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THE CRYSTAL STRUCTURE OF RAMSDELLITE FROM PIRIKA MINE

by

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(with 3 text-figures and 4 tables)

Abstract

Chemical composition and crystal structure of ramsdellite from Pirika mine, Hokkaido, Japan were studied. Chemical composition, determined by EPMA, shows that ramsdellite is pure manganese oxide and does not contain any other element. The crystallographic data, obtained by Rietveld analysis, indicate that ramsdellite has orthorhombic symmetry. Space group is Pnma and unit cell parameters are: a=4.513(1) Å, b=9.264(1) Å and c=2.859(1) Å. The structure consists of MnO_6 double chains (Byström, 1950). There are 4 symmetry-dependent MnO_6 octahedra in an unit cell and 2 symmetry-independent oxygen atoms in an MnO_6 octahedron. The difference of inter-atomic distances between Mn-O(1) and Mn-O(2) is larger than other manganese dioxide minerals. The distortion of MnO_6 octahedron is quite similar to that of groutite (α-MnOOH). These data suggest that ramsdellite was formed by oxidation of groutite.

Introduction

There are several kinds of manganese dioxide minerals such as pyrolusite, hollandite, cryptomelane, nsutite, birnessite and ramsdellite. Ramsdellite is a rare mineral and there are only two known occurrences in Hokkaido. Byström (1949) reported that ramsdellite contains double chains of linked MnO_6 octahedra. The double chains are linked together by sharing opposite corners of each double chain which gives orthorhombic symmetry. But there is no report on the precise crystal structure of this mineral primarily because no single crystal, natural or synthetic, is available for structural analysis.

The occurrence of ramsdellite in Hokkaido, has been reported by Hariya (1963) and Miura et al. (1983). Previous works show only x-ray powder diffraction data and neither chemical composition nor structural data of ramsdellite has been reported. We found radially extended, fine acicular crystals of ramsdellite in the Pirika mine. As the fine acicular crystals contain some cracks in it, single crystal method could not be attempted for structural study. We used the Rietveld method to determine the crystal structure and the chemical composition was analyzed by EPMA.

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Samples

The now closed Pirika mine, located 100 kilometer south-west of Sapporo, is a strata-bound manganese deposit. The deposit is associated with a sequence of tuff -breccia of Miocene age. The main manganese minerals are pyrolusite, manganite, groutite and ramsdellite (Hariya, 1959, Miura et al., 1983). Groutite and ramsdellite have similar structure but in the former half of the oxygen is replaced by OH. Ramsdellite occurs closely with groutite. The color of the specimen used for the study is black or silver-black with luster. The crystals show radially extended acicular forms. Groutite is not stable at high temperature. Powdered sample heated in air at 130℃ oxidized very slowly to ramsdellite (Dent Glasser and Smith, 1965). From the field relations, Miura et al. (1983) considered that ramsdellite in Pirika mine is an oxidation product of groutite.

Experiment

Chemical composition

The analyses were carried out using a JEOL JCMA-733 electron microprobe analyzer. The accelerating voltage was 15 kV and the beam current was 2×10^{-8} A. Table 1 shows the mean value of 8 analyses. Water content was measured 3 times, using the DuPont 902-H moisture evolution analyzer, and the mean value is also shown in table 1.

Structure refinement by x-ray powder diffraction

X-ray powder diffraction data were collected on a Philips APD1700 diffractometer with CuKα radiation (40kV, 40mA), using step scanning method

Table 1 Chemical analysis (wt%) of ramsdellite (n=8)

MnO_2	96.47	(0.63)
Fe_2O_3	0.18	(0.04)
Al_2O_3	0.28	(0.12)
MgO	0.36	(0.06)
Cr_2O_3	0.00	(0.00)
TiO_2	0.00	(0.00)
NiO	0.04	(0.04)
SiO_2	0.31	(0.08)
CaO	0.09	(0.05)
K_2O	0.01	(0.01)
Na_2O	0.01	(0.01)
H_2O*	1.86	(0.05)
Total	99.61	

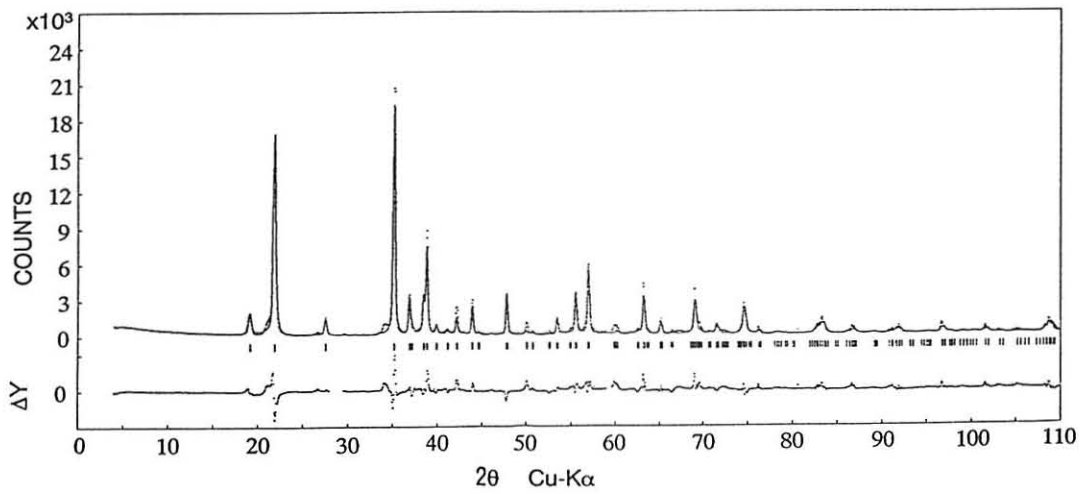
Standard deviatios are given in parentheses
* n=3

with 2θ range of 10° to 110°. The step size was 0.05° and the count time was 30 sec/step. The intensity of x-ray was counted after monochromatized by pyrolytic graphite.

In order to determine the crystal structure precisely, Rietveld analysis was performed. The program RIETAN (Izumi, 1985) was used for the calculations. Byström (1949) reported that the crystal system of ramsdellite is orthorhombic and the space group is D_{2h}^{16} (Pnma, in international table for x-ray crystallography, Vol. A) and the unit cell parameters are: a=4.533 Å, b=9.27 Å, c=2.87 Å, In the crystal model proposed by Byström, oxygen atom and manganese atom occupy the general equivalent position 4(c). Following previous worker's crystal axis setting, he changed the axial direction abc of D_{2h}^{16} to c'a'b'. We also select the same axial setting and used the structure model of Byström as input data for calculation. We select the space group Pnma and the coordinate of general equivalent position becomes $\pm(x, y, 1/4)$ $\pm(1/2-x, y+1/2, 1/4)$. The starting coordinates are:

Mn	:	x =	0.022	y =	0.136	z = 0.250
O(1)	:	x =	0.170	y =	−0.230	z = 0.250
O(2)	:	x =	−0.210	y =	−0.033	z = 0.250

For the unit cell parameters, the data proposed by Byström were used. The samples contain small amount of pyrolusite and the diffraction peaks of pyrolusite were observed. In the Rietveld process, the 2θ region of $28.0 \leqq 2\theta \leqq 29.5$ and $59.0 \leqq 2\theta \leqq 59.5$ were excluded.



Text-fig. 1 Observed and calculated x-ray diffraction patterns of ramsdellite. The dots are observed data and solid lines are calculated profiles. The vertical bar-marks indicate the positions of the calculated diffraction peaks. The difference between the observed and the calculated data (ΔY) is plotted below the vertical bar-marks.

Results

Table 1 shows the results of chemical analyses of ramsdellite. In the Rietveld calculation, background parameters, profile parameters, cell constants, atomic coordinates are optimized one by one. The temperature parameters of Mn and O(1) become negative in the first step, these values were fixed in calculation. The final R factor which represents the ratio of the observed structure factors to the

Table 2 Crystallographic data for ramsdellite

	Pirika Mine (this study)	Byström (1949)
Formula	MnO_2	MnO_2
Cell dimensions	a 4.513(1) Å	4.533 Å
	b 9.264(1) Å	9.27 Å
	c 2.859(1) Å	2.87 Å
	V 119.5 Å^3	120.6 Å^3
Z	4	4
D calc.	4.83	4.79

Standard deviations on the last digits are given in parentheses.

Table 3 Atomic coordinates and isotropic temperature factors.

Atom	positins	X	Y	Z	U
Mn	4 (c)	0.029 (3)	0.139 (1)	0.250	0.6
O(1)	4 (c)	0.215(13)	−0.209 (5)	0.250	0.8
O(2)	4 (c)	−0.277 (8)	−0.055 (6)	0.250	0.8

Standard deviations on the last digits are given in parentheses. Temperature factors are fixed in calculation.

Table 4 Manganese Oxygen distances in MnO_6 octahedron

Atoms	Vector	Groutite (a)	Ramsdellite (b)
MnI-O(1)III	A	2.178 Å	1.821 Å
MnI-O(1)II	B	1.896 Å	1.917 Å
MnI-O(2)II	C	1.968 Å	1.975 Å
MnI-O(2)I	D	2.340 Å	2.266 Å

(a) Glasser and Ingram (1967)

(b) Pirika mine

In groutite, OH occupy the O(2) position.

On the Vector, see Fig. 3.

symmetry code: I : X, Y, Z

II : −X, −Y, −Z

III : 1/2−X, Y+1/2, 1/2−Z

IV : −1/2+X, −Y−1/2, −1/2+Z

calculated structure factors becomes 12.5%.

Fig. 1 shows the observed and calculated x-ray diffraction patterns. The cell dimensions as determined using the Rietveld method, atomic coordinates and selected bond distances are given in Table 2, Table 3 and Table 4 respectively.

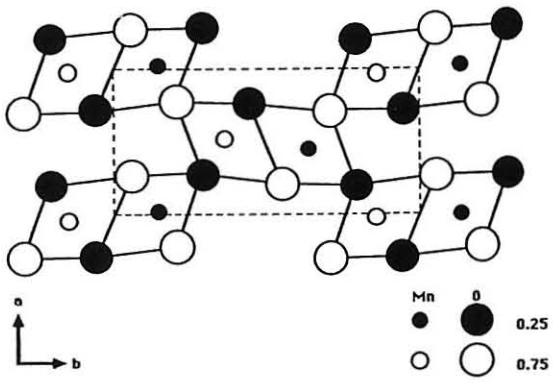
Discussion

Chemical composition

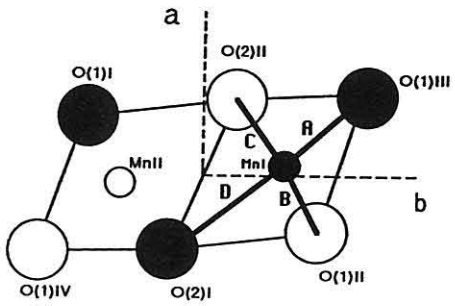
There are no report on the chemical composition of ramsdellite from Japan for any comparison with our data. Ramsdellite from Lake Valley, U. S. A. contains 0.8% Al_2O_3, 1.2% SiO_2, 0.2% TiO_2, 0.8% Fe_2O_3, 0.2% CaO and 1.3% H_2O (Byström, 1949). He considered that ramsdellite is pure MnO_2 mineral because it was not clear whether these elements were essential to ramsdellite or not. Ramsdellite from Pirika mine contains even lesser amounts of these elements except H_2O. So we also consider this mineral as pure MnO_2. As the water content is as high as 1.86%, it is possible that some of the oxygens are replaced by OH.

Basic structure

The cell dimensions optimized by Rietveld calculation, show a good agreement with the data reported by Byström (1949). The unit cell contains 4 MnO_2 molecules (Fig. 2). The MnO_6 octahedra share planes to form long chain. Two long chains share edges to form double chains and which are elongated parallel to the c -axis. Each double chain shares edges to form a framework structure. In the structure of hollandite or cryptomelane, double chains of MnO_6 octahedra are observed parallel to both [101] and [10$\bar{1}$] (monoclinic cell). But in ramsdellite, double chain is observed only in the b-axis and it does not have a tunnel structure.



Text-fig. 2 Projection down c of ramsdellite structure. The dashed line shows the unit cell. Filled circle and open circles are z=0.25 and z=0.75 respectively.



Text-fig. 3 Mn-O distances in ramsdellite structure. See table 4 for the vectors A, B, C, D.

Distortion of MnO_6 octahedra

Groutite (α-MnOOH) and ramsdellite have a similar structure. There are 4 symmetry-equivalent MnO_6 octahedra in an unit cell. The Mn-O inter atomic distances changes when groutite is oxidized to ramsdellite as shown in Table 4 and Fig. 3. The average Mn-O distance in hollandite, which has a tunnel structure consisting of MnO_6 double chain, is 1.922 Å (Miura, 1986). Whereas in manganese oxide, which has large tunnel consisting of double and pentagonal MnO_6 octahedron chain, the Mn-O distance is 1.946 Å (Tamada and Yamamoto, 1986). Ramsdellite from Pirika mine shows an average Mn-O distance of 2.041 Å, which is 6-7% larger than the other manganese dioxide minerals.

In the MnO_6 octahedron, inter-atomic distances of Mn-O(1) and Mn-O(2) are 1.89 Å and 2.07 Å respectively. The latter is 9.5% larger than the former one and in comparison to other manganese oxide minerals the difference between the two Mn-O distances are large. For example, in hollandite there are two independent MnO_6 octahedra and the difference between the maximum and minimum Mn -O distance in a MnO_6 octahedron are 4.3% and 3.8%. (Miura, 1986). The MnO_6 octahedron in ramsdellite is distorted and the distortion can be explained by the fact that the ramsdellite forms as an oxidation product of groutite (α-MnOOH). In the groutite structure, manganese is trivalent and half of the oxygen positions in ramsdellite structure is replaced by OH. The average Mn-OH distance is 5.7% larger than Mn-O distance. Diaspore (AlOOH), montroseite ((V. Fe)OOH), goethite (FeOOH) have similar crystal structure and the difference between X-O and X-OH (X=Al, Fe, Mn, etc.) in these minerals are 6.7%, 7.7% and 6.6% respectively (Dent Glasser and Smith, 1968). The distortion of octahedron is common in α-XOOH structures. Ramsdellite is a very rare mineral and the common manganese dioxide mineral is pyrolusite. It is possible that ramsdellite structure develops only when MnO_6 octahedra are distorted. This distortion is possible in MnOOH structure because half of oxygens in MnO_2 structure is replaced by OH. When these distortions occur, ramsdellite can be formed as an isomorph of groutite by oxidation. Ramsdellite structure may not be formed directly.

Conclusion

1. Ramsdellite from Pirika mine is pure manganese oxide and it does not contain any other essential element.
2. It has orthorhombic symmetry and the space group is Pnma. Unit cell dimensions are: a=4.513(1) Å, b=9.264(1) Å, c=2.859(1) Å.
3. Ramsdellite has double chains of distorted MnO_6 octahedra.
4. Ramsdellite is an oxidation product of groutite(α-MnOOH) and it's structure may not be formed directly.

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