41. *Jimboite, $Mn_3(BO_3)_2$, a New Mineral from the Kaso Mine, Tochigi Prefecture, Japan*

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(Comm. by Seitarô TSUBOI, M.J.A., March 12, 1963)

Introduction. In October, 1962, an unknown purple-brown mineral was found in manganese carbonate ores from the Kaso mine, Kanuma city, Tochigi prefecture. The chemical and X-ray studies reveal that it is a new manganese borate mineral, $Mn_3(BO_3)_2$, the manganese analogue of kotoite, $Mg_3(BO_3)_2$.

We propose the name jimboite for this new mineral, in honour of the late Professor Kotora Jimbo, the founder of the Mineralogical Institute, University of Tokyo.

This report presents the mode of occurrence, physical and chemical properties, and the results of the X-ray studies, together with the genetic considerations.

Occurrence. The Kaso mine is situated about 100 km north of Tokyo in the north-eastern part of the Ashio mountainland (Fig. 1). Here a thick accumulation of Carboniferous(?) to Permian geosynclinal sediments consists mainly of thin-bedded and massive cherts, slate, limestone, and basic igneous rocks. These rocks are more or less contact-metamorphosed near granitic intrusions of late Mesozoic age.[8]

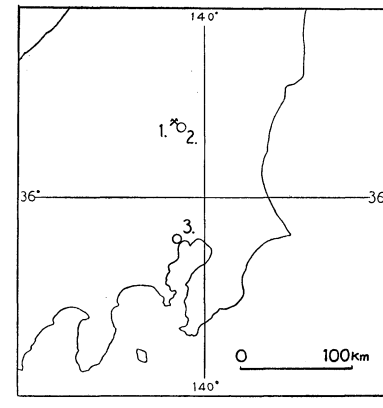

Fig. 1. Index map showing the location of the Kaso mine.
1. Kaso mine. 2. Kanuma. 3. Tokyo.

The manganese deposits of the Kaso mine are of bedded carbonate-silicate type and are closely associated with siliceous rocks of chert origin.[1),8),9)] Jimboite was found in the banded carbonate ores from the 18th level of the tabular orebody, which extends about 280 m vertically and 300 m horizontally with many pinch-and-swell structures. The orebody strikes northeasterly and dips 60–70° SE along the general trend of the country rocks. To the naked eye, the jimboite-bearing manganese-carbonate ore is brown to

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light grayish brown in colour, with fine bands of black jacobsite between aggregates of jimboite crystals (Fig. 2). In appearance, jimboite is difficult to distinguish from the other manganese minerals, but the development of cleavage is very diagnostic especially for larger grains, more than 5 mm in maximum length. Under the microscope, jimboite forms aggregate very often with individual anhedral crystals up to 5 mm in length. It also occurs in minute veinlets cutting the jacobsite and galaxite bands (Fig. 2). The other minerals in the assemblage are tephroite, alleghanyite series mineral, alabandite, pyrrhotite,

Fig. 2

Fig. 3

Figs. 2-3. Photomicrographs of jimboite from the Kaso mine, Tochigi prefecture.

2. Anhedral jimboite replacing fine aggregates of rhodochrosite and tephroite, and jimboite veinlets cutting jacobsite bands. ×23.

3. Coarse-grained jimboite containing abundant minute inclusions of tephroite, galaxite, etc. Note the traces of {101} parting of jimboite (center, in extinction). ×30.

galena, and chalcopyrite, and two undetermined minerals.

Physical Properties. Jimboite is light purplish brown with vitreous luster. It has perfect cleavage along {110}, and parting parallel to {101} as shown in Figs. 3 and 5. Twin plane and composition plane are {101}, and glide-twinning is sometimes observed in thin section and also in crushed or sliced crystals. The hardness is $5\frac{1}{2}$, and the specific gravity measured by pycnometer method is 3.98, close to the calculated value 4.00. Under the microscope, it is almost colourless. The {110} cleavage is developed in some grains in the marginal parts of the thin section. It is optically biaxial with $(+)2V=35°$ (on universal stage), $r>v$, and the refractive indices measured by immersion method are: $\alpha=1.792$, $\beta=1.794$, $\gamma=1.821$, $\gamma-\alpha=0.029$. Optical orientation is a$=X$, b$=Y$, c$=Z$, optical plane parallel to {010}. Fig. 5 is the photomicrograph of the thin section including a jimboite crystal sliced nearly perpendicular to c-axis. The mode of development of

cleavage is strikingly similar to that of kotoite with the same orientation (Fig. 4), suggesting the isomorphic relation between them.

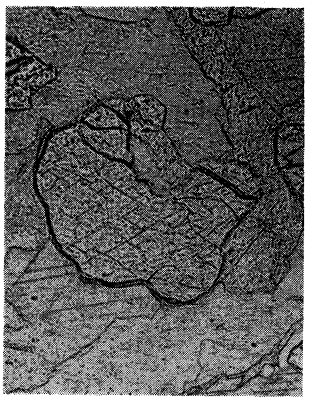

Fig. 4

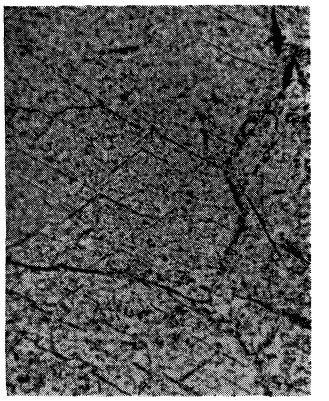

Fig. 5

Figs. 4–5. Photomicrographs of kotoite (left) and jimboite (right), cut perpendicular to c-axis.

4. A round grain of kotoite with distinct {110} cleavage surrounded by calcite grains. ×115.

5. A part of a jimboite grain showing the characteristic {110} cleavage. ×180.

Chemical Composition. The chemical analysis was done by the fourth author, on a small amount of hand-picked material including rhodochrosite, tephroite, and galaxite as impurities. The result is given in Table I, in which the method of recalculation to subtract the impurities is also shown. After this recalculation, the chemical composition of jimboite from the Kaso mine is $(Mn_{2.67}Mg_{0.23}Fe_{0.06})_{2.96}B_{2.02}O_{6.00}$ based on O=6 or $Mn_3(BO_3)_2$(jimboite end member) 90.0 mole %, $Mg_3(BO_3)_2$(kotoite end member) 7.8 mole %, and $Fe_3(BO_3)_2$ 2.2 mole %. Jimboite is soluble in HCl, H_2SO_4, and HNO_3.

X-Ray Studies. The X-ray studies include single-crystal and powder methods to obtain the crystal symmetry, space group, and cell constants. The single-crystal study carried out on a tiny cleavage piece using the Weissenberg goniometer showed the orthorhombic symmetry with possible space group D_{2h}^{12} or C_{2v}^{10}, and the former was preferred according to the absence of piezoelectric effect. The powder data are well coincident with those tabulated in A.S.T.M. Card No. 3–0759 as shown in Table II, in which the powder data for synthetic $Mn_3(BO_3)_2$ obtained by the authors are also compared. The unindexed diffraction in the standard material may be due to admixed MnO, the strongest diffraction of which is d=2.22Å.[4] The cell constants of jimboite, calculated from the powder data using quartz as the internal standard, coincide well with those measured by single-crystal study. Based on the cell constants, the specific gravity is calculated as 4.00

taking Z=2.

From the results of the chemical and X-ray studies, there is no doubt that this mineral is the manganese analogue of magnesium

Table I. Chemical analysis of jimboite (Analyst: J. Ito)

	Wt. %	Mol. quotient	less carbonate	less tephroite	less galaxite	No. of oxygen	No. of metal	No. of oxygen (O=6)	No. of metal (O=6)
B_2O_3	18.6	0.267				0.801	0.534	3.034	2.022
CO_2	6.1	0.139	−0.139						
SiO_2	3.3	0.055		−0.055					
MnO	65.3	0.921	−0.116	−0.099	−0.001	0.705	0.705	2.671	2.671
MgO	3.3	0.082	−0.012	−0.009		0.061	0.061	0.231	0.231
FeO	1.6	0.021	−0.002	−0.002		0.017	0.017	0.064	0.064
CaO	0.5	0.009	−0.009						
Al_2O_3	0.1	0.001			−0.001				
H_2O	0.1								
Insol	1.4								
	100.3								

Chemical composition: $(Mn_{2.67}Mg_{0.23}Fe_{0.06})_{2.96}B_{2.02}O_{6.00}$ as O=6

Molecular ratio:
$Mn_3(BO_3)_2$ (jimboite end member) 90.0 mole %
$Mg_3(BO_3)_2$ (kotoite end member) 7.8 mole %
$Fe_3(BO_3)_2$ 2.2 mole %

Table II. X-Ray powder data for synthetic $Mn_3(BO_3)_2$ and jimboite

1.		2.		3.				hkl
d(Å)	I	d(Å)	I	d(Å)	I	Q obs	Q cal	
4.10	31	4.11	40	4.09	70	0.060	0.060	011
3.59	20	3.62	40	3.59	60	0.078	0.078	101
2.77	100	2.79	100	2.77	90	0.130	0.130	121
2.57	75	2.61	30	2.59	50	0.149	0.150	130
		2.47	10b	2.47	10	0.165	0.165	031
				2.42	10	0.172	0.172	201
		2.39	10b	2.37	30	0.178	0.178	220
2.33	62	2.33	50	2.33	100	0.185	0.185	211
							0.186	002
2.26	17	2.26	10	2.26	30	0.196	0.196	131
2.22	75							
1.85	7							310
1.80	37	1.801	60	1.791	50	0.3117	0.3117	202
1.73	50	1.732	50	1.725	30	0.3359	0.3359	132
1.63	22	1.627	20	1.616	20	0.3825	0.3821	321
1.57	50	1.586	30	1.580	70	0.4007	0.4014	330
1.53	5							013
1.45	17							060
1.41	31	1.418	30	1.410	20	0.5029	0.5029	400
		a_0=5.672Å		a_0=5.640Å (calc. from (400))				
		b_0=8.744Å		b_0=8.715Å (calc. from (400), (132), (321), and (330))				
		c_0=4.661Å		c_0=4.637Å (calc. from (400) and (202))				

1. $Mn_3(BO_3)_2$, synthesized. A.S.T.M. Card No. 3-0759. Mo/ZrO_2 radiation.
2. $Mn_3(BO_3)_2$, synthesized by heating of $3MnCO_3+B_2O_3$ (with KHF_2) at about 700°C for 30 minutes. Fe radiation. b=broad.
3. Jimboite, the Kaso mine, Kanuma city, Tochigi prefecture. Fe radiation.

orthoborate kotoite, first described by the first author in 1939.[5]

Related Minerals. As already stated, chemical, X-ray, and some physical properties indicate that this mineral is the manganese analogue of kotoite, $Mg_3(BO_3)_2$. In Table III, the comparison with the cell constants, axial ratios, and optical properties including some old measurements are made.

Table III. Cell constants, axial ratios, and optical properties of synthetic $Mg_3(BO_3)_2$, kotoite, synthetic $Mn_3(BO_3)_2$, and jimboite

Materials	a_0(Å) b_0(Å) c_0(Å) a_0 : b_0 : c_0	α β γ $\gamma-\alpha$ (+)$2V$ Disp.	Authors
$Mg_3(BO_3)_2$ synthesized	5.398 8.420 4.505 0.6411: 1 :0.5350	1.6514 1.6521 1.6725 0.0211 22° $r>v$	Watanabe (1939)[5] Watanabe *et al.* (1963)[7]
$Mg_3(BO_3)_2$ synthesized	a : b : c= 0.6412: 1 :0.5494	1.6527 1.6537 1.6748 0.0221 24½° $r>v$	Mallard (1887)[2]
Kotoite The Hol Kol mine	5.398 8.426 4.510 0.6408: 1 :0.5353	1.652 1.653 1.673 0.021 21° $r>v$	Watanabe (1939)[5] Watanabe *et al.* (1963)[7]
Kotoite The Neichi mine	5.401 8.428 4.510 0.6408: 1 :0.5351	1.652 1.653 1.674 0.022 20° $r>v$	Watanabe *et al.* (1963)[7]
$Mn_3(BO_3)_2$ synthesized	5.672 8.744 4.661 0.6487: 1 :0.5331		This study
$Mn_3(BO_3)_2$ synthesized	a : b : c= 0.6511: 1 :0.5351		Mallard (1887)[2]
Jimboite The Kaso mine	5.640 8.715 4.637 0.6490: 1 :0.5327	1.792 1.794 1.821 0.029 35° $r>v$	This study

Synthesis. In order to confirm the supposed genesis of this mineral given in the succeeding article, the following procedure was taken to synthesize $Mn_3(BO_3)_2$. A mixture of $MnCO_3$ and B_2O_3 of mole ratio 3:1 with small amounts of KHF_2 as flux material was heated in air at about 700°C for 30 minutes using graphite powder as insulator to prevent the manganese from oxidation, and the product was examined by X-ray powder method. Though some subsidiary diffractions are present, most of them correspond to those of synthetic $Mn_3(BO_3)_2$ in A.S.T.M. Card No. 3-0759 (except the d=2.22Å diffraction) and of jimboite taken under the same recording condition of the X-ray diffractometer as given in Table II. The cell constants calculated in the same way as jimboite are: a_0=5.672Å, b_0=8.744Å, c_0=4.661Å.

Genesis. Comprehensive studies on manganese minerals from the Kaso mine was carried out by T. Yoshimura in 1938.[9] More than seventy species of various kinds of minerals including several new ones such as kasoite, were described in detail in his report. However, no borate was found at that time. Judging from the complexities of the mineral paragenesis, the genesis of the Kaso manganese deposits may not be

simple. It is the first author's opinion that the manganese carbonate ores were syngenetically formed with cherty rocks by submarine exhalative processes in the late Paleozoic geosynclinal zone. The manganese ores and associated sedimentary rocks were thermally metamorphosed by granitic intrusion of Cretaceous age. In connection with the pneumatolytic to hydrothermal activities of the granitic magma, a manganese borate such as jimboite was formed in manganese carbonate ores by a boron metasomatism as shown in the following reaction:

$$\underset{\text{Rhodochrosite}}{3MnCO_3} + B_2O_3 = \underset{\text{Jimboite}}{Mn_3(BO_3)_2} + 3CO_2$$

This is a kind of exchange reaction of boric acid with carbon dioxide and resembles the reaction of kotoitization in dolomite, or formation of kotoite-marble.[5),6),7)]

Acknowledgements. The authors wish to express their sincere thanks to Emeritus Professor S. Tsuboi, Professor R. Sadanaga, and Assistant Professor Y. Takeuchi of University of Tokyo for their kind suggestions and aids during the course of the present study. Further acknowledgements are also made to Dr. K. Sakurai of National Museum, and Mr. M. Imai and Mr. B. Gokan of Imai Mining Company for their kindness in collecting mineral specimens during field works at the Kaso mine. The authors are also indebted to Professor W. F. Jenks for his kind reading of the manuscript.

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