THE CRYSTAL STRUCTURE OF MONTROSEITE, A VANADIUM MEMBER OF THE DIASPORE GROUP*

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Abstract

An x-ray study of single crystals of montroseite, (V, Fe)O(OH), shows that the mineral has a structure analogous to that of diaspore, AlO(OH). Cell constants are given as: orthorhombic, space group $Pbnm$ (D_{2h}^{16}); $a=4.54$, $b=9.97$, $c=3.03$ Å; cell contents, four formula units. Atomic positions are given with interatomic distances, obtained as a result of a complete structure analysis by Fourier methods. Details of structure are compared with those of other members of the series.

Introduction

Among the many new vanadium minerals discovered during the past five years in the uranium-vanadium ore fields of the Colorado Plateaus is the black crystalline species named montroseite, described by Weeks, Cisney, and Sherwood (1953). It is the first distinct vanadium oxide mineral that has been reported, but current studies show that it is one of a series of structurally related oxides and hydroxides of vanadium in various valence states.

The x-ray patterns of montroseite are multiple, indicating the presence of two or more closely related phases. Rotation photographs show a short spacing of 3.0 Å along the prism axis. Weissenberg and precession photographs exhibit a strong sharp orthorhombic lattice and two weaker diffuse lattices in parallel position, of the same approximate dimensions and symmetry but with minor variations in spacings and intensities. These features suggest that the original montroseite phase corresponding to the sharp lattice has undergone alteration to other phases in which the basic structural framework is not changed. In this paper is described the complete refinement of the structure corresponding to the sharp lattice.

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X-ray Crystallography

As described in the previous paper by Weeks, Cisney, and Sherwood, the crystals are jet-black laths up to 0.5 mm. in length flattened normal to the a axis and elongated parallel to the c axis. There is a strong, almost fibrous cleavage parallel to (010) and (110), making it difficult to trim the crystals to suitable dimensions for x-ray study. The sharp spots are

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somewhat streaked, indicating a twisting of the crystal around [001] of as much as 10°. The diffuse spots are rather strongly developed, and close examination shows that there are two sets of them. The dimensions of the various lattices are given with an accuracy of about ±0.5 per cent in Table 1.

TABLE 1. LATTICE DIMENSIONS FOR MONTROSEITE AND RELATED DIASPORE-TYPE STRUCTURES

Species	Composition	a_0 (Å)	b_0 (Å)	c_0 (Å)	V (Å^3)
Montroseite	(V, Fe) O(OH)	4.54	9.97	3.03	136.9
Diffuse A	?	4.80	9.63	2.9_3	135.4
Diffuse B	VO_2	4.89	9.39	2.9_3	134.4
Diaspore[1]	AlO(OH)	4.40	9.39	2.84	129.9
Goethite[1]	FeO(OH)	4.64	10.0	3.03	140.6
Groutite[2]	MnO(OH)	4.58	10.76	2.89	142.5
Ramsdellite[3]	MnO_2	4.53	9.27	2.87	120.5

[1] Hoppe (1941).
[2] Collin and Lipscomb (1949).
[3] Byström (1949).

The extinctions, as shown by Weissenberg and precession photographs, are consistent with the space group *Pbnm* (D_{2h}^{16}), assuming the presence of a center of symmetry (and planes of symmetry normal to the *c* axis) analogous to other diaspore-type structures. Dimensions of these analogous structures are also given in Table 1.

CRYSTAL STRUCTURE ANALYSIS

Chemical analysis of montroseite did not indicate the chemical nature

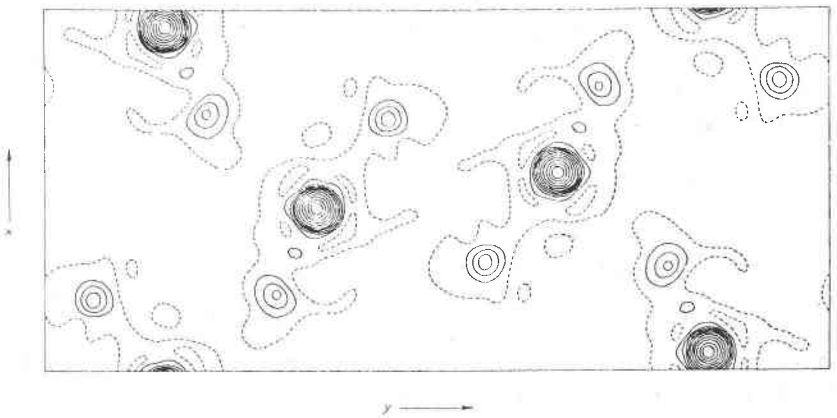

FIG. 1. Electron density projection along [001] of montroseite.

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR MONTROSEITE

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
020	18.2	−19.5	2.13.0	6.1	− 8.4
040	40.7	−46.0	2.14.0	16.8	18.8
060	31.1	36.6	2.15.0	13.1	13.5
080	4.9	5.6	2.16.0	10.4	−10.3
0.10.0	26.4	−34.8	2.17.0		6.1
0.12.0	9.2	−10.7	2.18.0	11.2	− 9.6
0.14.0	27.6	23.6	2.19.0		−10.5
0.16.0		− 4.3	2.20.0		3.6
0.18.0	12.1	−13.6			
0.20.0	14.1	18.7	310	10.6	3.8
			320	40.6	37.0
110	54.1	57.3	330	36.2	−22.0
120	32.7	22.2	340	4.9	− 5.3
130	51.9	−60.3	350		−10.8
140	50.3	−44.6	360	19.8	−24.4
150	13.5	− 3.5	370	19.4	30.2
160	9.2	−11.9	380	25.5	28.7
170	40.7	38.3	390		− 1.8
180		1.9	3.10.0	7.1	8.0
190	11.4	−14.7	3.11.0	8.4	−10.9
1.10.0		2.6	3.12.0	21.5	−25.2
1.10.0	27.0	−26.7	3.13.0		15.7
1.12.0		− 1.0	3.14.0		3.7
1.13.0	17.0	16.8	3.15.0		1.5
1.14.0		1.3	3.16.0	11.0	9.5
1.15.0	11.0	11.1	3.17.0	14.1	− 9.7
1.16.0	11.4	13.2	3.18.0		− 8.3
1.17.0	16.7	−17.0	3.19.0		− 2.6
1.18.0		− 2.3			
1.19.0		1.7	400	16.4	17.0
1.20.0		− 4.2	410	38.0	25.2
1.21.0	13.3	14.0	420		− 3.7
			430	16.4	25.3
200	18.8	17.7	440	7.8	− 8.0
210	13.9	35.7	450	22.5	−26.0
220	10.8	−11.7	460	7.2	7.1
230	12.1	− 0.4	470	8.8	3.9
240	50.7	−42.8	480		1.4
250	37.0	−37.1	490	21.4	32.8
260	23.3	23.8	4.10.0		− 6.6
270	5.7	1.5	4.11.0	10.4	−19.0
280	24.7	28.2	4.12.0		− 2.6
290	19.8	15.2	4.13.0	21.5	−15.6
2.10.0	20.2	−25.5	4.14.0		5.2
2.11.0	8.4	− 5.9	4.15.0		12.4
2.12.0		5.0	4.16.0		− 0.8

TABLE 2—(*continued*)

hkl	F_{obs}	F_{calc}
4.17.0		−2.5
4.18.0		−3.7
4.19.0	14.3	−10.5
510		8.5
520	29.6	32.1
530	10.4	−1.1
540	13.3	−15.0
550	7.1	6.2
560	20.2	−20.1
570		−8.1
580	19.6	21.9
590		−3.7
5.10.0	10.0	7.0
5.11.0		−1.6
5.12.0	18.2	−20.2
5.13.0		−6.6
5.14.0		2.6
5.15.0		3.9
5.16.0	16.8	13.4
600		−6.0
610	13.9	23.5
620		3.3
630	9.6	3.3
640		8.5
650	27.4	−28.2
660		−5.8
670		1.9
680		−6.6
690	21.2	12.7
6.10.0		5.4
6.11.0	9.8	−4.8
6.12.0		−1.5
6.13.0		−8.6
6.14.0		−5.3
6.15.0	12.3	14.2
710	10.2	−8.5
720	16.5	16.0
730	7.8	13.7
740	12.1	−13.0
750		−1.8
760	11.6	−12.8
770	12.3	−6.9
780	10.4	9.8
790		5.8
7.10.0		3.7
7.11.0	10.6	8.9
7.12.0		−8.3
800	20.0	−21.7
810	9.2	5.6
820		2.9
830		7.0
840	12.1	10.7
850		−6.9
860	10.6	−9.3
870		0.3
880		−1.4
890		10.6
8.10.0	11.4	11.9
910	9.6	−7.3
920		3.5
930	14.9	11.5
940		5.0
950		3.7
960		−2.1
970	5.5	−14.1
10.0.0	9.2	5.7
10.1.0		0.3
10.2.0		2.9
10.3.0		−0.2
10.4.0	11.2	11.9
10.5.0		1.2
10.6.0	8.2	−7.6
10.7.0		0.7
10.8.0	9.6	−10.4
11.1.0		−4.4
11.2.0		−3.6
11.3.0	8.8	9.0

of the mineral because some vanadium was replaced by iron. The true nature of the compound was suggested by the size of the unit cell and by the fact that the symmetry of the space group would allow a cell content of only four formula units of the type MO_2. The volume of the unit cell of montroseite is 137 Å^3, which will just accommodate 8 oxygen atoms in close packing (17.1 Å^3 per atom). In the space group *Pbnm* there are only four types of equipoint positions, three fourfold and one eightfold. The oxygen atoms will fit this scheme in several ways, but there can only be one type of vanadium atom in a fourfold position. Thus, the restrictions of unit-cell dimensions and symmetry lead to the empirical formula for montroseite of VO_2 or HVO_2. Reference to the tabulation of MO_2-type structures (Wyckoff, 1948) immediately suggests the comparison of montroseite with the diaspore structure type.

The structure of groutite, MnO(OH), as determined by Collin and Lipscomb (1949), was used as a starting point, and the montroseite structure refined by the usual iterative methods making use of Fourier synthesis and structure factor computations. The final electron density map is shown in Figure 1. The intensities used to determine the amplitudes for this Fourier synthesis were measured by comparing the density of spots on Weissenberg (*hk*0) photographs made with Mo$K\alpha$ radiation (films interleaved with nickel foil) against a calibrated strip made from reflections from the same crystal. The values of the structure amplitudes, F, so observed are listed in Table 2, together with those calculated from the final structure. The over-all temperature effect (which modifies the structure factor by the factor e^{-Bs^2}) as determined by a plot of log (F_{obs}/F_{calc}) against $s^2=(\sin\theta)^2/\lambda^2$ was found to have $B=0.4$ Å^2, thus indicating a rather strongly bound structure. The agreement between calculated and observed structure amplitudes is expressed in the usual manner in terms of R, the reliability factor:

$$R = \frac{\sum \left| |F_{obs}| - |F_{calc}| \right|}{\sum |F_{obs}|},$$

where $\sum |F_{obs}|$ is set equal to $\sum |F_{calc}|$. For the final structure, $R=0.21$ for 99 observed (non-zero) reflections. Absorption effects have been neglected.

The data for the final structure are shown in Table 3, where the parameters are given in fractions of the cell edge. This table also gives the data for diaspore and goethite as determined by Hoppe (1941, 1942), for groutite after Collin and Lipscomb (1949), and for ramsdellite after Byström (1949).

TABLE 3. PARAMETERS FOR MONTROSEITE AND OTHER DIASPORE-TYPE STRUCTURES

	M		O_I		O_{II}		R
	x	y	x	y	x	y	
Montroseite	−0.051	0.145	0.297	−0.197	−0.197	−0.051	0.213
Diaspore	−0.048	0.146	0.287	−0.199	−0.198	−0.056	0.114
Goethite	−0.045	0.146	0.31	−0.2	−0.20	−0.047	
Groutite	−0.036	0.140	0.27	−0.20	−0.21	−0.05	
Ramsdellite	0.022	0.136	0.167	−0.25	−0.211	−0.033	

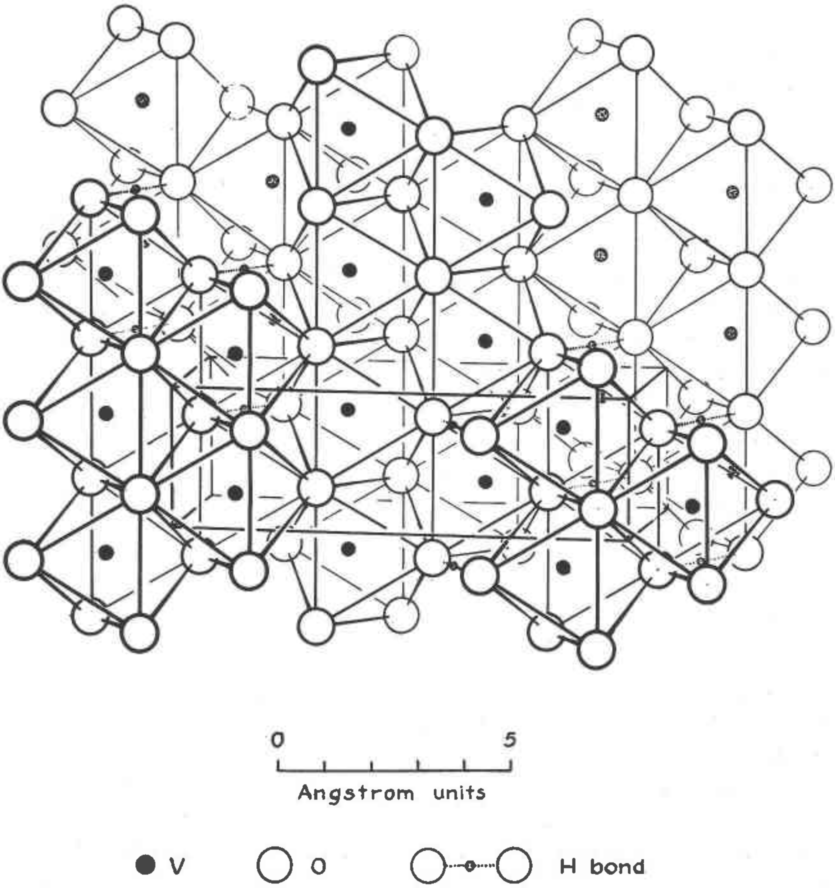

FIG. 2. Pictorial view of crystal structure of montroseite.

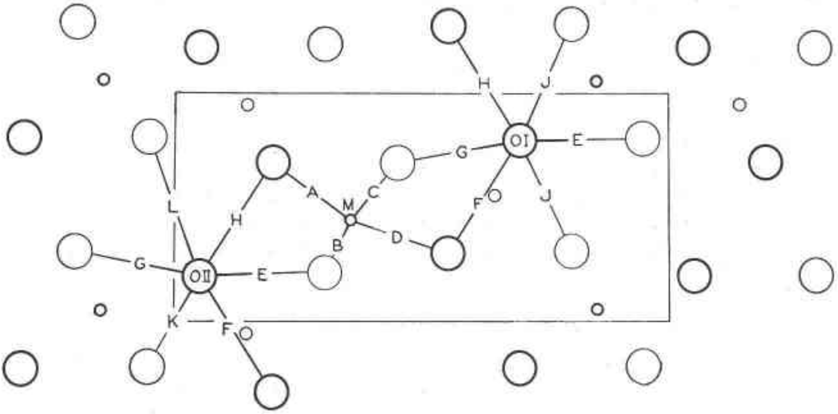

FIG. 3. Interatomic distances in montroseite.

FEATURES OF THE STRUCTURE

The well-known diaspore structure type, shown in a pictorial view in Figure 2, has been much discussed in standard works on crystal chemistry as an important example of a close-packed type of oxide structure (Pauling, 1940; Wells, 1950). A study of bond lengths reveals two outstanding characteristic features: (1) distortions in the octahedral coordination arising from edge-sharing in the chain and (2) the presence of hydrogen bonds between chains. All nearest neighbor interatomic distances, as shown in Figure 3, have been calculated for all structures except those of groutite and ramsdellite, for which accurate data are not yet available. These distances are given in Table 4. Distortion in the chain, expected as a result of the coulombic repulsion of the metal ions, is strongly evident from the short bonds from vanadium to exterior oxygen atoms (1.95 Å, A and B for montroseite) as compared with the longer bonds to interior oxygen atoms (average 2.13 Å, C and D). This effect is accompanied by a contraction to 2.55 Å of the O_{II}–O_{II} distance K, which is shared between octahedra. There seems to be a further dimensional compensation within the octahedron in the O_I–O_{II} distance F (2.68 Å). Other oxygen-oxygen distances are close to the normal van der Waals diameter, averaging 2.97 Å. These distances for goethite are also very consistent, averaging 2.97 Å, but in diaspore the average is reduced to 2.78 Å, indicating a higher degree of polarization of the oxygen atoms in the aluminum compound. The one remaining exception is the O_I-O_{II} distance H (2.72 Å) between chains, and this is the logical place to find the hydrogen atom. The distance is close to that found for most hydrogen bonds (Wells, 1950, p. 238). If the hydrogen atom could be located in this

TABLE 4. INTERATOMIC DISTANCES IN DIASPORE-TYPE STRUCTURES

(Lengths in Å, ±0.03)

Atoms	Vector	Montroseite	Diaspore	Goethite
$M-O_I$	A	1.95	1.84	1.89
	B(2)	1.95	1.86	2.02
$M-O_{II}$	C(2)	2.11	2.03	2.12
	D	2.16	1.99	2.05
O_I-O_{II}	E(2)	2.93	2.76	2.95
	F	2.67	2.62	2.85
	G(2)	2.94	2.78	2.94
	H	2.72	2.60	2.67
O_I-O_I	J(4)	2.93	2.80	2.94
	c-axis (2)	3.03	2.84	3.03
$O_{II}-O_{II}$	K(2)	2.55	2.48	2.56
	L(2)	3.30	3.19	3.31
M–M		3.30	3.12	3.54

structure, it would probably be found on a straight line joining O_I and O_{II}, approaching O_{II} more closely to compensate for the longer $V-O_{II}$ and shorter $V-O_I$ bonds.

CHEMICAL CONSTITUTION OF MONTROSEITE

The montroseite crystals studied in this investigation contained 8.8 per cent FeO (see Weeks, Cisney, and Sherwood, 1953), with iron to vanadium mol-ratio approximately 1:7. The oxidation potentials of Fe^{+2} and V^{+3} are such that the existence of ferric iron in the montroseite structure is unlikely. We may assume instead that Fe^{2+} replaces V^{+3} and that one V^{+4} ion is present for each Fe^{+2} ion.

It was stated earlier that crystals of montroseite give multiple *x*-ray patterns (see Table 1). The relative intensity of the lattices varies widely, but the diffuse B lattice seems to predominate. It is believed that it corresponds to an oxidized phase of composition VO_2. This explanation is consistent with the observations of Weeks, Cisney, and Sherwood that: (1) chemical analysis of montroseite shows a large excess of VO_2 and (2) powder patterns can be indexed on an orthorhombic lattice whose dimensions correspond most nearly with the diffuse B lattice as presented in this paper. Further work on the crystal structure and origin of the diffuse phases is in progress, and the results will be published later.

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