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HYDROGEN-ATOM POSITIONS IN *P4/nnc* VESUVIANITE

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ABSTRACT

The crystal structure of a large crystal (11.0 × 7.8 × 4.7 mm) of gem-quality Fe-bearing vesuvianite [*a* 15.533 (11), *c* 11.785(16) Å, *V* 2843(5) Å^3; ε 1.713(5), ω 1.710(5), 2*V* 0°(5); D 3.43 g cm^{-3}; 3.68 wt% FeO] from Kenya has been refined at 298 K by single-crystal neutron-diffraction methods to a weighted *R* value of 3.9% for 1448 unique Bragg reflections. No violations of *P4/nnc* space-group symmetry were observed on examination of the crystal by time-of-flight neutron methods. The protons are associated with oxygen atoms O(11) [H(1) 0.4592(7), 0.4814(9), 0.3083(8)] and O(10) [H(2) 0.25, 0.25, 0.280(10)], as predicted by bond-valence calculations. Difference-Fourier maps show a double minimum between adjacent O(10) atoms along *c*, indicating a statistical distribution of H(2) between two sites. The partial occupancy of the H(1) site (85%) is consistent with the substitution of fluorine for oxygen at the O(11) site. Although hydrogrossular and vesuvianite have similar structures and occur in many of the same environments, the neutron-diffraction results rule out the possibility of a hydrogarnet-type substitution [$(O_4H_4)^{4-}$ = $(SiO_4)^{4-}$] in this specimen. Its infrared spectrum (6500–7500 cm^{-1}) most closely resembles that of intermediate-fluorine, boron-poor vesuvianite.

Keywords: vesuvianite, crystal-structure refinement, neutron diffraction, hydrogen atoms.

SOMMAIRE

Nous avons affiné la structure d'un cristal unique de taille (11.0 × 7.8 × 4.7 mm) de vésuvianite gemme contenant du fer [*a* 15.533 (11), *c* 11.785(16) Å, *V* 2843(5) Å^3; ε 1.713(5), ω 1.710(5), 2*V* 0°(5); D 3.43 mg m^{-3}; 3.68 wt% FeO], provenant du Kenya. L'expérience de diffraction neutronique, effectuée à 298 K, a mené à un résidu pondéré de 3.98% en utilisant 1448 réflexions de Bragg uniques. Nous n'avons décelé aucune violation du groupe spatial *P4/nnc* à l'examen du cristal par la méthode du temps d'envol des neutrons. Les protons sont associés aux atomes d'oxygène O(11) [H(1) 0.4592(7), 0.4814(9), 0.3083(8)] et O(10) [H(2) 0.25, 0.25, 0.280(10)], comme le prédisent les valences de liaison calculées. Des projections par différence de Fourier montrent un minimum dédoublé entre atomes O(10) adjacents le long de *c*, indication d'une distribution statistique de H(2) entre deux sites. Le taux d'occupation du site H(1), 85%, concorde avec l'incorporation de fluor à la place de l'oxygène au site O(11). Quoique l'hydrogrossulaire et la vésuvianite possèdent des structures semblables et partagent certains milieux de croissance, les résultats de diffraction neutronique écartent la possibilité d'une substitution [$(O_4H_4)^{4-}$ = $(SiO_4)^{4-}$] comme on en

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trouve dans l'hydrogrenat. Le spectre d'absorption infrarouge dans l'intervalle 6500–7500 cm^{-1} est typique d'échantillons à teneurs intermédiaire en fluor et faible en bore.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, affinement de la structure cristalline, diffraction neutronique, atomes d'hydrogène.

INTRODUCTION

Although an extensive amount of work has been devoted to the crystal chemistry of vesuvianite (reviewed in Groat *et al.* 1992a), the precise location of the H atoms in high-symmetry (*P4/nnc*), boron-poor samples remains unknown. Recently, Groat *et al.* (1996) and Pavese *et al.* (1998) have determined the H position(s) in samples of high-symmetry, boron-rich vesuvianite and low-symmetry (*P4/n*), boron-poor vesuvianite, respectively. On the basis of bond-valence calculations, a number of investigators (*e.g.*, Yoshiasa & Matsumoto 1986) have proposed the existence of two types of hydroxyl groups in high-symmetry, boron-poor vesuvianite, but to date there has been no experimental confirmation of this result. In our quest for samples of garnet with high OH contents, we obtained a large, faceted gemstone that had been initially identified as hydrogrossular. The size of the crystal (11 × 8 × 5 mm) prevented preliminary characterization by X-ray diffraction, and the fact that the crystal was on loan meant that it could not be altered in any way. However, the unit cell determined from least-squares refinement of neutron data indicated that the crystal consists of vesuvianite rather than hydrogarnet. A decision was made to collect intensity data because the similarity of the FTIR spectrum to hydrogrossular suggested that a detailed analysis of the vesuvianite structure might provide information on the nature of the OH substitution in garnet. Although subsequent determination of the Si- and H-site occupancies confirmed that H is not incorporated in this particular specimen of vesuvianite *via* a hydrogarnet-type substitution [$(O_4H_4)^{4-} = (SiO_4)^{4-}$], the results of the refinement are reported here because of possible interest in the H-atom positions.

EXPERIMENTAL

The crystal of vesuvianite used for this study was obtained from the Gemological Institute of America (GIA sample no. 11631). It is an optically clear, birefringent, yellowish brown, faceted gemstone from an unspecified locality. On the basis of discussions with gemstone miners who viewed the stone, we conclude that it probably comes from a skarn deposit in crystalline limestone south of Bissel in the Kallad–Namanga area of Kenya, as described in Keller (1992). Pertinent chemical and crystallographic data are given in Table 1. Indices of refraction and optic axial angle (2*V*) were determined using a spindle stage modified to accept large crystals. Sharp extinction was observed, with no evidence of twinning. On the basis of optic sign, unit-cell parameters and chemical composition, the sample consists of boron-poor vesuvianite (Groat *et al.* 1992a).

Single-crystal neutron-diffraction data were collected at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and at the University of Missouri Research Reactor Facility (MURR). The space group was confirmed using the time-of-flight Laue technique at IPNS. A number of lattice planes were sampled in a solid volume of reciprocal space to determine the extinction conditions. No violations of space-group symmetry *P4/nnc* were observed. Ordering of atoms along the 4-fold axis has been shown to reduce the symmetry to *P4/n* (Giuseppetti & Mazzi 1983, Fitzgerald *et al.* 1986, Pavese *et al.* 1998). Intensity data were collected at 295 K at MURR using diffractometer 2XE. The unit-cell parameters were determined from least-squares refinement of 20 automatically centered reflections. Data-collection parameters are given in Table 1. Peak profiles were reduced to integrated intensities using the algorithm of Lehmann & Larsen (1974). The linear absorption coefficient (Table 1) was calculated using coherent and incoherent cross-sections taken from Bacon (1975).

Least-squares refinements were carried out using a modified version of ORFLS (Busing *et al.* 1962) and coherent neutron-scattering lengths from Koester (1977). Starting values for the positional parameters of

TABLE 1. MISCELLANEOUS INFORMATION FOR VESUVIANITE FROM KENYA

a (Å)	15.533(11)	MgO	3.85 wt.%	Mg	2.74 *apfu*
c	11.785(16)	Al_2O_3	15.55	Al	8.75
V ($Å^3$)	2837(5)	SiO_2	38.07	Si	18.19
Z	2	CaO	36.49	Ca	18.68
Space group	*P4/nnc*	TiO_2	0.44	Ti	0.16
Mass (g)	0.420	MnO	0.03	Mn	0.01
Volume (cm^{-3})	0.123	FeO	3.68	Fe^{2+}	1.47
D_m (g cm^{-3})	3.43	F	0.83	F	1.25
D_c	3.41	Total	98.99		
ϵ	1.713(5)	–(O=F)	–0.35		
ω	1.710(5)				
Optic axial angle (°)	0(5)				
Crystal size (mm)	11.0 × 7.8 × 4.7				

μ (cm^{-1})	0.63	Number of reflections based on pre-scan intensity check	5985
Range in transmission coefficient	0.62–0.87	Number of unique reflections after averaging, $\lvert F_o \rvert \geq 2.5\sigma \lvert F_o \rvert$	1448
λ (Å)	1.068	Maximum θ (°)	35
Scan mode	θ	R_{int} (%)	4.5
Step size (°)	0.1	wR (%)	3.9

TABLE 2. POSITIONAL PARAMETERS AND MUTIPLICITIES OF ATOMS, KENYA VESUVIANITE

Atom	Multiplicity	*x*	*y*	*z*
X(1)	2	–0.25	0.25	0.25
X(2)	8	–0.18912(16)	0.04467(16)	0.37925(24)
X(3)	8	–0.10081(18)	–0.18092(18)	0.88893(28)
X(4)	1.06 Ca	–0.25	–0.25	0.14809(94)
Y(1)	0.33 Fe + 0.67 Mg	–0.25	–0.25	0.03866(72)
Y(2)	4	0.0	0.0	0.0
Y(3)	2.04 Mg + 4.82 Al + 1.12 Fe + 0.16 Ti	–0.11277(16)	0.1213(16)	0.12610(24)
Z(1)	2	–0.25	0.25	0.0
Z(2)	8	–0.18061(19)	0.04075(18)	0.87166(27)
Z(3)	8	–0.08374(18)	–0.15045(18)	0.36392(26)
O(1)	8	–0.22076(13)	0.17280(13)	0.08532(18)
O(2)	8	–0.11709(13)	0.16033(14)	0.28020(18)
O(3)	8	–0.04733(13)	0.22270(13)	0.07472(19)
O(4)	8	–0.06106(13)	0.10596(13)	0.46961(17)
O(5)	8	–0.17072(14)	0.01384(14)	0.17913(19)
O(6)	8	–0.12029(15)	–0.27291(14)	0.05820(20)
O(7)	8	0.05582(14)	0.17305(15)	0.32111(20)
O(8)	8	–0.06069(13)	–0.09109(13)	0.06732(19)
O(9)	4	–0.14504(26)	–0.14504	0.25
O(10)	2	–0.25	–0.25	0.86539(55)
O(11)	6.56 O + 1.44 F*	–0.00309(15)	0.06136(15)	0.13598(20)
H(1)	6.56	0.45923(72)	0.48144(94)	0.30831(81)
H(2)	1	0.25	0.25	0.28069(966)

* F based on multiplicity of H(1) atom.

TABLE 3. ANISOTROPIC AND EQUIVALENT ISOTROPIC DISPLACEMENT FACTORS $(\times 10^4)$ OF THE KENYA VESUVIANITE

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
X(1)	160(12)	76(12)	186(21)	0	0	0	141(15)
X(2)	92(6)	81(6)	194(10)	10(4)	–14(5)	–4(6)	122(6)
X(3)	123(6)	116(6)	436(14)	42(5)	–77(7)	–57(7)	225(8)
X(4)	160(34)	160	320(57)	0	0	0	213(30)
Y(1)	44(25)	44	353(43)	0	0	0	147(23)
Y(2)	34(10)	37(10)	139(17)	17(2)	7(11)	29(11)	70(10)
Y(3)	54(6)	48(6)	160(10)	2(4)	0(6)	–8(6)	87(6)
Z(1)	49(14)	49	50(22)	0	0	0	49(12)
Z(2)	53(6)	37(6)	143(10)	–1(4)	7(7)	10(6)	78(7)
Z(3)	73(7)	39(6)	149(11)	11(5)	29(7)	–9(7)	87(7)
O(1)	97(5)	42(4)	151(8)	6(3)	–6(5)	10(5)	97(5)
O(2)	60(5)	78(5)	166(8)	–11(4)	–30(5)	1(5)	101(5)
O(3)	66(5)	37(5)	177(8)	4(3)	–8(5)	–19(5)	93(5)
O(4)	72(5)	37(4)	171(8)	7(4)	–20(5)	7(5)	93(5)
O(5)	81(5)	100(9)	193(8)	51(4)	5(5)	–6(5)	125(6)
O(6)	172(5)	66(5)	200(9)	28(4)	30(6)	45(5)	146(6)
O(7)	45(5)	142(5)	210(9)	24(4)	19(5)	–11(5)	132(6)
O(8)	43(5)	57(5)	189(8)	0(3)	28(5)	15(5)	96(5)
O(9)	100(8)	100	159(12)	–56(5)	–14(10)	14	120(9)
O(10)	59(16)	59	385(26)	0	0	0	168(21)
O(11)	64(5)	72(5)	181(8)	–29(4)	21(5)	–38(5)	106(5)
H(1)	1131(36)	2229(62)	606(43)	1281(39)	–302(31)	–632(40)	1322(42)
H(2)	291(47)	291	1914(930)	0	0	0	832(326)

the atoms were taken from Yoshiasa & Matsumoto (1986). The model was significantly improved with the inclusion of an isotropic, secondary extinction parameter ($g = 0.0986$) as a variable in the refinement (Coppens & Hamilton 1970). H-atom positions were located by difference-Fourier methods after convergence of initial refinements with isotropic displacement factors. Negative neutron density between *Y*(1) and O(10) as reported by Pavese *et al.* (1998) for *P4/n* vesuvianite was not observed. Difference-Fourier maps showed a double minimum between adjacent O(10) atoms along *c*, indicating a statistical distribution of H(2) between two sites. Refinement of the occupancy of the H(1) site indicated only partial occupancy (85%), which is consistent with an $OH^- = F^-$ substitution at the O(11) site (Groat *et al.* 1992b). All *Z* sites were found to be fully occupied; therefore, there is no evidence to support a hydrogarnet-type substitution $[(O_4H_4)^{4-} = (SiO_4)^{4-}]$ in this sample. On the basis of refinement of site occupancies, it was also determined that (1) the *X*(4) site is half-occupied by Ca, (2) the majority of Fe occupies the *Y*(3) site, and (3) the *Y*(1) site is only partially occupied by Fe. Site occupancies and positional parameters are given in Table 2. Anisotropic displacement parameters and selected interatomic distances and angles are presented in Tables 3 and 4, respectively. Root-mean-square displacements of atoms located along the 4-fold axes of rotation are tabulated in Table 5. The O(11)–H(1) bond length is unusually short [0.804 (10) Å] and has been corrected for the effect of thermal motion using the riding model (Busing & Levy 1957). Structure factors (Table 6) have been deposited and are available from the Depository of Unpublished Data, Canadian Institute for Science and Technology, National Research Council, Ottawa, Ontario K1A 0S2.

For the electron-microprobe analysis, the table of the faceted gemstone was placed over the bottom side of a brass disk with a 2.5 mm aperture, fastened in place with water-soluble glue, dried and carbon-coated. A small drop of silver was placed at the edge of the aperture to assure positive contact with the carbon coating on the stone. The disk was then mounted in a brass assembly to secure it in the JEOL 733 electron microprobe. Anorthite, fluorophlogopite, and pyrope–almandine garnet were used as standards.

Infrared (IR) spectroscopic measurements were obtained on a Nicolet 60SX FTIR instrument, generally following procedures discussed in Groat *et al.* (1995). The spectra were taken through two facets on opposite sides of the stone, which were oriented to allow light propagation normal to (100). For comparison, spectra were also obtained on a thick slab of sample "GEM" of Groat *et al.* (1995).

DISCUSSION

The Kenyan vesuvianite is chemically and structurally similar to the high-symmetry vesuvianite investigated by Yoshiasa & Matsumoto (1986) from the Nakatatsu mine, Fukui Prefecture, central Japan. However, because X-ray-diffraction methods were used in their study, these authors could not accurately locate the

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) OF KENYA VESUVIANITE

X(1)	–O(1) × 4	2.326(3)	*Y*(1)	–O(6) × 4	2.059(3)
	–O(2) × 4	2.516(3)		–O(10)	2.042(12)
Mean		2.421	Mean		2.056
X(2)	–O(1)	2.469(4)	*Y*(3)	–O(1)	1.919(3)
	–O(2)	2.417(4)		–O(2)	1.916(4)
	–O(3)	2.362(5)		–O(3)	1.969(3)
	–O(4)	2.449(4)		–O(4)	2.071(4)
	–O(5)^{1}	2.424(5)		–O(5)	1.998(4)
	–O(5)^{2}	2.333(4)		–O(11)	1.945(4)
	–O(6)	2.967(4)		–H(1)	2.515(10)
	–O(8)	2.322(4)	Mean *Y*–O		1.970
Mean		2.468			
X(3)	–O(3)	2.429(4)	*Y*(2)	–O(4) × 2	1.933(2)
	–O(6)	2.472(4)		–O(8) × 2	1.876(2)
	–O(7)^{3}	2.575(5)		–O(11) × 2	1.865(3)
	–O(7)^{4}	2.504(4)	*Y*(2)	–H(1)	2.364(9)
	–O(7)^{5}	2.382(4)	Mean *Y*–O		1.891
	–O(8)	2.599(5)			
	–O(10)	2.569(3)	*Z*(1)	–O(1) × 4	1.629(2)
	–O(11)	2.478(4)			
	–O(6)	2.952(4)	*Z*(2)	–O(2)	1.633(4)
Mean		2.551		–O(3)	1.633(4)
				–O(4)	1.666(4)
X(4)	–O(6) × 4	2.304(6)		–O(7)	1.618(4)
	–O(9) × 4	2.600(6)	Mean		1.638
Mean		2.452			
			Z(3)	–O(5)	1.629(4)
X(4)	–*X*(4)	2.403(3)		–O(6)	1.607(4)
X(4)	–*Y*(1)	1.290(3)		–O(8)	1.617(4)
				–O(9)^{a}	1.648(4)
O(10)	–O(10)	2.720(13)	Mean		1.625
O(10)	–H(2)^{6}	0.99(12)			
O(10)	–H(2)^{7}	1.72(11)	H(1)	–H(1)	1.458(18)
O(11)	–H(1)^{8}	0.804(10)	H(2)	–H(2)	0.724(8)
		[1.024(15)]^{b}			
O(7)	–H(1)^{9}	2.416(9)			
O(7)	–H(1)	2.624(11)	O(11)–H(1)–O(7)^{9}		109(1)
O(7)	–O(11)^{10}	2.784(4)	O(11)–H(1)–O(7)^{11}		105(1)
O(7)	–O(11)	2.934(4)			

Note: Numerical superscripts refer to symmetry operations: 1 (*x*, *y*, *z*), 2 (½–*x*, –*z*), 3 (–*x*, –*y*, –*z*), 4 (–*x*, ½+*y*, *z*), 5 (–*y*, –*x*, ½+*z*), 6 (½+*x*, –*y*, *z*), 7 (–*x*, –*y*, –*z* 8 (½–*y*, ½–*x*, *z*), 9 (½–*x*, ½–*y*, *z*), 10 (*y*, *x*, ½–*z*), 11 (½–*y*, ½–*x*, ½–*z*).

[a] bridging oxygen

[b] distance corrected for the effects of thermal motion.

TABLE 5. ROOT-MEAN-SQUARE (RMS) DISPLACEMENTS (Å) OF ATOMS ON THE AXES OF 4-FOLD SYMMETRY

Atom	RMS Displacement along *c*	Atom	RMS Displacement along *c*
Z(1)	0.071 (20)	O(10)	0.196 (9)
X(4)	0.179 (23)	H(2)	0.44 (15)
Y(1)	0.188 (16)		

position of the protons. Our results provide new information on the positions of the H atoms associated with O(11) and O(10) (Table 4, Fig. 1). The O(10) atom lies on the 4-fold rotation axis that passes through the channels in the structure. The H(2) atom is located at a distance of 0.99(12) Å from O(10) and can be bonded to either of the two O(10) atoms located along the channel. Thus there is a statistical distribution of H(2) atoms between the two sites; *i.e.*, the H(2)-atom sites have 50% average occupancy. The length of the O...H bond for O(10) is 1.72 (11) Å, which is similar to that predicted by Coda *et al.* (1970) based on analysis of IR data compiled by Nakamoto *et al.* (1955) for straight O–H...O hydrogen bonds [2.77(1) Å].

The O(11) atom lies on a general position and is bonded to an H(1) atom located at a distance of 1.024(15) Å (bond length corrected for the effects of thermal motion). It should be noted that the uncorrected bond-length observed for O(11)–H(1) is unusually short [0.804(10) Å], and could reflect static or dynamic disorder of the proton, which can lead to an apparent shortening in this distance. Proton disorder would not be unusual in view of the H-bond geometry. The two O(7) atoms are approximately equidistant from H(1) [2.416 (9) and 2.624(11) Å], and are involved in a weak, bifurcated H bond (Fig. 1). Corresponding O(11)–O(7) distances and O(11)–H(1)...O(7) angles are 2.784(4) Å, 109(1)° and 2.934(4) Å, 105(1)°, respectively.

The largest root-mean-square displacement is associated with H(2), which shows a statistical distribution between two sites (Table 5). Without low-temperature data, it is difficult to determine if the displacements observed for the other atoms represent true thermal motion or a disorder similar to that observed for H(2). However, note that in a neutron-diffraction refinement of the boron-enriched vesuvianite structure at 20 K, the O(10) and *Y*(1) displacements are essentially isotropic. The above atoms display very anisotropic behavior in the room-temperature X-ray refinement of the same material (Groat *et al.* 1996).

The mid-infrared spectrum of the Kenyan vesuvianite in the OH overtone region is essentially identical with that of sample "GEM" (Groat *et al.* 1995) (Fig. 2). Additional close similarities in the color, the Raman spectrum and in textures observed in cross-polarized light suggest that they are both from the same locality. The FTIR analysis of sample "GEM" equally applies to the Kenyan vesuvianite of this study. Both are examples of intermediate-fluorine, boron-poor vesuvianite. The dominant OH band at ~6970 cm^{-1} corresponds to the Mg,Al,F local configuration about the OH position at the *Y*(3)–*Y*(2) sites. The two bands at ~7175 and ~7095 cm^{-1} correspond respectively to Mg,Al,OH and Al,Al,OH local units, and the shoulder near 6745 cm^{-1} is attributed to Al,Al,F units. The weaker band near 5900 cm^{-1} is attributed to the OH band perturbed by Fe^{2+} in the *Y*(1) site. Thus all the OH overtones are accounted for, and there is no spectroscopic reason to

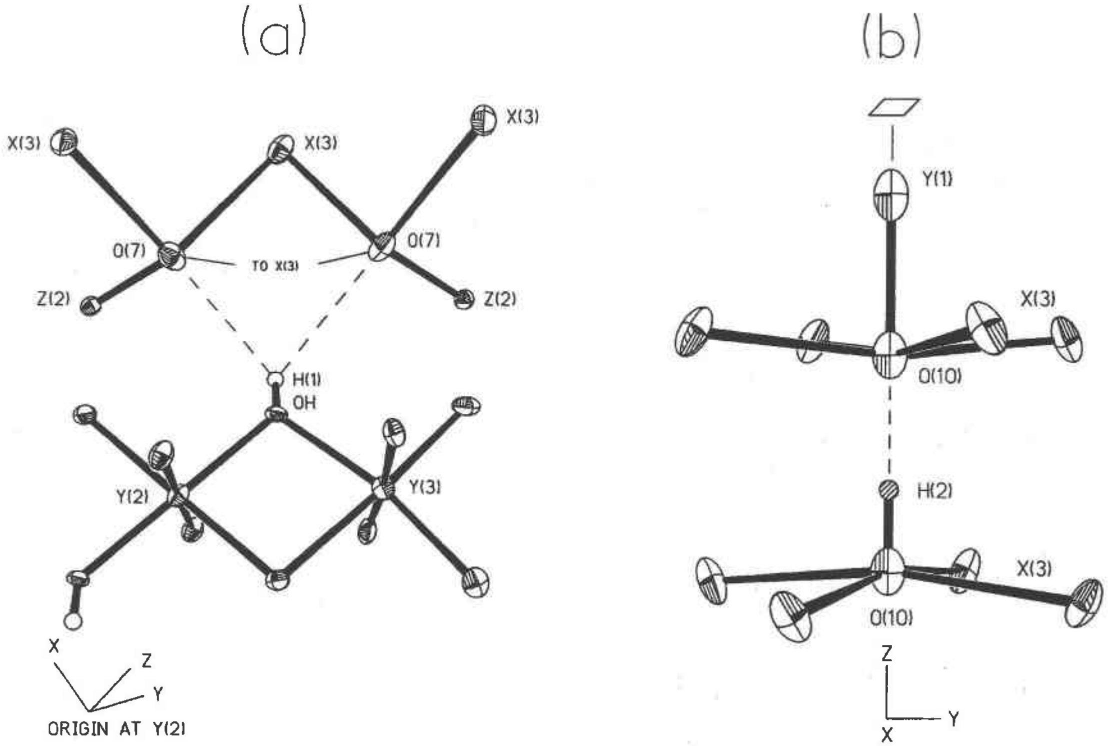

FIG. 1. A drawing of a portion of the structure of vesuvianite showing the local environment of O(11) (= OH) and O(10). Hydrogen bonds are indicated by dashed lines (from Groat *et al.* 1992b).

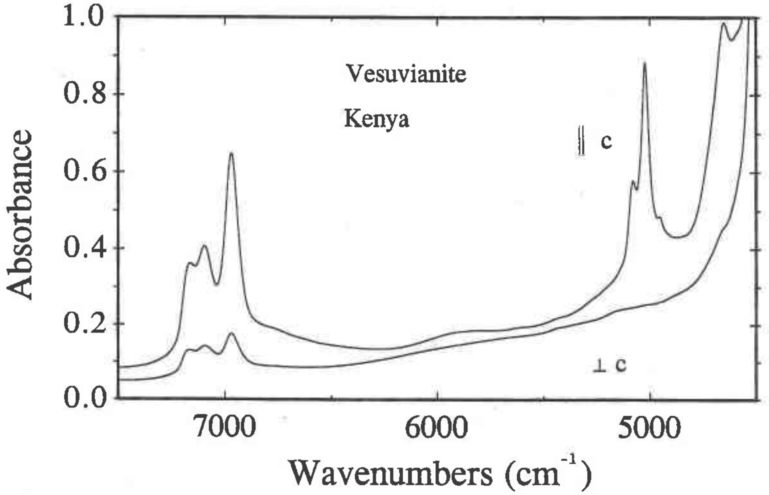

FIG. 2. The near-infrared absorption spectra of the Kenyan vesuvianite. The first overtones of the OH stretching modes are in the 7000 cm^{-1} and 5900 cm^{-1} regions.

invoke the hydrogarnet substitution, in accord with the results of the structure refinement.

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