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THE CRYSTAL CHEMISTRY OF Si $\rightleftharpoons$ Al SUBSTITUTION IN TOURMALINE

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ABSTRACT

The structures of nine gem-quality crystals of V-bearing uvite, $a \approx 15.95$, $c \approx 7.17$ Å, $V \approx 1580$ Å^3, $R3m$, have been refined to R indices of ~2.2% using graphite-monochromated Mo$K\alpha$ X-radiation; the crystals used for the X-ray data collection were analyzed using an electron microprobe. The Si content of these crystals is significantly less than 6 atoms per formula unit; assignment of $^{[4]}$Al sufficient to fill the *Si* site results in a linear relationship between <*Si*–O> and $^{[4]}$Al content. Examination of recent results of structure refinement for tourmaline shows no well-defined relationship between <*Z*–O> and constituent Z-cation radius. Conversely, there is a well-developed linear relationship between <*Y*–O> and constituent *Y*-cation radius. Site-scattering refinement shows F to be strongly to completely ordered at the O(1) site. There is no significant positional disorder at the O(1) or O(2) sites.

Keywords: tourmaline, uvite, crystal-structure refinement, site populations, chemical analysis, Si $\rightleftharpoons$ Al substitution.

SOMMAIRE

Nous avons affiné la structure de neuf cristaux gemmes d'uvite vanadifère, $a \approx 15.95$, $c \approx 7.17$ Å, $V \approx 1580$ Å^3, $R3m$, jusqu'à un résidu R d'environ 2.2% en utilisant un rayonnement X de Mo$K\alpha$ (monochromatisation au graphite). Les cristaux qui ont servi pour la collection des données ont été analysés par la suite avec une microsonde électronique. La teneur en Si de ces cristaux est inférieure à 6 atomes par unité formulaire; l'attribution de $^{[4]}$Al pour remplir le site *Si* mène à une relation linéaire entre <*Si* – O> et la teneur en $^{[4]}$Al. Une étude des résultats d'affinements récents de la structure de la tourmaline démontre l'absence d'une relation bien définie entre <*Z* – O> et le rayon de l'atome qui se trouve dans le site Z. Au contraire, nous trouvons une relation linéaire bien développée entre <*Y* – O> et le rayon de l'ion occupant le site *Y*. Un affinement de la dispersion des rayons X par les divers sites démontre que les atomes F ont une forte tendance à occuper le site O(1). Il n'y a pas de désordre de position important impliquant les sites O(1) et O(2).

(Traduit par la Rédaction)

Mots-clés: tourmaline, uvite, affinement de la structure cristalline, occupation des sites, composition chimique, substitution Si $\rightleftharpoons$ Al.

INTRODUCTION

As part of a general study on the crystal chemistry of tourmaline, here we examine the structural chemistry of uvite. We are attempting to derive relations between mean bond-length and constituent-cation radius for all cation sites in the tourmaline structure (Hawthorne *et al.* 1993, Burns *et al.* 1994). Such relationships will allow derivation of the oxidation states of transition metals and the patterns of cation order in chemically complex tourmalines by a combination of SREF (Structure REFinement) and EMPA (Electron MicroProbe Analysis). Because of the difficulty in establishing these relationships accurately for such complicated minerals as tourmaline, we have begun this work by focusing on Fe-free tourmaline in which there is no ambiguity introduced concerning the valence state of Fe. In this way, we initially dispense with one of the more intractable problems of the crystal chemistry of tourmaline; this can be addressed once we have a better understanding of the crystal chemistry of this group.

EXPERIMENTAL

The crystals used in this work are vanadium-bearing; they were collected in East Africa, and purchased in 1992 from a dealer who was unwilling to give the exact location, merely stating that it was a new find. Nine crystals were selected on the basis of color variation in the material available to us. The color varies through shades of green, and the intensity of the color increases with increasing V content.

TABLE 1. DATA COLLECTION AND REFINEMENT INFORMATION FOR UVITE CRYSTALS

	T72	T73	T74	T75	T76	T77	T78	T79	T80
a(Å)	15.949(1)	15.950(2)	15.940(1)	15.940(1)	15.938(2)	15.959(1)	15.955(1)	15.958(2)	15.957(1)
c(Å)	7.188(1)	7.174(1)	7.177(1)	7.163(1)	7.179(1)	7.175(1)	7.170(1)	7.180(1)	7.175(1)
V(Å^3)	1583.4(3)	1574.6(4)	1579.1(3)	1576.1(3)	1579.2(4)	1582.5(3)	1580.7(3)	1583.3(4)	1582.4(3)
<r>(mm)	0.21	0.19	0.14	0.20	0.19	0.16	0.21	0.22	0.18
R(az.)	2.38	1.34	1.78	1.29	1.51	3.11	1.67	1.44	1.72
R(az.)°	2.36	1.29	1.37	1.23	1.44	2.88	1.47	1.39	1.69
#I	1135	1136	1136	1131	1133	1139	1139	1139	1139
# $\|F_o\| > 5\sigma$	1129	1129	1119	1125	1126	1131	1136	1133	1129
R	2.47	2.18	2.08	1.99	2.17	2.48	2.25	2.02	2.00
wR	3.95	3.84	3.12	3.35	3.65	3.61	3.67	3.28	3.39
GOF*	1.16	1.36	1.15	1.20	1.21	1.20	1.03	1.22	1.32

° denotes corrected for absorption; space group is *R*3*m*, $Z = 3$, radiation/monochrometer is Mo/graphite

* GOF = goodness of fit

Collection of X-ray data

Each of the nine crystals selected for study was ground to an (approximate) sphere and mounted on a Nicolet *R*3*m* automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromatized Mo*K*α X-radiation. The cell dimensions (Table 1) were derived from the setting angles of the twenty-five automatically aligned reflections by least-squares methods. A total of 1101–1128 symmetry-independent reflections was measured for each crystal ($3 \leq 2\theta \leq 60°$), with index ranges $0 \leq h \leq 19$, $0 \leq k \leq 19$, $-11 \leq l \leq 11$; reflections forbidden by the *R*-lattice restriction were not measured. Two standard reflections were measured every 50 reflections; no significant changes in their intensities occurred during data collection. Each data set was corrected for Lorentz, polarization and background effects, and reduced to structure factors. An empirical absorption-correction, based on 36 ψ-scans for each of 11 reflections, was applied to each data set (*R*-azimuthal given in Table 1).

Refinement of the crystal structure

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout. The *R* indices are of the conventional form and are given as percentages.

Each refinement was done in the space group *R*3*m*, the space group of all tourmaline species (Dietrich 1985). Starting atomic positional parameters were those of tsilaisite (Nuber & Schmetzer 1984). The final cycles of refinement included anisotropic displacement-factors, site-scattering parameters for the *X*, *Y* and *Z* sites, an empirical isotropic-extinction correction and a refinable weighting factor g, given by $w = 1/[\sigma^2(F) + \mathrm{abs}(g)F^2]$. Structures were tested for absolute orientation and transformed as appropriate. Final *R*-indices (Table 1) range from 2.0% to 2.5%, and *wR* indices range from 3.1% to 3.9%. Refined positional parameters and equivalent isotropic displacement-factors are given in Table 2, selected interatomic distances in Table 3 and bond angles in Table 4, and refined site-scattering values in Table 5. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Chemical analysis

To ensure good chemical information for the site-population assignment, the single crystals used in the X-ray intensity-data collection were remounted, polished, carbon-coated and analyzed. Electron-microprobe analysis was done on a CAMECA SX–50 microprobe in the wavelength-dispersion mode. Beam conditions for all elements were 15 kV, beam current of 20 nA, and a spot diameter of 1 μm. Counting times for all element peak and background determinations were 20 s and 10 s, respectively. The analytical data were reduced and corrected using the (ϕpz) method (Pouchou & Pichoir 1984, 1985). The crystals were analyzed with the following standards: albite (Na), orthoclase (K), diopside (Ca, Si), fayalite (Fe), spessartine (Mn), olivine (Mg), chromite (Cr), titanite (Ti), VP_2O_7 (V), kyanite (Al) and fluor-riebeckite (F). The chemical data for each crystal are averages of 10 determinations taken uniformly over each crystal.

The analytical data are summarized in Table 6; structural formulae were initially calculated on the basis of 31 anions, assuming stoichiometric amounts of H_2O as OH^- (*i.e.*, OH + F = 4 atoms per formula unit,

TABLE 2. FINAL ATOMIC PARAMETERS FOR UVITE CRYSTALS[+][*]

		T72	T73	T74	T75	T76	T77	T78	T79	T80
X	x	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
	z	0.8408	0.8408	0.8408	0.8408	0.8408	0.8408	0.8408	0.8408	0.8408
	$U_{eq.}$	106(6)	136(7)	137(9)	136(10)	150(11)	136(9)	134(7)	129(7)	137(8)
Y	x	0.06346(3)	0.06326(3)	0.06324(3)	0.06305(4)	0.06302(3)	0.06313(3)	0.06326(3)	0.06327(4)	0.06322(3)
	y	0.93654(3)	0.93674(3)	0.93676(3)	0.93695(4)	0.93698(3)	0.93687(3)	0.93674(3)	0.93673(4)	0.93678(3)
	z	0.4401(3)	0.4384(3)	0.4388(4)	0.4356(5)	0.4376(4)	0.4366(4)	0.4372(3)	0.4369(3)	0.4375(4)
	$U_{eq.}$	59(3)	59(3)	66(3)	68(3)	63(3)	60(3)	52(3)	58(4)	62(3)
Z	x	0.26171(4)	0.26165(5)	0.26165(5)	0.26155(5)	0.26160(4)	0.26166(5)	0.26156(4)	0.26165(3)	0.26159(4)
	y	0.29802(4)	0.29806(4)	0.29799(5)	0.29793(5)	0.29802(4)	0.29801(5)	0.29796(4)	0.29795(3)	0.29800(4)
	z	0.4546(3)	0.4535(3)	0.4541(4)	0.4525(4)	0.4544(4)	0.4529(4)	0.4528(3)	0.4529(3)	0.4530(4)
	$U_{eq.}$	55(2)	55(2)	60(3)	58(3)	52(2)	54(2)	50(2)	52(2)	55(2)
Si	x	0.19044(3)	0.19043(4)	0.19035(5)	0.19044(4)	0.19022(4)	0.19040(4)	0.19042(3)	0.19041(3)	0.19043(3)
	y	0.19214(3)	0.19224(4)	0.19211(4)	0.19229(4)	0.19201(3)	0.19216(4)	0.19220(3)	0.19213(3)	0.19223(3)
	z	0.0686(3)	0.0669(3)	0.0672(4)	0.0652(4)	0.0676(4)	0.0657(4)	0.0659(3)	0.0660(3)	0.0662(3)
	$U_{eq.}$	54(2)	51(2)	58(2)	57(2)	52(2)	57(2)	53(2)	55(2)	56(2)
B	x	0.8903(1)	0.8903(1)	0.8901(1)	0.8902(1)	0.8902(1)	0.8902(1)	0.89019(9)	0.89018(9)	0.8902(1)
	y	0.1097(1)	0.1097(1)	0.1099(1)	0.1098(1)	0.1098(1)	0.1098(1)	0.10981(9)	0.10982(9)	0.1098(1)
	z	0.6167(5)	0.6150(5)	0.6155(6)	0.6145(6)	0.6153(6)	0.6144(6)	0.6143(5)	0.6148(4)	0.6143(5)
	$U_{eq.}$	69(7)	71(8)	71(11)	64(10)	75(8)	69(9)	74(7)	65(7)	71(8)
O(1)	x	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
	z	0.2945(5)	0.2930(4)	0.2928(4)	0.2907(4)	0.2943(4)	0.2919(4)	0.2910(4)	0.2922(4)	0.2924(4)
	$U_{eq.}$	57(7)	83(7)	102(7)	86(7)	49(8)	104(8)	84(8)	104(7)	85(7)
O(2)	x	0.93938(8)	0.93953(9)	0.9393(1)	0.9395(1)	0.93941(9)	0.93938(9)	0.93950(7)	0.93931(6)	0.93957(8)
	y	0.06062(8)	0.06047(9)	0.0607(1)	0.0605(1)	0.06059(9)	0.06062(9)	0.06050(7)	0.06069(6)	0.06043(5)
	z	0.5946(4)	0.5921(5)	0.5929(6)	0.5907(6)	0.5903(6)	0.5914(6)	0.5918(4)	0.5920(4)	0.5916(5)
	$U_{eq.}$	103(10)	94(10)	105(11)	99(11)	118(10)	99(10)	93(7)	98(6)	99(9)
O(3)	x	0.13406(8)	0.13410(9)	0.1341(1)	0.1339(1)	0.13371(9)	0.13382(9)	0.13403(8)	0.13397(8)	0.13402(8)
	y	0.86594(8)	0.86590(9)	0.8659(1)	0.8661(1)	0.86629(9)	0.86672(9)	0.86597(8)	0.86603(8)	0.86598(8)
	z	0.5574(4)	0.5561(4)	0.5574(5)	0.5552(5)	0.5566(5)	0.5559(5)	0.5559(4)	0.5558(4)	0.5559(5)
	$U_{eq.}$	86(5)	90(6)	94(8)	93(7)	106(6)	94(6)	84(5)	86(5)	91(5)
O(4)	x	0.90807(7)	0.90793(8)	0.9076(1)	0.90783(9)	0.90754(8)	0.90777(8)	0.90773(7)	0.90784(7)	0.90779(8)
	y	0.09193(7)	0.09207(8)	0.0924(1)	0.09217(9)	0.09246(8)	0.09223(8)	0.09227(7)	0.09216(7)	0.09221(8)
	z	−0.0040(4)	−0.0057(4)	−0.0052(5)	−0.0075(5)	−0.0050(5)	−0.0066(5)	−0.0063(4)	−0.0062(4)	−0.00674(5)
	$U_{eq.}$	103(5)	110(6)	114(7)	119(7)	103(6)	113(6)	118(5)	111(5)	115(6)
O(5)	x	0.09067(8)	0.09099(8)	0.0909(1)	0.09092(9)	0.09128(8)	0.09101(8)	0.09099(7)	0.09094(7)	0.09091(8)
	y	0.90933(8)	0.90901(8)	0.9091(1)	0.90908(9)	0.90872(8)	0.90899(8)	0.90901(7)	0.90906(7)	0.90909(8)
	z	−0.0255(4)	−0.0270(4)	−0.0263(5)	−0.0291(5)	−0.0258(5)	−0.0279(5)	−0.0278(4)	−0.0279(4)	−0.0279(4)
	$U_{eq.}$	92(5)	118(6)	108(7)	118(6)	107(6)	111(6)	112(5)	106(5)	111(6)
O(6)	x	0.1867(1)	0.1871(1)	0.1869(1)	0.1869(1)	0.1864(1)	0.1868(1)	0.18706(9)	0.18682(8)	0.18708(9)
	y	0.19583(9)	0.1962(1)	0.1962(1)	0.1963(1)	0.1958(1)	0.1961(1)	0.19627(9)	0.19610(8)	0.19627(9)
	z	0.2905(4)	0.2901(4)	0.2902(5)	0.2890(5)	0.2903(5)	0.2892(5)	0.2894(4)	0.2892(3)	0.28973(4)
	$U_{eq.}$	84(5)	84(5)	86(6)	86(6)	83(5)	84(5)	84(4)	81(4)	84(4)
O(7)	x	0.28472(9)	0.28497(9)	0.2850(1)	0.2853(1)	0.2850(1)	0.2854(1)	0.28528(8)	0.28511(7)	0.28518(9)
	y	0.28525(9)	0.2854(1)	0.2854(1)	0.2859(1)	0.2851(1)	0.2857(1)	0.28572(8)	0.28557(8)	0.28567(9)
	z	−0.0137(3)	−0.0147(4)	−0.0143(5)	−0.0158(1)	−0.0138(4)	−0.0154(5)	−0.0155(3)	−0.0156(3)	−0.01532(4)
	$U_{eq.}$	91(4)	81(5)	87(6)	86(6)	86(5)	88(5)	87(4)	88(4)	88(4)
O(8)	x	0.2702(1)	0.2703(1)	0.2703(1)	0.2701(1)	0.2703(1)	0.2702(1)	0.27036(9)	0.27020(8)	0.27027(9)
	y	0.2096(1)	0.2093(1)	0.2096(1)	0.2092(1)	0.2097(1)	0.2094(1)	0.20939(9)	0.20947(9)	0.20945(9)
	z	0.6254(3)	0.6245(4)	0.6248(5)	0.6237(5)	0.6257(5)	0.6238(5)	0.6238(4)	0.6240(3)	0.62417(4)
	$U_{eq.}$	102(5)	83(5)	95(6)	90(6)	94(5)	91(5)	81(4)	90(4)	90(4)

[*] X, Y and Z site-scattering refined using the scattering factors for Na, Al and Al, respectively.

[+] $U_{eq.} = U_{eq.} \times 10^4$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN UVITE CRYSTALS

	T72	T73	T74	T75	T76	T77	T78	T79	T80
X–O(2)b,f x3	2.436(2)	2.444(3)	2.445(3)	2.449(3)	2.456(3)	2.451(3)	2.446(2)	2.450(2)	2.447(2)
X–O(4)b,f x3	2.774(1)	2.771(1)	2.779(2)	2.767(2)	2.782(1)	2.774(1)	2.776(1)	2.774(1)	2.773(1)
X–O(5)b,f x3	2.683(1)	2.686(1)	2.685(1)	2.678(1)	2.696(1)	2.686(1)	2.685(1)	2.685(1)	2.683(1)
<X–O>	2.631	2.634	2.636	2.631	2.645	2.637	2.636	2.636	2.634
Y–O(3)	2.125(1)	2.131(2)	2.134(2)	2.136(2)	2.130(2)	2.133(2)	2.134(2)	2.132(2)	2.133(2)
Y–O(1)a	2.042(3)	2.035(3)	2.036(4)	2.026(4)	2.021(4)	2.030(3)	2.038(3)	2.033(2)	2.033(2)
Y–O(2)b x2	2.043(2)	2.035(3)	2.038(3)	2.036(3)	2.028(3)	2.040(3)	2.039(2)	2.044(2)	2.036(2)
Y–O(6)c x2	2.017(2)	2.018(2)	2.017(3)	2.011(3)	2.009(3)	2.014(3)	2.016(2)	2.014(2)	2.017(2)
<Y–O>	2.048	2.045	2.047	2.043	2.038	2.045	2.047	2.047	2.045
Z–O(6)	1.878(2)	1.869(3)	1.871(3)	1.867(3)	1.878(3)	1.873(3)	1.868(2)	1.873(2)	1.868(2)
Z–O(8)	1.924(3)	1.930(3)	1.923(3)	1.927(4)	1.926(3)	1.928(3)	1.928(3)	1.927(2)	1.929(3)
Z–O(3)a	1.987(2)	1.984(2)	1.986(3)	1.984(3)	1.984(2)	1.989(3)	1.986(2)	1.988(2)	1.986(2)
Z–O(7)d	1.959(2)	1.955(2)	1.956(3)	1.950(3)	1.958(3)	1.953(3)	1.953(2)	1.955(2)	1.954(2)
Z–O(7)e	1.899(3)	1.897(3)	1.895(4)	1.892(4)	1.895(3)	1.893(3)	1.894(3)	1.896(3)	1.896(3)
Z–O(8)e	1.894(2)	1.891(2)	1.891(3)	1.892(3)	1.888(3)	1.893(3)	1.891(2)	1.893(2)	1.891(3)
<Z–O>	1.924	1.921	1.920	1.919	1.922	1.922	1.920	1.922	1.921
Si–O(6)	1.599(3)	1.604(4)	1.603(5)	1.606(5)	1.602(4)	1.607(4)	1.606(3)	1.606(3)	1.607(3)
Si–O(7)	1.607(2)	1.607(2)	1.608(2)	1.611(2)	1.608(2)	1.613(2)	1.612(1)	1.611(1)	1.611(1)
Si–O(4)	1.634(1)	1.635(1)	1.632(2)	1.635(2)	1.631(2)	1.634(2)	1.634(1)	1.633(1)	1.636(1)
Si–O(5)	1.657(2)	1.654(2)	1.652(3)	1.654(3)	1.650(3)	1.654(3)	1.654(2)	1.656(2)	1.656(2)
<Si–O>	1.624	1.625	1.624	1.627	1.623	1.627	1.627	1.627	1.628
B–O(2)	1.366(1)	1.370(1)	1.367(1)	1.371(1)	1.370(1)	1.368(1)	1.372(1)	1.368(1)	1.374(1)
B–O(8)a x2	1.381(2)	1.378(2)	1.379(3)	1.374(3)	1.381(2)	1.378(2)	1.378(2)	1.379(2)	1.379(2)
<B–O>	1.376	1.375	1.375	1.373	1.377	1.375	1.376	1.375	1.377

Equivalent positions: a: y–x, y, z; b: y–x, –x, z; c: x, x–y, z; d: y–x+⅓, –x+⅔, z+⅔; e: –y+⅔, x–y+⅓, z+⅓; f: –y, x–y, z

apfu) and B_2O_3 (as BO_3^{3-}). The Li content was calculated as described by Burns *et al.* (1994).

DISCUSSION

Site-population determination by SREF is an electron-counting technique with spatial resolution and can be used for well-constrained analytical problems (Hawthorne & Grice 1990). Combined with EMPA of the actual crystal used to collect the X-ray intensity data, it provides extremely good characterization of chemical composition and site populations. We first derive the site populations from a combination of site-scattering values, the unit formula derived by EMPA, and stereochemical considerations at each site, and then we examine the variation in mean bond-length as a function of constituent-cation radii at each site.

B site

SREF is quite sensitive to the presence of B, particularly if it is in solid solution with another (possibly much heavier) scattering species (Hawthorne *et al.* 1995). In the present case, the *B* position is assigned as being fully occupied by B, and the observed equivalent isotropic-displacement factors are compatible with this assignment. The observed grand <*B*–O> distance of 1.375 Å is comparable with <$^{[3]}$B–O> distances in a wide range of mineral and inorganic structures. Thus the structure results are compatible with full occupancy of the *B* site by B. Any B significantly in excess of three atoms per formula unit would be visible, either by observed density at a new site or by a reduction of scattering and mean bond-length at the *Si* site. Neither of these situations is observed, and thus we may conclude that B is present in these crystals in (or very close to) the fixed stoichiometric amount of 3 apfu; unit formulae (Table 6) were calculated on this basis.

Si site

The electron-microprobe data indicate insufficient Si to fill the *Si* site in these crystals (Table 6), and Al was assigned to this site as suggested by the observed site-scattering values. From a review of data from the literature, Foit (1989) has shown that the <*Si*–O> distance in tourmaline is affected by the $^{[4]}$Al content.

TABLE 4. SELECTED BOND ANGLES (°) IN UVITE CRYSTALS

		T72	T73	T74	T75	T76	T77	T78	T79	T80
O(4)–Si–O(5)		100.3(1)	100.7(1)	101.0(1)	100.7(1)	101.5(1)	101.0(1)	101.0(1)	100.9(1)	100.7(1)
O(4)–Si–O(7)		111.0(1)	111.0(1)	110.7(2)	111.0(2)	110.5(1)	111.0(1)	111.0(1)	111.0(1)	110.9(1)
O(5)–Si–O(7)		110.6(1)	110.7(1)	110.7(2)	110.8(2)	110.6(2)	110.8(1)	110.8(1)	110.6(1)	110.7(1)
O(6)–Si–O(4)		111.7(1)	111.7(1)	111.8(2)	111.7(2)	111.7(2)	111.7(1)	111.6(1)	111.7(1)	111.8(1)
O(6)–Si–O(5)		111.1(1)	111.2(1)	111.0(2)	111.1(2)	110.9(2)	110.9(1)	111.1(1)	111.0(1)	111.2(1)
O(6)–Si–O(7)		111.6(1)	111.2(1)	111.2(2)	111.0(2)	111.3(1)	111.1(1)	111.0(1)	111.2(1)	111.1(1)
O(1)–Y–O(6)c	x2	97.6(1)	98.0(1)	97.9(1)	98.4(2)	98.3(2)	98.2(1)	98.0(1)	98.2(1)	98.2(1)
O(2)–Y–O(2)b		90.4(1)	90.6(2)	90.9(2)	90.5(2)	91.1(2)	90.7(1)	90.5(2)	90.6(1)	90.5(1)
O(3)–Y–O(2)b	x2	101.3(1)	101.4(1)	101.1(1)	100.9(2)	101.0(1)	100.9(1)	101.2(1)	100.9(1)	101.2(1)
O(6)–Y–O(6)c		89.2(1)	89.4(1)	89.1(2)	89.4(2)	89.2(1)	89.3(1)	89.5(1)	89.4(1)	89.4(1)
O(1)–Y–O(2)b	x2	83.9(1)	83.8(1)	84.1(1)	84.1(1)	83.8(1)	84.0(1)	84.0(1)	84.0(1)	83.8(1)
O(2)–Y–O(6)	x2	90.2(1)	90.0(1)	90.0(1)	90.0(1)	89.8(1)	89.9(1)	90.0(1)	90.0(1)	90.0(1)
O(3)–Y–O(6)b	x2	77.2(1)	76.7(1)	76.9(1)	76.6(1)	76.8(1)	76.8(1)	76.8(1)	76.9(1)	76.7(1)
O(3)–Z–O(7)e		94.4(1)	94.5(1)	94.3(1)	94.7(2)	94.6(1)	94.6(1)	94.5(1)	94.5(1)	94.6(1)
O(3)–Z–O(8)e		95.0(1)	94.8(1)	95.0(1)	94.9(1)	95.2(1)	95.0(1)	94.9(1)	95.0(1)	95.0(1)
O(6)–Z–O(8)		90.7(1)	90.5(1)	90.8(1)	90.6(1)	90.8(1)	90.6(1)	90.6(1)	90.7(1)	90.6(1)
O(7)d–Z–O(6)		92.4(1)	92.5(1)	92.5(2)	92.5(2)	92.7(1)	92.6(1)	92.5(1)	92.5(1)	92.5(1)
O(7)d–Z–O(8)		96.2(1)	96.0(1)	96.2(1)	96.2(1)	96.2(1)	96.2(1)	96.1(1)	96.3(1)	96.1(1)
O(7)e–Z–O(8)e		96.1(1)	96.2(1)	96.2(1)	96.1(1)	96.1(1)	96.2(1)	96.2(1)	96.1(1)	96.2(1)
O(3)–Z–O(6)		83.9(1)	83.9(1)	84.0(1)	83.8(1)	83.5(1)	83.7(1)	84.0(1)	83.8(1)	83.9(1)
O(3)–Z–O(8)		91.5(1)	91.7(1)	91.5(1)	91.5(1)	91.4(1)	91.4(1)	91.7(1)	91.5(1)	91.6(1)
O(6)–Z–O(8)e		95.0(1)	95.1(1)	94.9(2)	95.2(2)	95.1(2)	95.1(1)	95.1(1)	95.1(1)	95.2(1)
O(7)d–Z–O(7)e		90.6(1)	90.5(1)	90.6(1)	90.4(1)	90.6(1)	90.5(1)	90.4(1)	90.5(1)	90.5(1)
O(7)d–Z–O(8)e		77.6(1)	77.8(1)	77.6(1)	77.7(1)	77.6(1)	77.6(1)	77.7(1)	77.7(1)	77.7(1)
O(7)e–Z–O(8)		78.3(1)	78.3(1)	78.3(1)	78.3(1)	78.2(1)	78.2(1)	78.2(1)	78.3(1)	78.2(1)
O(2)b–X–O(2)b,f	x3	73.1(1)	72.6(1)	72.9(1)	72.4(1)	72.3(1)	72.6(1)	72.6(1)	72.7(1)	72.5(1)
O(2)b,f–X–O(4)b,f	x3	70.3(1)	70.3(1)	70.1(1)	70.1(1)	70.5(1)	70.1(1)	70.2(1)	70.1(1)	70.2(1)
O(2)b,f–X–O(5)b,f	x6	86.5(1)	86.4(1)	86.4(1)	86.3(1)	86.7(1)	86.3(1)	86.3(1)	86.3(1)	86.4(1)
O(4)b–X–O(4)b,f	x3	104.9(1)	105.3(1)	105.2(1)	105.6(1)	105.2(1)	105.5(1)	105.4(1)	105.4(1)	105.5(1)
O(4)b,f–X–O(5)b,f	x6	55.1(1)	55.3(1)	55.2(1)	55.4(1)	55.2(1)	55.3(1)	55.3(1)	55.3(1)	55.3(1)
O(8)a–B–O(2) x2		120.6(1)	120.8(2)	120.5(2)	120.7(2)	120.7(2)	120.7(1)	120.7(2)	120.6(1)	120.7(1)
O(8)–B–O(8)a		118.8(2)	118.3(2)	118.9(2)	118.7(2)	118.6(2)	118.6(2)	118.5(2)	118.8(1)	118.6(1)

However, the correlation between <*Si*–O> and [4]Al content was found to be low, probably because of inaccurate compositional data for the tourmaline crystals used for structure refinement. We have circumvented this problem by analyzing the actual crystals used for the collection of the X-ray intensity data. Figure 1 shows the variation in <*Si*–O> as a function of [4]Al content for the uvite crystals of this work and the crystals of manganiferous elbaite refined by Burns *et al.* (1994). There is a good linear correlation: <*Si*–O> = 1.620 + 0.0162 [4]Al, *r* = 0.961. The slope is very close to that predicted for a hard-sphere model, confirming that it is Al (rather than Mg or a fortuitous combination of Li and V) that occurs with Si at this site.

TABLE 5. SITE-SCATTERING (epfu) DERIVED BY SREF AND EMPA EXPRESSED AS EQUIVALENT ELECTRONS PER SITE

	X site		*Y* site		*Z* site	
	SREF	EMPA	SREF	EMPA	SREF	EMPA
T72	17.7(1)	18.2	35.1(2)	36.2	77.1(4)	77.5
T73	17.4(1)	17.8	35.2(2)	35.8	77.1(4)	77.8
T74	16.7(1)	17.2	35.6(2)	35.8	77.0(3)	78.0
T75	17.3(1)	17.8	35.8(2)	35.7	77.5(3)	78.3
T76	15.7(1)	15.9	36.0(2)	35.9	76.5(4)	78.5
T77	17.0(1)	17.2	35.9(2)	36.7	77.4(4)	79.1
T78	17.2(1)	17.8	35.1(2)	36.3	77.2(4)	78.7
T79	17.5(1)	17.7	35.5(2)	36.3	77.0(3)	78.5
T80	17.4(1)	17.4	35.9(2)	36.4	77.5(4)	78.9
<dev.>	1.7%		1.3%		1.3%	

Could there be significant occupancy of the *Si* site by B in these uvite structures? We may examine this possibility from two viewpoints: (1) site scattering, and (2) mean bond-length. Site-scattering refinement at the *Si* site converges to 84 electrons per formula unit (epfu) for a cross-section of these structures examined here. The mean Si content of these tourmaline crystals is ~5.6 apfu. If the balance of the *Si* site were filled with B, the scattering at the Si site would be 80.4 epfu, a value significantly different from those found by site-scattering refinements, which are compatible with virtually complete occupancy by atoms of atomic number (close to) 14. Tetrahedrally coordinated B has a radius of 0.11 Å (Shannon 1976), significantly less than that of Si (0.26 Å) and Al (0.39 Å). Any incorporation of B at the *Si* site would *decrease* the <Si–O>

TABLE 6. ELECTRON-MICROPROBE DATA* (WT%) FOR UVITE CRYSTALS

	T72	T73	T74	T75	T76	T77	T78	T79	T80
SiO_2	35.18	34.47	35.18	34.06	36.10	34.35	33.89	34.48	34.46
TiO_2	0.21	0.23	0.21	0.28	0.17	0.26	0.29	0.29	0.21
Al_2O_3	28.32	30.42	30.28	31.92	30.37	30.88	31.76	30.49	30.86
(B_2O_3)	10.52	10.58	10.66	10.66	10.80	10.69	10.69	10.66	10.69
V_2O_3	0.21	0.18	0.40	0.45	0.85	1.54	0.96	0.93	1.25
Cr_2O_3	0.03	0.04	0.04	0.05	0.07	0.17	0.17	0.08	0.13
MgO	14.58	13.58	13.54	12.79	13.33	13.15	12.94	13.53	13.24
CaO	4.59	4.33	3.99	4.40	3.45	4.11	4.44	4.40	4.28
Na_2O	0.54	0.72	0.91	0.65	1.16	0.81	0.64	0.64	0.70
Li_2O	0.03	0.08	0.12	0.17	0.14	0.08	0.13	0.08	0.10
(H_2O)	2.75	2.89	2.91	3	3	2.85	2.94	2.94	2.90
F	1.85	1.60	1.62	1.43	1.54	1.78	1.57	1.56	1.66
O=F	−0.78	−0.67	−0.68	−0.60	−0.65	−0.75	−0.66	−0.66	−0.70
Total	98.03	98.48	99.18	99.27	100.33	99.92	99.75	99.41	99.78
Si	5.813	5.664	5.734	5.551	5.810	5.584	5.512	5.625	5.604
Al	0.187	0.336	0.266	0.449	0.190	0.416	0.488	0.375	0.396
ΣSi	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Al	5.328	5.555	5.551	5.682	5.570	5.500	5.600	5.487	5.519
Mg	0.672	0.445	0.449	0.318	0.430	0.500	0.400	0.513	0.481
ΣZ	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Mg	2.919	2.882	2.841	2.790	2.768	2.687	2.738	2.777	2.729
Ti	0.026	0.028	0.026	0.034	0.021	0.032	0.035	0.036	0.026
V	0.028	0.024	0.052	0.059	0.110	0.201	0.125	0.122	0.163
Cr	0.004	0.005	0.005	0.006	0.009	0.022	0.022	0.010	0.017
Li	0.023	0.060	0.076	0.110	0.092	0.058	0.080	0.056	0.066
ΣY	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Ca	0.813	0.762	0.697	0.768	0.595	0.716	0.774	0.769	0.746
Na	0.173	0.229	0.288	0.205	0.362	0.255	0.202	0.202	0.221
ΣX	0.986	0.991	0.985	0.973	0.957	0.971	0.976	0.971	0.967
OH	3.033	3.168	3.165	3.263	3.216	3.085	3.192	3.195	3.146
F	0.967	0.832	0.835	0.737	0.784	0.915	0.808	0.805	0.854

* Li_2O, B_2O_3, H_2O estimated by stoichiometry; Fe, Zn, Cu, Mn, K not detected.

bond-length, whereas the data for the uvite crystals show that as the proportion of Si decreases, the <Si–O> bond-length *increases*. Indeed, assuming a hard-sphere model, we can predict the variation of the <Si–O> distance in these tourmaline crystals assuming complete occupancy of the *Si* site by (Si,B) and (Si,Al); these curves are shown in Figure 1. It is immediately apparent that the curve for Al incorporation at the Si site corresponds closely to the observed relationship, whereas the curve for B incorporation at the Si site is completely incompatible with the observed data.

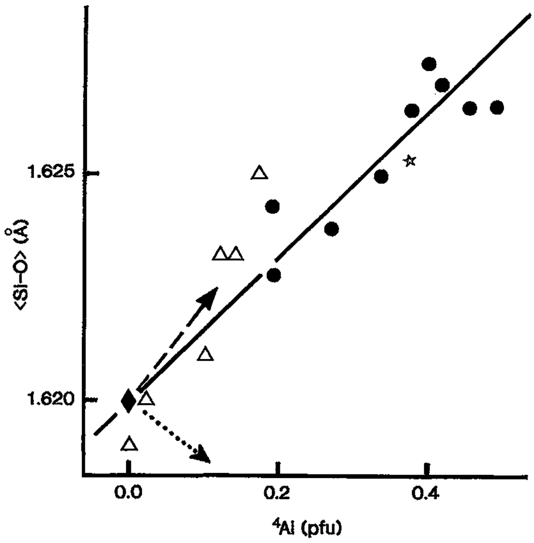

FIG. 1. Variation in <*Si*–O> as a function of $^{[4]}$Al content of the *Si* site; uvite crystals are shown as solid circles, elbaite crystals of Burns *et al.* (1994) are shown as triangles; the V-bearing tourmaline of Foit & Rosenberg (1979) is shown as a star, and the mean value for <*Si*–O> in several $^{[4]}$Al-free tourmaline crystals is represented by the black diamond. The broken line shows the ideal slope for a hard-sphere model of the Al ⇌ Si substitution; the dotted line shows the corresponding slope for a B ⇌ Si substitution.

Indeed, if we assume that the slight discrepancy between the ideal Al line and the observed data is due to B at the Si site (together with Al), the amount of B would only be 0.06 apfu at an Si content of 5.60 apfu. Furthermore, it should be noted that inductively caused deviations from the hard-sphere model are common in many structure-types, and the deviation of the ideal Al-substitution line and the observed data is well within the range of similar differences in other common structure-types. Thus we conclude that there is negligible B at the *Si* site in these uvite crystals.

Y + Z sites

It was shown by Hawthorne *et al.* (1993) that it is profitable to consider the variation in grand mean bond-length at the *Y* and *Z* sites as a function of constituent-cation radius, as this obviates any problems associated with erroneous assignment of cations to the *Y* and *Z* sites. Figure 2 shows this variation for the uvite crystals of this work and the crystals of manganiferous elbaite of Burns *et al.* (1994). The line on Figure 2 is the curve drawn by Grice & Ercit (1994) for their set of tourmaline crystals. There is good agreement among the three sets of data. The data for uvite lies slightly below the curve, the result of the higher F-content of the uvite crystals. Note that the aluminous elbaite of Gorskaya *et al.* (1982) also lies on this curve. Hawthorne *et al.* (1993) drew a similar curve, but one that differs considerably in slope from that of Grice & Ercit (1994). Most of the literature data used by Hawthorne *et al.* (1993) are reasonably compatible with the curve of Grice & Ercit (1994), but it seems likely that there are errors in some of the older refinements of the structure, probably related to the reported chemical compositions. The more modern data, essentially summarized by the data and line of Figure 2, indicate that there is a fairly well-developed relationship between the aggregate sizes and compositions of the *Y* and *Z* polyhedra. More data in the future will further refine the accuracy of this relationship, and make it useful as a compositional determinant.

Z site

It has been shown that Mg can occur at this site (Hawthorne *et al.* 1993, Grice & Ercit 1994), and the unit formulae derived from electron-microprobe results are consistent with this behavior; there is insufficient Al to fill the *Z* site completely, and the deficiency must be made up by Mg and perhaps small amounts of transition metals. This assignment is also reasonably

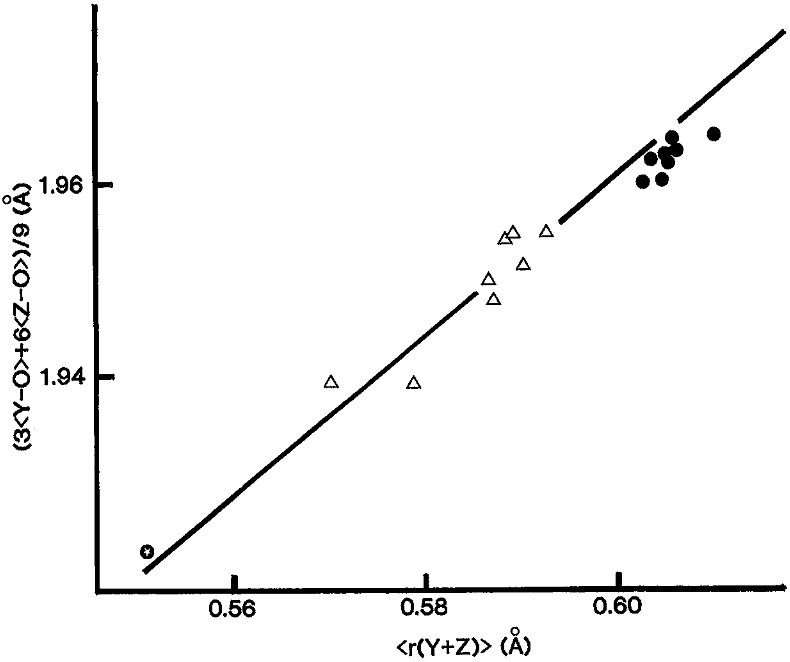

FIG. 2. Weighted mean bond-length of the *Y* and *Z* polyhedra as a function of the constituent-cation radius in uvite crystals (solid circles) and elbaite crystals (triangles); the line is that of Grice & Ercit (1994), and the encircled star represents the aluminous elbaite of Gorskaya *et al.* (1982).

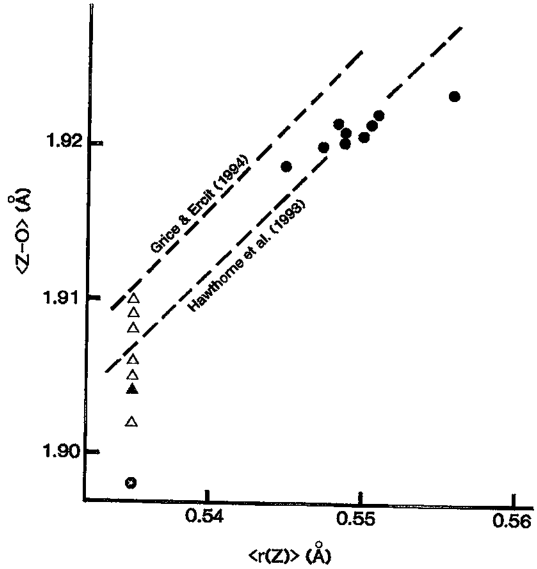

FIG. 3. Variation in <Z–O> distance as a function of constituent-cation radius. The legend is as in Figures 1 and 2; the filled triangle represents the elbaite of Grice & Ercit (1994).

compatible with the variation in <Z–O> bond-lengths within this group of crystals. Vanadium was arbitrarily split equally between the *Y* and *Z* sites; this leads to equally good agreement between refined site-scattering values and assigned cations at the *Y* and *Z* sites (Table 5), suggesting that this procedure is not too far from reality. Note that Foit & Rosenberg (1979) showed V^{3+} to occur at both the *Y* and *Z* sites in a sample of V-rich tourmaline. Figure 3 shows the variation in <Z–O> as a function of the mean constituent ionic radius of the *Z* cations assuming that all $^{[6]}$Al occurs at the *Z* site. There is a linear relationship with a slope of 0.41 and deviations of ≤0.001 Å. However, this relationship deviates significantly from a hard-sphere model slope of 1.0. Figure 3 also shows the data of Burns *et al.* (1994), Gorskaya *et al.* (1982), selected data from Grice & Ercit (1994), and the curves of Hawthorne *et al.* (1993) and Grice & Ercit (1994). The curve of Hawthorne *et al.* (1993) fits the elbaite and uvite data better than the curve of Grice & Ercit (1994); however, it does not fit the data of Grice & Ercit as well as their curve. Obviously, there are additional complications regarding the *Z* site in tourmaline that still remain to be untangled. Note also the range in <Z–O> distance for elbaite crystals, 1.898–1.910 Å (data from Gorskaya *et al.* 1982, Grice & Ercit 1994, Burns *et al.* 1994). Does this represent *Z* occupancy by other cations in addition to Al, or is it an inductive effect from other variations in the structure? The latter suggestion does not seem likely, as the range of distance occurs in a specific variety (elbaite) of tourmaline. However, if this range of <Z–O> distances is due to cations larger than Al at the *Z* site, it is apparent that the curves of Hawthorne *et al.* (1993) and Grice & Ercit (1994) overestimate the size of the *Z* octahedron for a given constituent-cation radius. Only additional data can resolve this problem.

Y site

The tourmaline samples examined here are essentially Fe-free, and hence there is no problem associated with determining the valence states of Fe. Furthermore, the spectroscopic results of Schmetzer (1982) show V to be present only in the trivalent state in all samples of tourmaline that he examined; this is also in accord with the lack of a heavy scatterer (*Z* > 14) at the tetrahedral site. Consequently, the resulting cations assigned to the *Y* site (Table 6) can be used to calculate the effective X-ray scattering at this site in each crystal, as modified for the proposed disorder of V^{3+} between the *Y* and *Z* sites. The X-ray scattering is actually measured by site-scattering refinement during the SREF procedure (Table 5). The agreement between the effective scattering at each site from the two methods is close, with a mean relative deviation of 1.3%. The measure of agreement between the two sets of data indicates a high level of accuracy in the determination of effective site-scattering by these two methods in the case of the uvite crystals examined here.

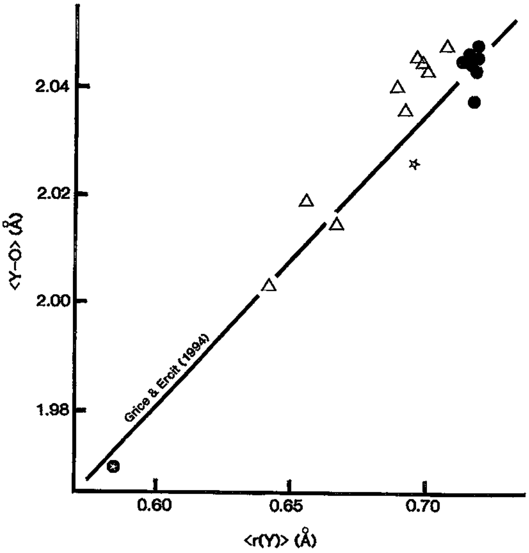

FIG. 4. Variation in <Y–O> distance as a function of constituent-cation radius; legend as in Figures 1 and 2.

The variation in <*Y*–O> as a function of the constituent-cation radius at the *Y* site is shown in Figure 4. Also shown are the data of Gorskaya *et al.* (1982), Burns *et al.* (1994) and the elbaite crystal of Grice & Ercit (1994), together with the curve of Grice & Ercit (1994). The latter curve fits the data much better than the curve of Hawthorne *et al.* (1993), and the *Y* site seems to be exhibiting much more consistent behavior than the *Z* site with reference to the structural data currently available.

X site

The electron-microprobe data show this site to contain significant Ca and Na, with no detectable K and insignificant amounts of vacancies. A comparison of the SREF and EMPA results is given in Table 5. The relative discrepancy between the two sets of results is similar to that observed at the *Y* and *Z* sites.

Anion disorder in the tourmaline structure

There are two aspects of order–disorder that affect the anion sites in the tourmaline structure: (1) OH–F substitution, and (2) positional disorder at the O(1) and O(2) sites.

OH–F substitution: The uvite crystals examined here have a relatively high F content (between 0.74 and 0.97 apfu), the F substituting for OH. In the tourmaline structure, the O(1) and O(3) anions are generally monovalent, and hence F can potentially substitute for OH at either or both of these sites. Grice & Ercit (1994) showed, using bond-valence arguments, that F orders at the O(1) site in a wide variety of tourmaline structures. The results of our refinements provide direct scattering evidence for the behavior of F. With the scattering at O(1) and O(3) assigned as O^{2-}, the equivalent isotropic-displacement factors are normal (*i.e.*, approximately equal to those of the divalent-anion sites in the structure at 0.009) for the O(3) site and anomalously low (<0.003>) at the O(1) site; this is typical for replacement of OH by F (Hawthorne 1979). Thus F is strongly to completely ordered at the O(1) site in these uvite crystals.

To further examine this effect, we refined the F–OH occupancy at the O(1) site. The refinements converged to significant F occupancies of O(1), and the displacement factors were more similar to those of the other anions in the structure (Table 2). A comparison of the refined F occupancy of O(1) with the F content determined by electron-microprobe analysis is given in Figure 5; the values are very similar, and indicate that F strongly to completely orders at the O(1) site.

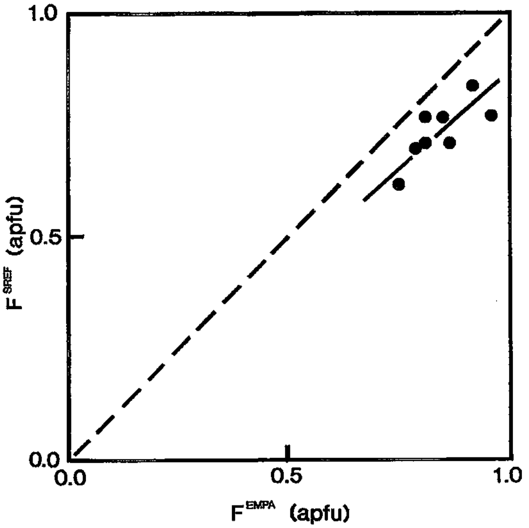

FIG. 5. Variation in refined F content of the O(1) site as a function of the F content of the crystal, as determined by electron-microprobe analysis.

Positional disorder: Burns *et al.* (1994) noted that in many refined structures of tourmaline, the anisotropic displacement parameters of the anions at the O(1) and O(2) sites are large and very strongly anisotropic compared to those of the other anions in the structure. They interpreted these features in terms of positional disorder induced by the local association of cations of very different size and charge. This being the case, tourmaline species without such variation in cation characteristics should not show such large and anisotropic displacement parameters. This is the case for the uvite crystals examined here. The equivalent isotropic displacement factors for O(1) and O(2) are similar to those of the other anions in the structure, and these anions do not have the same degree of anisotropy shown by the analogous anions in elbaite (Burns *et al.* 1994). This is in line with the site populations at the *X* and *Y* sites. In the uvite crystals examined here, the *Y* site is dominated by Mg, (~2.8 Mg apfu as compared with 3 *Y* apfu), and hence the O(1) anion is coordinated primarily by Mg. Similarly, the *X* site is completely occupied by Ca and Na; these cations are similar in size and differ in formal charge only by 1+, and hence will not induce significant disorder at O(2). Thus the lack of positional disorder involving anions in the uvite crystals examined here is in accord with the model of local order proposed by Burns *et al.* (1994).

Conclusions

(1) The Si content of these uvite crystals is significantly less than 6 apfu. Assignment of Al to the *Si* site in quantities sufficient to fill that site results in a linear variation in <*Si*–O> as a function of the amount of assigned $^{[4]}$Al.

(2) Examination of results of recent structure-refinements for tourmaline (this work, Burns *et al.* 1994, Grice & Ercit 1994) shows no well-defined relationship between <Z–O> and constituent Z-cation radius.
(3) There is a well-developed linear relationship between <Y–O> and constituent Y-cation radius for recently refined structures of tourmaline.
(4) Site-scattering refinement shows F to be strongly to completely ordered at the O(1) site in the uvite crystals examined here.
(5) The O(1) and O(2) anion positions do not show enhanced disorder in these uvite crystals, consistent with occupancy of the Y site dominantly by one type of cation (Mg), and the lack of significant amounts of vacancies at the X site.

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