oxygen, including Al^{3+}, Mn^{3+} or Mg^{2+}, but none of these in association with Ti^{4+} formed a calcium ferrite isomorph of the type $NaScTiO_4$ (Reid, Wadsley & Sienko, 1967). Cr^{3+} cannot form either structure, but prefers instead a hollandite $M^+Cr^{3+}Ti_3O_8$, where M is any one of the alkali metals Na, K, Rb or Cs. Although in each of these three structures Ti^{4+} and either a tri- or divalent metal are randomized in the available octahedral positions, more than a superficial stereochemical consideration is required to decide in advance whether any one of them is likely to form.

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Refinement of the Crystal Structure of Groutite, α-MnOOH

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The structure of α-MnOOH (groutite) has been refined from three-dimensional data. Large variations in Mn–O bond lengths can be attributed to the Jahn–Teller effect. Some other factors affecting metal-oxygen bond lengths are discussed.

Introduction

Groutite (α-MnOOH) was first studied by Gruner (1947) who determined its orthorhombic unit-cell dimensions (Table 1) and noted that it was isostructural with goethite (α-FeOOH) and diaspore (α-AlOOH). Collin & Lipscomb (1949) determined its space group (Pbnm) and general structure, but did not attempt any further refinement. In particular, they were not able to say whether there was any significant variation in the Mn–O bond lengths. The present study aimed to refine the structure and investigate this possibility.

Table 1. Unit-cell determinations of groutite (Å)

Reference	a	b	c
Gruner	4·56	10·70	2·85
Collin & Lipscomb	4·58	10·76	2·89
Present investigation	4·560	10·700	2·870

Experimental

Crystals were selected from a sample of groutite from the Cuyuna Range, Minnesota, kindly supplied by Dr Roy Phillips of the Geology Department, Durham University. Rotation and Weissenberg photographs, taken using Cu $K\alpha$ and Co $K\alpha$ radiation, confirmed that they were pure groutite and two of these crystals were selected for intensity measurements. The first (GX1) was a large jet-black wedge-shaped crystal, about 750 microns long and set about the a axis. The second (GX2) was a small, near-spherical crystal, about 200 microns in diameter, and was set about the c axis. The intensity measurements were made using a Hilger and Watts automatic linear diffractometer with Mo $K\alpha$ radiation and the data were processed on an Elliott 803B computer, mainly using programs kindly made available by Daly, Stephens & Wheatley (1963). After correction for Lorentz–polarization factors, the intensities were converted to structure amplitudes and placed

on an approximately absolute scale. Wilson's statistical method was used to estimate an initial overall temperature factor. No corrections were made for absorption or extinction.

Unit-cell dimensions (Table 1) were refined from powder data collected using Cu $K\alpha$ radiation with a Philips X-ray Diffractometer, Type PW 1050/1, calibrated against a silicon standard.

We are indebted to Mr G. G. Brebner and Dr F. E. Tocher of the Geology Department, Aberdeen University, who analysed GX1 with a Cambridge Geoscan Electron-Probe X-Ray Microanalyser and obtained the following result:

Experimental % Mn = 63·2

(Theoretical % Mn = 62·5).

This shows that no other metallic element could have been present as a contaminant in more than trace amounts.

Results

The unit-cell contains 4[MnOOH], so that all the atoms must lie on special positions. The structure proposed by Collin & Lipscomb places all atoms on the mirror plane with coordinates $(x, y, \frac{1}{4})$. Their parameters (Table 2) were taken as a starting point for a least-squares refinement (diagonal block approximation) using a procedure similar to that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). With the data from GX2, the initial R factor of 0·26 reduced to 0·027 after 5 cycles with isotropic temperature factors. The final structure factors are given in Table 3. No significant improvement was obtained by using anisotropic temperature factors. In the final cycle, the maximum shift in atomic coordinates was a half of the e.s.d. and the average shift 0·14 of the average e.s.d. The structure was therefore refined as far as the data would allow. The final parameters are given in Table 2.

Table 2. *Comparison of atomic parameters*

	Collin & Lipscomb Positional parameters		Present investigation Positional parameters (e.s.d. × 10⁴ in brackets)		Present investigation Isotropic temperature factor, U* (e.s.d. × 10⁴ in brackets)
	x	y	x	y	
Mn³⁺	−0·036	0·140	−0·0501 (2)	0·1401 (2)	0·0047 (1) Å²
O²⁻(1)	0·27	−0·20	0·2987 (8)	−0·1868 (8)	0·0038 (4)
O²⁻(2)	−0·21	−0·05	−0·1945 (8)	−0·0697 (8)	0·0044 (5)

$$* \quad U = B/8\pi^2$$

Table 3. *Observed and calculated structure factors for groutite, α-MnOOH*

The data from GX1 proved to be suffering badly from absorption and extinction, and the crystal had been used for analysis before correction factors could be estimated. Nevertheless, the positional parameters obtained after eliminating the four most badly affected planes from the calculation were not significantly different from those from GX2, although the R value was much higher (0·13) and the temperature factors were seriously affected.

Three-dimensional Fourier and difference syntheses were calculated from the data for GX2 to confirm the structure. The difference map showed no pronounced features.

Discussion

The oxygen atoms form distorted octahedra around the manganese atoms. In these octahedra, which share edges to form double strings parallel to c (Fig. 1), four of the bonds (Fig. 1, vectors B and C) forming a rough square about the manganese atom are considerably shorter than the other two [Fig. 1, vectors A and D; Table 4(a)]. This distortion is attributable to the Jahn–

Table 4

(a) Metal–oxygen bond distances (Å)

	Vector	Diaspore	Montroseite	Goethite	Manganite	Groutite
M–O(1)	A	1·858	1·94	1·89	2·199	2·178
M–(O1′)	B	1·851	1·96	2·02	$\left\{\begin{array}{c}1·878\\1·868\end{array}\right.$	1·896
M–O(2)	D	1·980	2·10	2·05	2·333	2·340
M–O(2′)	C	1·975	2·10	2·12	$\left\{\begin{array}{c}1·981\\1·965\end{array}\right.$	1·968
Approximate overall s.d.		±0·003	±0·017		±0·02	±0·003
	D–A	0·122	0·16	0·16	0·134	0·162
	C–B	0·124	0·14	0·10	0·10 (mean)	0·072

(b) Oxygen–oxygen bond distances in groutite

	Vector	
O(1) –O(2′)	E	2·97 Å
O(1′)–O(2′)	F	2·57₅
O(1′)–O(2)	G	3·13
O(1′)–O(1)	H	3·01₄
O(2) –O(2′)	J	2·72₆
O(1′)–O(2′)	(hydrogen bond)	2·62₆

(c) Bond angles in groutite

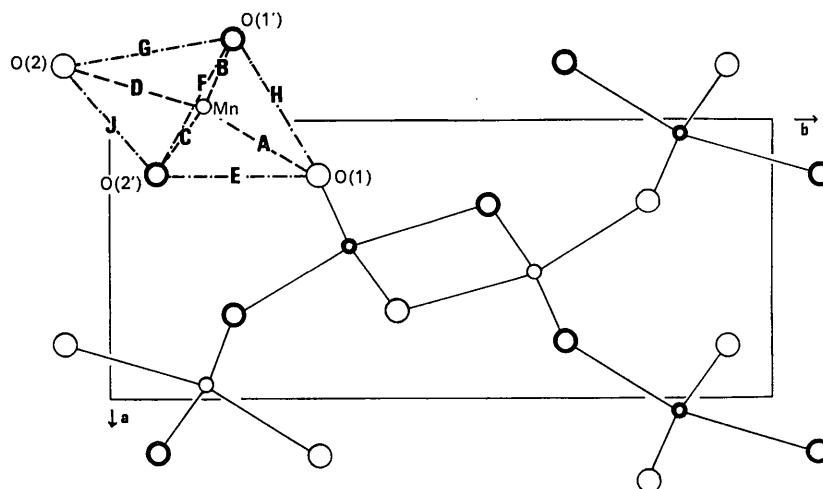| Vectors		Vectors	
A ∧ B	95·2°	B ∧ C	83·6
B ∧ D	94·8₅	B ∧ B	98·4°
D ∧ C	78·0	C ∧ C	93·6°
C ∧ A	91·6		

Fig. 1. Interatomic distance vectors in groutite (see Table 4). Large circles: oxygen; small circles: manganese; thin circles at height $z=\frac{1}{4}$; thick circles at height $z=\frac{3}{4}$.

Teller effect. Superimposed on this are smaller differences within the two groups, between Mn–O(1) and Mn–O(2).

It is interesting to compare the metal–oxygen bond lengths in groutite with those in the isostructural compounds diaspore (α-AlOOH), montroseite (VOOH) and goethite (α-FeOOH) and with those in manganite (γ-MnOOH), which has a different but related structure. Table 4(a) lists corresponding bond lengths for all five compounds.

Busing & Levy (1958) used neutron diffraction to place the hydrogen atoms in diaspore and found that O(2) was the oxygen atom of the hydroxyl group. In this case one would not expect to detect the Jahn–Teller effect, and the only major differences in bond lengths correspond to the difference between M–O and M–OH. Evans & Mrose (1955) did not attempt to distinguish OH from O in montroseite, but it is apparent that here too the hydrogen atom could be assigned to O(2). The much older data for goethite (Hoppe, 1941) show a similar trend. The structure of manganite was also investigated by neutron diffraction (Dachs, 1963) which established that the hydrogen was attached to the atom here called O(2). The relatively large error in those results reflects the difficulty of obtaining reliable intensity data from manganite, which exhibits pseudosymmetry, superstructure, and twinning. The bond lengths for manganite and groutite nevertheless correspond very closely. It therefore seems reasonable to assume that O(2) is the hydroxyl oxygen atom in groutite also.

Quite apart from the assignment of the hydrogen atom, the environments of O(1) and O(2) are different. O(1) is surrounded by three Mn atoms in a roughly coplanar triangle; it forms part of an edge between adjacent octahedra in a column parallel to c, and also one corner of a third octahedron. O(2) forms part of the edge just mentioned, and in addition belongs to two other edges shared between octahedra in adjacent columns; it forms the apex of a trigonal pyramid whose base consists of three manganese atoms. Octahedra tend to distort in such a way that the distance between metal atoms adjacent to shared edges increases [see

Table 4(b) and (c)]; thus the difference in environment alone might increase M–O(2) relative to M–O(1).

From this point of view it would be interesting to compare bond lengths with those in the isostructural γ-MnO₂, ramsdellite, in which differences in Mn–O lengths cannot be caused by the attachment of hydrogen atoms. Two structural studies of γ-MnO₂ have been reported. Byström (1949) found Mn–O bond lengths varying from 1·86 to 1·92 Å, but with no correlation between long bond lengths and Mn–O(2). Kondrashev & Zaslavskii (1951) appear to find such a correlation, but do not give sufficient experimental details to enable its significance to be assessed.

In any case, O(2) would be favoured for the OH group. Busing & Levy (1958) pointed out that in diaspore the hydrogen atom attached to O(2) does not need to approach the positively charged metal ions so closely as it would if attached to O(1); furthermore it completes a tetrahedral environment for O(2).

The distance O(1)–O(2) between adjacent octahedra, which is assumed to be a hydrogen bond, is 2·626 Å. This agrees well with the values found for the isostructural compounds and for manganite.

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