

Jōkokuite, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, a new mineral from the Jōkoku Mine, Hokkaido, Japan

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ABSTRACT

Jōkokuite, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, is a new hydrous manganese sulfate discovered at the drift wall of the 50 m level of the Jōkoku manganese-lead-zinc mine, southwestern Hokkaido. It occurs as post-mine stalactites up to about 5 cm long and 1 cm across, apparently precipitated secondarily from mine waters carrying components from manganese carbonates consisting mainly of rhodochrosite and manganoan calcite.

X-ray powder diffraction pattern shows that it is triclinic with $a=6.37\text{Å}$, $b=10.77\text{Å}$, $c=6.13\text{Å}$, $\alpha=98^\circ 46'$, $\beta=109^\circ 58'$, $\gamma=77^\circ 50'$, $Z=2$, and space group $P\bar{1}$ seems probable from the analogy with chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Wet chemical analysis gives the formula of $(\text{Mn}_{0.98}\text{Fe}_{0.04}\text{Zn}_{0.08})_{1.00}\text{S}_{1.00}\text{O}_{4.00} \cdot 5.07\text{H}_2\text{O}$, or ideally $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. Therefore, this is the manganese analogue of chalcantite, pentahydrate and siderite.

The mineral is pale pink with vitreous luster, and transparent to translucent. Streak is white. No discernible cleavage. Mohs hardness of aggregates is about 2.5. Specific gravity is 2.03 (meas.) and 2.094 (calc.). It is biaxial and optically negative, $2V$ about $70-80^\circ$, dispersion very weak. The indices of refraction are $\alpha=1.498$, $\beta=1.510$, $\gamma=1.517$, all ± 0.003 .

Introduction

In the course of investigation on the sulfate minerals from Jōkoku manganese-lead-zinc mine, southwestern Hokkaido, the pale pink colored stalactitic materials was collected in June 1976 by one of us (E. K.) from the drift wall of 50 m level of the No. 1 vein (1 Gō-Hi). Subsequent laboratory investigations showed the mineral to be the first natural occurrence of manganese sulfate pentahydrate, which has been expected to occur in nature for a long time (Palache *et al.*, 1951).

Synthetic manganese sulfate pentahydrate was studied by Regnault (1841), Cottrell (1900), Larsen and Glenn (1920), Taylor (1952) and other investigators (Mellor, 1932), but the mineralogical data are very scanty except its optical properties.

In this paper, the chemical, physical and optical properties of the mineral are presented together with the X-ray powder data.

The name is for the locality, Jōkoku Mine. Type material is preserved at Tohoku University. Both species and name have been approved before publication by the Commission on New Minerals and Mineral Names, IMA.

Occurrence

The Jōkoku Mine (lat. $41^\circ 42'N$.; long. $140^\circ 06'E$.), one of the most famous manganese mine in Japan, is located at Kaminokuni-machi, Hiyama District about 60 km south-west of Hakodate City, Hokkaido (Fig. 1).

The ore deposits are of about ten epithermal veins cutting Paleozoic formation consisting mainly of slate with some intercalations of chert, sandstone and limestone and Miocene volcanic rocks. Champion vein (Hon-Pi) occurs in a wide shear zone along the boundaries between Paleozoic slate and Tertiary andesitic breccia (Miura and Ohmura, 1961; Nishino, 1966; Ohta, Honda and Nishiyama, 1972).

The ore minerals are composed mainly of rhodochrosite associated

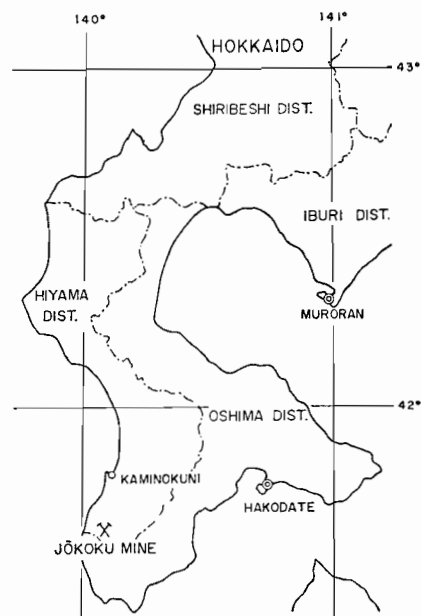


Fig. 1. Map showing the location of the Jôkoku Mine, Hokkaido, Japan.

with subordinate amounts of sphalerite, galena, pyrite, marcasite and some minor minerals. Gangue minerals are dolomite, ankerite, kutnahorite, quartz and small amounts of clay minerals such as chlorite, sericite and halloysite (Nambu and Kitamura, 1974).

In this mine, twelve species of hydrous sulfates occur as efflorescence on the drift walls, and are formed by precipitation from mine waters that have been in contact with oxidizing manganese ores. They are szmikite, gypsum, ilesite, rozenite, jôkokuite, siderotil hexahydrate, ferrohexahydrate, mallardite, melanterite, epsomite and goslarite (Nambu and Tanida, 1976).

Jôkokuite occurs as stalactites up to about 5 cm long and 1 cm across on the drift wall of 50 m level of No. 1 vein (Fig. 2). The

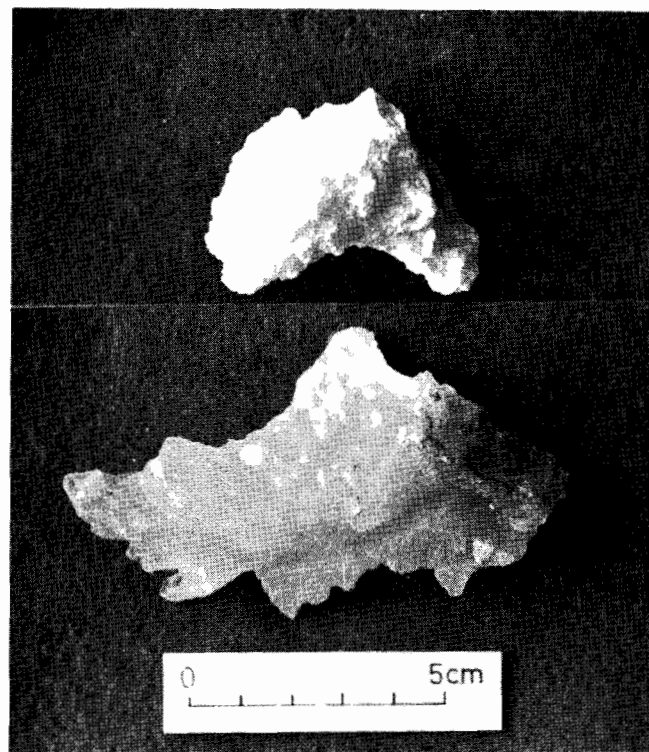


Fig. 2. Photographs of the stalactitic jôkokuites from the Jôkoku Mine. Upper, jôkokuite coated with a white powder of tetrahydrate (ilesite). Lower, fresh jôkokuite.

stalactites are composed of irregular and fine-grained crystals with mozaic texture and individual grains are less than 0.05 mm across.

Physical and optical properties

The stalactites of jôkokuite is pale pink in color with vitreous luster and transparent to translucent. Streak is white. It exhibits no discernible cleavage. Hardness of aggregates is about 2.5 (Mohs). The specific gravity measured by the Berman density balance is 2.03,

while the calculated value is 2.094.

The mineral is perfectly colorless in thin section. It is biaxial and optically negative with $2V=70-80^\circ$. Dispersion is very weak. The indices of refraction measured by immersion method using Na light at 20°C are $\alpha=1.498$, $\beta=1.510$, $\gamma=1.517$, all ± 0.003 .

These properties are compared with those of synthetic $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (Larsen and Glenn, 1920), synthetic $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Larsen and Glenn, 1920), synthetic $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ (Winchell and Winchell, 1951) and cuprian siderotil ($(\text{Fe}, \text{Cu})\text{SO}_4 \cdot 5\text{H}_2\text{O}$; Jambor and Trail, 1963) in Table 1.

Table 1. Optical properties of jōkokuite, chalcantite, pentahydrate and cuprian siderotil.

	1	2	3	4	5
α	1.498	1.495	1.516	1.428	1.515
β	1.510	1.508	1.539	1.492	1.525
γ	1.517	1.514	1.546	1.493	1.535
$\gamma-\alpha$	0.019	0.019	0.030	0.011	0.020
$2V$	$70-80^\circ$	rather large	56°	15°	$50-60^\circ$
Sign	negative	negative	negative	negative	negative
Dispersion	very weak		slight	$r < v$	

- 1: Jōkokuite, Jōkoku Mine, Hokkaido, Japan. Present study.
- 2: Jōkokuite (synthetic, Larsen and Glenn, 1920).
- 3: Chalcantite (synthetic, Larsen and Glenn, 1920).
- 4: Pentahydrate (synthetic, Winchell and Winchell, 1951).
- 5: Cuprian siderotil, Yerington, Nevada (Jambor and Trail, 1963).

Chemical composition

About 500 mg of very pale pink material purified by hand-picking was carefully analyzed by the normal wet methods, except for MnO determined by volumetric method (Nagashima, Codell and Fujiwara, 1964), ZnO by atomic absorption spectrometry, and H_2O by Penfield method. The results are shown in Table 2.

The empirical formula for the material calculated on the basis of 4 oxygen in anhydrous part is $(\text{Mn}_{0.93}\text{Fe}_{0.01}\text{Zn}_{0.03})_{1.00}\text{S}_{1.00}\text{O}_{4.00} \cdot 5.07\text{H}_2\text{O}$,

Table 2. Chemical analysis of jōkokuite from the Jōkoku Mine.

	Theoretical $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	Weight percentage	Molecular number	Atomic ratio based on O=4 in the anhydrous part	
MnO	29.42	27.34	0.3854	Mn	0.943
FeO		1.13	0.0157	Fe	0.038
ZnO		0.94	0.0116	Zn	0.028
MgO		0.00		S	1.000
CaO		0.00		O	4.000
SO_3	33.21	33.06	0.4129	H_2O	5.07
H_2O	37.37	37.68	2.0933		
Total	100.00	100.15			

which is very close to the ideal formula of $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$.

The mineral is easily soluble in water, and is commonly coated with a powder film of tetrahydrate (ilesite) formed by the dehydration on exposure in relatively dry air.

X-ray powder study

Because of the lack of appropriate single crystal, X-ray powder study on a part of purified material was made by the diffractometer method employing Mn-filtered Fe-radiation. The comparison of d -spacings and intensity ratios between jōkokuite and chalcantite (JCPDS Card No. 11-646) or siderotil (JCPDS Card No. 22-357) shows a close agreement. Therefore, it is considered that these three minerals are isostructural.

The X-ray powder diffraction pattern is satisfactorily indexed on a triclinic cell with $a=6.37\text{Å}$, $b=10.77\text{Å}$, $c=6.13\text{Å}$, $\alpha=98^\circ 46'$, $\beta=109^\circ 58'$, $\gamma=77^\circ 50'$, $Z=2$ in terms of the analogy with chalcantite and siderotil. Possible space group is $P1$ or $P\bar{1}$, the latter seems probable from the analogy with the two minerals mentioned above. The indexed powder

Table 3. X-ray powder data of jōkokuite from the Jōkoku Mine.

<i>hkl</i>	<i>d</i> calc.*	<i>d</i> obs.**	<i>I</i> / <i>I</i> ₁ **
010	10.38	10.4	4
100	5.836	5.84	100
110	5.651	5.66	56
020	5.189	5.19	13
111	4.977	4.98	61
011	4.881	4.88	18
110	4.664	4.67	8
120	4.392	4.39	23
111	4.090	4.09	11
021	3.994	3.99	19
021	3.722	3.72	22
101	3.568	3.57	4
120	3.510	3.51	7
030	3.460	3.46	3
130	3.316	3.32	8
111	3.283	3.28	25
121	3.205	3.21	6
121	3.075	3.076	16
201	3.015	3.015	3
221	2.974	2.975	17
200	2.918	2.916	18
012	2.819	2.821	19
112	2.729	2.727	72
130	2.723		
131	2.606	2.607	8
140	2.594	2.593	9
230	2.523	2.523	11
222	2.488	2.487	4
022	2.440	2.440	13
122	2.396	2.395	8
201	2.322	2.322	8
041	2.304	2.303	11
232	2.303		
032	2.291	2.290	27
240, 141	2.196	2.196	11
242	2.067	2.607	17
221	2.011	2.009	11
331	2.007		
310	1.994	1.994	8
312	1.981	1.981	11
320	1.971	1.969	20
332	1.905	1.904	16
013	1.859	1.858	9
023	1.839	1.838	8
312	1.801	1.799	9
142	1.797		
222	1.737	1.736	8
313, 142	1.697	1.696	20
321	1.693	1.692	13
311	1.622	1.622	31

* Calculated on the basis of a 6.37 Å, b 10.77 Å, c 6.13 Å, α 98°46', β 109°58', γ 77°50'.

** Pattern made at 20°C. Fe/Mn radiation.

Table 4. Unit cell parameters of jōkokuite, chalcantite, pentahydrate and cuprian siderotil.

	1	2	3	4
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.37	6.104	6.335	6.25
b (Å)	10.77	10.72	10.55	10.63
c (Å)	6.13	5.949	6.075	6.06
α	98°46'	97°34'	99°10'	97°15'
β	109°58'	107°17'	109°53'	109°40'
γ	77°50'	77°26'	75°00'	75°00'
V (Å ³)	384.9	361.85	367.67	365.9
$a:b:c$	0.591:1:0.569	0.569:1:0.555	0.600:1:0.576	0.588:1:0.570
Z	2	2	2	2
G calc.	2.094	2.282		2.17

1: Jōkokuite, Jōkoku Mine, Hokkaido, Japan. Present study.

2: Chalcantite (synthetic, Fisher, 1952).

3: Pentahydrate (synthetic, Hodenberg and Kühn, 1967).

4: Cuprian siderotil, Yerington, Nevada (JCPDS Card No. 22-357).

pattern is presented in Table 3, in which the calculated d -spacings are in good agreement with the measured values. In Table 4, crystallographic data of jōkokuite are compared with those of chalcantite, pentahydrate and siderotil.

Thermal analysis

DTA and TG of jōkokuite were carried out simultaneously in air by means of a Thermoflex unit made by Rigaku-Denki Co., Japan, using about 500 mg of hand-picked material. Heating rate was 10°C per minute.

The DTA and TG curves of jōkokuite are shown in Fig. 3. The DTA curve is characterized by the three distinctive endothermic peaks at 140°C, 328°C and 1,032°C, accompanying with the three weak but sharp endothermic peaks at 60°C, 83°C and 890°C. The TG curve shows three steps of weight loss, namely between room temperature

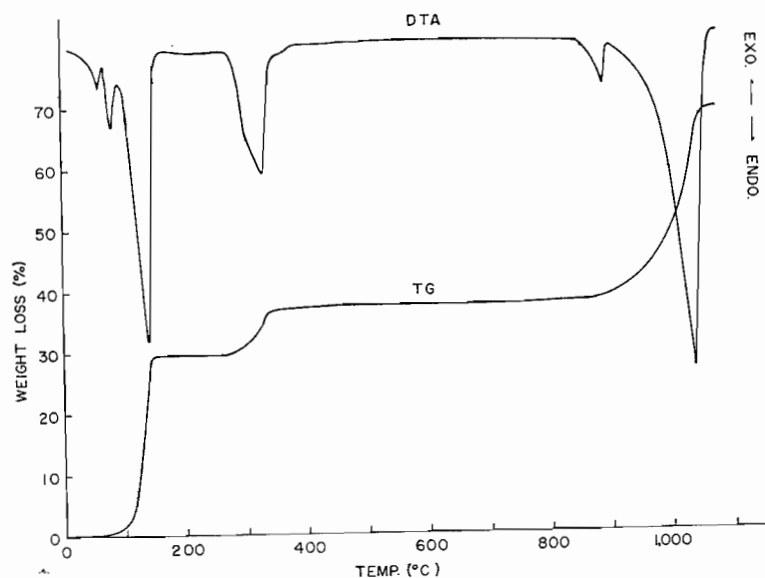


Fig. 3. DTA and TG curves of jôkokuite from the Jôkoku Mine.

and 160°C, between 270°C and 380°C, and between 800°C and 1,075°C, corresponding to the three distinctive endothermic peaks observed in the DTA curve.

The first and second steps of weight loss are due to the formation of manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and anhydrous phase (MnSO_4) by the dehydration of combined water, respectively. The third step is closely related to the expulsion of SO_3 , and the final product after heated to 1,080°C consists mainly of hausmannite. These phenomena were confirmed by the X-ray powder method and chemical analysis for heated materials at various temperatures.

Stability of jôkokuite

According to the observation of occurrence and measurements of temperature and humidity in the adit in which jôkokuite was found,

the mineral has apparently been precipitated from ground water at about 15°C and 98% or more humidity.

At this mine, the manganese sulfate heptahydrate, mallardite, too, occurs as aggregates of fine fibrous crystallite on the drift wall. However, the stalactitic form of jôkokuite suggests that it could not be formed by the dehydration of mallardite, but must have been precipitated immediately from cold solution.

On exposure to normal atmospheric condition (for example 20°C and 50% humidity) after standing for about a month, the stalactite of jôkokuite will dehydrate to tetrahydrate, ilesite, which can be ascertained by the X-ray powder method and chemical analysis.

On the other hand, Cottrell (1900) found that the four hydrates—mono-, tetra-, penta-, and heptahydrates—can exist in aqueous solution, and that the transition temperatures of $\text{MnSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{MnSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{MnSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$ are nearly 9°C and 27°C, respectively. Larsen and Glenn (1920) obtained the pentahydrate by evaporating an aqueous solution under reduced pressure at 23°C, and they showed that the pentahydrate altered slowly on standing in air to tetrahydrate. Recently Taylor (1952) found that the pentahydrate does not exist in contact with saturated solutions above 24.5°C from the study of the system $\text{MnSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$.

The results of synthetic studies, the dehydration experiments and the field evidence mentioned above indicate that the jôkokuite stalactite crystallized from mine water at temperature between about 25°C and several degrees, and the adit in which jôkokuite was found had been kept at the temperature and humidity favourable to the existence of the jôkokuite stalactite.

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REFERENCES

- COTTRELL, F.G. (1900) *Journ. Phys. Chem.*, **4**, 637-656.
 FISHER, D.J. (1952) *Amer. Miner.*, **37**, 95-114.
 HODENBERG, R. VON & KÜHN, R. (1967) *Kali und Steinsalz*, 326-327.
 JAMBOR, J.L. & TRAIL, R.J. (1963) *Can. Miner.*, **7**, 751-763.
 JCPDS Card No. 22-357.
 LARSEN, E.S. & GLENN, M.L. (1920) *Amer. Journ. Sci.*, **50**, 225-233.
 MELLOR, J.W. (1932) *A comprehensive treatise inorganic and theoretical chemistry*, **12**, 401-427.
 MIURA, H. & OHMURA, H. (1961) *Mining Geol. (Japan)*, **11**, 53-57 (in Japanese with English abstract).
 NAGASHIMA, K., CODELL, M. & FUJIWARA, S. (1964) *Bull. Chem. Soc. Japan*, **37**, 780-782.
 NAMBU, M. & KITAMURA, T. (1974) *Chigaku-Kenkyu*, **25**, 102-110 (in Japanese).
 NAMBU, M. & TANIDA, K. (1976) *Chigaku-Kenkyu*, **27**, 233-240 (in Japanese).
 NISHINO, J. (1966) *Mining Geol. (Japan)*, **16**, 132-142 (in Japanese with English abstract).
 OHTA, S., HONDA, T. & NISHIYAMA, Y. (1972) *Note of technical session on autumn meeting MMIJ*, F-1, 1-3 (in Japanese).
 PALACHE, C., BERMAN, H. & FRONDEL, C. (1951) *Dana's the system of mineralogy, Part II*, 487-493, John Wiley & Sons, New York.
 REGNAULT, H.V. (1841) *Ann. Chim. Phys.*, **1**, 129-207.
 TAYLOR, D. (1952) *Journ. Chem. Soc. London*, 2370-2375.
 WINCHELL, A.N. & WINCHELL, H. (1951) *Elements of optical mineralogy, Part II*, 160-162, John Wiley & Sons, New York.

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Short Communication

Inclusion dating and phase differentiation in minerals. H.S. VIRK and SURINDER SINGH, *Department of Physics, Punjabi University, Patiala-147002, India.*

Fission track technique developed by Fleischer, Price and Walker (1975) has been used for dating of minerals and estimation of their uranium contents. The technique is being exploited by the authors for mineral phase differentiation and dating of uraninite inclusions in mica pegmatites of Rajasthan state (India).

The experimental details for preparation of pegmatite samples and their fission track ages have been reported in an earlier communication to Mineralogical Journal (Virk and Singh Surinder, 1977). It is observed on careful microscope scanning that mica matrix is impregnated with a number of uranium bearing inclusions. On further etching of samples with 48 per cent HF acid the number of fossil fission tracks revealed in these inclusions is found to be a few hundred thousand times more than the corresponding number in inclusion free areas of the mica matrix. This situation is clearly demonstrated in the microphotographs (Virk and Singh Surinder, 1977).

For dating the inclusions, mica samples are irradiated in the CIRUS Reactor, Trombay, Bombay with a total thermal neutron dose of 10^{16} (nvt). The induced fission tracks in the inclusion free area are counted in the mica matrix itself. But due to large density of induced fission tracks arising from uraninite inclusions, it is preferred to use an external detector for their counting. Lexan polycarbonate and cellulose nitrate are considered most suitable for their detection efficiency and low uranium contents.

The fission track age of three uranium bearing inclusions has been