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NEW FIND OF GROUTITE, HMnO_2 , IN JAPAN

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Abstract

The writer has recently discovered in the Pirika mine, Hokkaido, the first groutite to be recorded.

Groutite, HMnO_2 , is a member of the diaspore-goethite group. It resembles manganite in general appearance as to color, streak, hardness and specific gravity, but its X-ray powder pattern, phase conversion at 445°C , luster, cleavage and pleochroism are different from manganite. The writer observed several characters of groutite from the Pirika mine.

Introduction

While engaged in a study of manganese oxide mineral in Hokkaido, Japan, the writer found beautiful radial aggregates of black minute crystals of a manganese mineral which had been thought to be manganite. However, X-ray powder diagram was prepared which gave a pattern entirely different from that of manganite.

X-ray examinations, microchemical-tests, ore microscopic observations and differential thermal analysis were undertaken to determine the mineral. On the basis of those measurements and examinations, the mineral is believed to be groutite; this represents the first recorded find of groutite in Japan.

An outline of the deposit

The Pirika mine, Imagane-machi, Setana-gun, Hokkaido, Japan, is situated about 2 Km north of the Pirika Station of the Setana line (Fig. 1). The mine has been worked for manganese ore for many years. Many similar manganese deposits of the so-called Pirika type are distributed in the Imagane district, which includes the green tuff area of south-western Hokkaido.

The district surrounding of the mine is geologically composed of



Fig. 1. Index map of the Pirika mine, Hokkaido, Japan

the Paleozoics, granite mass of Pre-Tertiary, green tuff, tuff breccia, and muddy rock of Neogene Tertiary and younger Quaternary deposits.

The manganese oxide deposits in Hokkaido are found to have been deposited concordantly or slightly oblique to stratifications of sediments. The mode of occurrence of many such deposits are controlled by geological structure: the Pirika type manganese deposits develop in a small geological basin in a restricted district. In those deposits layer arrangement of manganese ore was observed. In upper

bed pyrolusite predominates while in the lower manganite develops. Moreover the formation of those deposits was genetically related to sedimentation processes.

Occurrence

Groutite is found in the Motoyama deposit of the Pirika mine. The minute crystals are always in radial aggregate and nearly always are associated with manganite.

The manganite crystal usually is columnar, radiating. The crystal is striated vertically on the prismatic faces. Deep striations parallel to the elongation render impossible the measurement of any faces in the vertical zone.

The crystal of groutite is thin and platy in habit and forms a radial aggregate. Groutite is associated with manganite, quartz, barite and limonite.

Physical properties

The color of the groutite is dull black and the luster is submetallic, while manganite is brilliant dark steel-gray.

Cleavage of groutite is very perfect and yields brilliant reflections.

The streak is reddish dark brown like that of manganite. As to hardness it may be slightly softer than manganite.

The specific gravity determined on a gram of handpicked material is 4.182 recalculation to 4°C. This determination was made by pycnometer.

Microchemical tests

After decomposing the groutite by means of HCl (1:1), the presence of manganese was tested using ammonium molybdate solution. The presence of iron was in very small amount. Al, Ba, Ca, Na, and K were not found. Although the complete chemical analysis of the pure material has not been made, the presence of manganese was also proved by X-ray Fluorescence Spectrographic analysis.

Ore microscopic observation

The thin section of groutite is nonopaque. Under the ore microscope, the polished specimens of groutite show the following characters.

Polishing: a good polish

Reflection color: grayish white to pale brownish gray

Reflection pleochroism: distinct, similiary in air and oil immersion
(lightest) light grayish white
(darkest) pale brownish gray

Anisotropism under the crossed nicols: very strong, with polarization color; parallel to elongation, dark violet brown darker than manganite; perpendicular to elongation, pale brownish gray,

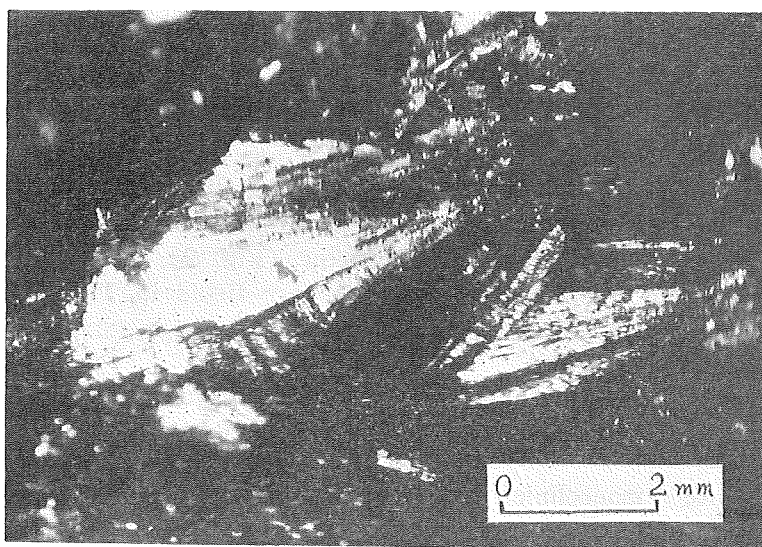


Photo. 1. Radial aggregates of groutite from the Pirika mine, Hokkaido, Japan

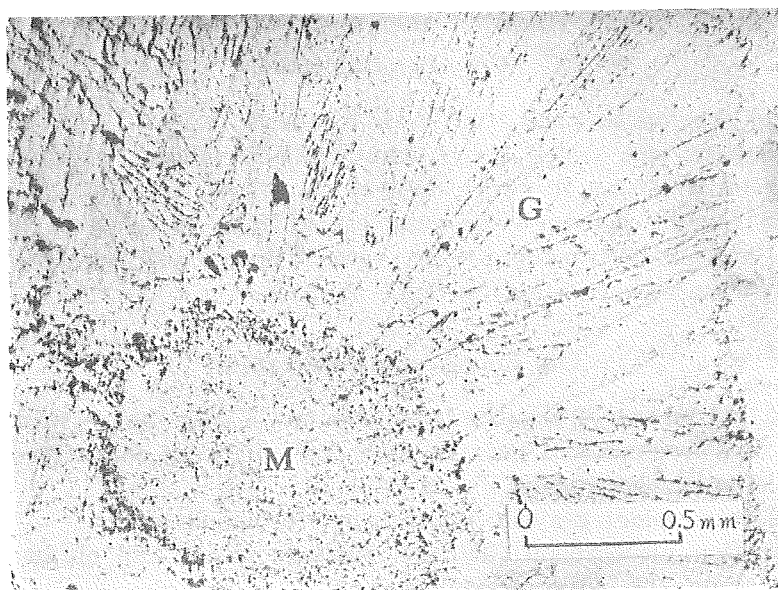


Photo. 2. Photomicrograph of a polished section of groutite from the Pirika mine, Hokkaido, Japan
G: groutite M: manganite

yellowish color stronger than manganite.

Form and texture (Photo. 2) : fibrous, needle-shaped, radial aggregate. Associated minerals are manganite, quartz, barite and limonite.

X-ray examination

The crystallography of groutite, which has been reported by J. W. GRUNER,⁵⁾ indicates that it is a member of the diaspore-goethite group.

X-ray powder diagram was made with unfiltered Fe radiation using Philips Geiger-counter X-ray spectrometer (Fig. 2). The interplaner spacings and the intensities of reflections are listed in Table 1. Such characters are with those of the groutite from iron mine of Cuyuna Range of Minnesota, U.S.A.

The lattice constants of groutite and manganite are;

Groutite³⁾ orthorhombic $a_0: 4.58\text{\AA}$ $b_0: 10.76\text{\AA}$ $c_0: 2.89\text{\AA}$
(HMnO_2)

Manganite³⁾ monoclinic $a_0: 8.86\text{\AA}$ $b_0: 5.24\text{\AA}$ $c_0: 5.70\text{\AA}$ $\beta: 90^\circ$
 $\text{MnO}(\text{OH})$

The lines of the powder photograph are shown in Table 1. The result is good agreement with that obtained by J. W. GRUNER⁵⁾ and P. RAMDOHR⁸⁾.

TABLE 1. X-ray powder data groutite

Cuyuna, Range, Minnesota, U. S. A. (by Gruner)			Cuyuna, Range, Minnesota, U. S. A. (by Ramdohr)		Pirika Mine		Manganite A. S. T. M. Card No.2-0429	
d (Å)	I	(hkl)	d (Å)	I	d (Å)	I	d (Å)	I
5.36	1	020	5.31	s	5.36	10		
4.17	10	110	4.17	ssst	4.19	73		
3.462	1-2	120	3.45	s	3.46	9	3.40	100
2.798	6	130	2.79	st	2.79	22		
2.675	6	040	2.66	st	2.67	30	2.65	80
2.524	1	021	2.52	s	2.53	7	2.52	40
2.369	6		2.36	st	2.37	40	2.41	80
2.303	5	140	2.29	st	2.30	20	2.26	60
2.210	2		2.20	m	2.21	13	2.18	60
2.008	1		2.00	s	2.00	2		
1.959	0.5	041	1.95	ss				
1.932	1	150	1.92	s	1.932	7		
1.798	0.5		1.79	ss	1.782	2		
1.763	2		1.75	s	1.763	6	1.77	80
1.732	1		1.73	s	1.735	5		
1.692	5		1.69	st	1.691	16	1.70	70
							1.66	80
							1.63	70
1.603	4		1.60	st	1.604	12		
1.559	0		1.55	s	1.559	3		
1.515	3	061	1.51	m	1.513	7	1.50	70
1.465	1		1.47	ss				
			1.45					
1.448	1		1.44	s	1.446	6		
1.435	2		1.43	s	1.438	7	1.43	70
1.398	1		1.39	s	1.397	3		
1.367	0.5-1		1.36	s	1.361	3		
1.345	1		1.34	s	1.344	2	1.32	70
1.304	0.5		1.30	ss			1.29	20
1.286	1	180?	1.28	s	1.278	3		
1.281	1							
1.267	1		1.26	s			1.26	20
1.258	1		1.253	s	1.259	2	1.24	20
1.220	1				1.218	3		
1.212	1	081	1.217	s/ss			1.21	20
1.202	1		1.208	s/ss				
			1.196	s			1.18	40
1.153	2		1.150	m	1.151	6	1.16	40
1.131	1-2		1.131	m	1.133	5	1.13	60
			1.117	ss			1.11	20
1.107	1		1.105	s			1.10	20
1.086	0.5		1.083	s/ss	1.084	3	1.08	20
1.077	0.5		1.075	ss				
			1.070	ss				
1.067	3	0,10,0	1.065	m	1.066	9		
			1.053	s	1.053	3		
			1.024	m/s				
			1.019	m/s	1.019	4		
			1.014	s/ss				
			1.001	st	1.001	5		

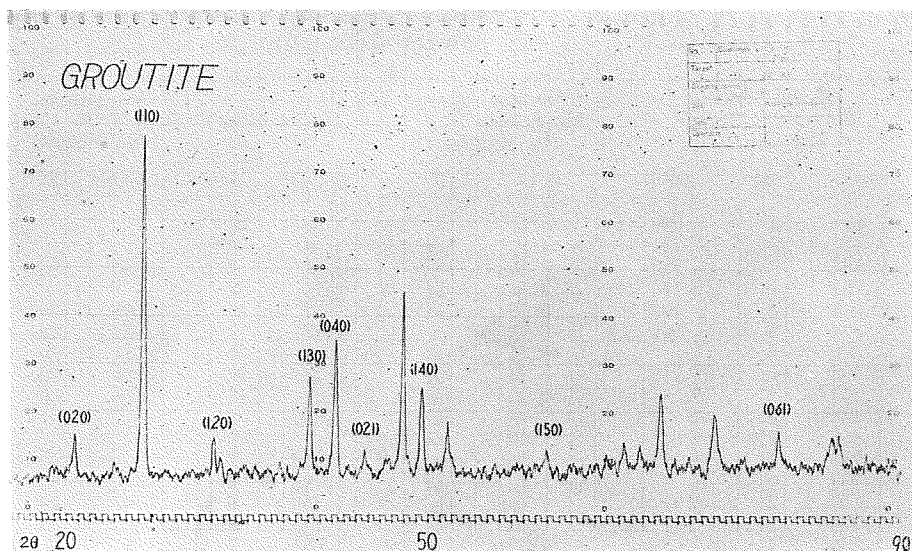


Fig. 2. X-ray powder diagram of groutite from the Pirika mine, Hokkaido, Japan

Differential thermal analysis curves and phase conversion by temperature

Differential thermal analysis curves for pure manganite have been

given by J. L. KULP and J. N. PERFETTI; no curve for groutite can be traced. The thermograms were made with conventional differential thermal analysis apparatus arranged by T. SUDO and others.⁹⁾ The heating rate was approximately 10°C per minute. The curve of groutite from the Pirika mine and that of manganite from the Yunosawa mine are as shown in Fig. 3.

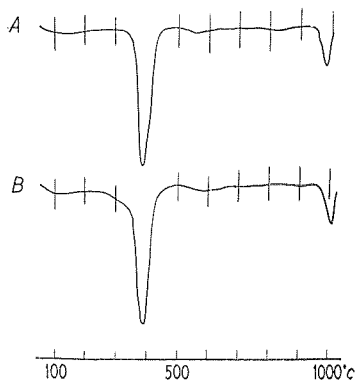


Fig. 3. Differential thermal analysis curves of manganite (A) from the Yunosawa mine and groutite (B) from the Pirika mine, Hokkaido, Japan

Groutite gives a curve very similar to that for manganite with two endothermic peaks. These curves have two remarkable endothermic peaks at approximately 395°C, corresponding to the dehydration, and an endothermic doublet at about 980-1020°C.

The effect of heat treatment of groutite and manganite on X-ray powder pattern was investigated. The results are shown in Table 2 and summarized:

- 1) The pattern of groutite almost disappears at the first endothermic reaction, corresponding to the dehydration to MnO_3 .
- 2) Pure manganite gives a strong peak at about 395°C , corresponding in respect to dehydration to MnO_2 . The pattern of MnO_2 almost disappears at 650°C and that of the second endothermic peak at about 985°C corresponding to the conversion of Mn_2O_3 to Mn_3O_4 .

The results of similar tests of manganite as reported by S. PAVLOVITCH⁷⁾ are different. E. J. RODE⁷⁾ has concluded that in vacuum Mn_2O_3 is formed while in air MnO_2 may be one of the products. Frequently curves for manganite shown an additional peak at $550\text{--}600^\circ\text{C}$ which J. L. KULP and J. N. PERFETTI have attributed to unidentified impurity; E. J. RODE, however, has considered it to relate to manganite and to represent in vacuum the conversion of Mn_2O_3 to a mixture of α and β - Mn_3O_4 or in air the decomposition of MnO_2 . However, it may be that the pattern of MnO_2 which appears at 550°C in the case of manganite represents a difference in electric charge of Mn for manganite and groutite.

TABLE 2. Main features of X-ray diffraction patterns

Original	at 550°C	at 650°C	at 1100°C
Manganite ($\text{MnO}(\text{OH})$)	$\text{MnO}_2 + \text{Mn}_2\text{O}_3$	Mn_2O_3	Mn_3O_4
Groutite (HMnO_2)	Mn_2O_3	Mn_2O_3	Mn_3O_4

Manganite and Groutite

M. J. BUERGER¹⁾ has shown that the bonding of hydrogen corresponds more closely to an OH ion in manganite. Similar bonds exist in boehmite and lepidocrocite.

J. W. GRUNER⁵⁾ has discussed the diaspore-goethite-groutite series and the boehmite-lepidocrocite-manganite series on the basis of unit cell volumes. R. L. COLLIN and W. N. LIPSCOMB²⁾ have shown the stability of manganite as compared with groutite. It is also possible that such distortions of the oxygen octahedra as they report occur in groutite as well.

Groutite is considerably larger in unit cell volume than manganite

and less stable under pressure and in elevated temperatures. For this reason it is also a rare mineral formed under unusual conditions as evidenced by its limited occurrence and association. But it will be considered a common mineral with further study.

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Reference

- 1) BUEGER M. J. (1936): The symmetry and crystal structure of manganite $\text{Mn}(\text{OH})\text{O}$. *Zeits. Krist.*, 95, 163-174.
- 2) COLLIN R. L. & LIPSCOMB W. N. (1949): The crystal structure of groutite, HMnO_2 . *Acta Cryst.*, 2, 104-106.
- 3) DANA's The system of mineralogy (1955).
- 4) DOI S. (1958): Manganese deposits of the Imagane Distrect, Hokkaido. Rept. Geol. Surv. Hokkaido, No. 20, 1-16.
- 5) GRUNER J. W. (1947): Groutite, HMnO_2 , a new mineral of the diaspore-goethite group. *Amer. Miner.*, 32, 654-659.
- 6) KULP J. L. & PERFETTI J. N. (1950): Thermal study of manganese oxides. *Miner. Mag.*, 29, 239-251.
- 7) MACHENZIE R. C. (1957): Differential thermal investigation of clays. *Miner. Soc.*, London, 320-321.
- 8) RAMDOHR P. (1956): Die manganerze. Symposium Sobre Yacimientos de Manganeso XX Congreso Geologico Internacional. Tomo 1. El manganeso en general, 19-73.
- 9) SUDO T. & others (1952): Studies on differential thermal analysis curves of Japanese clay minerals. *Jour. Geol. Soc. Japan*, 115-130.