray diffraction pattern of munakataite was obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered $\text{CuK}\alpha$ radiation. This diffraction pattern resembles the diffraction patterns of schmierite and linarite (Table 1). A single-crystal study was not carried out because of the small crystal size. It is considered to be monoclinic with the space group $P2_1/m$, analogous to schmierite. The unit cell parameters are as follows: $a = 9.766(8)$, $b = 5.666(5)$, $c = 9.291(10)$ \AA , $\beta = 102.40(8)^\circ$, $V = 502.1(8)$ \AA^3 , and $Z = 2$. Compared with the unit cell parameters of schmierite, $a = 9.922(3)$, $b = 5.712(2)$, $c = 9.396(3)$ \AA , $\beta = 101.96(3)^\circ$, and $V = 520.8$ \AA^3 (Effenberger, 1987), the *a*, *b*, and *c*-axes of munakataite are distinctly shorter due to the replacement of (SeO_4) with (SO_4). Since munakataite and schmierite have unit cells with twice the *c*-dimension of linarite, characteristic diffraction peaks of *l* having odd values such as 001, 10-1, 101, 11-1, and 201 can be observed for munakataite and schmierite, whereas the corresponding peaks are not observed in the diffraction pattern of linarite. These characteristic peaks are indicated in boldface in Table 1 for comparison.

CHEMICAL COMPOSITION

Chemical analyses of munakataite were carried out using a Link Systems energy dispersive X-ray spectrometer (QX-2000) for Pb, Cu, Ca, S, and Se (15 kV, 1 nA, 3 μm beam diameter). The standard materials used were PbSO_4 for Pb and S, chalcopyrite for Cu, wollastonite for Ca, and TeSe for Se. Sulfur and selenium were obtained from SO_3 and SeO_2 , respectively, according to FT-IR spectroscopy. The amount of H_2O could not be directly determined be-

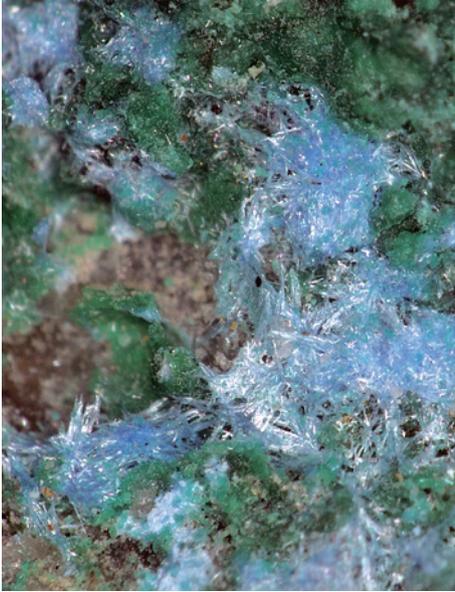


Figure 1. Photomicrograph of aggregates of munakataite crystals. Field view: approximately 1.8 mm wide.

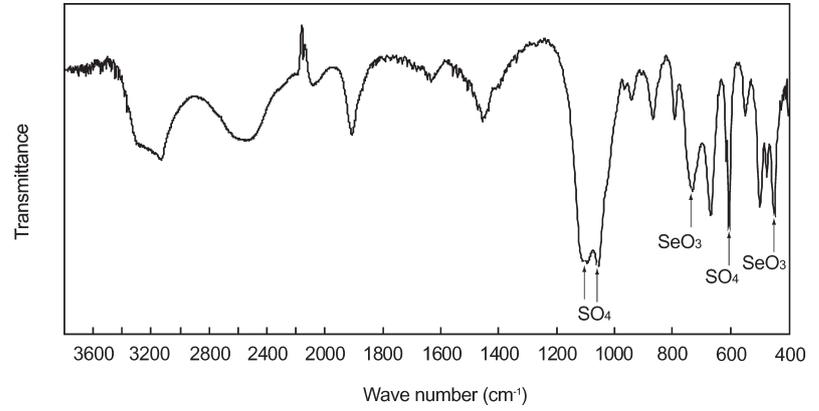


Figure 2. IR spectrum of munakataite.

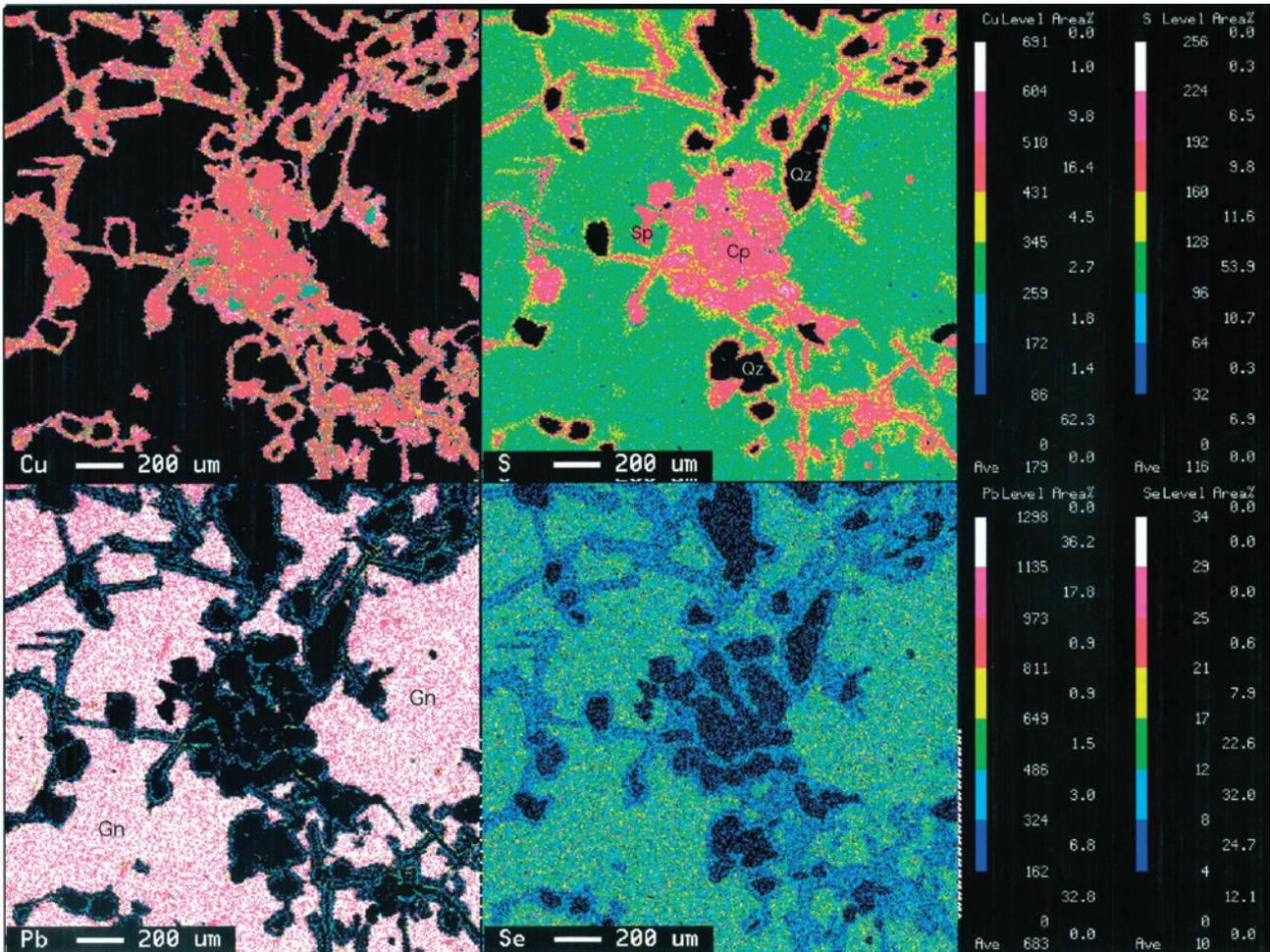


Figure 3. Element distribution color maps of galena including chalcopyrite. Abbreviations: Gn, galena; Cp, chalcopyrite; Sp, sphalerite; Qz, quartz.

Table 1. Comparison of X-ray powder diffraction data on munakataite, schmiederite, and linarite

			Munakataite			Schmiederite Effenberger (1987)			Linarite (PDF#30-0493)				
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i> / <i>I</i> ₀	<i>d</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>
1	0	0	9.50	9.54	13	9.7	20	10	9.46	11	1	0	0
0	0	1	9.04	9.07	3								
1	0	-1	7.38	7.42	3								
1	0	1	5.94	5.97	9	6.07	5						
1	1	0	4.86	4.87	44	4.92	42		4.849	40	1	1	0
0	1	1		4.81		4.85	6						
2	0	0	4.77	4.77	14	4.85	21	50	4.731	3	2	0	0
1	1	-1		4.50		4.54	3						
1	0	-2	4.47	4.49	57	4.52	47	50	4.521	60	1	0	-1
2	0	1	3.89	3.89	9	3.96	3						
1	0	2		3.79					3.805	9	1	0	1
2	0	-2	3.70	3.71	8	3.74	7	10	3.717	3	2	0	-1
2	1	0	3.65	3.65	14	3.7	7		3.625	30	2	1	0
0	1	2		{ 3.54 }		3.57	67	60	3.556	55	0	1	1
1	1	-2	3.53	{ 3.52 }	39	3.54	13						
2	1	1		3.21		3.26	4						
3	0	0	3.18	3.18	100	3.23	100	100	3.151	100	3	0	0
1	1	2		{ 3.15 }		3.19	89	90					
2	1	-2	3.14	{ 3.10 }	68	3.13	99	90	3.106	40	2	1	-1
0	0	3		3.03		3.06	5						
2	0	2	2.98	2.98	13	3.03	11	10	2.978	19	2	0	1
3	0	-2	2.92	2.91	2				2.912	2	3	0	-1
2	0	-3		2.85		2.86	31	30					
0	2	0	2.83	2.83	15				2.826	17	0	2	0
3	1	0	2.78	2.77	2	2.81	4		2.754	6	3	1	0
1	0	3		{ 2.72 }		2.76	4						
1	2	0	2.72	{ 2.72 }	22	2.74	33	40	2.707	30	1	2	0
1	1	-3		{ 2.71 }		2.73	7						
0	1	3	2.68	2.67	6								
2	1	2	2.64	2.64	6								
3	1	-2	2.59	2.59	10	2.62	18	20	2.587	25	3	1	-1
1	2	1		{ 2.56 }									
2	1	-3	2.52	{ 2.54 }	2								
1	1	3		2.45		2.48	4						
2	2	0	2.44	2.44	11	2.46	21	10	2.424	8	2	2	0
0	2	2	2.40	2.40	14	2.42	24	20	2.405	17	0	2	1
3	0	2		2.38					2.365	5	3	0	1
4	0	-2		{ 2.33 }		2.35	16	30	2.317	20	4	0	-1
1	0	-4	2.33	{ 2.32 }	18	2.34	14		2.344	4	1	0	-2
1	2	2		{ 2.27 }		2.29	13		2.267	20	1	2	1
0	0	4	2.27	{ 2.27 }	11	2.29	4	10					
2	2	-2		2.25					2.250	9	2	2	-1
2	0	-4	2.24	2.24	6	2.26	11		2.261	20	2	0	-2
4	1	0		{ 2.20 }		2.23	9	20					
3	1	2	2.20	{ 2.19 }	15	2.23	18		2.181	17	3	1	1
2	1	3		{ 2.16 }		2.19	7						
4	1	-2	2.16	{ 2.15 }	7	2.18	5		2.145	6	4	1	-1
1	1	-4		{ 2.15 }					2.164	19	1	1	-2
3	2	0		{ 2.12 }		2.14	22		2.104	12	3	2	0
1	0	4	2.12	{ 2.11 }	14	2.13	12	30	2.119	20	1	0	2
0	1	4		{ 2.11 }		2.13	3						
3	0	-4		2.07		2.082	4		2.081	4	3	0	-2
0	2	3		2.07		2.086	6						
2	2	2	2.05	2.05	5				2.049	8	2	2	1

Table 1. (Continued)

Munakataite						Schmiederite Effenberger (1987)			Linarite (PDF#30-0493)				
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>hkl</i> ₀	<i>d</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>
3	2	-2	2.03	2.03	6	2.049	16	20	2.027	20	3	2	-1
3	0	3	1.986	1.989	2	2.023	3						
3	1	-4	1.947	1.943	2	1.956	3						
5	0	-2	1.914	1.911	3	1.936	3						
5	0	0		1.908		1.941	3						
2	0	4	1.893	1.897	2	1.925	4		1.902	2	2	0	2
3	1	3	1.875	1.876	2								
4	0	-4		1.854		1.868	4						
1	3	0	1.853	1.853	6	1.868	4		1.847	5	1	3	0
4	1	2	1.842	1.840	12	1.873	16	10	1.830	12	4	1	1
4	2	0		1.824		1.849	10	10	1.813	20	4	2	0
3	2	2		1.820		1.846	5						
0	0	5		1.815		1.833	4	30					
5	1	-2	1.813	1.811	19	1.833	22		1.802	17	5	1	-1
5	1	0		1.808					1.793	14	5	1	0
1	2	-4	1.794	1.796	9	1.810	26	20					
0	2	4		1.771					1.777	7	0	2	2
1	1	-5		1.765		1.780	3						
2	2	-4		1.759		1.771	3		1.766	9	2	2	-2
2	3	0		1.756					1.750	5	2	3	0
0	3	2		1.744		1.758	8	10	1.742	8	0	3	1
2	1	-5	1.740	1.743	7	1.755	6						
4	2	1		1.734		1.760	3						
5	1	1	1.711	1.708	4	1.738	3						
1	3	2	1.692	1.691	6	1.706	13	20	1.688	5	1	3	1
2	3	-2	1.687	1.683	6	1.696	16	20	1.680	8	2	3	-1
2	3	-4		1.671					1.675	8	2	3	-2
5	0	-4		1.644		1.658	4		1.646	4	5	0	-2
1	1	5	1.641	1.643	6	1.662	6						
5	0	2		1.637					1.626	5	5	0	1
3	2	3		1.628		1.651	5						
3	1	4		1.614					1.613	5	3	1	2
4	2	2	1.605	1.604	5	1.628	8						
6	0	0		1.590					1.577	13	6	0	0
3	3	-2		1.585		1.598	4		1.580	8	3	3	-1
5	2	0	1.585	1.582	8	1.605	12	20	1.572	9	5	2	0
2	2	4		1.576		1.596	10	10					
4	2	-4	1.554	1.552	5	1.563	19	10					

cause of lack of material; however, it was calculated for charge balance as OH, as confirmed by FT-IR spectroscopy. Table 2 shows the average range of results of seven analyses. The empirical formula is $\text{Pb}_{2.03}(\text{Cu}_{1.94}\text{Ca}_{0.01})_{\Sigma 1.95}(\text{Se}^{4+}\text{O}_3)_{1.00}(\text{SO}_4)_{1.02}(\text{OH})_{3.92}$ based on $\text{Pb} + \text{Cu} + \text{Ca} + \text{Se} + \text{S} = 6 \text{ apfu}$. The simplified formula is $\text{Pb}_2\text{Cu}_2(\text{Se}^{4+}\text{O}_3)(\text{SO}_4)(\text{OH})_4$, which requires PbO 53.62, CuO 19.11, SeO_2 13.32, SO_3 9.62, and H_2O 4.33, total = 100.00 wt%.

DISCUSSION

Although S-rich schmiederite was introduced by Sarp and Burri (1987), no properties other than the chemical com-

position have been reported. Therefore, it may chemically correspond to munakataite. Munakataite resembles linarite and schmiederite in appearance; however, X-ray powder diffraction patterns can be used to differentiate munakataite from linarite and schmiederite. Moreover, the FT-IR measurement is a practical method to distinguish between munakataite and linarite or schmiederite.

No ore minerals, including Se, as major constituents are still known in the Kato mine, in spite of our examinations of a few ores. To determine the source of Se, we tried to detect traces of Se in the major minerals by using a WDS electron microprobe analyzer (JEOL 8800M). We were able to detect approximately 0.1 wt% Se in galena

Table 2. Chemical composition of munakataite

Constituent	wt%	Range	Standard dev.
PbO	53.71	53.24 - 54.09	0.29
CuO	18.33	17.74 - 19.81	0.74
CaO	0.04	0.00 - 0.26	0.10
SO ₃	9.73	8.13 - 11.16	1.09
SeO ₂	13.19	11.10 - 14.48	1.14
H ₂ O*	4.19		
Total	99.19		

* For charge balance.

including chalcopyrite (Table 3). Se is more or less homogeneously distributed in galena (Fig. 3); therefore, it is considered a clausthalite (PbSe) mole in a galena-clausthalite solid solution. This indicates that the condition for forming munakataite and other selenite minerals is not extremely rare. In fact, munakataite has also been found in the Kisamori mine, Akita Prefecture, Japan, which is a well known site of linarite, after the approval of munakataite as a new mineral (Toshiyuki Hiramata and Takashi Yamada, pers. comm.). We assume that more munakataite will be found in the form of light-blue fibrous aggregates, misidentified as linarite in various sites.

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Table 3. Chemical composition of galena

Constituent	wt%	Range	Standard dev.
Pb	85.76	85.18 - 86.13	0.38
S	13.26	13.04 - 13.66	0.22
Se	0.11	0.09 - 0.12	0.01
Total	99.13		

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