The Canadian Mineralogist
Vol. 36, pp. 1305-1310 (1998)

REFINEMENT OF THE CRYSTAL STRUCTURE OF TIENSHANITE: SHORT-RANGE-ORDER CONSTRAINTS ON CHEMICAL COMPOSITION

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ABSTRACT

The crystal structure of tienshanite, hexagonal, *a* 16.785(2), *c* 10.454(1) Å, *V* 2550.7(6) Å^3, *P6/m*, has been refined to an *R* index of 2.2% for 2353 observed (5σ) reflections measured with Mo*K*α X-radiation. The crystal used in the collection of the X-ray intensity data was subsequently analyzed using an electron microprobe in wavelength-dispersion mode. Site populations were assigned on the basis of the refined site-scattering values, the formula unit calculated from the electron-microprobe data, and the mean bond-lengths. There is significant positional disorder at the *Ti* site, which is occupied by Ti^{4+} and Nb^{5+}. The refined structure results in a revised chemical formula for tienshanite: $K\,Na_3\,(Na,K,\square)_6\,(Ca,Y,RE)_2\,Ba_6\,(Mn^{2+},Fe^{2+},Zn,Ti)_6\,(Ti,Nb)_6\,Si_{36}\,B_{12}\,O_{114}\,[O_{5.5}(OH,F)_{3.5}]\,F_2$. Formulae can be written for the Ti^{4+}- and Nb^{5+}-bearing end-members. However, local bond-valence requirements impose certain compositional constraints associated with local order involving (Ti^{4+},Nb^{5+}) and [(OH,F),O]. Thus tienshanite compositions can extend from Ti^{4+}_6 to $Ti^{4+}_3Nb^{5+}_3$.

Keywords: tienshanite, crystal structure, chemical formula, electron-microprobe analysis.

SOMMAIRE

Nous avons affiné la structure cristalline de la tienshanite, hexagonale, *a* 16.785(2), *c* 10.454(1) Å, *V* 2550.7(6) Å^3, *P6/m*, jusqu'à un résidu *R* de 2.2% pour 2353 réflexions observées (5σ) mesurées en rayonnement Mo*K*α. Nous avons ensuite analysé le même cristal avec une microsonde électronique en dispersion d'énergie. L'occupation des sites a été assignée selon les valeurs de la dispersion des rayons X aux divers sites, l'unité formulaire calculée à partir des données à propos de la composition, et la longueur moyennes des liaisons. Il y a un désordre important de position au site *Ti*, où logent Ti^{4+} et Nb^{5+}. L'affinement de la structure mène à une formule chimique révisée de la tienshanite: $K\,Na_3\,(Na,K,\square)_6\,(Ca,Y,RE)_2\,Ba_6\,(Mn^{2+},Fe^{2+},Zn,Ti)_6\,(Ti,Nb)_6\,Si_{36}\,B_{12}\,O_{114}\,[O_{5.5}(OH,F)_{3.5}]\,F_2$. Il est possible d'écrire des formules pour les pôles Ti^{4+} et Nb^{5+}. Toutefois, les valences locales de liaisons imposent certaines restrictions à cause d'une mise en ordre locale impliquant (Ti^{4+},Nb^{5+}) et [(OH,F),O]. Ainsi, la composition de la tienshanite peut aller de Ti^{4+}_6 à $Ti^{4+}_3Nb^{5+}_3$.

(Traduit par la Rédaction)

Mots-clés: tienshanite, structure cristalline, formule chimique, données de microsonde électronique.

INTRODUCTION

Tienshanite (Dusmatov *et al.* 1967) is a complex alkali borosilicate from a quartz – aegirine – microcline pegmatite that occurs in alkali syenite from Dara-i-Pioz, Tajikistan. The crystal structure of tienshanite was solved and refined by Malinovskii *et al.* (1977), who showed it to be a sheet silicate and assigned the formula $K\,Na_9\,Ca_2\,Ba_6\,(Mn,Fe)_6\,(Ti,Nb,Ta)_6\,Si_{36}\,B_{12}\,O_{123}\,(OH)_2$. As this formula has variable components at two positions, there are several end-member compositions algebraically possible, *e.g.*, $K\,Na_9\,Ca_2\,Ba_6\,Mn^{2+}_6\,Ti^{4+}_6\,Si_{36}\,B_{12}\,O_{123}\,(OH)_2$ and $K\,Na_9\,Ca_2\,Ba_6\,Mn^{2+}_6\,Nb_6\,Si_{36}\,B_{12}\,O_{123}\,(OH)_2$. Anovitz & Hemingway (1996) pointed out that the formula proposed is not electronically neutral for the Mn^{2+} and Ti end-member. The present study was done to resolve this problem.

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EXPERIMENTAL

The material used in the present study is from Dara-i-Pioz, Tajikistan, and was provided by D.I. Belakovskiy. Tienshanite has been described as hexagonal, and we found no diffraction evidence for departure from this symmetry. However, the crystals show slightly biaxial optics, with a very small value of 2*V*. The crystal used in the collection of the X-ray intensity data was ground to an ellipsoid and mounted on a Siemens *P*4 automated four-circle diffractometer. Cell dimensions (Table 1) were derived from the setting angles of 33 automatically aligned reflections. Intensities were measured from 4 to 60° 2θ over the index ranges $\bar{2} \le h \le 21, \bar{2} \le k \le 21, \overline{14} \le l \le 14$ with scan speeds varying between 2 and 30° 2θ/min. A total of 7619 reflections was collected, giving 2634 unique reflections with an *R*(merge) index of 2.1%. Psi-scan data were measured on 18 reflections at increments of 6°, and an ellipsoidal absorption correction reduced *R*(azimuthal) from 4.1 to 1.7%. Intensities were corrected for absorption, Lorentz, polarization and background effects, and were reduced to structure factors; of the 2634 unique reflections, 2353 were classed as observed ($I_o > 5\sigma$ I). Following completion of the refinement, the crystal used in the collection of the X-ray intensity data was analyzed with an electron microprobe according to the method of Hawthorne *et al.* (1993). The standards used were as follows: benitoite (Si,Ti), synthetic $MnNb_2O_6$ (Nb), manganotantalite (Ta), spessartine (Mn), arfvedsonite (Fe), gahnite (Zn), witherite (Ba), diopside (Ca), YAG (Y), orthoclase (K), albite (Na) and fluororiebeckite (F).

TABLE 1. MISCELLANEOUS INFORMATION FOR TIENSHANITE

a (Å)	16.785(2)	Crystal size (mm)	0.13 x 0.15 x 0.21
c	10.454(1)	Radiation.	Mo*K*α/Graphite
V (Å³)	2550.7(5)	Total no. of I	7619
Sp. Gr.	*P*6/*m*	No. of |*F*|	2634
Z	1	No. of |F_o| > 5σ	2353
		R(azimuthal) %	4.1 → 1.7
		R(obs) %	2.2
		wR(obs) %	2.2

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{½}$, $w = 1/\sigma^2 F^*[1-\exp(-2.5\{\sin\theta/\lambda\}^2)]$

STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC system of programs; *R* indices are of the form given in Table 1. Structure refinement was initiated in the space group *P*6/*m* using the coordinates and site assignments of Malinovskii *et al.* (1977). Full-matrix refinement of all positional and displacement variables for an

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS* FOR TIENSHANITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ba	0.18579(1)	0.50676(1)	0	157(1)	131(1)	113(1)	0	0	68(1)	136(1)
Ti(1)	0.34879(9)	0.41959(6)	0	–	–	–	–	–	–	41(2)†
Ti(2)	0.3746(6)	0.4342(4)	0	–	–	–	–	–	–	41(2)†
Mn	0.13608(3)	0.22088(3)	0	100(3)	116(3)	87(2)	0	0	62(2)	97(2)
Ca	1/3	2/3	1/2	56(3)	56(3)	49(3)	0	0	28(1)	54(2)
K	0	0	1/2	237(8)	237(8)	222(9)	0	0	118(4)	232(6)
Na(1)	0.5180(1)	1/2	1/2	–	–	–	–	–	–	164(6)
Na(2)	0.1875(1)	0.3419(1)	1/2	176(8)	234(8)	194(7)	0	0	52(6)	224(6)
Si(1)	0.32540(4)	0.50460(4)	0.27216(5)	65(2)	66(3)	59(2)	–9(2)	–4(2)	36(2)	62(2)
Si(2)	0.36326(4)	0.34795(4)	0.28635(5)	73(3)	68(2)	76(2)	2(2)	–8(2)	42(2)	69(2)
Si(3)	0.19159(4)	0.16323(4)	0.28020(5)	81(3)	72(3)	83(2)	–0(2)	–2(2)	44(2)	76(2)
B	0.1763(2)	0.5125(2)	0.3728(2)	63(9)	65(9)	48(8)	–1(7)	3(7)	25(8)	62(7)
O(1)	1/2	1/2	0	71(15)	113(15)	248(16)	0	0	18(12)	157(12)
O(2)	0.3718(1)	0.3513(1)	0.1332(1)	168(8)	116(7)	64(6)	1(5)	–7(6)	95(6)	106(6)
O(3)	0.0445(1)	0.2890(1)	0.3381(2)	144(8)	102(7)	132(6)	–12(6)	–21(6)	75(6)	120(6)
O(4)	0.3611(1)	0.5147(1)	0.1267(1)	145(8)	101(7)	73(6)	–6(6)	15(6)	68(6)	103(6)
O(5)	0.3248(1)	0.4150(1)	0.3381(2)	159(6)	131(7)	91(6)	20(6)	20(6)	114(7)	109(6)
O(6)	0.0770(1)	0.4598(1)	0.3582(1)	73(7)	90(7)	112(7)	–26(5)	–4(6)	37(6)	93(6)
O(7)	0.2275(2)	0.3586(2)	0	106(11)	161(12)	223(11)	0	0	67(10)	163(9)
O(8)	0.1877(1)	0.1605(1)	0.1287(1)	156(8)	145(8)	87(6)	–5(6)	–1(6)	96(7)	120(6)
O(9)	0.2079(1)	0.6126(1)	0.3576(1)	111(7)	51(7)	106(6)	4(5)	–29(6)	32(6)	93(5)
O(10)	0.2201(1)	0.4850(1)	0.2731(1)	65(7)	125(7)	79(6)	–27(6)	–6(5)	53(6)	87(5)
O(11)	0.5011(2)	0.2931(2)	1/2	99(10)	81(9)	47(8)	0	0	48(8)	75(8)
O(12)	0.1785(1)	0.0681(1)	0.3431(2)	198(8)	99(7)	118(7)	–5(6)	–7(6)	83(7)	134(6)
F	1/3	2/3	0	135(10)	135(10)	390(21)	0	0	67(5)	220(10)

* $U \times 10^4$

† constrained to be equal

anisotropic-displacement model, together with variable site-scattering of the *Ti*, *Mn*, *Ca*, *K*, *Na*(1) and *Na*(2) sites, converged to an *R* index of ~2.5%. The equivalent isotropic-displacement factor for the site designated as OH by Malinovskii *et al.* (1977) was anomalously small, suggesting that this site is occupied predominantly by F. The electron-microprobe composition showed tienshanite to contain 3.61 F *apfu*, in agreement with the structural indication that the OH site is actually occupied by F. This site was re-designated as *F* and considered as occupied by F (~2.0 F *apfu*, atoms per formula unit); the remaining 1.61 F was assigned later in the refinement procedure. The *Ti* and *Na*(1) sites showed very anisotropic displacements, suggestive of positional disorder. The *Na*(1) site was considered as disordered in the *x* direction off its special position ½ ½ ½. The *Ti* site was considered as split into two positions, labeled *Ti*(1) and *Ti*(2). The chemical composition of this crystal shows that the *Ti* [= *Ti*(1) + *Ti*(2)] site is occupied by ~1.8 Nb + 4.2 Ti *apfu*. The *Ti*(1) site was considered to be occupied by 1.0 Ti *apfu*, and the *Ti*(2) site was assigned as (3.2 Ti + 1.8 Nb) *apfu*. The disordered sites were assigned isotropic-displacement parameters, and the *Ti*(1) and *Ti*(2) displacement parameters were constrained to be equal. Full-matrix refinement of all variables converged to an *R* index of 2.2%. Final positional and displacement parameters are given in Table 2, and selected interatomic distances and angles are given in Table 3; observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR TIENSHANITE

B–O(6)		1.451(3)	*Si*(2)–O(2)		1.606(2)
B–O(9)		1.496(3)	*Si*(2)–O(3)c		1.642(2)
B–O(10)		1.477(3)	*Si*(2)–O(5)		1.645(2)
B–O(11)a		1.480(2)	*Si*(2)–O(6)c		1.608(2)
<*B*–O>		1.476	<*Si*(2)–O>		1.625
Si(1)–O(4)		1.611(2)	*Si*(3)–O(3)c		1.634(2)
Si(1)–O(5)		1.650(2)	*Si*(3)–O(8)		1.585(2)
Si(1)–O(9)b		1.616(2)	*Si*(3)–O(12)		1.638(2)
Si(1)–O(10)		1.628(2)	*Si*(3)–O(12)a		1.644(1)
<*Si*(1)–O>		1.626	<*Si*(3)–O>		1.625
Ti(1)–O(1)		2.200(1)	*Ti*(2)–O(1)		1.824(9)
Ti(1)–O(2),d	x2	1.961(2)	*Ti*(2)–O(2),d	x2	1.953(6)
Ti(1)–O(4),d	x2	2.004(2)	*Ti*(2)–O(4),d	x2	1.984(7)
Ti(1)–O(7)		1.763(3)	*Ti*(2)–O(7)		2.138(9)
<*Ti*(1)–O>		1.982	<*Ti*(2)–O>		1.973
Ti(1)–*Ti*(2)		0.376(8)	*Mn*–O(7)		2.037(2)
			Mn–O(8),d	x2	2.114(2)
Ba–O(1)a		3.063(1)	*Mn*–O(8)a,e	x2	2.107(2)
Ba–O(2)a,e	x2	2.912(2)	<*Mn*–O>		2.096
Ba–O(4)f,g	x2	2.858(1)			
Ba–O(4),d	x2	3.168(2)	*Ca*–O(9)	x6	2.358(2)
Ba–O(7)		2.901(4)	*Ca*–O(11)	x3	2.510(3)
Ba–O(10),d	x2	2.971(2)	<*Ca*–O>		2.409
Ba–F		2.587(1)			
<*Ba*–O>		2.943	*K*–O(12)	x12	3.090(2)
Na(1)–O(5)h,i	x2	2.846(2)	*Na*(2)–O(3),l	x2	2.699(2)
Na(1)–O(6)c,j	x2	2.258(2)	*Na*(2)–O(5),l	x2	2.617(2)
Na(1)–O(6)b,k	x2	2.340(2)	*Na*(2)–O(11)a		2.517(2)
<*Na*(1)–O>		2.481	*Na*(2)–O(12)a,m	x2	2.888(2)
			Na(2)–O(10),l	x2	3.221(2)
Na(1)–*Na*(1)		0.604(5)	<*Na*(2)–O>		2.819
Si(1)–O(5)–*Si*(2)		131.4(1)	*B*–O(9)–*Si*(1)		136.8(1)
			B–O(10)–*Si*(1)		127.0(1)
			B–O(6)–*Si*(2)		128.9(2)

a: $x-y, x, z$; b: $\bar{y}+1, x-y+1, z$; c: $y, y-x, z$; d: $x, y, \bar{z}$; e: $x-y, x, \bar{z}$; f: $y-x, \bar{x}+1, z$; g: $y-x, \bar{x}+1, \bar{z}$; h: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; i: $\bar{x}+1, \bar{y}+1, z$; j: $y, y-x, \bar{z}+1$; k: $\bar{y}+1, x-y+1, \bar{z}+1$; l: $x, y, \bar{z}+1$; m: $x-y, x, \bar{z}+1$

ELECTRON-MICROPROBE ANALYSIS

The results of electron-microprobe analysis are given in Table 4. As the impetus for this work was to resolve a problem with the chemical formula of tienshanite, a large number of elements were sought (Table 4) but not detected. The unit formula was calculated on the basis of 125 anions with OH + F = 5.5 *apfu*; the justification for this procedure is discussed below. Comparing our chemical composition with that reported by Dusmatov *et al.* (1967), we found significant F, Y, (Ti + Nb + Ta) in excess of 6 *apfu*, and (Na + K) less than 10 *apfu*.

SITE POPULATIONS

The results of site-scattering refinement are given in Table 5. The results of electron-microprobe analysis are necessary to interpret the site-scattering results.

TABLE 4. CHEMICAL COMPOSITION (wt%) AND UNIT FORMULA* (*apfu*) FOR TIENSHANITE

SiO_2	43.09	Si	36.19
B_2O_3	(8.28)		
TiO_2	7.26	B	12
Nb_2O_5	4.66		
Ta_2O_5	0.11	Ti	4.17
MnO	6.32	Nb	1.77
FeO	1.03	Ta	0.03
ZnO	0.51	Σ	5.97
BaO	18.23		
CaO	1.61	Mn	4.50
Y_2O_3	0.83	Fe	0.72
K_2O	2.09	Zn	0.32
Na_2O	4.35	Ti	0.42
F	1.36	Σ	5.96
H_2O	0.34		
O = F	–0.57	Ba	6.00
Total	99.50	Ca	1.45
		Y	0.37
		K	2.24
		Na	7.08
		F	3.61
		OH	(1.89)
		Σ	5.50

Not detected: Mg, Al, P, S, Cl, Sc, V, Cr, Co, Ni, Cu, Ga, Ge, As, Se, Sr, Zr, Mo, Cd, In, Sn, Sb, Te, Cs, Tl, Pb, Bi.

* Normalized on the basis of 125 anions.

TABLE 5. CATION SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR TIENSHANITE

Site	Site scattering	Site population	Predicted site-scattering	$\langle X–\phi\rangle^{*}_{calc}$	$\langle X–\phi\rangle_{obs}$
Ti(1)	145(1)	3.2 Ti + 1.8 Nb	144	1.98	1.98
Ti(2)	20(1)	1.0 Ti	22	1.98	1.97
Mn	150.6(3)	4.53 Mn + 0.72 Fe + 0.32 Zn + 0.43 Ti	151.0	2.08	2.10
Ba	336	6.0 Ba	336	2.93	2.94
Ca	53.1(2)	1.5 Ca + 0.4 Y + (0.1 RE)	52.0	2.52	2.41
K	19.4(1)	1.0 K	19.0	3.02	3.09
Na(1)	33	3.0 Na	33	2.40	2.48
Na(2)	74.3(7)	4.09 Na + 1.25 K + 0.66 □	68.7	>2.69	2.82

* Calculated by summing the constituent ionic radii; values from Shannon (1976)

However, we need a reasonable basis for calculating the unit formula. At this stage of the refinement, the anion composition of tienshanite was not yet decided, and hence we did not initially use an anion-renormalization scheme. The <*Si*–O> distances indicated that the *Si* sites are occupied completely by Si, and hence we normalized the formula initially on the basis of 36 Si *apfu*. The final values (Table 4) do not differ substantially from these initial values.

There are three types of cation sites in tienshanite that can be differentiated in terms of the coordination environments. Site scattering and average <*T*–O> distances confirm that the three *Si* sites are occupied by Si, and the *B* site is fully occupied by B.

The octahedrally coordinated *Ti* site consists of two positionally disordered sites, labeled *Ti*(1) and *Ti*(2), that are displaced 0.376(8) Å from each other. The refined occupancies and average <*Ti*–O> distances are 145(1) *epfu* (electrons per formula unit), <*Ti*(1)–O> = 1.982 Å for the *Ti*(1) site, and 20(1) *epfu*, <*Ti*(2)–O> = 1.973 Å for the *Ti*(2) site. This is consistent with (3.2 Ti + 1.8 Nb) *apfu* at the *Ti*(1) site and 1 Ti *apfu* at the *Ti*(2) site (Table 5). The [5]-coordinated *Mn* site has a <*Mn*–O> distance of 2.10 Å and a refined site-scattering value of 150.6(3) *epfu* (average of 25.1 *e* per site), and is therefore occupied by transition metals. The Mn, Fe and Zn atoms inferred from the chemical analysis are assigned to this site, and the remaining Ti from the unit formula (left over after assignment of Ti to the *Ti* site) completes the 6 *apfu* site-requirement. The observed site-scattering and <*Mn*–O> distance are in good agreement with values calculated from this cation assignment (Table 5).

The remaining cation sites are occupied by large cations with coordination numbers ranging from [6] to [12]. There are 6.00 Ba *apfu*, in accord with the refinement results (Table 5). For a coordination number of [11], the <*Ba*–ϕ> distance calculated from the sum of the radii is 2.93 Å, in good agreement with the observed value of 2.94 Å. The [9]-coordinated *Ca* site contains 53.1(2) *epfu* (average of 26.55 *e* per site); therefore, in addition to the 1.5 Ca indicated by the unit formula, there must be additional scattering species (with >20 electrons /atom) at this site. The 0.40 Y indicated by the unit formula and an additional 0.10 *REE* were assigned to fill the *Ca* site. The [12]-coordinated *K* site has a refined site-scattering value of 19.4(1) *epfu*, in accord with complete occupancy of this site by K; this leaves 1.2 K *apfu* to be assigned to remaining sites in the structure. The positionally disordered *Na*(1) site is coordinated by six O-atoms and has a site-scattering value of 33 *epfu*, in agreement with the assigned 3 Na *apfu*. The only site remaining to be considered is the [9]-coordinated *Na*(2) site, which must hold the Na and K remaining to be assigned from the unit formula. The 4.09 Na + 1.25 K assigned to the *Na*(2) site sums to 5.34 *apfu*; the remainder of this site is occupied by 0.66 vacancies. The 68.7 *epfu* calculated from this assigned *Na*(2) is less than the refined value of 74.3(7) *epfu*, but the origin of this discrepancy is not clear. There are 77.3 cations from the chemical formula (Table 4) per 125 anions, and 77.3 assigned cations (Table 5), in good agreement with the proposed 0.7 □. Stereochemical details of the cation coordinations are given in Table 3. Full details of the structure topology are discussed by Malinovskii *et al.* (1977).

CHEMICAL COMPOSITION OF TIENSHANITE

Malinovskii *et al.* (1977) gave the chemical formula of tienshanite as $K\ Na_9\ Ca_2\ Ba_6\ (Mn,Fe)_6\ (Ti,Nb,Ta)_6\ Si_{36}\ B_{12}\ O_{123}\ (OH)_2$. However, as pointed out by Anovitz & Hemingway (1996), this formula is not neutral for a Ti^{4+} end-member, but has an aggregate charge of 6^-.

Chemical composition of the crystal examined

Tienshanite from Dara-i-Pioz, Tajikistan, has $\sim Ti_{4.2}Nb_{1.8}$ at the *Ti* site, and hence although the charge deficit is less than that for the ideal Ti^{4+} end-member, it is still very large. Presumably, higher-valence-cation substituents have been overlooked, or some of the anion

TABLE 6. BOND-VALENCE (*vu*) TABLE FOR TIENSHANITE

	K	*Ba*	*Na*(1)	*Na*(2)	*Ca*	*Mn*	*Ti*(1)	*Ti*(2)	*B*	*Si*(1)	*Si*(2)	*Si*(3)	Σ
O(1)		$0.13^{\times2}\rightarrow$					$0.31^{\times2}\rightarrow$	$0.16^{\times2}\rightarrow$					1.20
O(2)		$0.19^{\times2}\downarrow$					$0.62^{\times2}\downarrow$	$0.11^{\times2}\downarrow$			1.05		1.97
O(3)				$0.12^{\times2}\downarrow$							0.95	0.97	2.04
O(4)		$0.22^{\times2}\downarrow$ $0.11^{\times2}\downarrow$					$0.55^{\times2}\downarrow$	$0.11^{\times2}\downarrow$		1.04			2.03
O(5)			$0.09^{\times2}\downarrow$	$0.14^{\times2}\downarrow$						0.93	0.94		2.10
O(6)			$0.24^{\times2}\downarrow$ $0.21^{\times2}\downarrow$						0.81		1.04		2.30
O(7)		0.18				0.49	1.06	0.07					1.80
O(8)						$0.41^{\times2}\downarrow$ $0.41^{\times2}\downarrow$						1.11	1.93
O(9)					$0.36^{\times6}\downarrow$				0.71	1.02			2.09
O(10)		$0.17^{\times2}\downarrow$		$0.05^{\times2}\downarrow$					0.75	0.99			1.96
O(11)				0.18	$0.24^{\times3}\downarrow$				$0.74^{\times2}\rightarrow$				1.90
O(12)	$0.08^{\times12}\downarrow$			$0.08^{\times2}\downarrow$								0.96 0.95	2.07
F		$0.34^{\times3}\rightarrow$											1.02
Σ	0.96	2.03	1.08	0.96	2.88	2.13	3.71	0.67	3.01	3.98	3.98	3.99	

sites assigned as O-atoms by Malinovskii *et al.* (1977) may contain (F,OH). We looked for forty elements in tienshanite (Table 4) in search of these "missing" components. We found additional higher-valence cations in the form of Y^{3+} (substituting for Ca) and more Ti^{4+} (substituting for Mn^{2+}). Moreover, we found 3.61 F *apfu* and inferred an additional 1.89 OH *apfu*. We may further test for the presence and location of such components *via* bond-valence analysis.

The bond-valence arrangement for tienshanite is shown in Table 6, calculated from the parameters of Brown & Altermatt (1985) and Brown (1981). First, the anion identified as F has an incident bond-valence sum of 1.02 *vu* (valence units) and is not bonded to atoms at the *Ti* site; this sum is in accord with the *F* site being occupied by a monovalent anion. Second, the O(3), O(5), O(6), O(8), O(9), O(10), O(11) and O(12) anions have incident bond-valence sums of ~2 *vu* and hence are identified as O^{2-}; the remaining anions [O(1), O(2), O(4) and O(7)] have incident bond-valence sums significantly less than 2 *vu*, and hence can potentially be OH^- groups if the incident bond-valence from the atoms at the *Ti* site does not bring their sums close to 2 *vu*.

Next, we need to consider the identity of the O(1) and O(7) anions. The O(1) anion is bonded to two Ba atoms (for an incident bond-valence of 0.26 *vu*, Table 6), and to two atoms at the *Ti* sites. The constitu-

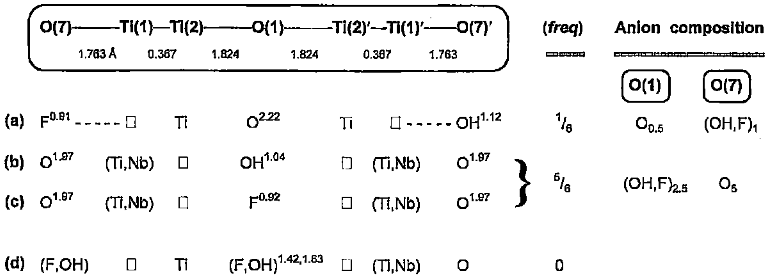

FIG. 1. Local (short-range) arrangements of atoms around the O(1) and O(7) sites in the structure of tienshanite. The linear arrangement of sites and their associated intersite distances are boxed; possible arrangements of cation occupancies [labeled (a)–(d)] are shown below. The superscripts of the anions O, OH and F are the incident bond-valence sums for these arrangements of cations and anions, and the anions are assigned accordingly: they sum ~1 *vu* for (OH,F), and ~2 *vu* for O. The relative frequency and anion content of these local arrangements are shown to the right of the figure.

ents of the O(1) and O(7) sites are strongly affected by the positional disorder at the *T*(1) and *T*(2) sites. In order to resolve this problem, we need to consider the possible short-range (SR) configurations possible; these are shown diagrammatically in Figure 1. The sites involved occur in a chain with a (long-range) center of symmetry at the O(1) site; this symmetry means that the long-range (average) arrangement must conform to $\bar{1}$ symmetry, but any short-range (local) arrangement need not conform to $\bar{1}$ symmetry. Figure 1 shows all of the symmetrically distinct arrangements of cations [labeled (a)–(d)], together with the observed interatomic distances and the local incident bond-valence sums calculated for anion occupancy by both O and F. For arrangement (a), both *Ti*(2) sites are occupied by $\mathrm{Ti^{4+}}$; the incident bond-valence sum at O(1) is 2.22 *vu*, and hence O(1) = $\mathrm{O^{2-}}$ in this case; the incident bond-valence sums at O(7) are 1.12 and 0.91 for O and F, respectively, and hence O(7) = (OH,F). For arrangements (b) and (c), *Ti*(1) is occupied by (Ti,Nb); the incident bond-valence sums at O(1) are 1.04 and 0.92 for O and F, respectively, and hence O(1) = (OH,F); the incident bond-valence sum at O(7) is 1.97 *vu*, and hence O(7) = $\mathrm{O^{2-}}$. Arrangement (d), with both *Ti*(1)' and *Ti*(2) occupied, gives incident bond-valence sums between 1.42 and 1.63 *vu*, and hence are not possible (at least without the presence of an almost symmetrical H-bond, which does not have the necessary acceptor anion). Arrangements (b) and (c) contain all the Nb in the crystal, and hence we may calculate the frequency of occurrence of these arrangements (Fig. 1). In turn, this provides us with the total anion contents of the O(1) and O(7) sites. Thus the chemical composition of the crystal examined here is $\mathrm{K\ Na_3\ (Na_{4.09}K_{1.25}\square_{0.66})_{\Sigma 6}\ (Ca_{1.50}Y_{0.40}RE_{0.10})_{\Sigma 2}\ Ba_6\ (Mn^{2+}_{4.53}Fe^{2+}_{0.72}Zn_{0.32}Ti^{4+}_{0.43})_{\Sigma 6}\ (Ti_{4.20}Nb_{1.80})_{\Sigma 6}\ Si_{36}\ B_{12}\ O_{114}\ O_{5.5}\ (OH_{1.9}F_{1.6})\ F_2}$.

Ideal end-members

Significant substitutions in tienshanite involve □ at *Na*(2), (Y + *RE*) at *Ca*, $\mathrm{Ti^{4+}}$ at *Mn*, (Ti,Nb) at *Ti* and (OH,F,O) at O(1) and O(7). We may write the Ti- and Nb-bearing end-members as follows:

$\mathrm{K\ Na_3\ Na_6\ Ca_2\ Ba_6\ Mn^{2+}_6\ Ti^{4+}_6\ Si_{36}\ B_{12}\ O_{114}\ O_3\ (OH)_6\ F_2}$

$\mathrm{K\ Na_3\ Na_6\ Ca_2\ Ba_6\ Mn^{2+}_6\ Nb^{5+}_6\ Si_{36}\ B_{12}\ O_{114}\ O_9\ F_2}$

However, it is obvious from Figure 1 that the O(1) and O(7) sites cannot show this complete range of composition. If arrangement (a) is the only arrangement present, then the Ti-bearing end-member composition results. However, if only arrangements (b) and (c) are present, then the minimum (OH,F) content of O(1) + O(7) is $\mathrm{O_6(OH,F)_3}$. Hence the maximum Nb content of tienshanite is 3.0 *apfu*, and the resulting composition is $\mathrm{K\ Na_3\ Na_6\ Ca_2\ Ba_6\ Mn^{2+}_6\ (Nb^{5+}_{3.0}Ti^{4+}_{3.0})_{\Sigma 6}\ Si_{36}\ B_{12}\ O_{114}\ O_6\ (OH,F)_3\ F_2}$

Thus tienshanite provides us with another example of local order restricting the possible range of solid solution in a mineral.

ACKNOWLEDGEMENTS

We thank D.I. Belakovskiy of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, for the sample of tienshanite. This work was supported by Natural Sciences and Engineering Research Council of Canada grants to FCH. We are grateful to Drs. John M. Hughes and Robert T. Downs, who reviewed our manuscript.

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Received June 30, 1998, revised manuscript accepted October 10, 1998.