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POSITIONAL DISORDER OF OXYGEN IN GARNET: THE CRYSTAL-STRUCTURE REFINEMENT OF SCHORLOMITE

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ABSTRACT

The structure of a crystal of schorlomite garnet with composition $\{Ca_{2.87}Mg_{0.10}Na_{0.04}\}$ $[Ti_{1.06}Fe^{3+}_{0.63}Al_{0.14}Fe^{2+}_{0.06}Zr_{0.04}Mg_{0.04}Mn_{0.03}V_{0.01}]$ $(Si_{2.35}Fe^{3+}_{0.34}Fe^{2+}_{0.31})O_{12}$, and an a parameter of 12.157(3) Å, has been refined using Mo$K\alpha$ X-ray-diffraction data to an R_w of 0.042. The oxygen atom in the structure is modeled by a split isotropic position, which results from significant occupancy of the tetrahedral site by iron. Lengths of bonds between tetrahedrally coordinated cations and the two oxygen atoms are consistent with silicon-oxygen and iron-oxygen distances observed in other garnet structures.

Keywords: schorlomite, garnet, structure refinement.

SOMMAIRE

Nous avons affiné la structure d'un cristal de schorlomite ayant une composition $\{Ca_{2.87}Mg_{0.10}Na_{0.04}\}$ $[Ti_{1.06}Fe^{3+}_{0.63}Al_{0.14}Fe^{2+}_{0.06}Zr_{0.04}Mg_{0.04}Mn_{0.03}V_{0.01}]$ $(Si_{2.35}Fe^{3+}_{0.34}Fe^{2+}_{0.31})O_{12}$ et un paramètre a de 12.157(3) Å, par diffraction X en utilisant un rayonnement Mo$K\alpha$, et ce, jusqu'à un résidu R_w de 0.042. Les sites occupés par l'oxygène dans cette structure ont été simulés par une position isotrope à deux sous-sites, qui découle du fait que le site à coordinence tétraédrique contient une fraction importante de fer. La longueur des liaisons entre les cations à coordinence tétraédrique et les deux atomes d'oxygène concordent avec les distances Si–O et Fe–O observées dans la structure d'autres grenats.

(Traduit par la Rédaction)

Mots-clés: schorlomite, grenat, affinement de la structure.

INTRODUCTION

Schorlomite is a species of silicate garnet containing more than one atom of titanium per formula unit (>15 wt.% TiO_2) (Deer *et al.* 1982). Schorlomite forms a solid-solution series with andradite; titanian andradite is commonly given the varietal name "melanite". The structural role of iron and titanium in Ti-rich garnet is complex because the tetrahedral site is usually deficient in silicon. Several investigators have examined the site occupancies of Fe and Ti in the schorlomite structure using Mössbauer spectroscopy (Dowty 1971, Huggins *et al.* 1977a, b, Koritnig *et al.* 1978, Schwartz *et al.* 1980, Wu & Mu 1986, Kühberger *et al.* 1989). Schorlomite crystallizes with the garnet structure (space group $Ia3d$) and has the general formula $\{X_3\}[Y_2](Z_3)O_{12}$. The X cation site is eight-coordinated, the Y cation site is six-coordinated, and the Z cation site is four-coordinated (*cf.* review by Novak and Gibbs 1971). In schorlomite, the major atomic species distributed over these cation sites are Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ti^{4+}, Al^{3+} and Si^{4+}. The crystal structure of synthetic and natural schorlomite has been investigated by neutron powder-diffraction (Weber *et al.* 1975) and single-crystal X-ray diffraction (Bi *et al.* 1983), respectively. The purpose of the present study is to re-examine the crystal structure of natural schorlomite by single-crystal X-ray diffraction to help understand the complex chemical substitutions that occur in this mineral.

EXPERIMENTAL METHODS

Sample description

The sample of schorlomite selected is a primary anhedral megacryst approximately 8 cm in diameter, collected from a pegmatitic section of the melteigite

TABLE 1. CHEMICAL COMPOSITION OF SCHORLOMITE FROM THE ICE RIVER COMPLEX*

oxide	wt. %	cation**	atoms
SiO_2	27.42	Si	2.348
TiO_2	16.43	Ti	1.058
ZrO_2	0.93	Zr	0.039
Al_2O_3	1.36	Al	0.137
Fe_2O_3	15.05	Fe^{3+}	0.970
FeO	5.14	Fe^{2+}	0.368
V_2O_3	0.20	V^{3+}	0.014
MnO	0.44	Mn	0.032
MgO	1.06	Mg	0.135
CaO	31.24	Ca	2.866
Na_2O	0.23	Na	0.038
H_2O+	0.04	H_4	0.005
Total	99.54		8.01

*from Locock *et al.* (1995);
**normalized on the basis of 12 oxygen atoms.

unit of the Ice River alkaline intrusive complex, Yoho National Park, British Columbia. This sample was selected for this study on the basis of its chemical homogeneity and lack of zoning (Locock *et al.* 1995). No evidence of optical anisotropy or zoning were observed by transmitted or reflected light microscopy. The chemical composition and formula of this specimen (Table 1) have been reported by Locock *et al.* (1995).

Diffracted X-ray intensities were measured from a 0.10-mm sphere using an Enraf–Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo$K\alpha$ X-radiation. The unit-cell dimension [a 12.157(3) Å] was determined by least-squares fitting of 25 automatically centered reflections in the 2θ scan-range of 24 – 32°. Intensities of three reflections were monitored at one-hour intervals, with variations of less than 2%. A total of 3512 reflections were collected ($0 < 2\theta < 90°$), with index ranges $0 \leq h \leq 13$, $0 \leq k \leq 17$, and $0 \leq l \leq 19$. The data were corrected for Lorentz, polarization, spherical absorption ($\mu R = 4.4$) and background effects, and reduced ($R_{sym} = 4.2\%$) to structure factors: of the 529 unique reflections measured, 197 were classed as observed [$|F| \geq 3\sigma_F$]. Crystallographic calculations were done using XTAL3.0 software (Hall & Stewart 1990) to determine and refine atomic positions and the displacement factors, with the neutral-atom scattering factors of Cromer & Mann (1968). Lists of structure factors for the various models have been deposited with the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

RESULTS

Initially we hoped that we could determine the distribution of cations among the sites within the schorlomite structure by least-squares refinement of site occupancies. As an initial trial, unconstrained refinement of the site occupancies was done assuming that sites are fully occupied and that iron or silicon would occupy the tetrahedral site (Z), iron or titanium would occupy the octahedral site (Y), and calcium or magnesium would occupy the eight-coordinated site (X). This procedure gave results that are inconsistent with the bulk composition of the sample (Table 1) and the site occupancies determined previously by Mössbauer spectroscopy and XANES (Locock *et al.* 1995). Specifically, insufficient Fe was assigned to the Z site and an excess of magnesium was assigned to the X site.

The XANES spectra of this schorlomite (Locock *et al.* 1995) are consistent with tetravalent Ti occupying the octahedral site only. Mössbauer spectra (Locock *et al.* 1995) show that the tetrahedral site is occupied by both Fe^{3+} and Fe^{2+} (in addition to silicon). These observations were incorporated into the structural model as follows: the Z site is completely filled by Si, Fe^{2+} and Fe^{3+} in relative amounts consistent with Mössbauer spectroscopy. The X site contains all the Ca and Na, and sufficient Mg to fill the site. The Y site contains the remaining atomic species, consistent with the chemical composition (Table 1). Refinement of this model, which involved a single oxygen with an anisotropic displacement factor, converged to $R_w = 0.043$. Atomic positions and isotropic displacement factors are given in Table 2.

The displacement factor for oxygen is larger than that observed by Novak & Gibbs (1971) for a wide variety of garnets (Table 2). In addition, the highest thermal motion of the oxygen, when refined with an anisotropic temperature-factor, is closely aligned parallel to the Si–O bond. In most silicates, however, the largest displacements of the oxygen atoms are approximately 90° to the bond direction (Downs *et al.* 1990). Difference-Fourier synthesis shows positive density near the oxygen position. Therefore, instead of a single position for the oxygen, two partially filled oxygen positions were assigned, with the occupancies equal to the amount of silicon and iron predicted to be in the tetrahedral site by Mössbauer spectra. The least-squares refinement converged quickly and resulted in an R_w of 0.042 (17 parameters), which is an improve-

TABLE 2. ATOMIC COORDINATES, DISPLACEMENT FACTORS[a] AND BOND LENGTHS (Å)

	model 1	model 2		model 1	model 2
O1–x	0.0368(4)	0.0406(7)	Z–U (iso)	0.012(1)	0.013(1)
y	0.0488(4)	0.0479(8)	U11	0.014(3)	0.017(3)
z	0.6528(4)	0.6556(8)	U22	0.011(2)	0.010(2)
U(iso)	0.011(2)	0.006(2)			
			Y– U(iso)	0.0070(3)	0.0071(3)
O2–x		0.521(3)	U11	0.0070(4)	0.0071(4)
y		0.448(3)	U12	0.001(1)	0.001(1)
z		0.360(3)			
U(iso)		0.006(7)	X–U(iso)	0.0061(9)	0.0058(8)
			U11	0.003(2)	0.000(2)
U11	0.016(3)		U22	0.008(1)	0.009(1)
U22	0.006(3)		U23	0.006(2)	0.006(2)
U33	0.012(3)				
U12	−0.003(2)				
U13	0.009(2)				
U23	−0.002(2)				

	model 1	model 2	andradite[b]		model 1	model 2	andradite[b]
O1–Z	1.703(5)	1.646(9)	1.643	O1–X	2.370(5)	2.388(9)	2.366
O2–Z		1.94(3)		O1–X^1	2.510(5)	2.534(9)	2.500
				O2–X		2.31(3)	
O1–Y	2.000(5)	2.04(1)	2.024	O2–X^1		2.43(3)	
O2–Y		1.84(3)					

[a] The form of the displacement factor is $\exp[-2\pi^2[U(1,1)h^2a^{*2} + U(2,2)k^2b^{*2} + U(3,3)l^2c^{*2} + 2U(1,2)hka^*b^* + 2U(1,3)hla^*c^* + 2U(2,3)klb^*c^*]]$.

[b] Novak & Gibbs (1971).

ment over a model with a single isotropic oxygen atom (R_w = 0.045, 13 parameters). The resulting magnitudes of the isotropic displacement factors are similar to those in other garnet structures (Table 2), with the notable exception that the displacement factor for the tetrahedrally coordinated cation is larger than that for the other cations in the structure. This observation is contrary to what is observed in most natural garnets, in which the tetrahedrally coordinated cation exhibits the lowest displacement-factor (Novak & Gibbs 1971). Attempts to refine the occupancies at the metal sites with this split-oxygen model did not converge owing to high correlation between cation site-occupancies and oxygen displacement-factors. Therefore, it is not possible to exclude the possibility that Al may occupy the *Z* site, based on the X-ray data presented here.

DISCUSSION

A split oxygen model is supported by the observed bond-lengths to the *Z* cation, which are 1.646(9) Å and 1.94(3) Å. These values are close to predicted Si–O bond lengths of 1.64 Å for *d*(Si–O) and 1.87 Å for *d*(Fe^{3+}–O) using the radii from Shannon (1976) and assuming a radius for a four-coordinated oxygen of 1.38 Å. The *Z*–O distance of 1.94(3) Å is similar to that observed for ten synthetic rare-earth iron garnets, 1.871 Å, that have only Fe^{3+} in the tetrahedral site (Hawthorne 1981). The occurrence of Fe^{2+} at the *Z* site will further increase the *Z*–O distance. The O2–O1–*T* angle is 165(6)°, indicating that (1) there is very little relative rotation of the tetrahedra when either O1 or O2 form the coordination and (2) the O1–O2 vector is aligned closely with the shared edge between the *X* and *Y* site. The largest values in the difference-Fourier map occur near the *Z* site. There is a maximum of 4 $e/Å^3$ at the site, and several minima of −2 $e/Å^3$ within 0.3 Å of the site. It is probable, given the observed split-oxygen position, that the difference density at the *Z* site is the result of the displacement of the tetrahedrally coordinated cation from the 24*d* position.

In this sample of schorlomite, the *X* site is almost completely filled with calcium, so the contents of the *X* site do not vary appreciably among unit cells. The *Y* site contains predominantly titanium, ferric and ferrous iron and aluminum. The bond lengths from O2 to the *Y* site and the *X* site are, as expected, shorter than in the single-oxygen model. However, the *Y*–O2 bond shows a shortening of 8%, which is considerably greater than the percentage shortening of the other bonds. This bond is 1.84(3) Å, which is too short for a

TABLE 3. COMPARISON OF POLYHEDRAL VOLUME, QUADRATIC ELONGATION AND ANGLE VARIANCE[a] OF MODEL 1 AND MODEL 2

		MODEL 1	MODEL 2	
		0 atoms	01 atoms	02 atoms
Polyhedral volume	Z-site	2.496(9)	2.27(1)	3.67(7)
	Y-site	10.68(3)	11.30(4)	8.1(1)
	X-site	24.87(5)	25.44(9)	22.4(3)
Quadratic elongation	Z-site	1.009	1.007	1.017
	Y-site	1.000	1.000	1.019
	X-site	---	---	---
Angle variance	Z-site	35.73	26.95	70.53
	Y-site	0.0138	2.95	74.15
	X-site	---	---	---

[a] Calculated using the Volcal program (Hazen & Finger 1982).

titanium bond. Aluminum and Fe^{3+} could occupy the smaller *Y*-site formed by O2. Substitution of Fe for Si at the tetrahedral site is then coupled with substitution of Al and Fe^{3+} at the *Y* site. Table 3 compares the volumes of the cation sites in the two models. It can be seen that if the oxygen is in the O2 position, the volume of the tetrahedral site is much larger and the octahedral site is much smaller relative to the case where the oxygen occupies the O1 position. It is not unreasonable to propose local order such that a relatively large low-valence cation at the *Z* site is associated with a smaller high-valence cation at the *Y* site. This atomic substitution results in a lowering of the symmetry within the unit cell, and if these displacements were correlated among unit cells, the garnet would no longer exhibit cubic symmetry. Koritnig *et al.* (1978) reported X-ray-diffraction peaks from a sample of schorlomite from the Harz Mountains, Germany, that show a splitting inconsistent with cubic symmetry. Guinier films (Cu radiation) of the schorlomite studied here show no such splitting.

The structure refinement of schorlomite reported by Bi *et al.* (1983) also showed that the oxygen atom has the largest and most anisotropic displacement of the atomic positions. Unfortunately, they also calculated negative displacement factors for silicon, so that a detailed comparison is not possible. In their powder neutron-diffraction study, Weber *et al.* (1975) did not determine individual atomic displacement-factors, but they did observe a Z–O distance of 1.74 Å for a single oxygen model.

CONCLUSIONS

Oxygen is disordered over two positions in this sample of schorlomite. This disorder is the result of occupancy of the *Z* site by cations of very different radii. This pattern of occupancy results in well-separated sites for oxygen that can be distinguished by X-ray diffraction.

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