

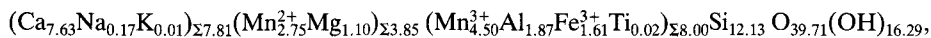
Okhotskite, a new mineral, an Mn³⁺-dominant member of the pumpellyite group, from the Kokuriki mine, Hokkaido, Japan

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Abstract

Okhotskite, an Mn³⁺-dominant pumpellyite-group mineral, is monoclinic, $A2/m$, $a = 8.887$, $b = 6.000$, $c = 19.53$ Å, $\beta = 97.08^\circ$, $Z = 1$. The formula is



which simplifies to $\text{Ca}_8(\text{Mn}^{2+}, \text{Mg})_4(\text{Mn}^{3+}, \text{Al}, \text{Fe}^{3+})_8\text{Si}_{12}\text{O}_{56-n}(\text{OH})_n$. Strong lines in the X-ray powder diffraction pattern are: 4.76(60)(004, 111), 3.87(70)(202), 2.96(100)(115, 300), 2.88(25)(022), 2.72(70)(302), 2.67(45)(304, 311), 2.55(45)(024, 313) and 2.38(45)(304).

Its colour is deep orange with a pale orange streak and vitreous lustre. Transparent. Non-fluorescent. H 6 (Mohs). Density (calc.) = 3.40 g/cm³. Optically biaxial negative, $2V(\text{meas}) = 46(5)^\circ$, $2V(\text{calc}) = 46^\circ$, dispersion indiscernible. Refractive indices: $\alpha = 1.782(5)$, $\beta = 1.820(5)$, $\gamma = 1.827(5)$. Orientation: $Y = b$, $c \wedge Z = 9-14^\circ$ in acute angle of β . Pleochroism is distinct: X yellow, Y and Z deep orange. Absorption: $X < Y < Z$.

This mineral occurs as fine prisms up to 0.2 mm long and forms aggregates in network veinlets cutting hematite ore from the Kokuriki mine in the Tokoro district, eastern Hokkaido, Japan. Associated minerals are: hematite, piemontite, quartz, neotocite, bementite, apatite, Mn-oxides, inesite and rhodochrosite. The mineral is named okhotskite for the Sea of Okhotsk, along which the mine is located.

KEYWORDS: okhotskite, new mineral, pumpellyite group, Hokkaido, Japan.

Introduction

PUMPELLYITE-group minerals are represented by the chemical formula, $W_8X_4Y_8Z_{12}O_{56-n}(\text{OH})_n$, and named after the most dominant Y-site cation (Passaglia and Gottardi, 1973); pumpellyite (with Al_Y) (Palache and Vassar, 1925), julgoldite (with Fe_Y³⁺) (Moore, 1971) and shuiskite (with Cr_Y) (Ivanov *et al.*, 1981). Although Kato *et al.* (1981) found pumpellyite-(Mn²⁺) containing Mn²⁺ as the most dominant divalent cation in the X-site, no member with Mn³⁺ as the most dominant Y-site cation has been found. The present study describes the first occurrence of an Mn³⁺-dominant pumpellyite-group mineral, from the Kokuriki mine. The mineral is named okhotskite for the Sea of Okhotsk, along which the mine is located. The mineral and its name have been approved

by the Commission on New Minerals and Mineral Names, IMA.

Occurrence

The Tokoro Belt, a tectonic unit occupying the eastern side of the Central Axial Zone of Hokkaido, is made up of an upper Jurassic greenstone complex and upper Cretaceous clastic sedimentary rocks. The former is called the Nikoro Group and the latter the Yubetsu and Saroma Groups (Kiminami *et al.*, 1983; Iwata *et al.*, 1983; Research Group of the Tokoro Belt, 1984; Iwata and Tajika, 1986). The investigated area is underlain by the Nikoro and Saroma Groups.

Stratabound manganiferous hematite ore deposits occur in a member of the Nikoro Group which

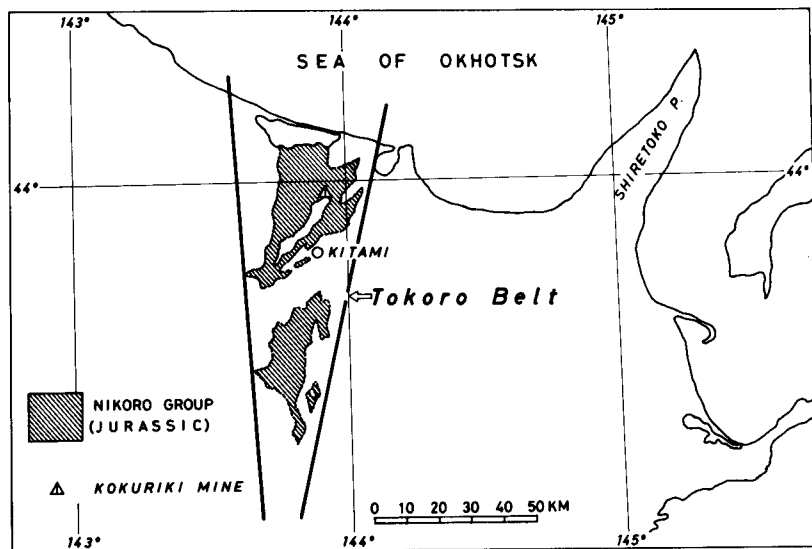


FIG. 1. Index map showing the location of the Kokuriki mine.

consists mainly of greenstones, associated with small amounts of chert and limestone (Bamba, 1984; Research Group of Tokoro Belt, 1984), and suffered low-grade metamorphism of high-pressure intermediate type (Sakakibara, 1986). The ore bodies occupy a space between radiolarian chert and basaltic pillow lava. The former is the hanging wall and the latter the footwall.

The Kokuriki mine, containing several ore deposits, is located at Hiyoshi, in the Tokoro district facing the Okhotsk Sea, about 20 km north of Kitami City (Fig. 1). Massive manganese iron ore with 33% Fe and 10% Mn on average was produced during the period 1930–1964, but the mine is not operating at present.

The ore specimens studied were collected from the mine dump. Okhotskite occurs in veinlets cutting hematite ore. Microscopic observation reveals that okhotskite forms aggregates of prisms of various size, up to 0.2 mm long (Fig. 2). Fibrous pumpellyite containing various amounts of Mn is also observed as aggregates coexisting with piemontite in quartz veinlets or pools. In addition neotocite, bementite and fluorapatite are observed, forming veinlets or pools. Hematite forms aggregates of very fine grained or dusty crystals, associated with very small amounts of Mn oxides. The hematite is very pure, containing a maximum of 0.38 wt. % Mn. In other ore specimens, inesite, baryte and rhodochrosite occur in the veinlets (Togari *et al.*, 1986).

Physical and optical properties

Okhotskite is deep orange in colour with a pale orange streak and shows a vitreous lustre. It is transparent and non-fluorescent. One set of cleavages is observed in thin section. The hardness of the aggregate is 6 on Mohs' scale. Although its density could not be measured because of the small grain size, the value calculated from the empirical formula is 3.40 g/cm³ (Mandarino, 1981).

The mineral is optically biaxial negative with $2V(\text{meas.}) 46(5)^\circ$ and $2V(\text{calc.}) 46^\circ$. Dispersion is indiscernible. Refractive indices measured by the immersion method are: $\alpha = 1.782(5)$, $\beta = 1.820(5)$ and $\gamma = 1.827(5)$ (589 nm). Orientation is $Y = b$ and $c \wedge Z = 9\text{--}14^\circ$ in the acute angle of β . It is strongly pleochroic with axial colours: X yellow, Y and Z deep orange. Absorption is $X < Y < Z$.

Chemical data

Chemical analysis was carried out with an Hitachi XMA-5A and a Jeol 50A electron microprobe, with correction by the method of Bence and Albee (1968) and Albee and Ray (1970), using the following standards: wollastonite (Ca, Si), synthetic spinel (Mg, Al), synthetic MnO (Mn), synthetic rutile (Ti), synthetic magnetite (Fe) and anorthoclase (Na, K). H₂O was determined by TG. Fe

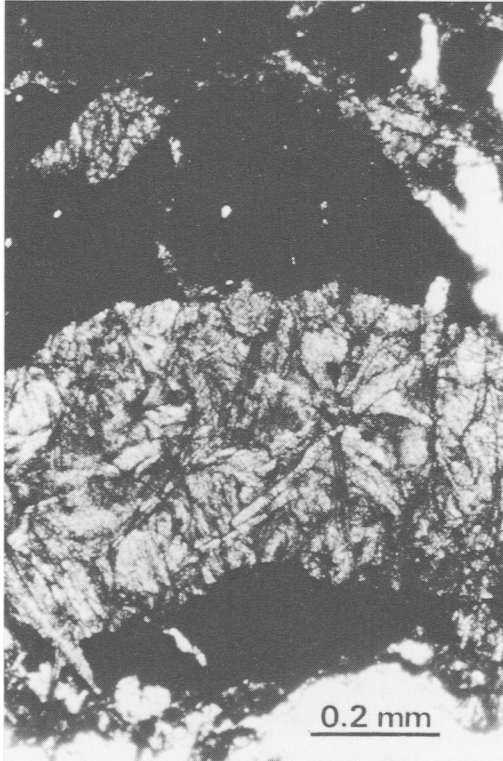


FIG. 2. Photomicrograph of okhotskite with hematite (black) and quartz (white).

was confirmed as trivalent by Mössbauer spectroscopy. The structural formula was calculated based on the rules set out by Passaglia and Gottardi (1973): Al, Ti and Fe^{3+} were placed in the Y-site; Mn^{3+} was added until the Y-site was fully occupied, and the remaining Mn was placed in the X-site as Mn^{2+} with Mg (Kato *et al.*, 1981).

The analytical results are: SiO_2 34.25, TiO_2 0.09, Al_2O_3 4.49, Fe_2O_3 6.03, Mn_2O_3 16.69, MnO 9.18, MgO 2.08, CaO 20.11, Na_2O 0.25, K_2O 0.03, H_2O 6.89, Total 100.09 wt %. The empirical formula calculated from the analysis on the basis of 56 oxygen ions is: $(\text{Ca}_{7.63}\text{Na}_{0.17}\text{K}_{0.01})_{\Sigma 7.81}(\text{Mn}_{2.75}\text{Mg}_{1.10})_{\Sigma 3.85}(\text{Mn}_{4.50}\text{Al}_{1.87}\text{Fe}_{1.61}\text{Ti}_{0.02})_{\Sigma 8.00}\text{Si}_{12.13}\text{O}_{39.71}(\text{OH})_{16.29}$. The simplified formula is: $\text{Ca}_8(\text{Mn}^{2+}, \text{Mg})_4(\text{Mn}^{3+}, \text{Al}, \text{Fe}^{3+})_8\text{Si}_{12}\text{O}_{56-n}(\text{OH})_n$ with $\text{Mn}^{3+} > (\text{Al} + \text{Fe}^{3+})$.

The described mineral may be specified as okhotskite-(Mn^{2+}) because of dominant Mn^{2+} in the X-site. It is noted that pumpellyite-(Mn^{2+}) from the Ochiai mine, Japan, contains moderate amounts of Mn^{3+} in the Y-site and that one spot analysis gave $\text{Mn}^{3+} > \text{Al}$ (Kato *et al.*, 1981).

Mössbauer spectroscopy

The Mössbauer spectrum was obtained using a 5 mCi ^{57}Co in Pd source at room temperature. Mössbauer data were accumulated in 512 channels of a multichannel analyser by using a constant acceleration spectrometer. The Doppler velocity was calibrated using a metal iron foil. The absorber consisted of 200 mg of finely ground powder, which was pressed on an Al-foil, 4 cm^2 in area. The sample also contained a moderate amount of piemontite, which could not be completely separated from the sample. The Lorentzian spectrum fit was obtained by a least-squares method with line widths and intensities constrained to be equal at each site. The LSF program of Shinno and Maeda (1981) was used for computer analysis and the quality of the fit was judged by χ^2 values.

The Mössbauer spectrum and hyperfine parameters are shown in Fig. 3 and Table 1 respectively.

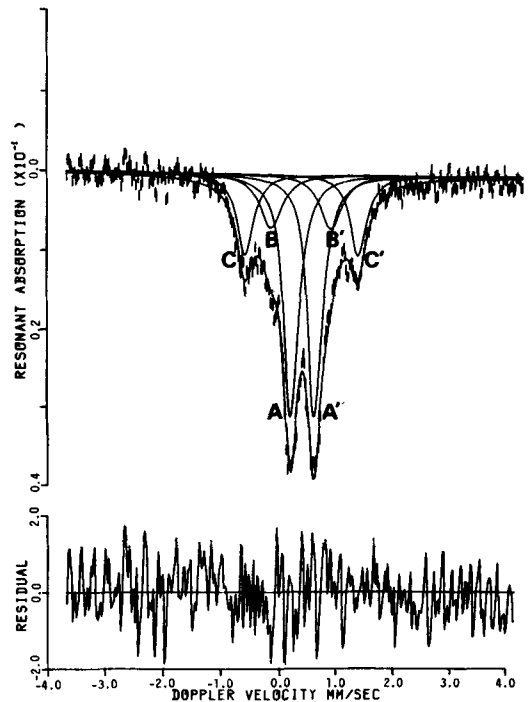


FIG. 3. ^{57}Fe Mössbauer spectrum of okhotskite at room temperature. Doublets AA' and BB' belong to Fe^{3+} in pumpellyite, and CC' to Fe^{3+} in piemontite.

vely. The spectrum consists of three doublets. One doublet is identified as belonging to Fe^{3+} in the M3-site of piemontite (Bancroft *et al.*, 1967;

Table 1. ⁵⁷Fe Mössbauer hyperfine data at room temperature and assignment

Doublet	IS	QS	FWHM	AR	Assignment
AA'	0.39	0.41	0.31	62	Fe ³⁺ in pumpellyite
BB'	0.34	1.04	0.35	15	Fe ³⁺ in pumpellyite
CC'	0.35	1.91	0.33	23	Fe ³⁺ in piemontite

* IS=isomer shift (mm/s). QS=quadrupole splitting (mm/s). FWHH=full width at half height (mm/s). AR=area ratio (%). Standard deviations of IS, QS and FWHH are ± 0.02 mm/s and those of AR ± 2 %.

Dollase, 1973), and the remaining two doublets are identified as belonging to Fe³⁺ in okhotskite. The method for assignment of two doublets to the X- and Y-sites has not been established as yet.

Crystallography

Single-crystal X-ray studies could not be carried out because of the small crystal size and their aggregated form. However, the X-ray powder diffraction pattern (Cu-K α radiation) was indexed by analogy with pumpellyite (Table 2), and gave the following unit-cell data; monoclinic *A2/m*, *a*

Table 2. X-ray powder diffraction pattern of okhotskite

I	d _{obs.}	d _{calc.}	hkl	I	d _{obs.}	d _{calc.}	hkl
60	4.76	{ 4.85 4.73 4.49 4.41	{ 004 111 104 200	30	2.096	{ 2.100 2.095 2.091 2.086	{ 320 402 322 217
30	4.43	{ 4.49 4.41	{ 104 200	20	1.915	{ 1.920 1.911	{ 404, $\bar{4}$ 15 033
15	3.96	4.04	104	10	1.906	{ 1.908 1.905	{ 413 226
70	3.87	3.83	202	20	1.873	1.885	028
15	3.84	3.81	113	45	1.815	{ 1.813 1.808	{ 317 128
25	3.43	3.44	211	10	1.724	{ 1.730 1.725 1.724	{ 233 406 135, $\bar{4}$ 24
20	3.093	3.078	204	25	1.669	1.676	228
15	3.025	3.000	020	30	1.636	1.638	331
100	2.961	{ 2.957 2.940	{ 115 300	20	1.627	{ 1.629 1.626 1.621	{ $\bar{3}$ 33 426 037
25	2.879	2.866	022	15	1.588	{ 1.587 1.585	{ $\bar{4}$ 19 319
70	2.720	2.722	302	20	1.561	1.561	335
45	2.665	{ 2.663 2.655	{ $\bar{3}$ 04 311	15	1.514	1.522	328
45	2.553	{ 2.551 2.544	{ 024 313	15	1.512	1.500	040
10	2.511	2.514	017	25	1.492	{ 1.495 1.487 1.482	{ 426 237 042
20	2.500	2.499	215				
10	2.491	{ 2.492 2.480	{ $\bar{1}$ 17 220				
45	2.384	2.386	304				
30	2.376	2.364	222				
30	2.214	{ 2.210 2.205	{ $\bar{4}$ 02 400				
40	2.197	2.198	026				
25	2.164	2.176	126				

= 8.887(5), *b* = 6.000(4), *c* = 19.53(2) Å, β = 97.08(6)°, *V* = 1033(3) Å³, *Z* = 1. The *a*:*b*:*c* ratio calculated from the unit-cell parameters is 1.4812:1:3.2550. With *c* < *a* it is 3.2550:1:1.4812.

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