

Site occupancy refinement of osumilite

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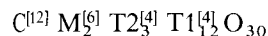
Crystal structure / Osumilite

Abstract. The structure of osumilite from Nain, Labrador, $(\text{Na}_{0.14}\text{K}_{0.86})^{[12]}(\text{Mg}_{1.44}\text{Fe}_{0.56})^{[6]}(\text{Mg}_{0.23}\text{Fe}_{0.16}\text{Al}_{2.61})^{[4]}(\text{Si}_{10.36}\text{Al}_{1.64})^{[4]}\text{O}_{30}$ is hexagonal with space group $P6/mcc$, $a_0 = 10.126(2)$, $c_0 = 14.319(3)$ Å, $Z = 2$ and $D_x = 2.63$ g/cm³, and was refined to R (unweighted) = 0.033 and R (weighted) = 0.026 using 590 nonequivalent reflections.

The basic structure determined by Brown and Gibbs (1969) was confirmed. It was shown, however, that part of both Fe^{2+} and Mg^{2+} enter the T2 position (T2–O distance 1.772 Å) and are not strongly fractionated between this and the octahedral M position (M–O distance 2.135 Å). No other site contains Mg^{2+} or Fe^{2+} in this osumilite.

1. Introduction

The crystallochemical formula of osumilite may, according to the structure determination by Brown and Gibbs (1969) and the survey of the crystal chemistry of milarite-type minerals by Forbes et al. (1972), be written as



where C is mainly occupied by Na^+ and K^+ , M by Mg^{2+} and Fe^{2+} , T2 by Al^{3+} and Fe^{3+} , and T1 by Si^{4+} and Al^{3+} .

The basic structure determined by Brown and Gibbs (1969) and confirmed in the present study is depicted in Figure 1. The tetrahedra around the T positions build a three-dimensional framework, where the T1 constitute hexagonal double rings interconnected by the T2 tetrahedra and additionally linked by the M octahedra. The C positions are situated between the stacks of hexagonal double rings. Forbes et al. (1972) list further potential cation sites.

A number of osumilite analyses determined since then [cf. compilations in Berg and Wheeler (1976), and Maijer et al. (1977)] can be fitted to the above

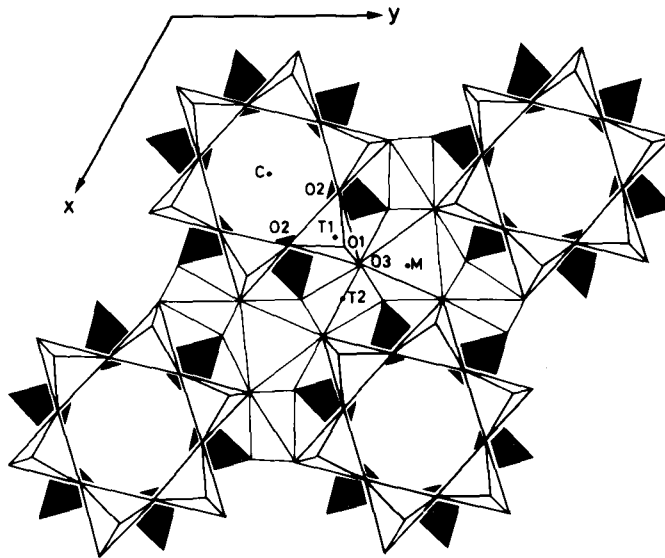


Fig. 1. Projection of the osumilite structure along [001]

formula only if some of the divalent cations are assigned to the T2 position, because these analyses show less than 15 ($\text{Si}^{4+} + \text{Al}^{3+} + \text{Fe}^{3+}$) and more than 2 ($\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Mn}^{2+}$) per formula unit. This assignment might be considered feasible because in the minerals of the roedderite group, which show close structural similarities with osumilite, the T2 position is largely or exclusively filled by Mg (Khan et al., 1972). If this is correct, osumilite may show a temperature-dependent $\text{Mg}^{2+} - \text{Fe}^{2+}$ exchange equilibrium between tetrahedral and octahedral sites. This distribution can, however, not be extracted from the crystal structure analyses available so far, because the site occupancies have not been refined yet, and the interpretation of the Mössbauer spectra is ambiguous (see below).

On the basis of optical absorption studies and structural analogies to cordierite Goldman and Rossman (1978) seriously questioned the above relationships. According to them, the T2 position contains trivalent cations only and is only partially occupied. Part of the Fe^{2+} was assigned to the C site. For instance for the Nain osumilite, which has also been studied by us, Goldman and Rossman give a formula $(\text{Na}_{0.10}\text{K}_{0.89}\text{Fe}_{0.37})^{12}(\text{Mg}_{1.43}\text{Fe}_{0.53}\text{Mn}_{0.01})^{6} \text{Al}_{2.66}^{4} \text{Si}_{10.30} \text{Al}_{1.70}^{4} \text{O}_{30}$. The Mössbauer spectra of osumilites also reported by these authors exhibit at least three different doublets due to Fe^{2+} and can thus not easily be reconciled with either of the above structural models because these show only two different positions containing Fe^{2+} . However, next-nearest neighbor interactions may be invoked to explain the spectra.

The aims of the present study were the identification of the Fe-bearing sites, the Mg–Fe distribution and the occupancy of the T2 site.

2. Experimental methods

Chemical analysis. Microprobe analysis of the Nain osumilite supplied by J. Berg and performed on the crystal serving for the structure determination yielded the molecular proportions given in Table 1, on the basis of 30 oxygens. Mössbauer spectra confirmed earlier observations by Goldman and Rossman (1978) that the iron present in this sample is at least 95% ferrous. Compared to the average analysis given by Berg and Wheeler (1976) our sample is slightly higher in Fe. The chemical composition derived from the structure refinement (see below) is also compiled in Table 1.

Data collection and structure refinement. A crystal measuring $0.28 \times 0.16 \times 0.60$ mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and $\theta - 2\theta$ scan ($\theta_{\max} = 30^\circ$). The intensities of 3985 reflections were measured; 2985 of these had $|F_o| \geq 3\sigma(|F_o|)$. Symmetry equivalent intensities were averaged to give 590 unique reflections used for the subsequent refinement. The standard deviations, $\sigma(F_o)$, were estimated using the formula presented by Stout and Jensen (1968).

Lorentz, polarization and absorption corrections (Busing et al., 1957) were applied [$\mu(\text{MoK}\alpha) = 15.6 \text{ cm}^{-1}$]. The structure was refined by full-matrix, least-squares analysis with the program SHELX-76 (Sheldrick, 1976), starting with the atomic coordinates given by Brown and Gibbs (1969). The atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV, 1974, for neutral atoms. Only for K and Na the scattering factors for ions were used. Anisotropic refinement of the crystal structure converged at R (unweighted) = 0.033 and R (weighted) = 0.026 $\{R_{\text{weighted}} = [\sum w (|F_o| - |F_c|)^2]^{1/2} / (\sum w F_o^2)^{1/2}, w = 1/\sigma^2\}$.

The site occupancy refinement was started with mutual release of the site occupation factors, temperature factors and the x, y, z parameters of the O atoms. This provided R (weighted) = 0.0253. For the final refinement the following assumptions have been made: The Si value obtained from the microprobe analysis was assigned to the T1 position and the Al value of the analysis was used to fill the rest of T1 and part of T2. It cannot be expected that Si occupies in part T2 because the angles O3–T2–O3 are distorted and the temperature factor of O3 is too small. The final refinement, therefore, started from the x, y, z parameters, temperature factors and site occupancies for Na, K, Mg and Fe obtained from the initial refinement cycles, whereas Al and Si occupancies in T1 and T2 were taken from and constrained to the values of the analysis. Positional and thermal parameters were also constrained. The calculations converged at R (weighted) = 0.0259.

Table 1. Positional and thermal parameters with standard deviations. The anisotropic temperature factors have the form $T = \exp [-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2} + 2U_{12} hka^*b^* + 2U_{13} hla^*c^* + 2U_{23} klb^*c^*)]$. s.o.f. = site occupation factor = number of atoms per 30 total oxygens

site	x	y	z	s.o.f. micro- probe	s.o.f. X-ray	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C ^{Na} K	0	0	$\frac{1}{4}$	0.13 0.87	0.14(1) 0.86(1)	0.0258(7)	0.0258(7)	0.0287(13)	0	0	0.0129(3)
M ^{Mg} Fe ²⁺	0.3333	0.6667	$\frac{1}{4}$	1.38 0.62	1.44(1) 0.56(1)	0.0048(3)	0.0048(3)	0.0082(7)	0	0	0.0024(2)
T(2) ^{Al} Mg Fe ²⁺	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	2.61 0.24 0.15	2.61 0.23(1) 0.16(1)	0.0093(4)	0.0093(4)	0.0054(7)	0	0	0.0072(4)
T(1) ^{Al} Si	0.2476(1)	0.3522(1)	0.3920(1)	1.64 10.36	1.64 10.36	0.076(13) 0.0050(5)	0.070(13) 0.0070(5)	0.042(13) 0.0036(7)	-0.015(10) 0.0019(5)	-0.005(10) 0.0016(5)	0.031(10) 0.0041(4)
O(1)	0.2841(3)	0.4058(3)	$\frac{1}{2}$	6.0	6.0	0.0258(13)	0.0204(12)	0.0074(13)	0	0	0.0093(10)
O(2)	0.2833(2)	0.2154(2)	0.3684(1)	12.0	12.0	0.0365(11)	0.0294(10)	0.0207(11)	0.0009(8)	0.0032(8)	0.0258(9)
O(3)	0.3532(2)	0.4922(2)	0.3213(1)	12.0	12.0	0.0128(7)	0.0180(8)	0.0128(9)	0.0050(7)	0.0010(6)	0.0070(6)

This minimum for the site occupancies is obviously very well defined: Starting from arbitrary initial site occupancies for Na, K, Mg and Fe (e.g. Na > K in C, Fe > Mg in M and Fe > Mg in T2) led to exactly the same result for the site occupancies of these cations. A list of structure factors may be obtained from the authors upon request.

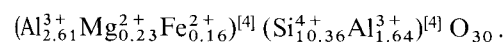
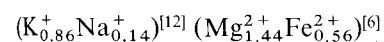
3. Results

The N(Z) test carried out with the MULTAN program system is in agreement with the space group $P6/mcc$ reported for osumilite by Brown and Gibbs (1969). Lattice constants obtained were $a_0 = 10.126(2)$, $c_0 = 14.319(3)$ Å, $Z = 2$. The calculated density ($D_x = 2.63$ g/cm³) agrees well with the range of densities determined by Berg and Wheeler (1976) for osumilites from the same locality (2.62–2.64 g/cm³).

A list of positional and thermal parameters with estimated standard deviations and site occupation factors is given in Table 1. Interatomic distances and angles are compiled in Table 2. Despite the slight differences in chemical composition of the osumilites studied (e.g. absence of ferric iron in the sample studied by us) the general agreement with the values reported by Brown and Gibbs (1969) is excellent.

Both in the present data set and that given by Brown and Gibbs (1969) the temperature factors of the oxygen atoms are anomalously high, in particular those of the O1 and O2 atoms. One might suspect that these values indicate a microtwinning on the scale of the unit cell. Such a hypothesis could then also explain the deviations from uniaxial optical behaviour. However, a high-resolution electron microscope study of the sample by M. Czank did not reveal any indication of microtwinning and the cause for the elevated temperature factors of the oxygens remains, therefore, unknown.

The refinement led to the following structural formula:



The close correspondence between this calculated composition and that determined by probe analysis is evident from Table 1.

It is thus clear that the T2 position contains cations in addition to Al and is not only partly occupied as suggested by Goldman and Rossman (1978). Inspection of the *B* and *D* sites (Forbes et al., 1972), which are potential cation sites, too, indicated no electron density in these sites, and they are obviously not occupied in the structure of osumilite, at least not in the Nain osumilite studied.

Table 2. Interatomic distances (Å) and angles (°)

[T1–O] tetrahedra					
T1–O distances		O–O distances		O–T1–O angles	
T1–O1	1.619(1)	O2–O2	2.594(2)	105.5(3)	
T1–O2	1.626(2)	O2–O3	2.613(2)	106.4(1)	
T1–O2	1.632(2)	O2–O3	2.677(3)	110.5(1)	
T1–O3	1.632(2)	O1–O2	2.677(3)	111.8(1)	
mean	1.627	O1–O3	2.681(2)	111.1(1)	
		O1–O2	2.693(3)	111.2(1)	
		mean	2.656	109.4	
[T2–O] tetrahedra					
T2–O distances		O–O distances		O–T2–O angles	
T2–O3	× 4 1.772(2)	O3–O3	× 2 2.573(3)	× 2	93.1(1)
mean	1.772	O3–O3	× 2 2.897(3)	× 2	109.7(1)
all other ≥	3.110	O3–O3	× 2 3.180(3)	× 2	127.6(1)
		mean	2.883	mean	110.1
[M1–O] octahedra					
M1–O distances		O–O distances		O–M1–O angles	
M1–O3	× 6 2.135(2)	O3–O3	× 3 2.573(3)	× 3	74.1(1)
mean	2.135	O3–O3	× 3 2.979(3)	× 3	88.5(1)
all other ≥	3.839	O3–O3	× 6 3.248(3)	× 6	99.1(1)
		mean	3.012	mean	90.2
[C1–O] polyhedra		T–O–T angles			
C1–O2	× 12 3.099(2)	T1–O3–T2	124.5(1)		
C1–O3	× 12 4.566(2)	T1–O1–T1	145.5(2)		
C1–O1	× 12 5.114(2)	T1–O2–T1	153.6(5)		

An independent check for the incorporation of divalent cations into the T2 site may be obtained by considering the T2–O bond length (Table 2). The value of 1.772(2) Å is higher than that expected for a tetrahedron occupied by Al only (1.756 Å, cf. Brown and Gibbs, 1969), even if the effects of tetrahedral distortion on T–O bond lengths are considered (Cohen et al., 1977), and agrees well with that calculated from ionic radii given by Shannon (1976) for tetrahedral Al³⁺, Mg²⁺ and Fe²⁺ weighted according to the site occupancy determined above (1.769 Å).

No evidence contrary to the assignment of Si to only the ring (T1) site was encountered. In this respect osumilite is analogous to low-cordierite (Hochella et al., 1979) where the tetrahedra interconnecting the six-membered rings contain Al only and Si is confined to the tetrahedra of the rings. On the other hand, no Si – Al order is present within the six-membered double rings of osumilite, whereas low-cordierite exhibits Si – Al order in the ring sites as well.

The distribution of Fe^{2+} and Mg^{2+} over the tetrahedral and octahedral sites deserves an additional comment: Defining a distribution coefficient $K = x_{\text{Mg}}^{[4]} x_{\text{Fe}}^{[6]} / x_{\text{Fe}}^{[4]} x_{\text{Mg}}^{[6]}$, where x_i^n is the molar fraction of the element i on the site n , a value of 0.56 is obtained, i.e. Mg^{2+} and Fe^{2+} are not very strongly fractionated between the octahedral and the tetrahedral T2 position, with ferrous iron showing a slight preference for the tetrahedral relative to the octahedral site. This result is in qualitative agreement with the observation of e.g. Navrotsky and Kleppa (1967) and Reznitskii (1976) that in the spinel structure Mg^{2+} and Fe^{2+} show – within the limits of error – identical site preference energies and do not significantly fractionate between octahedral and tetrahedral sites in these structures. In view of these results we do not expect a strong temperature dependence of the Fe–Mg distribution in osumilite, which might be supported by the only very minor changes in the Mössbauer spectra of heated versus untreated osumilite (Goldman and Rossman, 1978).

4. Summary and Conclusions

The present study has shown that in osumilite part of the Mg^{2+} and Fe^{2+} can enter the T2 position and that these cations are restricted to T2 and M. The assignment given by Goldman and Rossman (1978) for Fe^{2+} can thus not be correct. On the other hand, the model presented here is also consistent with the compositional variation observed in synthetic, Fe-free osumilites. These may show an excess of Mg over the two octahedral sites per formula unit (Olesch and Seifert, 1981). It should be pointed out, however, that the interpretation of the Mössbauer spectra of $^{57}\text{Fe}^{2+}$ in osumilites remains an open question, as well as the deviation from hexagonal symmetry that is manifested in the optical properties of some osumilites (Goldman and Rossman, 1978) and possibly indicated by the high and anisotropic temperature factors of the oxygen atoms according to the present X-ray study.

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