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Sterlinghillite, a Rare Manganese Arsenate, from the Gozaisho Mine, Fukushima Prefecture, Japan

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Abstract Sterlinghillite is found in rhodonite-braunite ore from the Gozaisho mine, Fukushima Prefecture, in association with brandtite and an undetermined manganese lead arsenate mineral. This is the second occurrence of this mineral in the world. The representative chemical analysis by EPMA gave MnO 42.76, As_2O_5 46.40, H_2O 10.84 (by difference) total 100 wt. %, yielding the empirical formula $Mn_{2.99}As_{2.00}O_8 \cdot 2.98H_2O$ on the basis of O=8 in anhydrous part. The strongest lines in the X-ray powder diffraction pattern by a Gandolfi camera are 11.3 (vvs), 6.48 (s), 4.96 (m), 3.67 (m), and 3.23 (vs). The cell parameters in monoclinic symmetry are estimated from the powder diffraction pattern: a=12.39 (2), b=11.23 (2), c=11.62 (2) Å, β=98.45 (5)°, V=1599.3 Å^3.

Key words: sterlinghillite, Gozaisho mine, Fukushima Prefecture, Japan, X-ray, chemical data.

Introduction

Sterlinghillite, a very rare manganese arsenate hydrate, $Mn_3(AsO_4)_2 \cdot 4H_2O$, was reported from the Sterlinghill mine, Ogdensburg, Sussex Co., New Jersey, USA, but the crystallography has not been known due to the lack of sufficient sample (Dunn, 1981). Only one specimen of the mineral was found and it occurs as a product presumably by the decomposition of löllingite on löllingite–franklinite–willemite–calcite ore.

The Gozaisho mine is the well known locality of many manganese arsenates such as manganberzeliite (Matsubara, 1975), sarkinite, geigerite (Kato *et al.*, 1990), villyaellenite and arseniopleite (Matsubara *et al.*, 1998). Recently, the third and fourth authors recognized an unfamiliar mineral among the arsenate-bearing ores collected from the dump. The X-ray and chemical studies by the first and second authors have proved it to be sterlinghillite as the second occurrence in the world. It associates

with brandtite and an undetermined manganese lead arsenate mineral.

Occurrence

The ore deposit of the Gozaisho mine (36°59.7′N, 140°42.4′E) is located at Iwaki City, Fukushima Prefecture, Japan, and involved within basic schist of epidote-amphibolite facies belonging to the Gozaisho metamorphic rocks. The ore bodies are generally lentiticular and stratiform in small scale, and composed of two type ores. One is braunite ore with rhodonite, rhodochrosite and nambulite, and the other is hausmannite ore with manganosite, rhodochrosite, tephroite, alleghanyite and sonolite. Rare manganese arsenates and Sb-bearing minerals such as lågbanite (Matsubara *et al.*, 1986) and romeite (Matsubara *et al.*, 1996) are found only in braunite ore as the later stage products affected by any hydrothermal activities.

The studied material is black stained manganese ore and is composed of mainly fine-grained braunite with minor quartz and rhodonite. The aggregates of sterlinghillite and other arsenates occur as bundles or subparallel prisms reaching 5 mm in length on rhodonite-rich part. They are colorless but look slightly pink tint because of the color coming through underlain rhodonite. It is very difficult to distinguish each other by naked eyes. Under the electron microscope they fill the interstices of rhodonite and quartz grains as irregular aggregates under 0.5 mm in diameter. The aggregates include minute arsenian apatite and djurleite. BEI indicates that ster-

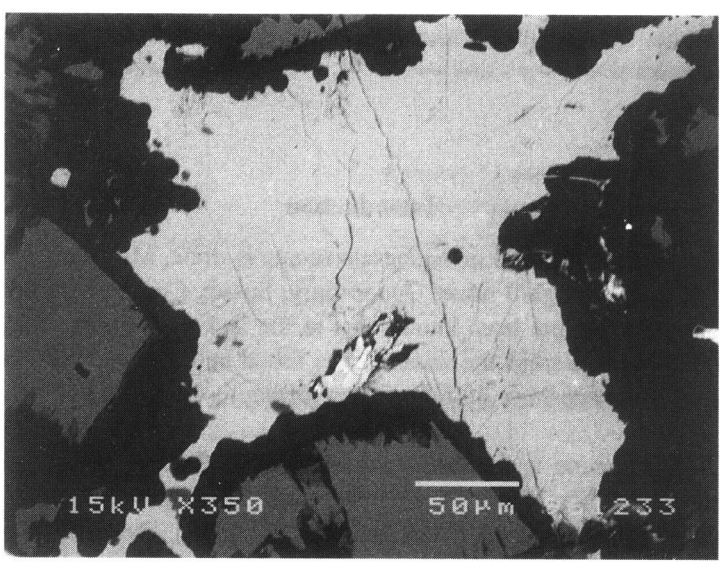

Fig. 1. Back-scattered electron image (BEI) of sterlinghillite (light) in association with rhodonite (gray) and quartz (dark). The grain of sterlinghillite includes small aggregate of brandtite and an undetermined manganese lead arsenate in lower part.

linghillite is almost homogeneous (Fig. 1), whereas brandtite-dominant part is highly heterogeneous (Figs. 2, 3). The heterogeneity owes the various proportion of Ca, Mn and Pb, and also the substitution by sterlinghillite. We have recognized only two ster-

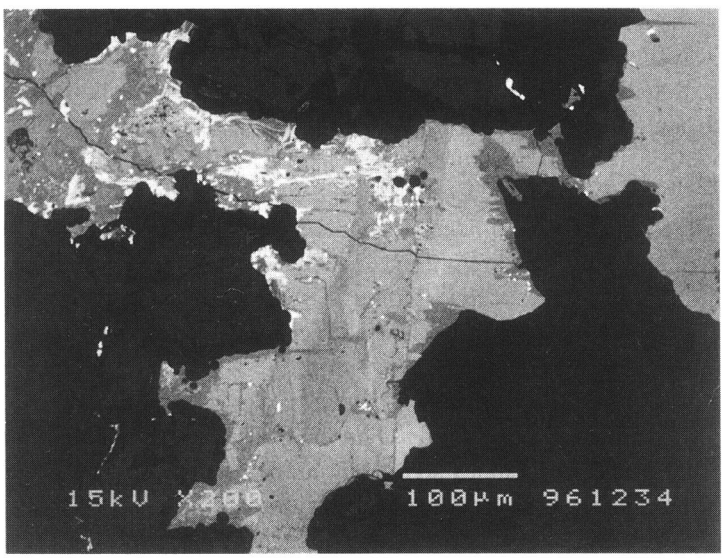

Fig. 2. Back-scattered electron image of aggregate of inhomogeneous brandtite (light gray to gray) in association with sterlinghillite (dark gray), an undetermined manganese lead arsenate (bright) and/or rhodonite and quartz (dark).

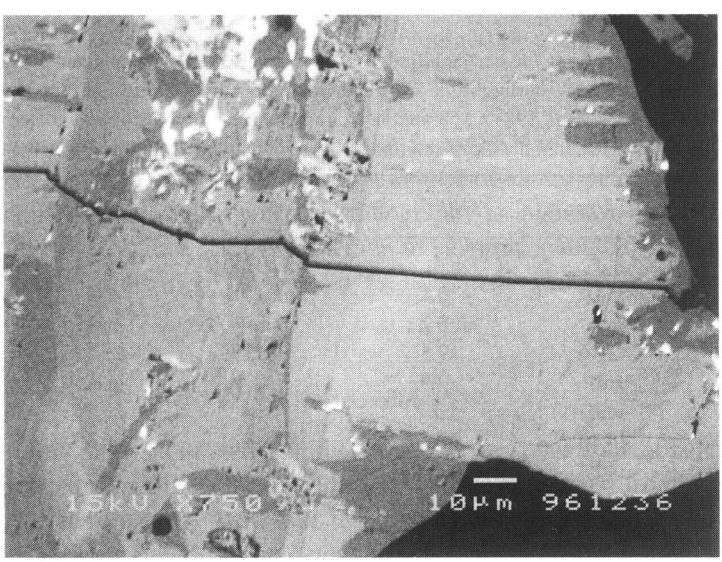

Fig 3. Enlarged back-scattered electron image of the center part of Fig. 2.

linghillite-bearing pieces divided from one specimen until now.

Chemical Composition

Chemical analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000) for Si, Al, Mg, Ca, Na, K, Fe, Mn, Pb, Sr, As and P. The contents of Si, Al, Mg, Ca, Na, K, Fe, Pb, Sr and P in sterlinghillite and Si, Al, Mg, Na, K and P in brandtite and an undermined manganese lead arsenate were under the detection limits, respectively. Standard materials and detailed analytical procedure have been reported by Yokoyama *et al.* (1993). The figures of the representative analyses of sterlinghillite, brandtite, an undermined manganese lead arsenate and arsenian apatite from the Gozaisho mine are presented in Table 1 together with the data for sterlinghillite from the original locality (Dunn, 1981). The empirical formula of the present sterlinghillite is $Mn_{2.99}As_{2.00}O_8 \cdot 2.98H_2O$ on the basis of O=8 in anhydrous part. The ratio of manganese and arsenic in sterlinghillite is nearly ideal but water content is too small to theoretical formula. The empirical formula of the present brandtite is $(Ca_{1.95}Pb_{0.09})_{\Sigma 2.04}Mn_{1.02}As_{1.98}O_8 \cdot 2.25H_2O$ on the basis of O=8 in anhydrous part. It is noteworthy that brandtite includes significant amounts of lead. The general formula of an undermined manganese lead arsenate (bright parts in Figs. 2, 3) can be written into $Pb(Mn,Ca,Pb)Mn_3(AsO_4)_3 \cdot nH_2O$ ($n \approx 3$). The M^{2+}/As ratio of 5/3 resembles that of the Gozaisho arseniopleite in which small amount of Pb is included (Matsubara *et al.*, 1998). However, water content assumed from the difference of total weight percentages suggests that the mineral is structurally different from arseniopleite or alluaudite group minerals. The zoning pattern is observed in arsenian apatite due to the

Table 1. Chemical analyses for sterlinghillite, brandtite, an undetermined manganese lead arsenate and arsenian apatite. 1: sterlinghillite from the Gozaisho mine. 2: sterlinghillite from Ogdensburg, New Jersey (Dunn, 1981). 3: brandtite from the Gozaisho mine. 4: an undetermined manganese lead arsenate from the Gozaisho mine. 5: arsenian apatite from the Gozaisho mine.

Wt. %	1	2	3	4	5
CaO	n.d.	n.d.	23.31	2.51	48.46
MgO	n.d.	0.1	n.d.	n.d.	n.d.
FeO	n.d.	0.2	n.d.	n.d.	n.d.
MnO	42.76	39.5	15.43	25.52	1.10
ZnO	n.d.	2.9	n.d.	n.d.	n.d.
PbO	n.d.	n.d.	4.14	28.76	n.d.
As_2O_5	46.40	44.7	48.48	36.45	29.02
P_2O_5	n.d.	n.d.	n.d.	n.d.	18.41
H_2O*	10.84	12.6	8.64	6.76	
Total	100	100	100	100	96.99

*: by difference, n.d.: not detected

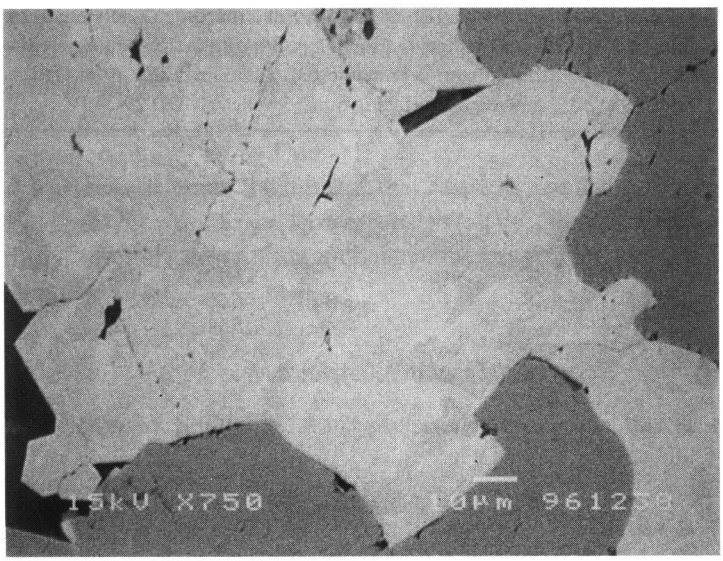

Fig. 4. Back-scattered electron image of arsenian apatite showing weakly zoning between As-rich (light) and P-rich (light gray) parts.

substitution of P by As (Fig. 4). The As/P ratio of the most As-rich apatite reaches 0.97 as indicated in Table 1.

X-ray Study

The X-ray powder diffraction data were obtained by a Gandolfi camera (diameter=114.6 mm) using Cu/Ni radiation. The diffraction data of sterlinghillite with those of subordinate brandtite are given in Table 2, in which those of sterlinghillite from Ogdensburg (Dunn, 1981) and brandtite from the Harstig mine (ICDD 29-348) were compared. As we can obtain no single crystal of sterlinghillite due to close association with brandtite, the correct crystallography is unknown like as the original sterlinghilite. However, the cell parameters in monoclinic symmetry can be estimated from the powder diffraction pattern: a=12.39 (2), b=11.23 (2), c=11.62 (2) Å, β=98.45 (5)°, V=1599.3 Å^3.

Discussion

The present analysis of sterlinghillite suggests the water content is less than that of the original sterlinghillite (Dunn, 1981). This may be derived from the water loss damaged by electron beam. However, the difference among them is small, and the correct water content could not be determined because both were analysed with the electron microprobe. The measured density of the original sterlinghillite is 2.95 g/cm^3

Table 2. X-ray powder diffraction data for sterlinghillite and brandtite. 1: mixture of sterlinghillite and brandtite from the Gozaisho mine. Diffraction peaks with indices are for sterlinghillite and that with symbol at remarks column is brandtite (B). 2: sterlinghillite from Ogdensburg, New Jersey (Dunn, 1981). 3: brandtite from Harstig mine, Sweden (ICDD 29-348).

			1			2		3	
h	k	l	$d_{calc.}$	$d_{obs.}$	I	remarks	d	I	d	I
0	1	0	11.2	11.3	vvs		11.12	100		
1	1	1	6.42	6.48	s	+B	6.39	30	6.482	25
							6.11	2		
1	0	$\bar{2}$	5.52	5.52	vw		5.50	2		
				5.14	w	B			5.151	20
1	1	$\bar{2}$	4.96	4.96	m		5.01	10	4.993	10
2	1	1	4.65	4.69	vw		4.73	10		
									4.403	10
									4.237	10
0	2	2	4.02	3.96	w		3.96	2		
1	2	$\bar{2}$	3.94							
				3.81	w	B			3.790	20
3	0	1	3.68	3.67	m		3.692	30		
				3.43	w	B			3.424	30
				3.37	m	B			3.373	55
									3.294	5
2	2	2	3.21	3.23	vs	+B	3.209	100	3.241	70
				3.17	vw	B			3.178	5
				3.01	m	B			3.010	100
4	0	$\bar{2}$	2.89	2.88	w		2.880	40		
4	0	1	2.86	2.85	w		2.848	40		
0	4	0	2.81	2.81	w		2.814	5		
									2.799	5
3	3	0	2.76	2.76	w		2.751	60		
									2.700	5
1	4	1	2.64	2.64	w	+B	2.629	10	2.642	5
3	3	$\bar{2}$	2.59	2.60	w		2.603	10		
							2.553	2		
5	0	$\bar{1}$	2.47	2.47	vw		2.465	10		
4	2	$\bar{3}$	2.35	2.35	vw	+B	2.341	2	2.345	5
							2.298	2		
				2.27	vw	B			2.271	15
							2.217	2		
									2.192	5
							2.171	2	2.154	5
				2.13	w	B			2.118	5
							2.049	2	2.072	5
6	1	$\bar{2}$	1.989	1.983	vw		1.975	5		
2	5	2	1.948	1.946	w	+B	1.939	5	1.949	5
									1.926	5
									1.899	10
5	4	$\bar{1}$	1.855	1.855	vw		1.855	5	1.874	5
							1.843	10		
				1.826	vw	B			1.824	5

which may be lower than real one due to the highly porous nature (Dunn, 1981). The calculated density of the present material is 3.09 g/cm^3 from the estimated cell parameters by assumption of the ideal formula, $Mn_3(AsO_4)_2 \cdot 3H_2O$, and Z=6. This is corresponding to about 5% addition to 2.95 g/cm^3 and may be allowed to exist in the predicted range over 2.95 g/cm^3 by Dunn (1981).

There are no reports about the mineral that has the chemical composition corresponding to the present manganese lead arsenate to date. This mineral is a possibly new mineral, but the fully description must have the crystallographic study after the find of more large grains.

Acknowledgements

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References

Dunn, P. J., 1981. Sterlinghillite, a new hydrated manganese arsenate mineral from Ogdensburg, New Jersey. *Amer. Mineral.*, **66**, 182–184.

Kato, A., S. Matsubara & K. Sekiuchi, 1990. Geigerite from the Gozaisho mine, Fukushima Prefecture, Japan. *Abstr. Japanese Assoc. Min. Petrol. and Econ. Geol., 1990 Annual Meeting*, 184. (In Japanese.)

Matsubara, S., 1975. Manganberzeliite from the Gozaisho mine, Fukushima Prefecture, Japan. *Journ. Mineral. Soc. Japan*, **12**, 238–252. (In Japanese.)

Matsubara, S., A. Kato, K. Sekiuchi & E. Hashimoto. 1986. Lågbanite from the Gozaisho mine, Fukushima Prefecture, Japan. *Abstr. Mineral. Soc. Japan, 1986 Annual Meeting*, 39. (In Japanese.)

Matsubara, S., A. Kato, M. Shimizu, K. Sekiuchi & Y. Suzuki, 1996. Romeite from the Gozaisho mine, Iwaki, Japan. *Mineral. Journ.*, **18**, 155–160.

Matsubara, S., R. Miyawaki, A. Kato, T. Mouri, Y. Suzuki & F. Matsuyama, 1998. Arseniopleite from the Gozaisho mine, Fukushima Prefecture, Japan. *Abstr. Japanese Assoc. Min. Petrol. and Econ. Geol., 1998 Annual Meeting*, 176. (In Japanese.)

Yokoyama, K., S. Matsubara, Y. Saito, T. Tiba & A. Kato, 1993. Analyses of natural minerals by energy-dispersive spectrometer. *Bull. Natn. Sci. Mus., Tokyo*, Ser. C, **19**, 115–126.