Bull. Natn. Sci. Mus., Tokyo, Ser. C, 27(1, 2), pp. 45–50, June 22, 2001

Manganoan Wallkilldellite, a Manganese Arsenate, from the Gozaisho Mine, Fukushima Prefecture, Japan

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Abstract Wallkilldellite is found in rhodonite-rhodochrosite-braunite ore from the Gozaisho mine, Fukushima Prefecture, in association with villyaellenite. The average chemical analysis of 5 analyses by EPMA gave CaO 8.89, MnO 34.06, CuO 0.67, SiO_2 0.51, As_2O_5 28.92, H_2O 26.95 (by difference) total 100 wt.%, yielding the empirical formula $(Ca_{2.45}Mn_{1.55})_{\Sigma 4.00}(Mn_{5.86}Cu_{0.13})_{\Sigma 5.99}(As_{3.88}Si_{0.13})_{\Sigma 4.01}O_{16}(OH)_8 \cdot 19.08H_2O$ on the basis of total cations = 14 in anhydrous part. The strongest lines in the X-ray powder diffraction pattern by a Gandolfi camera are 11.7 (100) (002), 3.27 (85) (110), 2.90 (50) (008), 2.13 (60) (120; 121), and 1.632 (80) (220). The cell parameters in hexagonal symmetry calculated from the powder diffraction pattern are: a=6.52(1), c=23.1(1) Å, V=850.4 Å^3.

Key words: wallkilldellite, arsenate, Gozaisho mine

Introduction

Wallkilldellite, a extremely rare calcium manganese arsenate hydrate, $Ca_4Mn_6^{2+}As_4O_{16}(OH)_8 \cdot 18H_2O$, was reported from the Sterlinghill mine, Ogdensburg, Sussex Co., New Jersey, USA, together with kittatinnyite, Si and Mn^{3+} analogue of wallkilldellite, $Ca_4Mn_4^{3+}Mn_2^{2+}Si_4O_{16}(OH)_8 \cdot 18H_2O$, from the Franklin mine (Dunn and Peacor, 1983). The original wallkilldellite was reported as the last stage mineral forming radial and irregular aggregates of dark red platy crystals in association with a manganoan cuproan adamite in franklinite-willemite-calcite ore.

The Gozaisho mine is the unique locality in Japan of many rare manganese arsenates such as sterlinghillite (Matsubara *et al.*, 2000). The third author has recognized an unusual mineral among his collection from the Gozaisho mine. Although the appearance of original wallkilldellite is different with that of the Gozaisho's material, the X-ray and chemical studies indicate it to be wallkilldellite except Ca-poor nature. This paper is for the description of Gozaisho's wallkilldellite as the second find in the world.

Occurrence

The location and geology of the ore deposit of the Gozaisho mine (36°59.7′N,

Table 1. The mineral list of different forming stage at the Gozaisho mine.

	Primary	Hydrothermal activities	Secondary
Element			copper
Sulfides		djurleite, digenite, bornite, chalcopyrite, galena, molybdenite, pyrite	
Oxides	hausmannite, manganosite, jacobsite, iwakiite, quartz	hematite, crednerite, romeite, quartz pyrophanite	cuprite, pyrolusite, cryptomelane
Carbonates	rhodochrosite	rhodochrosite, calcite	malachite
Sulfates	barite (fine aggregates)	barite (vein)	brochantite
Arsenates		manganberzeliite, sarkinite, geigerite, villyaellenite, arseniopleite, sterlinghillite, conichalcite, brandtite, wallkilldellite	
Silicates	braunite (fine aggregates)	braunite (coarse crystal), tephroite, alleghanyite, sonolite, spessartine, långbanite, aegirine, manganocummingtonite, rhodonite, nambulite, phlogopite, ganophyllite, helvite, microcline, albite	neotocite

140°42.4′E) is already reported in some papers (e.g. Matsubara *et al.*, 1996; Matsubara *et al.*, 2000). The manganese arsenates occur as the later stage products affected by any hydrothermal activities, and are found only in braunite-rhodonite ore which has a few rhodochrosite (Table 1).

The aggregates of wallkilldellite occur as very thin veinlets under 0.5 mm in thickness cutting braunite-rhodonite ore like other manganese arsenates. The veinlets are composed of extremely fine micaceous platy crystals and a few prismatic crystals of villyaellenite. The individual crystal of wallkilldellite is hexagonal plate under 15 μm in diameter, and the crystals form rosette aggregates (Fig. 1). The present wallkilldellite is pale reddish brown to light brown with pale light brown streak despite the original material is dark red with light orange streak.

Chemical Composition

Chemical analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000) for Mg, Si, P, Ca, Mn, Fe, Cu, Zn and As. The contents of Mg, Fe and Zn were under the detected limit. Standard materials and detailed analytical procedure have been reported by Yokoyama *et al.* (1993). The figures of the average analysis of wallkilldellite from the Gozaisho mine is presented in Table 2 together with the data for the original wallkilldellite and kittatinnyite

Fig. 1. SEM images of wallkilldellite in association with villyaellenite.
(Top) Wallkilldellite appears rosette aggregates composed of micaceous platy crystals and prismatic crystals of villyaellenite are visible in lower part. (Bottom) Enlarged SEM image of wallkilldellite aggregates.

(Dunn and Peacor, 1983). The empirical formula of the present wallkilldellite is $(Ca_{2.45}Mn_{1.55})_{\Sigma 4.00}(Mn_{5.86}Cu_{0.13})_{\Sigma 5.99}(As_{3.88}Si_{0.13})_{\Sigma 4.01}O_{16}(OH)_8 \cdot 19.08H_2O$ on the basis of total cations = 14 in anhydrous part. In comparison with the theoretical formula of wallkilldellite, the result shows obviously deficiency of Ca and excess of Mn. We

Table 2. Chemical compositions for wallkilldellite and kittatinnyite.

Wt.%	1	1′	2	3
MgO	n.d.		0.9	0.0
CaO	8.89	8.13–9.85	12.4	17.3
MnO	34.06	32.78–36.16	27.0	10.6
Mn_2O_3				23.6
FeO	n.d.		0.3	0.0
CuO	0.67	0.00–1.36	3.3	0.0
ZnO	n.d.		0.0	0.3
SiO_2	0.51	0.26–0.88	1.7	18.2
As_2O_5	28.92	26.97–30.53	27.4	0.8
Total	73.05		73.0	70.8
		Atomic Proportions		
Mg			0.33	
Ca	2.45		3.31	4.04
Mn	7.41		5.69	5.88
Fe			0.06	
Cu	0.13		0.62	
Zn				0.05
Si	0.13		0.42	3.97
As	3.88		3.56	0.09

n.d.; not detected
1: Average of 5 analyses of wallkilldellite from the Gozaisho mine.
1′: Range.
2: Wallkilldellite from Sterling Hill, New Jersey, USA (Dunn and Peacor, 1983).
3: Kittatinnyite from Franklin, New Jersey, USA (Dunn and Peacor, 1983).

consider the substitution of Mn for Ca is not unreasonable. Although the site of a few Cu could not be determined, we assigned it at the Mn-site because ionic radius of Cu is close to Mn rather than Ca. Dunn and Peacor (1983), however, considered that Cu occupies at the Ca-site. As theoretical number of water molecules is assumed as 18 per formula, calculated water molecules by difference are slightly high like the case of Dunn and Peacor (1983).

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 wallkilldellite are given in Table 3, in which those of wallkilldellite from the Sterling Hill mine and kittatinnyite from the Franklin mine (Dunn and Peacor, 1983) were compared. We can obtain no single crystal of wallkilldellite due to extremely small size, and therefore the correct crystallography is unknown. However, Dunn and Peacor (1983) suggested the

Table 3. X-ray powder diffraction data for wallkilldellite and kittatinnyite.

1				2			3		
d_{obs}	d_{cac}	I	h k l	d	I	h k l	d	I	h k l
11.7	11.6	100	0 0 2	11.5	100	0 0 2	11.2	100	0 0 2
5.64	5.65	45	1 0 0	5.61	90	1 0 0	5.61	60	1 0 0
				5.05	10	1 0 2	5.03	30	1 0 2
				4.56	40	1 0 3			
				4.06	5	1 0 4	4.00	5	1 0 4
				3.92	2	0 0 6	3.80	30	0 0 6
3.27	3.26	85	1 1 0	3.25	40	1 1 0	3.25	30	1 1 0
2.90	2.89	50	0 0 8	2.936	10	0 0 8			
2.83	2.84	40	1 1 4	2.844	60	1 1 4	2.822	50	1 1 4, 2 0 0, 1 0 7
	2.82		2 0 0	2.810	1	2 0 0			
2.79	2.80	30	2 0 1						
2.73	2.74	25	2 0 2	2.748	50	2 0 2	2.733	60	2 0 2
							2.637	2	2 0 3
2.55	2.54	25	2 0 4	2.545	50	2 0 4	2.525	40	2 0 4
2.47	2.49	12	1 1 6						
2.40	2.41	15	2 0 5						
2.34	2.34	20	1 0 9				2.313	5	1 0 9
2.32	2.32	35	1 1 7						
	2.31		0 0 10	2.349	40	0 0 10	2.279	40	0 0 10
				2.182	20	1 1 8			
2.13	2.13	60	1 2 0	2.136	30	1 2 0	2.133	30	2 0 7, 1 2 0
	2.13		1 2 1						
				2.101	20	2 1 2	2.090	20	2 1 2
2.06	2.06	15	2 1 3				2.050	2	2 1 3
2.00	2.00	10	2 1 4				2.002	2	2 0 8
							1.949	2	1 0 11
1.883	1.885	5	1 1 10	1.886	2		1.885	5	
				1.794	5		1.784	10	
				1.727	2				
							1.704	2	
							1.673	1	
1.632	1.630	80	2 2 0	1.611	5		1.628	30	
1.594	1.591	10	2 0 12				1.609	2	
							1.574	10	
				1.492	2				
				1.446	5				
1.376	1.376	5	2 2 9	1.425	2		1.412	20	
				1.341	5		1.324	5	

1: wallkilldellite from the Gozaisho mine, Fukushima Prefecture, Japan. *a* 6.52(1), *c* 23.1(1) Å.

2: wallkilldellite from Sterling Hill mine, N. J., USA (Dunn & Peacor, 1983). *a* 6.506(7), *c* 23.49 (3) Å.

3: kittatinnyite from Franklin, N. J., USA (Dunn & Peacor, 1983). *a* 6.498(4), *c* 22.78(2) Å.

space groups $P6_3/mmc$, $P6_3mc$ or $P\bar{6}_2c$ from Weissenberg photographs. The calculated cell parameters for the present wallkilldellite with refer to the original result are a=6.52(1), c=23.1(1) Å, V=850.4 Å^3. The value of a is almost same to the original a=6.506(7) Å, but that of c is slightly small to the original c=23.49(3) Å.

Conclusions

The present wallkilldellite is characterized less Ca content than the original one (Dunn and Peacor, 1983). This may cause different color between two materials. We can explain smaller c dimension of Gozaisho's material due to increasing of Mn whose ionic radius is generally smaller than that of Ca. This suggests the arrangement of Ca-polyhedra form a layer parallel to (001) like mica structure. The presence of slight Si content, also, suggests a part of Mn is Mn^{3+} because of valence balance. The calculated density of the present wallkilldellite is 3.01 g/cm^3, which is considerably higher than the original ones, 2.85(5) g/cm^3 (measured) and 2.90 g/cm^3 (calculated), due to the higher Mn content.

Wallkilldellite is the last stage mineral during hydrothermal activities forming many manganese arsenate hydrates such as villyaellenite, sarkinite, geigerite, brandtite, arseniopleite, and sterlinghillite at the Gozaisho mine.

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