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MALLARDITE FROM THE JÔKOKU MINE, HOKKAIDO, JAPAN

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Mallardite, $MnSO_4 \cdot 7H_2O$, reported only from its original locality, the Lucky Boy mine, Utah (Carnot, 1879), was found from the Jôkoku mine, Hokkaido, Japan. The mineral occurs as efflorescences which are composed of aggregates of minute fibers or prismatic crystals on the walls of mine passages.

X-ray powder diffraction pattern shows that it is monoclinic with $a_0 = 14.15$, $b_0 = 6.50$, $c_0 = 11.06$Å, $\beta = 105°36'$, $Z = 4$ and space group $P2_1/c$ seems probable from the analogy with melanterite and bieberite. Wet chemical analysis leads to an emperical formula of $(Mn_{0.90}, Mg_{0.11})_{1.01}S_{1.00}O_{4.00} \cdot 6.8H_2O$, showing the material to be very close to the ideal formula $MnSO_4 \cdot 7H_2O$.

The mineral is colorless with vitreous luster, and transparent to translucent. Powdered material is white in color. It is readily soluble in cold water. Specific gravity is 1.838 (calc.). Optically biaxial possitive with large optic axial angle. Extinction angle is $Z \wedge c = 44°$. Refractive indices measured by the immersion method are $\alpha = 1.462$, $\beta = 1.465$, $\gamma = 1.474$, and $\gamma - \alpha = 0.012$, all ± 0.003.

Studies on the stability relation among synthetic manganese sulfate hydrates (Cottrell, 1900) and the field evidence in adits where the material was collected indicate that mallardite is formed at temperatures below about 10°C and under high relative humidity.

INTRODUCTION

Mallardite was originally described by Carnot (1879) from the Lucky Boy mine, Utah which is the only one definite locality of the mineral. Its identification is based only on chemical analysis and optical properties which are lacking in refractive indices, so that mineralogical data of this mineral are very scanty. Moreover, a cuprian and zincian variety is said to occur in the Bayard area of the Central District, Grand County, New Mexico (Palache, Berman and Frondel, 1951), but no reliable data of these minerals are known.

This very rare mineral was found by one of the authors (E.K.) in adits of 80 meter level of the Jôkoku mine in February, 1977. In this paper, the mode of occurrence and mineralogical properties of mallardite from the mine are presented together with brief discussion on its stability and genesis.

OCCURRENCE

The Jôkoku mine, the largest producer of manganese in Japan, is located at

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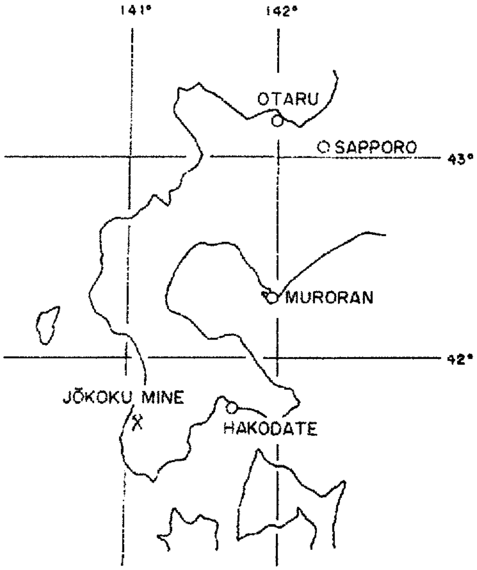

Fig. 1 Map showing the location of Jôkoku mine, Hokkaido, Japan.

Kaminokuni-machi, Hiyama District about 60 km southwest of Hakodate, Hokkaido (Fig. 1.). The ore deposits are composed of about ten epithermal fissure-filling manganese-zinc-lead veins cutting Paleozoic slate and Miocene volcanic rocks (Miura and Ômura, 1961; Nishio, 1966). But, recently pyrometasomatic manganese-zinc-lead deposits have been proved to occur in the paleozoic limy rocks, being developed around the lower part of veins (Ohta, Honda and Nishiyama, 1971).

The ore minerals are composed mainly of rhodochrosite associated with subordinate amounts of sphalerite, galena and pyrite, and with many kinds of minor minerals. Gangue minerals include quartz, dolomite, ankerite, kutnahorite, manganoan calcite and a small quantity of clay minerals such as chlorite, sericite and kaolin minerals (Nambu and Kitamura, 1974). These are altered in the zones of oxidation to limonite consisting of goethite and lepidochrosite, and to various manganese dioxide minerals such as nsutite, cryptomelane, pyrolusite, lithiophorite, manganite and wad. In adition, plumbogummite occurs rarely in the aggregates of goethite and quartz.

Mallardite was found in adits of the 80 meter level of the Jôkoku mine. Localities are shown in Fig. 2. The mineral occurs mainly as delicate fibrous efflorescences and occasionally crusts on the adit wall. It appears directly on the surface of rhodochrosite and other manganese-bearing minerals such as manganoan calcite and

Fig. 2 Locality map of mallardite at the 80 m level of Jôkoku mine. Sample from No. 1 was used for the present study. Uwaban and Shitaban mean a hanging wall and a foot wall, respectively. ○:Locality

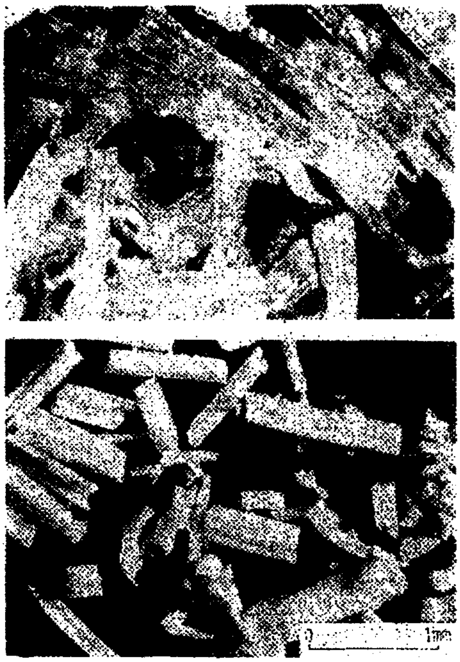

Fig. 3 Photographs of fresh mallardite (upper) and jôkokuite pseudomorph (lower) derived from the dehydration of mallardite on exposure to dry air at ordinary room temperature.

kutnahorite, and occasionally as pore or fracture-filling in mother rocks.

Under the microscope, they consist of aggregate of hair-like, needle-like and long columnar crystals, generally between about 0.5 and 12 mm in length, and between 0.2 and 1 mm across (Fig. 3).

Mallardite is ordinarily not associated with other sulfate minerals, but rarely admixed with jôkokuite ($MnSO_4 \cdot 5H_2O$) and/or ilesite ($MnSO_4 \cdot 4H_2O$).

The material from the location No. 1 in Fig. 2 was used for the present study.

PHYSICAL AND OPTICAL PROPERTIES

The needles of mallardite are colorless with vitreous luster and transparent to translucent. The powdered material is white in color. It is too fine to measure the hardness and the specific gravity. The calculated specific gravity is 1.838, which is slightly lower than the measured value 1.846 for artificial $MnSO_4 \cdot 7H_2O$ (Günther, 1912).

A distinct cleavage is observed on (001) under the petrographic microscope. It is biaxial positive with a large optic angle, extinction angle is $z \wedge c = 44°$, and refractive indices measured by the immersion method using Na light at 12°C are $\alpha = 1.462$, $\beta = 1.465$, $\gamma = 1.474$, (all ± 0.003) and $\gamma - \alpha = 0.012$. These values are somewhat lower than those of other members of the melanterite group. Optical properties of mallardite are compared with those of melanterite and bieberite in Table 1.

Table 1 Optical properties of mallardite, melanterite and bieberite.

	1	2	3
Color	colorless	pale green	carmine
Opt. sign	+	+	−
2V	large	86°	near 90°
Dispersion	slight	r>v, weak, inclined	slight
α	1.462	1.471	1.477
β	1.465	1.478	1.483
γ	1.474	1.486	1.489
$\gamma-\alpha$	0.012	0.015	0.012

1: Mallardite, Jôkoku mine, Hokkaido, Japan. Present study.
2: Melanterite (Synthetic, Larsen and Glenn, 1920).
3: Bieberite (Synthetic, Larsen and Glenn, 1920).

CHEMICAL COMPOSITION

Chemical analysis was made by the normal wet method on the handpicked pure materials after the confirmation of their purity through the x-ray powder method.

The results are compared with those of mallardite from Lucky Boy mine, Utah (Carnot, 1879) and theoretical value of $MnSO_4 \cdot 7H_2O$ in Table 2. The material from Jôkoku mine contains 1.59% of MgO which substitutes for MnO.

The empirical formula for the Jôkoku material calculated on the basis of O=4 in the anhydrous part is

Table 2 Chemical analysis of mallardites from Jôkoku mine, Hokkaido and Lucky Boy mine, Utah.

	1	2	3
MnO	23.56	23.6	25.60
FeO	0.00		
ZnO	0.00		
MgO	1.57	0.6	
CaO	0.00	0.7	
SO_3	29.09	29.8	28.89
H_2O	44.39	44.5	45.51
Insol.	1.39	0.6	
Total	100.51	100.0	100.00

Atomic ratio based on O=4 in the anhydrous parts.

	1	2	3
Mn	0.903	0.92	1.00
Mg	0.108	0.04	
Ca	0.000	0.04	
S	0.996	1.00	1.00
O	4.000	4.00	4.00
H_2O	6.831	6.83	7.00

1: Jôkoku mine, Hokkaido, Japan. Present study.
2: Lucky Boy mine, Utah (Carnot, 1879).
3: Theoretical $MnSO_4 \cdot 7H_2O$.

$(Mn_{0.90}Mg_{0.11})_{1.01}S_{1.00}O_{4.00} \cdot 6.8H_2O$, showing the material to be very close to the theoretical $MnSO_4 \cdot 7H_2O$.

X-RAY POWDER STUDY

X-ray powder data on a part of purified material used for chemical analysis was obtained by the diffractometer method employing Mn-filtered Fe-radiation. The comparison of d-spacings and intensity ratios between mallardite and melanterite ($FeSO_4 \cdot 7H_2O$; JCPDS Card No. 22-633) or bieberite ($CoSO_4 \cdot 7H_2O$; JCPDS Card No. 16-487) shows a close agreement. Therefore, it is considered that these three minerals are isostructural.

The x-ray powder diffraction pattern is successfully indexed on a monoclinic cell with $a_0=14.15$, $b_0=6.50$, $c_0=11.06$Å, $\beta=105°36'$, Z=4 in terms of the analogy with melanterite and bieberite. Possible space group is $P2_1/c$ by the same reason as the above. The indexed x-ray powder pattern is presented in Table 3, and unit cell dimensions and calculated specific gravity together with those of melanterite and bieberite are summarized in Table 4.

Table 3 X-ray powder data of mallardite from the Jôkoku mine.

hkl	d (calc.)Å*	d (obs.)Å**	I/I_1
110	5.869	5.85	8
$\bar{1}02$	5.486	5.49	72
111	4.905	4.92	100
$\bar{2}02$	4.882	4.88	56
102	4.562	4.57	33
211	4.035	4.04	25
311	3.755	3.79	47
202	3.737	3.74	16
112	3.735		
020	3.251	3.26	36
113	3.207	3.21	12
$\bar{2}13$	3.127	3.13	31
302	3.073	3.07	12
410	3.018	3.02	9
$\bar{1}22$	2.787	2.805	13
$\bar{2}04$	2.757	2.758	39
411	2.735	2.732	9
$\bar{5}03$	2.663	2.660	17
$\bar{3}04$	2.626	2.626	19
104	2.491	2.490	14
222	2.435	2.431	13
023	2.398	2.400	39
502	2.199	2.186	5_B
612	2.192		
$\bar{3}24$	2.096	2.096	4
$\bar{3}15$	2.055	2.056	12
015	2.025	2.025	8
422	2.019	2.017	14
$\bar{1}24$	1.977	1.975	17
331	1.886	1.890	9
404	1.869	1.870	16
620	1.862	1.862	15
$\bar{2}06$	1.843	1.842	20
$\bar{1}25$	1.829	1.829	6
$\bar{4}06$	1.793	1.792	6
711	1.767	1.763	8
$\bar{6}24$	1.734	1.733	4
506	1.733		

* Calculated on the basis of $a_0=14.15$, $b_0=6.50$, $c_0=11.06$ Å, $\beta=105°36'$.
** Pattern at 18°C. Fe/Mn radiation.

Table 4 Unit cell parameters of mallardite, melanterite and bieberite.

	1	2	3
System	monoclinic	monoclinic	monoclinic
S.G.	$P2_1/c$	$P2_1/c$	$P2_1/c$
a_0 (Å)	14.15	14.077	14.040
b_0 (Å)	6.50	6.509	6.495
c_0 (Å)	11.06	11.054	10.925
β	105°36'	105°36'	105°27'
V (Å³)	980.1	975.71	960.17
Z	4	4	4
$a_0:b_0:c_0$	2.177:1:1.701	2.1627:1:1.6983	2.162:1:1.682
D. (calc.)	1.878	1.893	1.942

1: Mallardite, Jôkoku mine, Hokkaido, Japan. Present study.
2: Melanterite (JCPDS Card, No.22-633).
3: Bieberite (JCPDS Card, No.16-487).

THERMAL ANALYSIS

DTA and TG of mallardite were carried out simultaneously in air by means of a Thermoflex unit made by Rigaku-Denki Co., Japan, using about 350 mg of pure material. Heating rate was 10°C per minute.

The DTA and TG curves are shown in

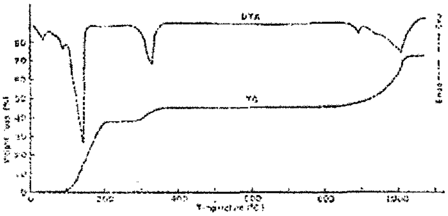

Fig. 4 DTA and TG curves of mallardite from Jôkoku mine.

Fig. 4. It is characterized by the three distinctive endothermic peaks at 163°C, 325°C and 1,005°C, accompanying with the three faint but sharp endothermic peaks at 25°C, 90°C and 895°C.

The TG curve shows three steps of weight loss, namely between room temperature and 200°C, between 260°C and 360°C, and between 725°C and 1,025°C.

The first and second steps of weight loss are due to the formation of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) and anhydrous sulfate ($MnSO_4$) by the dehydration of crystalline water, respectively. The third step is derived from expelled SO_3, and the final product after heated to 1,080°C consists mainly of hausmannite. These phenomena were examined by the x-ray powder method and chemical analysis.

From the comparison between TG curve and DTA, it may be concluded that three peaks at 25°C, 90°C and 163°C are due to the dehydration of about 85% water which corresponds to about 6 molecules of water, and the peak at 325°C may be caused by the loss of the remained 1 molecule of water. Lastly, the two peaks at 895°C and 1,005°C are due to vaporization of SO_3.

GENESIS AND STABILITY OF MALLARDITE

The efflorescences of mallardite on the adit wall apparently precipitated secondarily from surface and mine waters carrying components from manganese carbonate consisting mainly of rhodochrosite and manganoan calcite, and from sulfide minerals such as pyrite, sphalerite and galena.

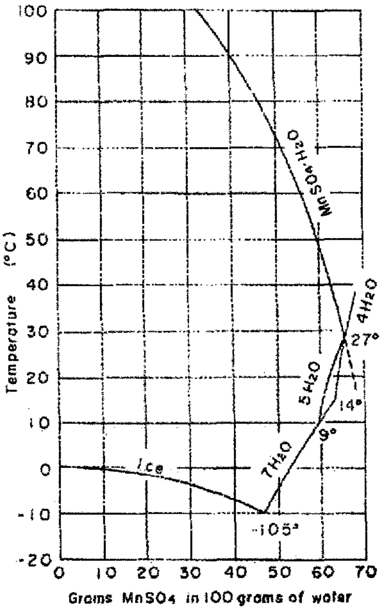

Fig. 5 The solubility of manganous sulfate in water (Cottrell, 1900, rewritten by Mellor (1932))

The occurrence of this mineral in the adit of 80 m level of Jôkoku mine is limited to the cold season from November to June in which the adit temperature is below about 15°C and relative humidity is over about 98 per cent. In other seasons, as the adit temperature will rise to over about 15°C, mallardite dehydrates gradually to jôkokuite or to ilesite. However, the morphological aspects of jôkokuite and ilesite show that a part of them are precipitated immediately from relatively warm solution above about 15°C.

On exposure to air for several days at 20°C and 60 per cent relative humidity, mallardite dehydrated to form a white powdery material, which on x-ray examination proved to be tetrahydrate without forming an intervening pentahydrate phase.

On the other hand, the stabilities of the hydrates of manganous sulfate with 1, 4, 5 and 7 molecules of water of crystallization were determined by Cottrell (1900) for temperatures between -10°C and +100°C. The ranges of their stability in the presence of aqueous solution are illustrated in Fig. 5. This figure indicates that the transition temperatures of $MnSO_4 \cdot 7H_2O \rightleftarrows MnSO_4 \cdot 5H_2O + 2H_2O$ and $MnSO_4 \cdot 5H_2O \rightleftarrows MnSO_4 \cdot H_2O + 4H_2O$ are nearly 9°C and 27°C respectively, and that tetrahydrate having the transition temperature of nearly 14°C from pentahydrate is an unstable phase.

Experimental studies on the phase equilibrium in the systems of manganous sulfate and water made by Cottrell (1900), and the natural conditions of temperature and humidity in adits where mallardite was formed will suggest that the mineral crystallized from mine water at temperatures below about 10°C and under suturated humidity.

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北海道上国鉱山産マラード鉱について

南部松夫・谷田勝俊・北村　強・加藤栄一

上国鉱山の80mレベルの諸坑道から，本邦新産（世界で二番目）のマラード鉱が発見された。長さ0.5～12mm，径0.2～1mmの毛状ないし柱状の多数の微細結晶が霜柱状に集合して，坑道壁面に付着しているのが普通である。絹糸状光沢を有し，無色透明ないし半透明，比重（計算値）1.838，(001）面に劈開が明瞭である。二軸性正であって光軸角は大，消光角(Z∧c) 44°，屈折率は $\alpha=1.462$，$\beta=1.465$，$\gamma=1.474$（±0.003）である。O=4として計算した組成式は $(Mn_{0.90}Mg_{0.11})_{1.01}S_{1.00}O_{4.00}\cdot 6.8H_2O$ である。単斜晶系，$P2_1/c$，$Z=4$，$a_0=14.15$，$b_0=6.50$，$c_0=11.06$Å，$\beta=105°36'$。この鉱物は，産状および $MnSO_4$-H_2O 系の平衡実験から約10°C以下の温度，飽和に近い湿度条件下で晶出したことが推定される。