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Geology and Mineralogy

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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

By

Howard T. Evans, Jr., and Stanley Block

October 1953

Trace Elements Investigations Report 368

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*This report concerns work done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

USGS - TEI-368

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

By

Howard T. Evans, Jr., and Stanley Block

ABSTRACT

An X-ray study of single crystals of montroseite, (V,Fe)O(OH), shows that it 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 A, b = 9.97, c = 3.03; 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. A diffuse auxiliary X-ray lattice produced by montroseite crystals is interpreted as arising from an oxidized phase of composition VO_2, and having a similar structure, analogous to ramsdellite, MnO_2. A process of low-temperature oxidation during which the main structural framework is not disturbed is postulated, as in the case of the alteration of lepidocrocite and magnetite to maghemite, and goethite to hematite.

INTRODUCTION

Among the many new vanadium minerals discovered during the last five years in the Colorado Plateaus uranium-vanadium ore fields 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 2.97 A 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.

This work is part of a program undertaken by the Geological Survey on behalf of the Division of Research of the Atomic Energy Commission.

X-RAY CRYSTALLOGRAPHY

As described in the paper by Weeks, Cisney, and Sherwood (1953) the crystals are jet-black laths up to 0.5 mm in length flattened normal to the <u>a</u> axis and elongated parallel to the <u>c</u> 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 somewhat streaked indicating a twisting of the crystal around [001] of as much as 10°. The diffuse spots are rather strongly developed, and close examinations shows that there are two sets of them. The dimensions of the various lattices are given with an accuracy of about ± 0.5 percent in table 1.

Table 1.--Lattice dimensions of montroseite and related structures

Species	Composition	a_o(A)	b_o(A)	c_o(A)	V (A^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 structures of the same type. Dimensions of these analogous structures are also given in table 1.

CRYSTAL STRUCTURE ANALYSIS

Chemical analysis of montroseite did not indicate the chemical nature of the mineral because of some replacement of vanadium by iron. The true nature of the compound was suggested by the size of the unit cell and 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 A^3, which will just accommodate 8 oxygen atoms in close packing (17.1 A^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 be only 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 (hk0) photographs made with MoKα 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 $B = 0.4$ A^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

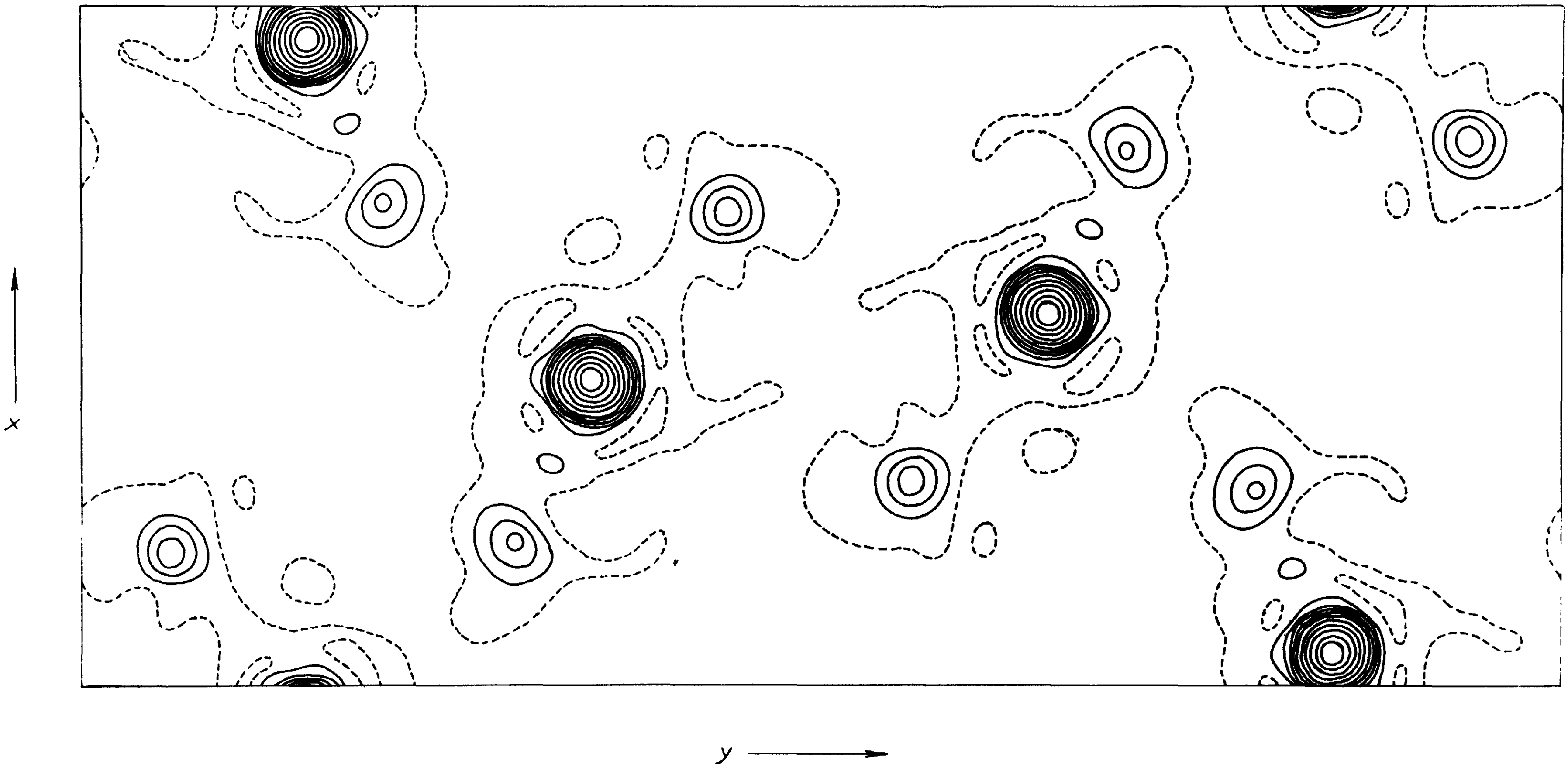

Figure 1. Projection along the c axis of electron density in montroseite.

Table 2.--Observed and calculated structure factors for montroseite

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
020	18.2	-19.5	1.13.0	17.0	16.8
040	40.7	-46.0	1.14.0		1.3
060	31.1	36.6	1.15.0	11.0	11.1
080	4.9	5.6	1.16.0	11.4	13.2
0.10.0	26.4	-34.8	1.17.0	16.7	-17.0
0.12.0	9.2	-10.7	1.18.0		- 2.3
0.14.0	27.6	23.6	1.19.0		1.7
0.16.0		- 4.3	1.20.0		- 4.2
0.18.0	12.1	-13.6	1.21.0	13.3	14.0
0.20.0	14.1	18.7			
			200	18.8	17.7
110	54.1	57.3	210	13.9	35.7
120	32.7	22.2	220	10.8	-11.7
130	51.9	-60.3	230	12.1	- 0.4
140	50.3	-44.6	240	50.7	-42.8
150	13.5	- 3.5	250	37.0	-37.1
160	9.2	-11.9	260	23.3	23.8
170	40.7	38.3	270	5.7	1.5
180		1.9	280	24.7	28.2
190	11.4	-14.7	290	19.8	15.2
1.10.0		2.6	2.10.0	20.2	-25.5
1.11.0	27.0	-26.7	2.11.0	8.4	- 5.9
1.12.0		- 1.0	2.12.0	(5.0)	(5.0)

Table 2.--Continued

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
2.13.0	6.1	- 8.4	3.16.0	11.0	9.5
2.14.0	16.8	18.8	3.17.0	14.1	- 9.7
2.15.0	13.1	13.5	3.18.0		- 8.3
2.16.0	10.4	-10.3	3.19.0		- 2.6
2.17.0		6.1			
2.18.0	11.2	- 9.6	400	16.4	17.0
2.19.0		-10.5	410	38.0	25.2
2.20.0		3.6	420		- 3.7
			430	16.4	25.3
310	10.6	3.8	440	7.8	- 8.0
320	40.6	37.0	450	22.5	-26.0
330	36.2	-22.0	460	7.2	7.1
340	4.9	- 5.3	470	8.8	3.9
350		-10.8	480		1.4
360	19.8	-24.4	490	21.4	32.8
370	19.4	30.2	4.10.0		- 6.6
380	25.5	28.7	4.11.0	10.4	-19.0
390		- 1.8	4.12.0		- 2.6
3.10.0	7.1	8.0	4.13.0	21.5	-15.6
3.11.0	8.4	-10.9	4.14.0		5.2
3.12.0	21.5	-25.2	4.15.0		12.4
3.13.0		15.7	4.16.0		- 0.8
3.14.0		3.7	4.17.0		- 2.5
3.15.0		1.5	4.18.0		- 3.7
			4.19.0	14.3	-10.5

Table 2.--Continued

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
510		8.5	680		- 6.6
520	29.6	32.1	690	21.2	12.7
530	10.4	- 1.1	6.10.0		5.4
540	13.3	-15.0	6.11.0	9.8	- 4.8
550	7.1	6.2	6.12.0		- 1.5
560	20.2	-20.1	6.13.0		- 8.6
570		- 8.1	6.14.0		- 5.3
580	19.6	21.9	6.15.0	12.3	14.2
590		- 3.7			
5.10.0	10.0	7.0	710	10.2	- 8.5
5.11.0		- 1.6	720	16.5	16.0
5.12.0	18.2	-20.2	730	7.8	13.7
5.13.0		- 6.6	740	12.1	-13.0
5.14.0		2.6	750		- 1.8
5.15.0		3.9	760	11.6	-12.8
5.16.0	16.8	13.4	770	12.3	- 6.9
			780	10.4	9.8
600		- 6.0	790		5.8
610	13.9	23.5	7.10.0		3.7
620		3.3	7.11.0	10.6	8.9
630	9.6	3.3	7.12.0		- 8.3
640		8.5			
650	27.4	-28.2	800	20.0	-21.7
660		- 5.8	810	9.2	5.6
670		1.9			

Table 2.--Continued

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
820		2.9	10.0.0	9.2	5.7
830		7.0	10.1.0		0.3
840	12.1	10.7	10.2.0		2.9
850		- 6.9	10.3.0		- 0.2
860	10.6	- 9.3	10.4.0	11.2	11.9
870		0.3	10.5.0		1.2
880		- 1.4	10.6.0	8.2	- 7.6
890		10.6	10.7.0		0.7
8.10.0	11.4	11.9	10.8.0	9.6	-10.4
910	9.6	- 7.3	11.1.0		- 4.4
920		3.5	11.2.0		- 3.6
930	14.9	11.5	11.3.0	8.8	9.0
940		5.0			
950		3.7			
960		- 2.1			
970	5.5	-14.1			

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 related structures

	M		OI		OII		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	-0.20	-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	

FEATURES OF THE STRUCTURE

The well-known diaspore structure type, shown in a pictorial view in figure 2, has been 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: distortions in the octahedral coordination arising from edge-sharing in the chain; and the presence of hydrogen bonds between chains. All nearest neighbor interatomic distances, as shown in figure 3, have been calculated for all structures except groutite and ramsdellite, for which

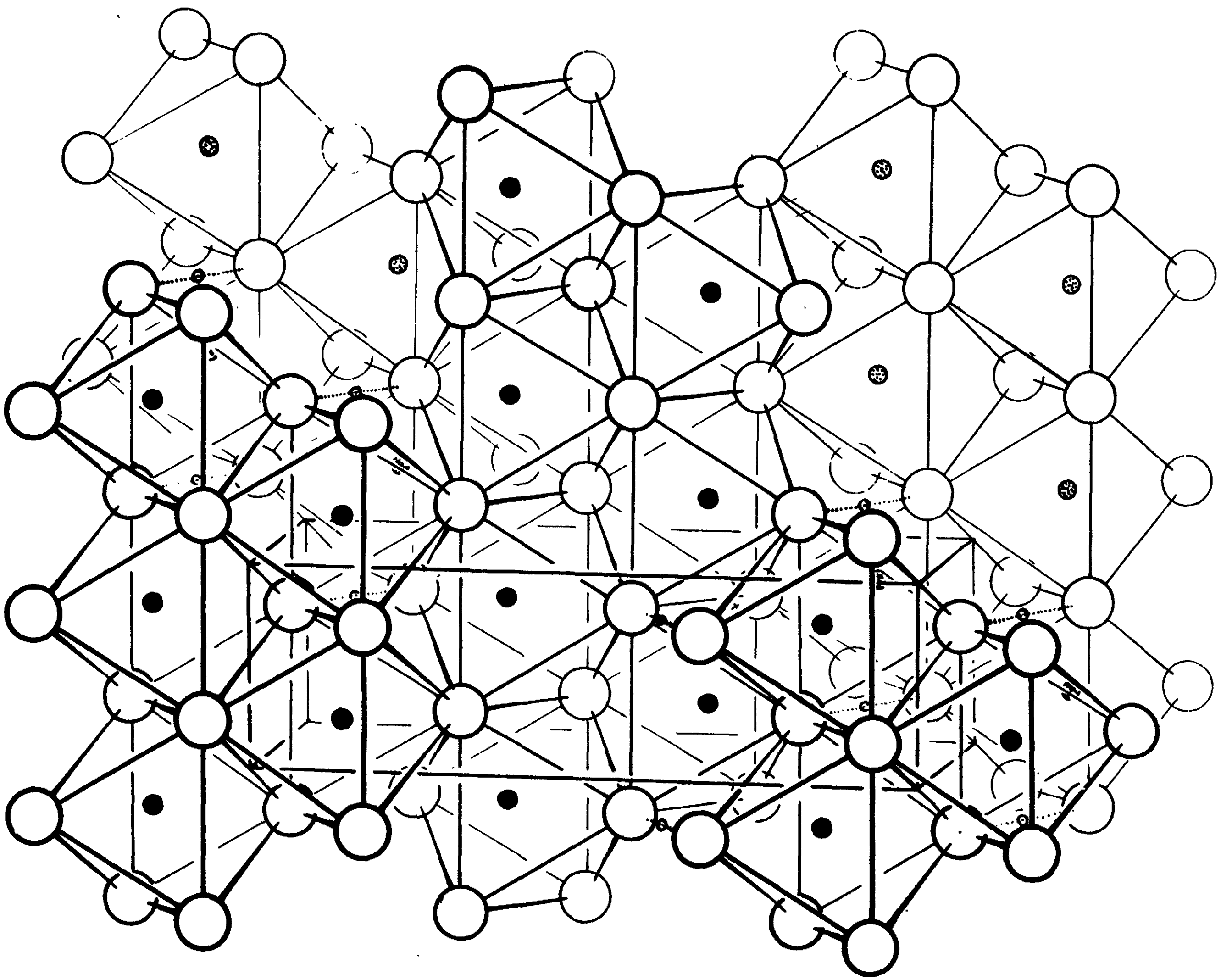

Figure 2. Pictorial view of the montroseite crystal structure.

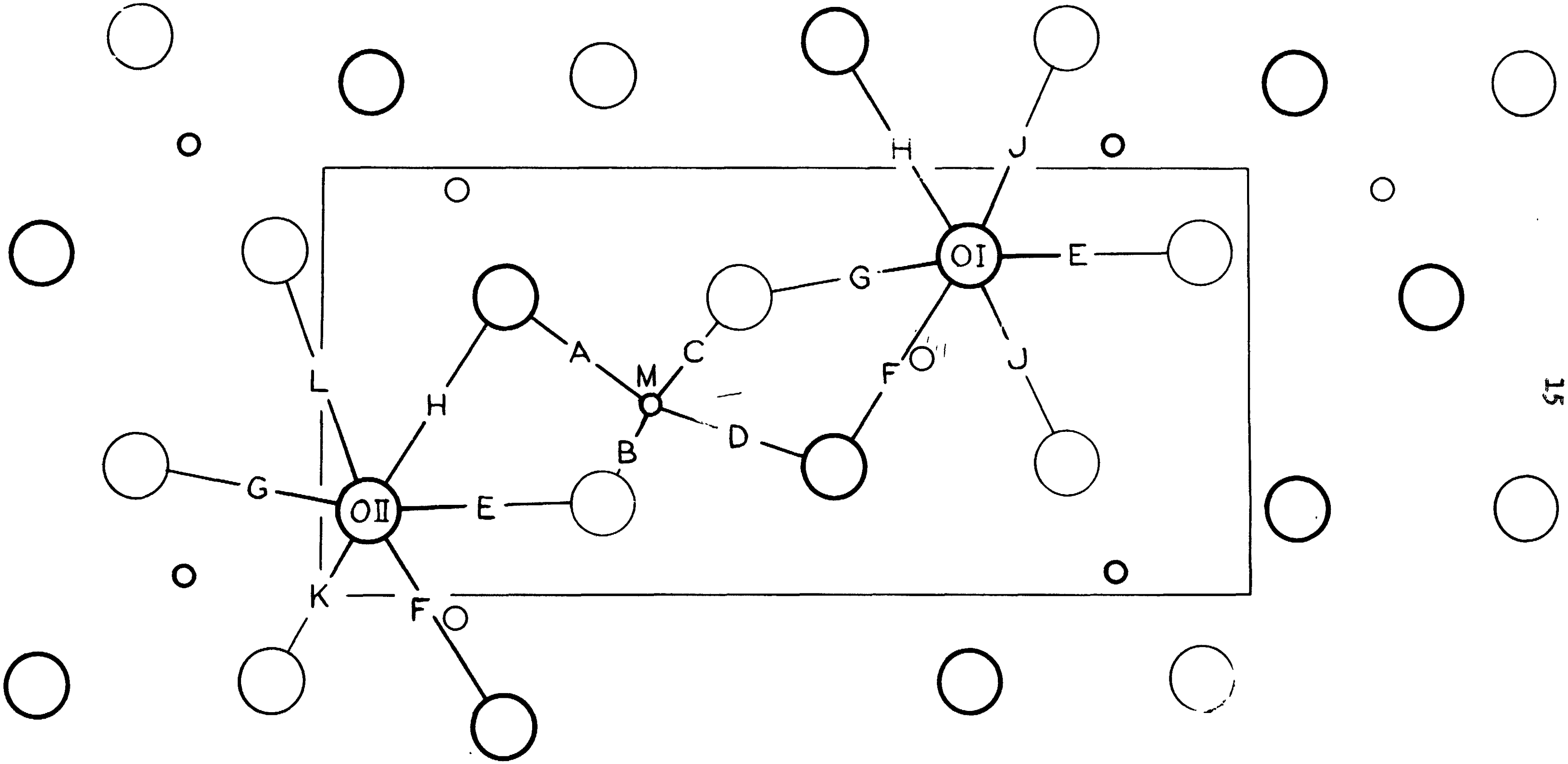

Figure 3. Projection along the c axis of the montroseite crystal structure.

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 A, A and B for montroseite) as compared with the longer bonds to interior oxygen atoms (average 2.13 A, C and D). This effect is accompanied by a contraction to 2.55 A of the OII - OII distance K which is shared between octahedra. There appears to be a further dimensional compensation within the octahedron in the OI - OII distance F (2.68 A). Other oxygen-oxygen distances are close to the normal van der Waals diameter, averaging 2.97 A. These distances for goethite are also very consistent, averaging 2.97 A, but in diaspore the average is reduced to 2.78 A, indicating a higher degree of polarization of the oxygen atoms in the aluminum compound. The one remaining exception to these generalizations is the OI - OII distance H (2.72 A) 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 structure, it would probably be found on a straight line joining OI and OII, approaching OII more closely to compensate for the longer V-OII and shorter V-OI bonds.

CRYSTAL CHEMISTRY AND ALTERATION

The montroseite crystals studied in this investigation came from the Bitter Creek mine, and contained 8.8 percent FeO (Weeks, Cisney, and Sherwood, 1953), with the 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 extremely unlikely. We may assume instead that Fe^{2+} replaces V^{3+} and that one V^{4+} ion is present for each Fe^{2+} ion.

Table 4.--Interatomic distances in diaspore-type structures. (Lengths in A, ± 0.03)

Atoms	Vector	Montroseite	Diaspore	Goethite
M-OI	A	1.95	1.84	1.89
	B (2)	1.95	1.86	2.02
M-OII	C (2)	2.11	2.03	2.12
	D	2.16	1.99	2.05
OI-OII	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
OI-OI	J (4)	2.93	2.80	2.94
	c-axis (2)	3.03	2.84	3.03
OII-OII	K (2)	2.55	2.48	2.56
	L (2)	3.30	3.19	3.31
M-M		3.30	3.12	3.54

It was stated earlier that crystals of montroseite give multiple X-ray patterns. (See table 1.) One of the orthorhombic lattices is sharp, whereas the other two are diffuse, and all are similar and parallel in orientation. A plausible explanation of these observations can be developed by postulating that the sharp lattice corresponds to the original crystal structure (V,Fe)O(OH) as it was deposited, which has subsequently been subjected to alteration to other phases corresponding to the diffuse lattices. The alteration presumably has proceeded without changing the hexagonal close-packed oxygen framework, through the migration of hydrogen atoms and iron and vanadium ions or electrons. One obvious product of oxidation is VO_2, which might be expected, by analogy with ramsdellite, to have a polymorph with the diaspore structure. It is suggested that the stronger of the two diffuse lattices corresponds to VO_2. The fate of the iron in the alteration process is harder to predict. Goethite is certainly not one of the products. Possibly the weaker diffuse lattice corresponds to an iron-vanadium phase.

Artificial VO_2 has been reported by Goldschmidt (1926) (according to measurements of W. Zachariasen) to have the tetragonal cassiterite-type (SnO_2) structure. It may be that the diaspore structure which the vanadium dioxide presumably takes on by alteration of the original hydroxy compound (montroseite) is metastable and can exist only when such alteration takes place at low temperatures so that the hexagonal close-packed oxygen framework is not disturbed. This situation is analogous to the formation of maghemite, Fe_2O_3, by alteration from lepidocrocite, FeO(OH) (Sosman and Posnjak, 1925) and from magnetite, Fe_3O_4 (Newhouse, 1929). Here, the stable form of Fe_2O_3 is hematite, which has a hexagonal close-packed oxygen framework, but the metastable maghemite, whose structure is related to magnetite, retains at low temperatures the original cubic close-packed arrangement of magnetite and lepidocrocite. Correspondingly, goethite (see above) alters invariably to hematite.

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