

## POLYPHITE AND SOBOLEVITE: REVISION OF THEIR CRYSTAL STRUCTURES

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### ABSTRACT

The crystal structures of polyphite,  $\text{Na}_5(\text{Na}_4\text{Ca}_2)\text{Ti}_2[\text{Si}_2\text{O}_7](\text{PO}_4)_3\text{O}_2\text{F}_2$ , triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a$  5.3933(2),  $b$  7.0553(3),  $c$  26.451(1) Å,  $\alpha$  95.216(1),  $\beta$  93.490(1),  $\gamma$  90.101(1)°,  $V$  1000.44(8) Å<sup>3</sup>, and sobolevite,  $\text{Na}_{12}\text{Ca}(\text{NaCaMn})\text{Ti}_2(\text{Ti Mn})[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_3\text{F}_3$ , monoclinic, space group  $Pc$ ,  $Z = 2$ ,  $a$  7.0755(5),  $b$  5.4106(4),  $c$  40.623(3) Å,  $\beta$  94.42(1)°,  $V$  1552.8(3) Å<sup>3</sup>, from the Khibina–Lovozero alkaline complex, Kola Peninsula, Russia, have been refined (for the holotype single crystal of polyphite) to residual  $R$  values of 3.7 and 4.3%, respectively, using 5849 and 9030 observed ( $|F_o| > 4\sigma F$ ) reflections collected with a single-crystal diffractometer fitted with a CCD detector and  $\text{MoK}\alpha$  X-radiation. The single crystals were subsequently analyzed with an electron microprobe, resulting in significant revision of both chemical formulae. There is a close relation among the structures of polyphite, sobolevite and quadruphite,  $\text{Na}_{14}\text{Ca}_2\text{Ti}_4[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_4\text{F}_2$ . This type of structure consists of two structural blocks, Ti-silicate ( $TS$ ) and alkali-cation ( $AC$ ), stacked along [001]. There is also a close relation among the silicophosphate minerals polyphite, sobolevite, quadruphite and nacaphite,  $\text{Na}(\text{Na,Ca})_2(\text{PO}_4)\text{F}$ . The  $TS$  block has a three-layered structure consisting of a central sheet of octahedra and two adjacent heteropolyhedral sheets. The  $AC$  block consists of nacaphite-like trimeric clusters that link along [100] to form an infinite chain. The  $TS$  and  $AC$  blocks link together through an intermediate ( $I$ ) layer of Na polyhedra and P tetrahedra. In polyphite, sobolevite and quadruphite, all cations are arranged as close-packed layers parallel to (001) and characterized by a plane unit-cell approximately  $5.4 \times 7$  Å with  $\gamma \approx 90^\circ$ .

**Keywords:** polyphite, sobolevite, crystal structure, Khibina–Lovozero, Kola Peninsula, Russia.

### SOMMAIRE

Nous avons affiné les structures cristallines de la polyphite,  $\text{Na}_5(\text{Na}_4\text{Ca}_2)\text{Ti}_2[\text{Si}_2\text{O}_7](\text{PO}_4)_3\text{O}_2\text{F}_2$ , triclinique, groupe d'espace  $P\bar{1}$ ,  $Z = 2$ ,  $a$  5.3933(2),  $b$  7.0553(3),  $c$  26.451(1) Å,  $\alpha$  95.216(1),  $\beta$  93.490(1),  $\gamma$  90.101(1)°,  $V$  1000.44(8) Å<sup>3</sup> (monocristal holotypique), et de la sobolevite,  $\text{Na}_{12}\text{Ca}(\text{NaCaMn})\text{Ti}_2(\text{Ti Mn})[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_3\text{F}_3$ , monoclinique, groupe d'espace  $Pc$ ,  $Z = 2$ ,  $a$  7.0755(5),  $b$  5.4106(4),  $c$  40.623(3) Å,  $\beta$  94.42(1)°,  $V$  1552.8(3) Å<sup>3</sup>, provenant du complexe alcalin de Khibina–Lovozero, péninsule de Kola, en Russie, jusqu'aux résidus  $R$  de 3.7 et 4.3%, respectivement, en utilisant 5849 et 9030 réflexions observées ( $|F_o| > 4\sigma F$ ) prélevées avec un diffractomètre et un rayonnement  $\text{MoK}\alpha$ , muni d'un détecteur CCD. Les monocristaux ont par la suite été analysés avec une microsonde électronique, ce qui a mené à une révision importante des deux formules. Il y a une étroite relation parmi les structures de la polyphite, la sobolevite et la quadruphite,  $\text{Na}_{14}\text{Ca}_2\text{Ti}_4[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_4\text{F}_2$ . De telles structures contiennent deux modules structuraux, un contenant le Ti et le silicate ( $TS$ ) et l'autre, le cation alcalin ( $AC$ ), empilés le long de [001]. Il y a aussi une étroite relation parmi les minéraux silicophosphatés polyphite, sobolevite, quadruphite et nacaphite,  $\text{Na}(\text{Na,Ca})_2(\text{PO}_4)\text{F}$ . Le module  $TS$  a une structure à trois couches contenant un feuillet central d'octaèdres avec deux feuillets hétéropolyédriques adjacents. Le bloc  $AC$  contient des groupes trimériques semblables à la nacaphite liés le long de [100] pour former une chaîne infinie. Les modules  $TS$  et  $AC$  sont liés l'un à l'autre par l'intermédiaire d'une couche  $I$  de polyèdres Na et de tétraèdres P. Dans la polyphite, la sobolevite et la quadruphite, tous les cations sont agencés en couches à empilement compact parallèles à (001) et possédant une maille planaire d'environ  $5.4 \times 7$  Å, avec  $\gamma \approx 90^\circ$ .

(Traduit par la Rédaction)

**Most-clés:** polyphite, sobolevite, structure cristalline, Khibina–Lovozero, péninsule de Kola, Russie.

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## INTRODUCTION

Polyphite and sobolevite are alkali titanium silicate minerals from hyperagpaitic pegmatitic rocks of the Khibina–Lovozero alkaline complex, Kola Peninsula, Russia (Khomyakov 1995, Khomyakov *et al.* 1983, 1992). Khomyakov and co-investigators reported the following chemical formulae: for sobolevite,  $\text{Na}_{14} \text{Ca}_2 \text{Mn Ti}_3 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_4$ , and for polyphite,  $\text{Na}_{17} \text{Ca}_3 \text{Mg} (\text{Ti}, \text{Mn})_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_6 \text{O}_2 \text{F}_6$ , on the basis of electron-microprobe data, together with results of a semiquantitative analysis for fluorine. Thus there was no possibility to calculate empirical formulae on an anion basis. Sokolova *et al.* (1987b, 1988) reported crystal structures and general structural formulae of polyphite,  $\text{Na}_{17} \text{Ca}_3 \text{Mg} (\text{Ti}, \text{Mn})_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_6 \text{O}_2 \text{F}_6$ ,  $a$  5.412(2),  $b$  7.079(3),  $c$  26.56(1) Å,  $\alpha$  95.21(4),  $\beta$  93.51(2),  $\gamma$  90.10(3)°,  $V$  1111.4 Å<sup>3</sup>,  $Z = 1$ , space group  $P1$ ,  $R$  5.0%, and sobolevite,  $\text{Na}_{11} (\text{Na}, \text{Ca}) (\text{Mg}, \text{Mn}) \text{Ti}_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_3 \text{F}_3$ ,  $a$  7.078(1),  $b$  5.4115(7),  $c$  40.618(10) Å,  $\alpha$  90.01(2),  $\beta$  93.19(2),  $\gamma$  90.00(1)°,  $V$  1553.5(5) Å<sup>3</sup>,  $Z = 2$ , space group  $P1$ ,  $R$  7.8%. The crystal structures of polyphite, sobolevite and the related mineral quadruphite,  $\text{Na}_{14} \text{Ca}_2 \text{Ti}_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_4 \text{F}_2$  (Sokolova *et al.* 1987a, Sokolova & Hawthorne 2001), consist of two types of block that differ both in chemical composition and bond topology: (1) a Ti-silicate (*TS*) block, and (2) a (Na,Ca)-phosphate or alkali-cation (*AC*) block. Structural relations of Ti-silicate minerals with a three-layered *TS* block (consisting of a close-packed sheet of octahedra and two adjacent heteropolyhedral sheets of tetrahedra and octahedra) have been discussed extensively in recent years (Egorov-Tismenko & Sokolova 1990, Ferraris 1997, Sokolova 1998, Christiansen *et al.* 1999). Egorov-Tismenko & Sokolova (1990) showed that the *TS* block corresponds to the structure of seidozerite,  $\text{Na}_4 \text{Mn Ti} (\text{Zr}_{1.5} \text{Ti}_{0.5}) [\text{Si}_2\text{O}_7]_2 \text{O}_2 (\text{F}, \text{OH})_2$  (Simonov & Belov 1960, Christiansen *et al.* 2003). In the structures of quadruphite, polyphite and sobolevite, the *AC* block corresponds to a fragment of the structure of nacaphite,  $\text{Na} (\text{NaCa}) (\text{PO}_4) \text{F}$  (Sokolova *et al.* 1989, Sokolova & Hawthorne 2001). Quadruphite, polyphite and sobolevite commonly form intergrowths with lomonosovite,  $\text{Na}_{10} \text{Ti}_4 [\text{Si}_2\text{O}_7]_2 [\text{PO}_4]_2 \text{O}_4$  (Belov *et al.* 1977); from a structural perspective, they also can be regarded as derivatives of lomonosovite.

The original crystal-structure determinations of polyphite and sobolevite are not completely satisfactory, first of all because they relied on formulae calculated on a cation basis,  $\text{Si} = 4$  *apfu* (atoms per formula unit), with unknown contents of F. In the original work, no absorption correction was done, and there was some ambiguity as to the degree of order of Mn and Mg at the junction of the *TS* and *AC* blocks. We have refined the structures of polyphite and sobolevite, and discuss the refined chemical formulae and details of cation and anion order in their structures.

## ELECTRON-MICROPROBE ANALYSIS

Chemical analyses of polyphite (holotype crystal) and sobolevite single crystals were done with a Cameca SX-50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA and a beam size of 20 µm. Standards were as follows: fluorapatite: Ca, P, F; tugtupite: Na, Si, Cl; forsterite: Mg; titanite: Ti; spessartine: Mn; strontianite: Sr; zircon: Zr;  $\text{MnNb}_2\text{O}_6$ : Nb; witherite: Ba; fayalite: Fe; manganotantalite: Ta. Data were reduced using the  $\phi(\rho z)$  procedure of Pouchou & Pichoir (1985). The chemical compositions of polyphite (holotype) and sobolevite crystals are given in Table 1 (mean of ten determinations for each fragment), and the unit formulae were calculated on the basis of 23 (21O + 2F) and 36 (33O + 3F) anions *pfu* (per formula unit), respectively:  $\text{Na}_{8.72} \text{Ca}_{1.40} \text{Sr}_{0.03} \text{Mg}_{0.30} \text{Mn}_{0.68} \text{Fe}_{0.07} \text{Ti}_{1.41} \text{Nb}_{0.19} \text{Zr}_{0.19} \text{P}_{2.96} \text{Si}_{2.04} \text{O}_{20.94} \text{F}_{2.06}$  and  $\text{Na}_{13.62} \text{Ca}_{1.63} \text{Sr}_{0.03} \text{Mg}_{0.39} \text{Mn}_{1.02} \text{Fe}_{0.10} \text{Ti}_{2.42} \text{Nb}_{0.51} \text{Zr}_{0.09} \text{P}_{4.01} \text{Si}_{4.13} \text{O}_{33.08} \text{F}_{2.92}$ . The formulae differ (see constituents shown in bold) from the following empirical formulae on which the first structure-determinations of polyphite and sobolevite were based (Khomyakov *et al.* 1992, 1983):  $\text{Na}_{8.23} \text{Ca}_{1.35} \text{Sr}_{0.03} \text{Ba}_{0.06} \text{Mg}_{0.30} \text{Mn}_{0.72} \text{Fe}_{0.03} \text{Ti}_{1.36} \text{Nb}_{0.19} \text{Zr}_{0.12} \text{P}_{2.99} \text{Si}_{2.00} \text{O}_{20.29} \text{F}_{2.45}$  and  $\text{Na}_{13.47} \text{Ca}_{1.60} \text{Mg}_{0.21} \text{Mn}_{0.79} \text{Fe}_{0.11} \text{Ti}_{2.67} \text{Nb}_{0.46} \text{P}_{3.94} \text{Si}_{4.00} \text{O}_{33.19} \text{F}_{0.52}$ , and with corresponding generalized structural formulae for polyphite,  $\text{Na}_{17} \text{Ca}_3 \text{Mg} (\text{Ti}, \text{Mn})_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_6 \text{O}_2 \text{F}_6$ , and sobolevite,  $\text{Na}_{11} (\text{Na}, \text{Ca}) (\text{Mg}, \text{Mn}) \text{Ti}_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_3 \text{F}_3$  (Sokolova *et al.* 1987b, 1988).

TABLE 1. CHEMICAL COMPOSITIONS\* (wt.%) AND UNIT FORMULAE (*apfu*) OF POLYPHITE AND SOBOLIVITE

	Polyphite	Sobolevite		Polyphite	Sobolevite
P <sub>2</sub> O <sub>5</sub>	22.37	19.61	P	2.96	4.01
Nb <sub>2</sub> O <sub>5</sub>	2.69	4.65			
SiO <sub>2</sub>	13.03	17.11	Si	2.04	4.13
TiO <sub>2</sub>	11.97	13.32			
ZrO <sub>2</sub>	2.42	0.75	Nb	0.19	0.51
FeO	0.49	0.50	Zr	0.19	0.09
MnO	5.11	4.99	Mg	0.13	0.39
MgO	1.29	1.07	Ti <sup>4+</sup>	1.41	2.42
CaO	8.38	6.31	Fe <sup>**</sup>	0.07	0.10
SrO	0.31	0.22	Mn <sup>2+</sup>	0.02	0.47
Na <sub>2</sub> O	28.75	29.10	Σ	2.01	3.98
F	4.16	3.83			
			Mn <sup>2+</sup>	0.66	0.55
O=F	-1.75	-1.61	Mg	0.17	0.00
			Ca	1.40	1.63
Total	99.22	99.85	Sr	0.03	0.03
			Na	8.72	13.62
			Σ	10.98	15.83
			F	2.06	2.92
			O	20.94	33.08

\* Ta<sub>2</sub>O<sub>5</sub>, HfO<sub>2</sub> and BaO: not detected; \*\* Fe<sup>3+</sup> in sobolevite, Fe<sup>2+</sup> in polyphite.

COLLECTION OF X-RAY DATA  
AND STRUCTURE REFINEMENT

Single-crystal X-ray-diffraction data for polyphite (holotype) and sobolevite were collected with a Siemens P4 diffractometer fitted with a 4K CCD detector, using MoK $\alpha$  X-radiation. An empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) was used for refinement of the structures. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1992).

*Polyphite*

The intensities of 11684 reflections with  $\bar{7} < h < 7, \bar{9} < k < 9, \bar{37} < l < 37$  were collected using 15 s per 0.2° frame. The refined unit-cell parameters were obtained from 6707 reflections ( $I > 10\sigma I$ ) and are given in Table 2. The crystal structure of polyphite was refined in space groups  $P1$  and  $P\bar{1}$  using atom coordinates from Sokolova *et al.* (1987b), with corresponding  $R_1$  values of 3.4 and 3.7%, respectively. Analysis of the cation polyhedra confirmed the presence of an inversion center in the crystal structure of polyphite, and the space group  $P\bar{1}$  was adopted. Final atom-parameters for polyphite are given in Table 3, selected interatomic distances are listed in Table 4, assigned site-occupancies are given in Table 5, and bond valences are presented in Table 6.

*Sobolevite*

The intensities of 17784 reflections with  $\bar{9} < h < 9, \bar{7} < k < 7, \bar{57} < l < 57$  were collected using 15 s per 0.2° frame. The refined unit-cell parameters were obtained from 6594 reflections ( $I > 10\sigma I$ ) and are given in Table 2. For sobolevite, we used triclinic [ $a$  7.0753(5),  $b$  5.4104(4),  $c$  40.622(3) Å,  $\alpha$  90.015(1),  $\beta$  93.159(1),  $\gamma$  90.006(1)°,  $V$  1552.7(3) Å<sup>3</sup>] and monoclinic (see Table 2) versions of the unit cell for integration of intensities of reflections. The crystal structure of sobolevite was refined in five space groups:  $P1$  and  $P\bar{1}$  (triclinic system) and  $P2_1/c$ ,  $P2_1$  and  $Pc$  (monoclinic system). Corresponding final  $R_1/R_{\text{int}}$  indices are as follows: 4.6/0.0 ( $P1$ ), 6.8/1.1 ( $P\bar{1}$ ), 7.4/2.0 ( $P2_1/c$ ), 5.3/1.9 ( $P2_1$ ) and 4.3/2.0 ( $Pc$ ). On the basis of the lowest  $R$  indices, the latter space-group,  $Pc$ , was chosen for the crystal structure of sobolevite. Note that the space group  $Pc$  allows the most complete degree of Ca–Na order possible within the AC block, whereas other three space groups (excluding  $P1$ , with the lowest symmetry) give *averaged* scattering over the sites in the AC block. The details of X-ray data collection and structure refinement are given in Table 2. Final atom-parameters for sobolevite are given in Table 7, selected interatomic distances are listed in Table 8, assigned site-occupancies are given in Table 9, and bond valences are presented in Table 10. Final observed and calculated structure-factors for polyphite and sobolevite may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

## POLYPHITE

TABLE 2. MISCELLANEOUS DATA CONCERNING THE REFINEMENT OF POLYPHITE AND SOBOLEVITE

	Polyphite*	Sobolevite*
$a$ (Å)	5.3933(2)	7.0755(5)
$b$	7.0553(3)	5.4106(4)
$c$	26.451(1)	40.623(3)
$\alpha$ (°)	95.216(1)	90
$\beta$	93.490(1)	93.156(1)
$\gamma$	90.101(1)	90
$V$ (Å <sup>3</sup> )	1000.44(8)	1552.8(3)
Space group	$P\bar{1}$	$Pc$
$Z$	2	2
Absorption coefficient (mm <sup>-1</sup> )	2.36	2.3
$D_{\text{max}}$ (g.cm <sup>-3</sup> )	3.07**	3.03***
$D_{\text{calc}}$ (g.cm <sup>-3</sup> )	3.1	3.098
$F(000)$	906.4	1405.7
Crystal size (mm)	0.09 × 0.13 × 0.16	0.16 × 0.18 × 0.24
Radiation	MoK $\alpha$	MoK $\alpha$
2 $\theta$ range for data collection (°)	60.03	59.98
$R(\text{int})$ (%)	1.3	2
Reflections collected	11684	17784
Unique reflections	5849	9030
$F_o > 4\sigma F$	5604	8902
Refinement method	Full matrix least-squares on $F^2$ ; fixed weights proportional to $1/\sigma(F)$	
Goodness of fit on $F^2$	1.18	1.163
Final $R$ index (%) [ $F_o > 4\sigma F$ ]	3.73	4.31
$R$ index (%) (all data)	3.96	4.37
$wR_2$ (%)	9.04	9.86
GoF	1.18	1.064

\* data were collected from holotype crystals.

\*\* Khomyakov *et al.* (1992).\*\*\* Khomyakov *et al.* (1983).*Coordination of the cations*

The structure of polyphite consists of two blocks ( $TS$  and  $AC$ ) stacked along  $[001]$  with an intermediate layer between them, denoted as  $I$  in Figure 1.

*The  $T$  (=  $Si + P$ ) sites:* There are two unique  $Si$  sites in the crystal structure of polyphite, with  $\langle Si-O \rangle$  1.605 and 1.624 Å, respectively. The  $Si(1)$  and  $Si(2)$  tetrahedra link through O(10), forming an  $[Si_2O_7]$  group with an Si–O–Si angle of 137.0°, and the  $Si$  tetrahedra are confined to the heteropolyhedral sheet of the  $TS$  block. There are three unique  $P$  sites within the  $AC$  block, each of which is surrounded by a tetrahedral arrangement of O atoms, with  $\langle P-O \rangle$  distances in the range 1.534–1.538 Å.

*The octahedral sites of the  $TS$  block:* There are two unique  $M$  sites, each of which is coordinated by six anions in an octahedral arrangement. The  $M(1)$  octahedron occurs within the heteropolyhedral (H) sheet (of tetrahedra and octahedra); the  $M(2)$  site belongs to the (O) sheet of octahedra in the central part of the block. The  $M(1)$  site is involved in shorter  $\langle M-O \rangle$  bonds than the  $M(2)$  site: 1.973 Å compared to 2.031 Å (Table 4). The higher refined site-scattering value of 25.65 *epfu*

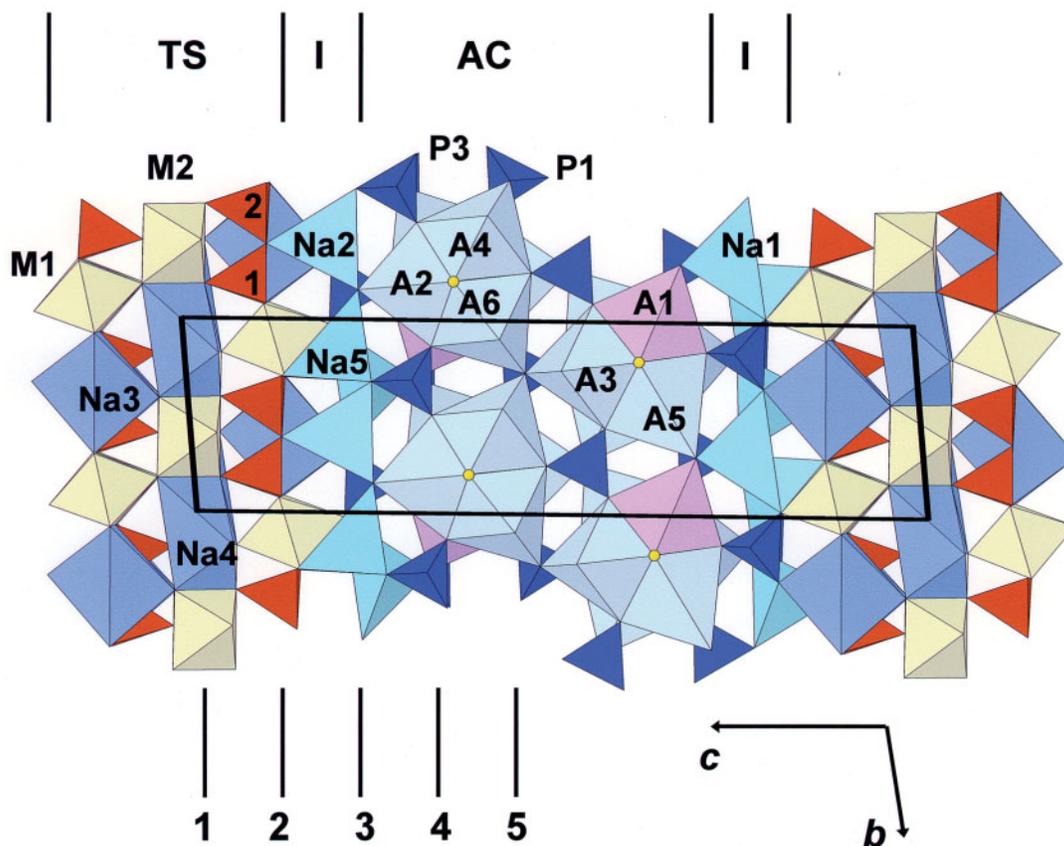


FIG. 1. The crystal structure of polyphite viewed down [100]. *TS*: Ti-silicate block, *AC*: alkaline-cation block, *I*: intermediate layer. Vertical lines 1–5 show the positions of “close-packed” cation layers for a symmetrically unique part of the structure. *M* octahedra are yellowish, *Na* octahedra are light navy-blue, Si tetrahedra are orange, P tetrahedra are purple, [4]- and [5]-coordinated Na polyhedra are greenish blue, Na-dominant A octahedra are greyish blue, Ca-dominant A octahedra are pink, F atoms are shown as yellow circles.

for *M*(1) indicates that most of the stronger-scattering species (Nb and Zr) occur at this site, together with the dominant  $Ti^{4+}$ . However,  $\langle M(2)-O \rangle$  is significantly larger than  $\langle M(1)-O \rangle$ , indicating that the larger scattering species occur at *M*(2), *i.e.*,  $Fe^{2+}$ , Mg and  $Mn^{2+}$ , possibly with some Zr. This results in the site populations given in Table 5. There is good agreement between the observed and calculated site-scattering values, and the observed and predicted mean bond-lengths order in the correct sequence.

Within the O sheet, there is one unique *Na*(4) site, octahedrally coordinated by O atoms, with  $\langle Na(4)-O \rangle = 2.444 \text{ \AA}$ . Within the H sheet, there is one unique *Na*(3) site, octahedrally coordinated by six O-atoms with  $\langle Na(3)-O \rangle = 2.549 \text{ \AA}$ .

*The octahedrally coordinated sites of the AC block:* There are six unique A sites within this block, each

FIG. 2. The crystal structure of polyphite: (a) the octahedron O-sheet in the *TS* block; (b) a close-packed layer of Na and M cations corresponding to the O sheet shown in (a); (c) the heteropolyhedral H-sheet in the *TS* block; (d) a close-packed layer of Na, Si and M cations corresponding to the H sheet shown in (c); (e) linkage of O and H sheets, Na atoms of the H sheet are shown as circles; (f) |AB| sequence of close-packed layers of cations corresponding to the O sheet (black) and H sheet. All cations of the O sheet are shown as black circles. Legend as in Figure 1; *Na*, *M* and *Si* sites are shown as blue, yellowish and orange circles in (b), (d) and (e);  $t_1$  and  $t_2$  translations correspond to unit-cell axes of about 5.4 and 7.1 Å.

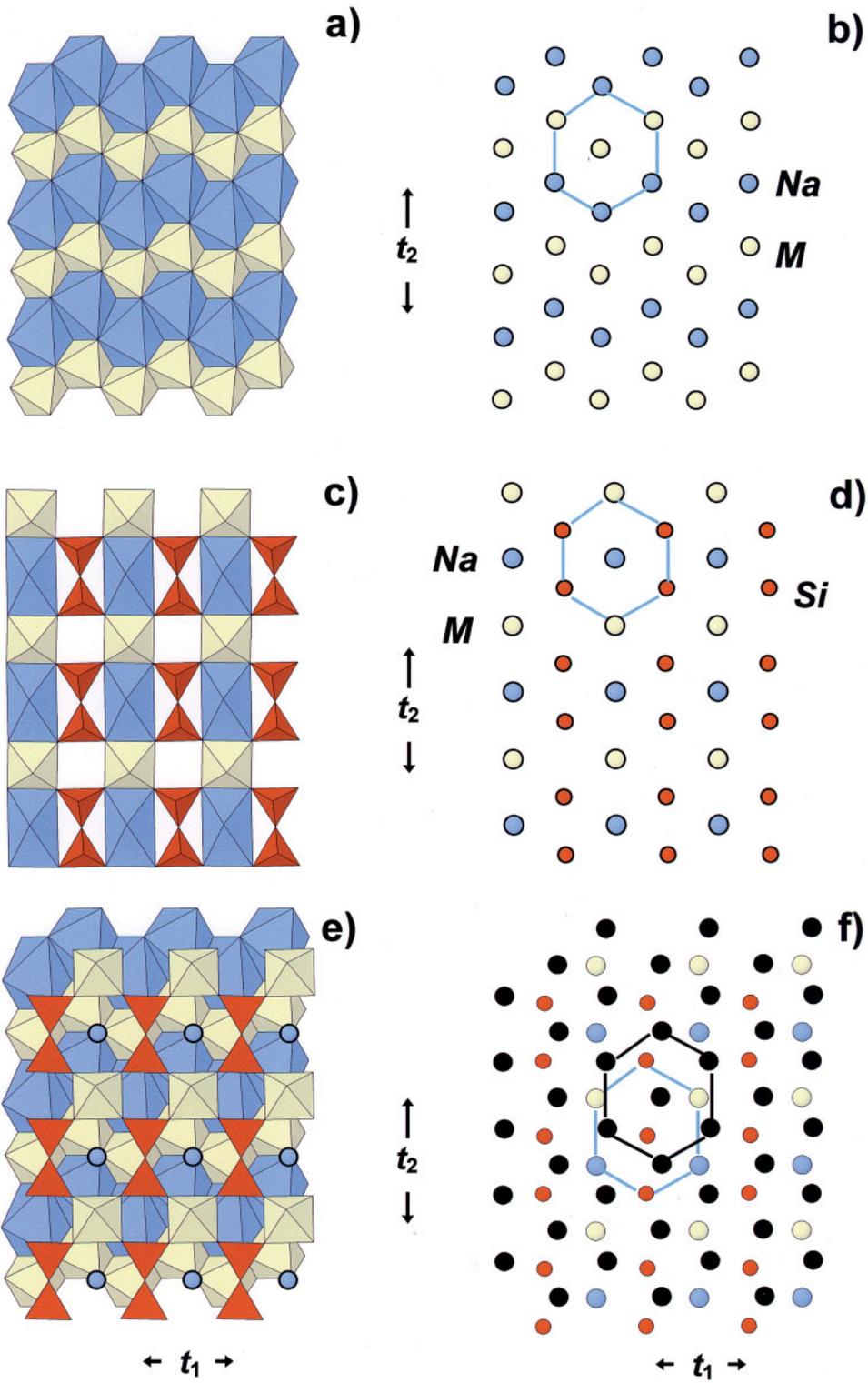


TABLE 3. ATOM PARAMETERS AND DISPLACEMENT FACTORS FOR POLYPHITE

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
M(1)	0.13165(6)	-0.10753(5)	0.11831(1)	0.00509(17)	0.00571(18)	0.00889(18)	0.00093(12)	0.00055(12)	0.00019(11)	0.00654(11)
M(2)	0.22811(8)	0.61396(6)	0.00406(2)	0.0161(2)	0.0095(2)	0.0080(2)	0.00085(14)	-0.00034(15)	0.00279(15)	0.01124(14)
A(1)	0.22160(13)	-0.04447(9)	0.35026(3)	0.0220(4)	0.0172(3)	0.0168(3)	0.0018(2)	0.0023(2)	-0.0008(2)	0.0186(2)
A(2)	0.67082(14)	0.17653(11)	0.31741(3)	0.0104(4)	0.0135(4)	0.0090(4)	0.0013(3)	0.0002(3)	-0.0005(3)	0.0110(3)
A(3)	0.77837(16)	0.76266(12)	0.54343(3)	0.0189(5)	0.0139(5)	0.0118(4)	0.0003(3)	0.0016(3)	0.0028(3)	0.0149(3)
A(4)	0.73596(16)	0.46190(11)	0.41983(3)	0.0221(5)	0.0111(4)	0.0088(4)	0.0002(3)	-0.0025(3)	-0.0022(3)	0.0142(3)
A(5)	0.21592(19)	0.43500(15)	0.34468(4)	0.0198(6)	0.0151(5)	0.0166(6)	0.0034(4)	0.0025(4)	0.0023(4)	0.0170(3)
A(6)	0.7387(2)	0.98070(16)	0.42440(4)	0.0260(6)	0.0169(6)	0.0170(6)	0.0039(4)	0.0009(4)	0.0003(4)	0.0198(4)
Na(1)	0.1808(3)	0.66982(18)	0.23045(5)	0.0367(7)	0.0170(6)	0.0280(7)	0.0040(5)	0.0054(6)	0.0003(5)	0.0270(3)
Na(2)	0.6214(3)	0.38767(19)	0.21296(5)	0.0311(8)	0.0171(7)	0.0185(7)	-0.0002(5)	-0.0023(5)	0.0036(5)	0.0225(4)
Na(3)	0.1324(2)	0.38779(17)	0.12660(4)	0.0218(6)	0.0213(6)	0.0152(5)	0.0026(4)	-0.0006(4)	0.0001(5)	0.0195(2)
Na(4)	-0.2427(2)	0.88253(16)	-0.00295(5)	0.0128(5)	0.0152(5)	0.0280(6)	-0.0064(5)	-0.0070(4)	0.0032(4)	0.0195(3)
Na(5)	0.6373(2)	0.91134(16)	0.19672(4)	0.0272(6)	0.0129(5)	0.0161(5)	-0.0009(4)	-0.0007(5)	-0.0021(4)	0.0189(2)
P(1)	0.28000(12)	0.73333(9)	0.46176(2)	0.0128(3)	0.0103(3)	0.0098(3)	0.0012(2)	0.0008(2)	0.0001(2)	0.01095(13)
P(2)	0.12365(12)	0.15773(9)	0.23490(3)	0.0131(3)	0.0103(3)	0.0109(3)	0.0003(2)	0.0008(2)	0.0005(2)	0.01146(13)
P(3)	0.73298(12)	0.68636(10)	0.30796(3)	0.0131(3)	0.0102(3)	0.0102(3)	0.0012(2)	0.0002(2)	0.0010(2)	0.01209(13)
Si(1)	0.63422(13)	0.17405(10)	0.09611(3)	0.0132(3)	0.0077(3)	0.0089(3)	0.0009(2)	0.0001(2)	-0.0001(2)	0.00993(14)
Si(2)	0.62121(13)	0.60845(9)	0.10685(3)	0.0111(3)	0.0070(3)	0.0077(3)	0.0004(2)	-0.0002(2)	0.0000(2)	0.00866(13)
O(1)	0.1802(5)	0.5498(3)	0.43195(9)	0.0508(15)	0.0201(11)	0.0188(11)	-0.0031(9)	0.0006(10)	-0.0157(10)	0.0303(6)
O(2)	0.8826(6)	0.0831(4)	0.11853(10)	0.0570(18)	0.0507(17)	0.0249(13)	-0.0105(12)	-0.0167(12)	0.0439(15)	0.0458(8)
O(3)	0.3927(6)	0.0756(5)	0.11318(10)	0.0605(19)	0.0591(19)	0.0284(14)	-0.0100(13)	0.0185(13)	-0.0496(16)	0.0496(9)
O(4)	0.5823(4)	0.5958(3)	0.04495(7)	0.0207(9)	0.0133(9)	0.0074(8)	0.0006(7)	-0.0001(7)	0.0002(7)	0.0139(14)
O(5)	0.1789(4)	-0.0258(3)	0.20012(7)	0.0227(10)	0.0121(9)	0.0116(9)	0.0002(7)	-0.0003(7)	0.0033(7)	0.0156(4)
O(6)	0.6287(4)	0.6795(3)	0.25292(8)	0.0307(11)	0.0204(10)	0.0141(9)	0.0023(8)	-0.0072(8)	-0.0008(8)	0.0220(4)
O(7)	0.0186(4)	0.6935(3)	0.30991(9)	0.0144(9)	0.0273(11)	0.0272(11)	0.0064(9)	0.0004(8)	0.0007(8)	0.0228(4)
O(8)	0.6329(4)	0.1810(3)	0.03572(7)	0.0178(9)	0.0187(9)	0.0089(8)	0.0007(7)	0.0005(7)	-0.0000(7)	0.0152(4)
O(9)	0.0787(4)	0.4105(3)	0.03788(7)	0.0180(9)	0.0112(8)	0.0099(8)	0.0018(6)	0.0012(7)	-0.0001(7)	0.0130(4)
O(10)	0.6342(4)	0.3909(3)	0.12426(7)	0.0394(12)	0.0077(8)	0.0109(9)	0.0010(7)	0.0011(8)	0.0025(8)	0.0193(4)
O(11)	0.5663(4)	0.7295(4)	0.4638(1)	0.0138(9)	0.0341(13)	0.03189(12)	0.0101(10)	0.0012(9)	0.0017(9)	0.0261(5)
O(12)	0.1133(4)	-0.1768(3)	0.04920(7)	0.0157(9)	0.0242(10)	0.0104(9)	0.0008(7)	0.0002(7)	-0.0024(7)	0.0169(4)
O(13)	0.1887(5)	0.3376(3)	0.21064(8)	0.0413(13)	0.0114(9)	0.0158(10)	0.0031(7)	0.0010(9)	-0.0048(8)	0.0228(5)
O(14)	0.3845(4)	0.6985(3)	0.13465(8)	0.0236(10)	0.0336(12)	0.0125(9)	-0.0005(8)	0.0007(8)	0.0171(9)	0.0234(5)
O(15)	0.8744(4)	0.7061(4)	0.13204(8)	0.0260(11)	0.0368(13)	0.0121(9)	0.0008(9)	0.0014(8)	-0.0212(10)	0.0251(5)
O(16)	0.1892(5)	0.9058(3)	0.43481(9)	0.0384(13)	0.0200(11)	0.0208(11)	0.0091(9)	0.0030(9)	0.0122(9)	0.0259(5)
O(17)	0.2804(5)	0.1511(3)	0.28513(8)	0.0370(13)	0.0247(11)	0.0131(10)	0.0014(8)	-0.0049(9)	0.0037(9)	0.0252(5)
O(18)	0.1917(5)	0.7468(3)	0.51586(8)	0.0378(13)	0.0250(11)	0.0113(9)	0.0021(8)	0.0083(9)	0.0021(9)	0.0244(5)
O(19)	-0.1530(4)	0.1554(3)	0.24535(11)	0.0165(10)	0.0242(12)	0.0503(16)	-0.0080(11)	0.0097(10)	-0.0002(8)	0.0307(6)
O(20)	0.6514(5)	0.5081(4)	0.33222(10)	0.0313(12)	0.0343(13)	0.0300(13)	0.0199(11)	-0.0012(10)	-0.0098(10)	0.0309(6)
O(21)	0.6389(5)	0.8645(4)	0.33874(10)	0.0428(15)	0.0365(14)	0.0254(12)	-0.0151(11)	-0.0045(11)	0.0209(12)	0.0362(6)
F(1)	-0.0360(3)	0.2038(3)	0.37737(7)	0.0128(7)	0.0245(9)	0.0266(9)	0.0034(7)	0.0012(7)	0.0014(6)	0.0212(4)
F(2)	0.4706(3)	0.2107(2)	0.38948(6)	0.0135(7)	0.0202(8)	0.0191(8)	0.0004(6)	-0.0003(6)	0.0000(6)	0.0177(3)

coordinated by four O-atoms and two F-atoms. The following cations occur at the A sites: Na, Ca,  $Mn^{2+}$ , Mg and Sr, ordered in terms of decreasing content in the AC block. The  $\langle A(1-4)-O \rangle$  distances (2.335, 2.246, 2.359 and 2.387 Å, respectively) are significantly shorter than the  $\langle A(5)-O \rangle$  and  $\langle A(6)-O \rangle$  distances (2.413 and 2.407 Å, respectively), and hence the smaller available cations, Mg and  $Mn^{2+}$ , must occur at the A(1-4) sites. Thus the A(5) and A(6) sites are occupied by Na and Ca. We assign the minor amount of Sr to the A(1) site, which has the highest site-scattering value (17.6 *epfu*). The resultant site-populations (Table 5) show reasonable agreement between observed and calculated  $\langle A-O \rangle$  distances. Calcium is dominant only at one site, A(1), as indicated by the high site-scattering. The A(2-6) sites are Na-dominant. Substitution of Na and  $Mn^{2+}$  at a site is fairly common in these minerals: previously, it has been described for vuonnemite,  $Na_{10}(Na,Mn)TiNb_2[Si_2O_7]_2(PO_4)_2O_3(F,O)$  (Ercit *et al.* 1998) and quadruphite,  $Na_{14}Ca_2Ti_4[Si_2O_7]_2(PO_4)_4$

$O_4F_2$  (Sokolova & Hawthorne 2001). Bond-valence calculations for O and F atoms are in accord with this distribution of cations (Table 6).

*The Na sites of the I layer:* There are two unique Na sites, Na(1) and Na(2), tetrahedrally coordinated by O atoms with a range of  $\langle Na-O \rangle$  distances from 2.227 to 2.452 Å. There is one Na(5) site coordinated by five O-atoms with a  $\langle Na(5)-O \rangle$  distance of 2.429 Å. The bond valences (Table 6) were calculated with the universal curves of Brown (1981). It is pertinent to this work that Na and Mg are represented by the same universal bond-valence curve. Calculation of the bond-valence sums incident at the Na sites of the I layer results in values of 0.87–1.09 *vu* (Table 6), indicating occupancy by Na and not by (Mg,Mn) as reported by Sokolova *et al.* (1987b).

Based on the SREF (Structure REFinement) results and bond-valence calculations, the end-member formula of polyphite is  $Na_5(Na_4Ca_2)Ti_2[Si_2O_7](PO_4)_3O_2F_2, P\bar{1}, Z = 2$ .

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR POLYPHITE

<i>M</i> (1)–O(2)	1.903(2)	<i>A</i> (1)–O(7)	2.291(2)	<i>A</i> (3)–O(1)	2.362(3)	<i>A</i> (5)–O(1)	2.395(3)
<i>M</i> (1)–O(3)	1.929(2)	<i>A</i> (1)–O(16)	2.312(2)	<i>A</i> (3)–O(27)	2.328(3)	<i>A</i> (5)–O(7)	2.345(2)
<i>M</i> (1)–O(5)	2.188(2)	<i>A</i> (1)–O(17)	2.339(2)	<i>A</i> (3)–O(22)	2.361(3)	<i>A</i> (5)–O(17)	2.472(3)
<i>M</i> (1)–O(12)	1.845(2)	<i>A</i> (1)–O(21)	2.371(3)	<i>A</i> (3)–O(20)	2.387(3)	<i>A</i> (5)–O(20)	2.452(3)
<i>M</i> (1)–O(14)	1.991(2)	<i>A</i> (1)–F(1)	2.327(2)	<i>A</i> (3)–F(1)	2.435(2)	<i>A</i> (5)–O(12)	2.376(2)
<i>M</i> (1)–O(15)	1.982(2)	<i>A</i> (1)–F(2)	2.367(2)	<i>A</i> (3)–F(2)	2.284(2)	<i>A</i> (5)–O(5)	2.439(2)
< <i>M</i> (1)–O>	1.973	< <i>A</i> (1)–O,F>	2.278	< <i>A</i> (3)–O,F>	2.364	< <i>A</i> (5)–O,F>	2.413
<i>M</i> (2)–O(4)	2.147(2)	<i>A</i> (2)–O(17)	2.224(3)	<i>A</i> (4)–O(1)	2.468(3)	<i>A</i> (6)–O(11)	2.353(3)
<i>M</i> (2)–O(4) <sub>a</sub>	2.176(2)	<i>A</i> (2)–O(19)	2.175(3)	<i>A</i> (4)–O(11)	2.343(3)	<i>A</i> (6)–O(16)	2.492(3)
<i>M</i> (2)–O(8)	2.039(2)	<i>A</i> (2)–O(20)	2.340(3)	<i>A</i> (4)–O(18)	2.365(2)	<i>A</i> (6)–O(18)	2.389(3)
<i>M</i> (2)–O(9)	1.956(2)	<i>A</i> (2)–O(21)	2.330(3)	<i>A</i> (4)–O(20)	2.386(3)	<i>A</i> (6)–O(20)	2.368(3)
<i>M</i> (2)–O(9) <sub>b</sub>	1.934(2)	<i>A</i> (2)–F(1)	2.166(2)	<i>A</i> (4)–F(1)	2.428(2)	<i>A</i> (6)–F(1)	2.457(2)
<i>M</i> (2)–O(12)	1.939(2)	<i>A</i> (2)–F(2)	2.242(2)	<i>A</i> (4)–F(1)	2.330(2)	<i>A</i> (6)–F(2)	2.386(2)
< <i>M</i> (2)–O>	2.031	< <i>A</i> (2)–O,F>	2.246	< <i>A</i> (4)–O,F>	2.387	< <i>A</i> (6)–O,F>	2.408
Tetrahedrally and [5]-coordinated Na-sites							
<i>Na</i> (1)–O(5)	2.360(2)	<i>Na</i> (2)–O(6)	2.227(3)	<i>Na</i> (5)–O(5) <sub>c</sub>	2.518(2)		
<i>Na</i> (1)–O(6)	2.452(3)	<i>Na</i> (2)–O(10)	2.354(2)	<i>Na</i> (5)–O(6)	2.310(2)		
<i>Na</i> (1)–O(7)	2.317(3)	<i>Na</i> (2)–O(13)	2.356(3)	<i>Na</i> (5)–O(14)	2.466(3)		
<i>Na</i> (1)–O(13)	2.356(2)	<i>Na</i> (2)–O(19)	2.244(3)	<i>Na</i> (5)–O(15)	2.546(3)		
< <i>Na</i> (1)–O>	2.371	< <i>Na</i> (2)–O>	2.295	<i>Na</i> (5)–O(19)	2.305(3)		
				< <i>Na</i> (5)–O>	2.429		
Octahedrally coordinated Na-sites							
<i>Na</i> (3)–O(2)	2.521(4)	<i>Na</i> (4)–O(4)	2.682(2)	<i>Si</i> (1)–O(2)	1.592(3)	<i>Si</i> (2)–O(4)	1.632(2)
<i>Na</i> (3)–O(3)	2.623(4)	<i>Na</i> (4)–O(8) <sub>b</sub>	2.255(2)	<i>Si</i> (1)–O(3)	1.584(3)	<i>Si</i> (2)–O(10)	1.643(2)
<i>Na</i> (3)–O(9)	2.367(2)	<i>Na</i> (4)–O(8) <sub>d</sub>	2.372(2)	<i>Si</i> (1)–O(8)	1.602(2)	<i>Si</i> (2)–O(14)	1.614(2)
<i>Na</i> (3)–O(13)	2.285(2)	<i>Na</i> (4)–O(9)	2.381(2)	<i>Si</i> (1)–O(10)	1.640(2)	<i>Si</i> (2)–O(15)	1.603(2)
<i>Na</i> (3)–O(14)	2.563(3)	<i>Na</i> (4)–O(12) <sub>b</sub>	2.618(2)	< <i>Si</i> (1)–O>	1.605	< <i>Si</i> (2)–O>	1.624
<i>Na</i> (3)–O(15)	2.641(3)	<i>Na</i> (4)–O(12) <sub>e</sub>	2.356(2)				
< <i>Na</i> (3)–O>	2.549	< <i>Na</i> (4)–O>	2.444	<i>Si</i> (1)–O(10)– <i>Si</i> (2)	137.0(1)		
<i>P</i> (1)–O(1)	1.533(2)	<i>P</i> (2)–O(5)	1.559(2)	<i>P</i> (3)–O(6)	1.525(2)		
<i>P</i> (1)–O(22)	1.542(2)	<i>P</i> (2)–O(24)	1.523(2)	<i>P</i> (3)–O(21)	1.539(2)		
<i>P</i> (1)–O(23)	1.532(2)	<i>P</i> (2)–O(20)	1.535(2)	<i>P</i> (3)–O(28)	1.538(2)		
<i>P</i> (1)–O(1)	1.530(2)	<i>P</i> (2)–O(25)	1.534(2)	<i>P</i> (3)–O(31)	1.538(2)		
< <i>P</i> (1)–O>	1.534	< <i>P</i> (2)–O>	1.538	< <i>P</i> (3)–O>	1.535		

TABLE 5. REFINED OCTAHEDRAL-SITE SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR POLYPHITE

Scattering species	SREF value ( <i>epfu</i> )	Site population ( <i>apfu</i> )	Predicted site-scattering ( <i>epfu</i> )	< <i>X</i> – $\phi$ > <sub>calc</sub> * (Å)	< <i>X</i> – $\phi$ > <sub>obs</sub> (Å)
<i>M</i> (1)	Nb, Ti 51.3(1)	1.56 Ti + 0.38 Nb + 0.06 Zr	52.3	1.995	1.973
<i>M</i> (2)	Nb, Ti 46.2(1)	1.26 Ti + 0.13 Fe <sup>2+</sup> + 0.31 Zr + 0.26 Mg + 0.04 Mn	47.6	2.031	2.033
<i>A</i> (1)	Ca, Na 35.2(1)	0.82 Ca + 0.72 Na + 0.40 Mn + 0.06 Sr	36.6	2.359	2.335
<i>A</i> (2)	Ca, Na 28.8(1)	1.10 Na + 0.46 Mn + 0.34 Mg + 0.10 Ca	29.7	2.304	2.246
<i>A</i> (3)	Ca, Na 28.0(1)	1.32 Na + 0.42 Ca + 0.26 Mn	29.4	2.371	2.359
<i>A</i> (4)	Ca, Na 29.4(1)	1.10 Na + 0.70 Ca + 0.20 Mn	31.1	2.374	2.387
<i>A</i> (5)	Ca, Na 24.1(1)	1.60 Na + 0.40 Ca	25.6	2.396	2.413
<i>A</i> (6)	Ca, Na 23.6(1)	1.64 Na + 0.36 Ca	25.2	2.396	2.407

\* radii from Shannon (1976).

### Topology of the structure

The structure of polyphite consists of *TS* and *AC* blocks stacked along [001] with an *I* layer between them (Fig. 1). The *TS* block has a three-layered structure consisting of a central sheet of octahedra and two adjacent heteropolyhedral sheets. The central sheet of octahedra at  $z \approx 0$  is a local close-packing of *M*(2) and *Na*(4) octahedra (Figs. 2a, b). There are two symmetri-

cally distinct zig-zag chains of edge-sharing octahedra within the sheet; Sokolova & Hawthorne (2004) designated this type of edge-sharing chain of octahedra as a *brookite* chain, as it occurs in the crystal structure of brookite, TiO<sub>2</sub>. In the *TS* block, *Na*(4) octahedra form the first brookite-type chain, and *M*(2) octahedra form the second chain. The size of the regular *M*(2) octahedron is less than the size of the irregular *Na*(4) octahedron, and substitution of Mg and Mn<sup>2+</sup> ( $r$  [<sup>6</sup>Mg]

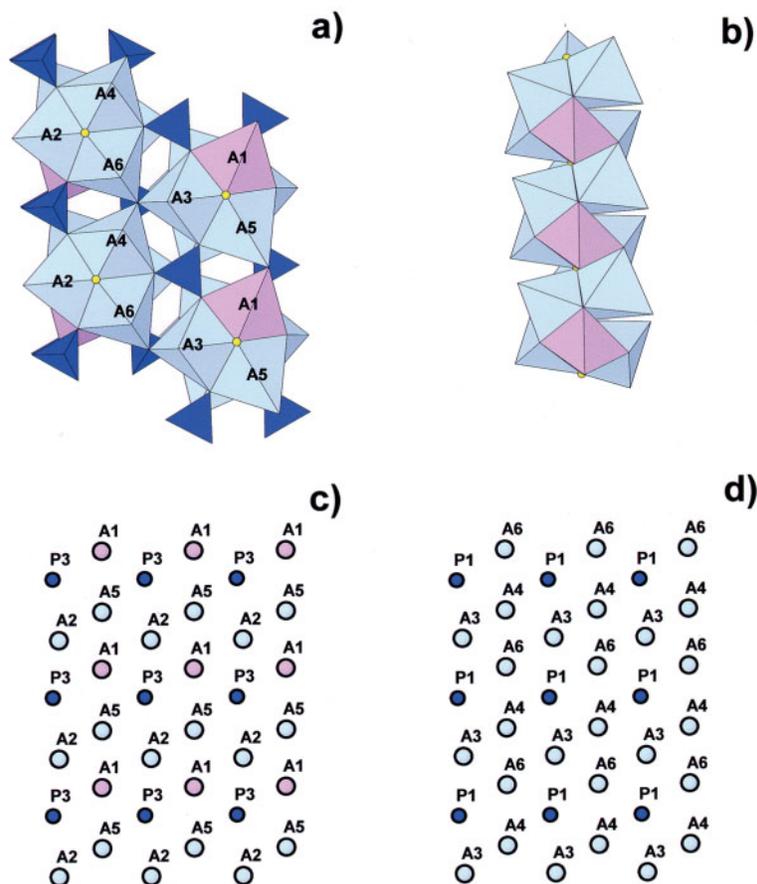


FIG. 3. The crystal structure of polyphite: (a) the AC block viewed down [100]; (b) the infinite chain of octahedron clusters rotated  $\sim 60^\circ$  relative to each other; (c) and (d) close-packed layer of A and P atoms at  $z \approx 0.65$  and  $0.56$ . Legend as in Figure 1; Na- and  $M^{2+}$ -dominant A sites and P sites are shown as blue, pink and purple circles in (c) and (d).

$= 0.72$  and  $r [^{60}\text{Mn}^{2+}] = 0.83 \text{ \AA}$  (Table 5) for Na ( $^{60}\text{r} = 1.02 \text{ \AA}$ ) (Shannon 1976) promotes linkage between the two compositionally different types of brookite chains. Within the O sheet, the M and Na octahedra each share three common edges. The Na(4) octahedron is also elongate along the b axis in order to promote this linkage. In each of the two H sheets (located at  $z \approx -0.12$  and  $0.12$ ),  $[\text{Si}_2\text{O}_7]$  groups share common edges with M(1) octahedra, giving rise to large hexagonal voids that incorporate the Na(3) octahedra (Fig. 2c) [which share edges with M(1) octahedra in the plane of the sheet]. The central O-sheet links to the adjacent H-sheets through common vertices of  $(\text{SiO}_4)$  tetrahedra, M(1) and Na(3) octahedra of the H sheet, and M(2) and Na(4) octahedra of the O sheet (Fig. 2e). An array of inversion centers extends along the O sheet, making the two H sheets symmetrically equivalent (Fig. 2f).

The AC block (Fig. 3a) can be described in terms of nacaphite-like *trimeric clusters* of octahedra (Sokolova & Hawthorne 2001). The key motif in the structure of the AC block is the trimer of octahedra [as in nacaphite,  $\text{Na}(\text{Na,Ca})_2(\text{PO}_4)\text{F}$ ]. Three A octahedra share a single edge, and also each shares a face with two adjacent octahedra; the central axis of each cluster is an edge (formed by two F atoms) that is common to all three constituent octahedra (Fig. 3a). These trimeric clusters link to form a convoluted chain of octahedra (Fig. 3b) that extends in the a direction. Clusters adjacent in the chain are rotated  $\sim 60^\circ$  relative to each other and connect by sharing both faces and edges. Two octahedra of the cluster are connected to the next trimer through two common faces, and the remaining octahedra link through common edges. The chain shows pseudo-hexagonal symmetry described by a  $6_3$  axis along the

sequence of common [F(1)–F(2)] edges that defines the central axis of the chain. Combination of two clusters corresponds to a sequence of two [F(1)–F(2)] edges of 2.700 and 2.731 Å with an  $\angle$  F–F–F = 166.5° (sum = 5.431 Å), defining the  $a$  repeat and giving an  $a$  unit-cell parameter of 5.3933(2) Å. There are six  $A$  sites within the  $AC$  block, corresponding to two unique trimeric clusters. The ratio of divalent to monovalent cations is 0.60. The thickness of the  $AC$  block along the  $c$  axis is about 12 Å, corresponding to two infinite chains of octahedron clusters.

In polyphite, the  $I$  layer is characterized by  $Na$  sites with coordination numbers of [4] and [5] (Table 4). The  $Na$  polyhedra link to  $P(2)$  tetrahedra to form a rather irregular layer (Fig. 4b). This layer is situated

at the junction of the  $TS$  and  $AC$  blocks, and can be regarded as a derivative of the  $AC$  block (Figs. 1, 5a). The thickness of this layer is approximately that of one  $Na$  polyhedron.

#### SOBOLEVITE

##### Coordination of the cations

The structure of sobolevite also consists of  $TS$  and  $AC$  blocks stacked along [001] with an intermediate layer between them (Fig. 5b).

*The  $T (= Si + P)$  sites:* There are four unique  $Si$  sites in the crystal structure of sobolevite, with a grand  $\langle Si-O \rangle$  distance of 1.621 Å. The  $Si(1)$  and  $Si(3)$  tetrahedra

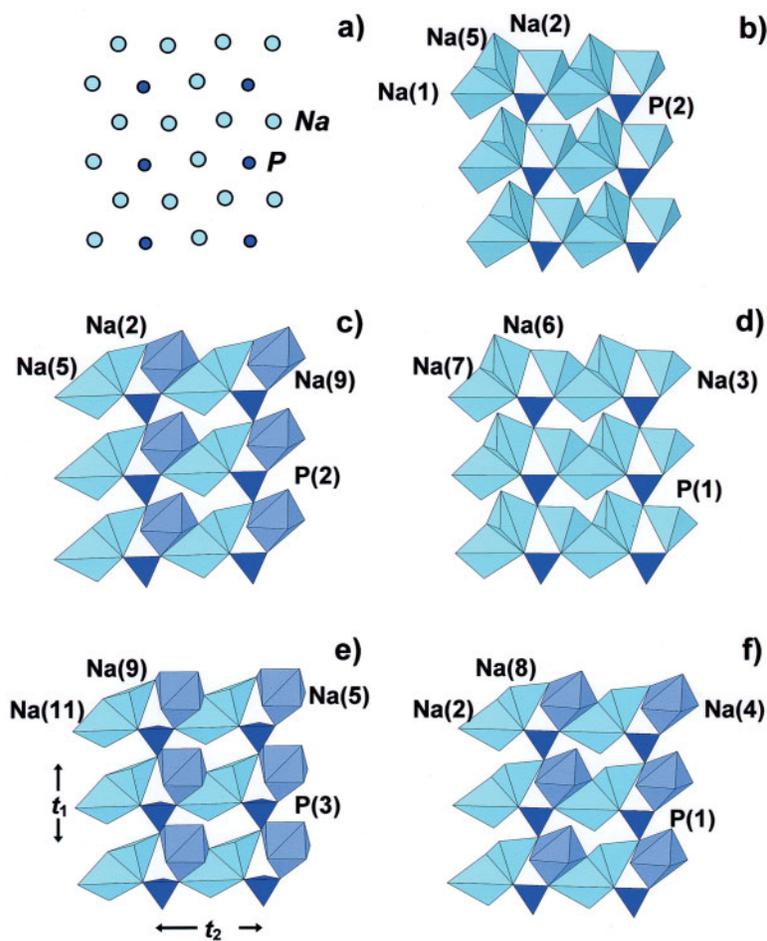


FIG. 4. The  $I$  layer: (a) a close-packed layer of Na and P atoms within the intermediate layer; (b) in polyphite,  $z \approx 0.21$ ; (c) and (d) in sobolevite;  $z \approx 0.43$  and 0.70; (e) and (f) in quadruphite,  $z \approx 0.20$  and 0.75. The [4]- and [5]-coordinated Na polyhedra are greenish blue, [6]-coordinated Na polyhedra are light navy-blue, and the  $P$  tetrahedra are purple. In (a), Na and P atoms are greenish blue and purple circles.

link through O(16), and the Si(2) and Si(4) tetrahedra link through O(15), forming [Si<sub>2</sub>O<sub>7</sub>] groups with a mean Si–O–Si angle of 137.2°. There are four unique P sites within the alkali-cation block, all of which are coordinated by tetrahedra of O atoms with <P–O> distances in the range 1.526–1.549 Å.

*The octahedral sites of the TS block:* There are four unique M sites, each coordinated by an octahedral arrangement of O atoms. The M(1) and M(2) octahedra occur within the H sheets, and the M(3) and M(4) sites belong to the O sheet of octahedra in the central part of the block. Two pairs of sites, [M(1) and M(2)], and [M(3) and M(4)], are related by pseudo-inversion centers located in the O sheet: both refined site-scattering values and mean bond-lengths are very similar (Table 9). The M(1,2) sites are characterized by shorter <M–O> bonds than the M(3,4) sites: 1.980 and 1.965 Å versus 2.056 and 2.043 Å (Table 8). The higher refined site-scattering values of 25.80 and 24.90 *epfu* for M(1) and M(2) indicate that the dominant Ti<sup>4+</sup> occurs at these sites, together with the more strongly scattering species (Nb, Zr and Fe<sup>3+</sup>). The <M(3,4)–O> distances are significantly greater than the <M(1,2)–O> distances, indicating that the larger scattering species, *i.e.*, Mg and Mn<sup>2+</sup>, occur at M(3,4). This results in the site populations given in Table 9; note the good agreement between the observed and calculated site-scattering values and the observed and predicted mean bond-lengths.

Within the O sheet, there are two unique Na sites, Na(4) and Na(12), with a grand <Na–O> equal to 2.444 Å. Bond-valence calculations show that two anion

sites of the O sheet, OF(2) and OF(23), are occupied by O and F atoms in the ratio 1 : 1; together with F at the F(1) and F(2) sites, this gives a total of 3 F *apfu*, in accord with the F content determined by electron-microprobe analysis (Table 1). Within the H sheets, there are two unique Na sites, [6]-coordinated Na(8) and [5]-coordinated Na(10), with <Na(8)–O> = 2.482 and <Na(10)–O> = 2.481 Å.

*The octahedrally coordinated sites of the AC block:* There are six unique sites within this block, each coordinated by four O atoms and two F atoms. The following cations occur at these sites: Na, Ca, Mn<sup>2+</sup> and Sr, ordered in terms of decreasing content in the AC block. There is complete order of Ca at the Ca site, with <Ca–O> = 2.383 Å, and Na at two sites, Na(1) and Na(11), with <Na–O> = 2.415 and 2.435 Å, respectively. The <A(1–3)–O> distances are 2.346, 2.278 and 2.309 Å, respectively. The highest scattering, 16 *epfu*, occurs at the A(3) site, and the longest mean distance involves the A(1) site, and so we assign the maximal amount of Na and 0.06 *apfu* Sr to the A(1) site. The A(1) and A(2) sites are dominated by Na, whereas the A(3) site is dominated by divalent cations, Ca and Mn<sup>2+</sup>. The resultant site-populations (Table 9) show reasonable agreement between observed and calculated <A–O> distances. Bond-valence calculations for O and F atoms are in accord with this distribution of cations (Table 10).

*The Na sites of the I layer:* There are two unique I layers in the crystal structure of sobolevite. One layer has two distinct Na sites, Na(3) and Na(7), tetrahedrally coordinated by O atoms, with <Na–O> equal to 2.300

TABLE 6. BOND-VALENCE\* (*vu*) TABLE FOR POLYPHYTE

	P(1)	P(2)	P(3)	Si(1)	Si(2)	M(1)	M(2)	A(1)	A(2)	A(3)	A(4)	A(5)	A(6)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Σ
O(1)	1.27									0.24	0.21	0.23							1.95
O(2)				1.08	0.82													0.17	2.07
O(3)				1.11	0.76													0.14	2.01
O(4)					0.97		0.38												
O(5)		1.18				0.40	0.41											0.13	1.89
O(6)			1.30											0.22				0.17	1.97
O(7)			1.25					0.31					0.25	0.19	0.28			0.24	2.01
O(8)				1.06			0.55							0.24					2.05
O(9)							0.68											0.27	2.10
O(10)							0.69											0.22	2.10
O(11)	1.24			1.04	0.95													0.22	2.21
O(12)						0.96	0.68		0.26	0.27			0.24						2.01
O(13)		1.30																0.14	2.00
O(14)																		0.22	2.00
O(15)					1.02	0.65												0.16	2.01
O(16)	1.27				1.04	0.67												0.14	2.01
O(17)		1.26						0.30	0.24					0.19					2.00
O(18)			1.28					0.27	0.30				0.20						2.03
O(19)				1.26						0.23	0.25		0.23						1.99
O(20)										0.33					0.28			0.25	2.12
O(21)			1.25							0.23		0.24	0.20						1.92
F(1)								0.26	0.24					0.24					1.99
F(2)								0.22	0.25	0.16	0.17	0.17	0.20	0.24					1.18
Σ	5.06	5.00	5.05	4.29	3.98	4.26	3.39	1.57	1.56	1.34	1.35	1.20	1.33	0.87	1.00	1.09	1.19	1.00	
AG**	5.00	5.00	5.00	4.00	4.00	4.19	3.57	1.64	1.45	1.45	1.34	1.20	1.18	1.00	1.00	1.00	1.00	1.00	

\* bond valences (*vu*) from curves of Brown (1981) for Ca, Na, Sr, Mg, Nb, Ti<sup>4+</sup>, Zr, P, Si, Fe<sup>3+</sup>, Mn<sup>2+</sup>.

\*\* aggregated charge.

TABLE 7. ATOM PARAMETERS AND DISPLACEMENT FACTORS FOR SOBOLEVITE

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
M(1)	0.30679(11)	0.65537(16)	0.14054(2)	0.0079(4)	0.0064(4)	0.0127(5)	-0.0023(3)	0.0002(3)	-0.0032(3)	0.0090(3)
M(2)	-0.03714(11)	0.84831(16)	-0.01221(2)	0.0061(4)	0.0038(4)	0.0056(4)	0.0011(3)	0.0013(3)	0.0034(3)	0.0051(3)
M(3)	0.52398(16)	0.5229(2)	0.06679(3)	0.0150(6)	0.0167(6)	0.0078(5)	0.0019(4)	0.0013(4)	0.0030(4)	0.0131(4)
M(4)	-0.25318(15)	0.9826(2)	0.06153(3)	0.0083(5)	0.0238(6)	0.0126(6)	0.0005(4)	0.0004(4)	0.0040(4)	0.0149(4)
A(1)	0.3720(3)	0.3620(5)	-0.20778(5)	0.0161(11)	0.0268(13)	0.0000(9)	-0.0013(8)	-0.0028(7)	-0.0019(9)	0.0144(6)
A(2)	0.1332(3)	-0.1806(4)	-0.23131(6)	0.0133(12)	0.0168(11)	0.0169(12)	-0.0028(8)	0.0080(8)	-0.0010(8)	0.0154(7)
A(3)	0.1403(3)	0.3293(4)	-0.14189(5)	0.0247(10)	0.0233(10)	0.0158(9)	-0.0014(6)	-0.0045(7)	-0.0024(7)	0.0215(6)
Ca	-0.10012(19)	-0.1402(3)	-0.16378(4)	0.0112(6)	0.0158(6)	0.0234(7)	-0.0034(5)	0.0050(5)	-0.0013(4)	0.0167(3)
Na(1)	-0.1112(4)	0.3569(5)	-0.21275(7)	0.0111(12)	0.0140(12)	0.0146(12)	0.0047(9)	-0.0019(9)	-0.0024(9)	0.0133(5)
Na(2)	0.4107(5)	0.3090(8)	-0.07527(10)	0.0291(18)	0.044(2)	0.0332(18)	-0.0154(15)	0.0024(13)	0.0099(15)	0.0353(9)
Na(3)	-0.1408(5)	0.1952(7)	0.20108(8)	0.0205(15)	0.044(2)	0.0215(14)	0.0198(13)	0.0057(11)	-0.0033(13)	0.0284(8)
Na(4)	0.0227(5)	0.5150(6)	0.06698(10)	0.0107(12)	0.0156(12)	0.0404(17)	-0.0004(12)	0.0085(11)	0.0004(10)	0.0220(6)
Na(5)	0.6813(4)	0.8643(6)	-0.08480(7)	0.0183(13)	0.0272(15)	0.0118(12)	0.0040(10)	-0.0024(10)	-0.0007(11)	0.0192(6)
Na(6)	0.3256(4)	0.1764(6)	0.19063(8)	0.0134(12)	0.0325(16)	0.0112(12)	0.0037(11)	0.0022(9)	-0.0038(11)	0.0190(6)
Na(7)	0.5909(5)	0.6472(8)	0.21383(11)	0.0148(15)	0.048(2)	0.050(2)	-0.0177(18)	0.0007(14)	-0.0029(14)	0.0376(10)
Na(8)	0.8201(4)	0.6544(5)	0.14646(7)	0.0128(12)	0.0167(13)	0.0164(13)	-0.0013(10)	-0.0038(10)	-0.0023(10)	0.0154(6)
Na(9)	-0.0613(5)	0.3318(6)	-0.06369(9)	0.0161(13)	0.0171(13)	0.0243(14)	0.0035(11)	0.0050(11)	0.0008(10)	0.0190(6)
Na(10)	0.4527(5)	0.8461(6)	-0.01722(8)	0.0345(18)	0.0221(15)	0.0155(14)	0.0050(11)	0.0054(13)	-0.0008(13)	0.0239(7)
Na(11)	0.3834(5)	0.8641(6)	-0.15845(8)	0.0181(14)	0.0259(16)	0.0197(14)	0.0034(11)	0.0032(11)	-0.0006(11)	0.0205(6)
Na(12)	0.2575(5)	0.0006(5)	0.06354(8)	0.0295(15)	0.0120(12)	0.0208(13)	0.0097(10)	0.0111(11)	0.0076(10)	0.0204(6)
P(1)	0.1053(3)	0.7026(3)	0.21542(4)	0.0162(8)	0.0190(8)	0.0075(6)	0.0017(6)	0.0054(5)	-0.0005(6)	0.0140(3)
P(2)	0.1661(2)	0.8018(3)	-0.08850(4)	0.0071(7)	0.0152(7)	0.0148(7)	-0.0012(6)	-0.0020(5)	0.0006(6)	0.0125(3)
P(3)	-0.3834(3)	0.1110(4)	0.26344(5)	0.0152(8)	0.0216(8)	0.0193(8)	-0.0007(7)	0.0065(6)	-0.0047(7)	0.0185(3)
P(4)	0.6556(2)	0.3876(3)	-0.13664(4)	0.0114(6)	0.0110(6)	0.0047(6)	0.0018(5)	-0.0042(5)	0.0047(6)	0.0092(3)
Si(1)	0.0150(2)	0.1477(3)	0.12600(4)	0.0062(7)	0.0064(7)	0.0133(7)	0.0029(5)	-0.0037(5)	0.0017(5)	0.0088(3)
Si(2)	-0.3133(2)	0.3426(3)	-0.00553(4)	0.0029(6)	0.0129(8)	0.0112(7)	-0.0013(5)	-0.0015(5)	0.0045(5)	0.0091(3)
Si(3)	0.5846(3)	0.1624(3)	0.13313(5)	0.0169(8)	0.0091(7)	0.0102(7)	0.0024(5)	0.0033(6)	-0.0042(6)	0.0120(3)
Si(4)	0.2574(3)	0.3607(4)	0.00121(4)	0.0129(7)	0.0148(8)	0.0090(7)	-0.0024(6)	0.0049(6)	-0.0033(6)	0.0121(3)
O(1)	0.3415(9)	0.6553(10)	0.09629(14)	0.034(3)	0.018(3)	0.024(3)	-0.0041(19)	0.001(2)	0.001(2)	0.0252(12)
OF(2)	0.5262(7)	0.8184(9)	0.03928(10)	0.011(2)	0.025(2)	0.0000(15)	-0.0043(15)	0.0010(14)	0.0024(17)	0.0121(9)
O(3)	0.5160(8)	0.4078(9)	0.15191(12)	0.023(2)	0.011(2)	0.020(2)	-0.0110(17)	-0.0029(18)	0.0042(17)	0.0179(10)
O(4)	0.15912(10)	0.52131(10)	-0.09211(19)	0.041(4)	0.007(2)	0.058(4)	-0.010(2)	0.011(3)	0.003(2)	0.0351(15)
O(5)	0.6809(6)	0.2961(11)	-0.09997(10)	0.012(2)	0.038(3)	0.0000(15)	0.0148(17)	-0.0042(13)	-0.0077(18)	0.0165(10)
O(6)	0.4948(8)	0.9219(11)	0.14830(12)	0.028(2)	0.024(2)	0.015(2)	-0.0007(18)	-0.0068(17)	-0.014(2)	0.0225(11)
O(7)	0.6624(9)	0.6698(10)	-0.13496(14)	0.038(3)	0.016(2)	0.022(2)	-0.0082(18)	0.001(2)	-0.014(2)	0.0256(12)
O(8)	0.4622(7)	0.3099(12)	-0.15261(16)	0.011(2)	0.031(3)	0.037(3)	0.001(2)	-0.009(2)	-0.0109(19)	0.0267(12)
O(9)	0.1137(9)	0.9077(12)	0.14060(12)	0.036(3)	0.038(3)	0.0094(19)	0.013(2)	0.0012(19)	0.025(3)	0.0277(13)
O(10)	0.3625(8)	0.8832(12)	-0.07250(12)	0.018(2)	0.035(3)	0.009(2)	-0.001(2)	0.0007(17)	-0.006(2)	0.0208(10)
O(11)	0.7112(8)	0.3219(9)	0.03483(11)	0.031(3)	0.012(2)	0.0026(17)	-0.0018(14)	0.0047(17)	-0.0016(17)	0.0152(9)
O(12)	0.5642(7)	0.1773(10)	0.09333(13)	0.0057(19)	0.035(3)	0.017(2)	0.007(2)	-0.0011(16)	0.0016(17)	0.0194(10)
O(13)	-0.0306(6)	0.1285(10)	0.08699(11)	0.0109(18)	0.022(2)	0.012(2)	-0.0066(17)	0.0085(14)	0.0069(16)	0.0147(9)
O(14)	0.0025(6)	0.8718(9)	-0.06568(11)	0.0015(16)	0.022(2)	0.0099(18)	0.0050(16)	-0.0015(13)	0.0048(15)	0.0111(8)
O(15)	0.4583(6)	0.3425(11)	-0.01683(13)	0.0000(17)	0.034(3)	0.018(2)	-0.0048(19)	0.0032(15)	0.0023(17)	0.0171(10)
O(16)	-0.1887(8)	0.1441(10)	0.14434(12)	0.020(2)	0.025(3)	0.010(2)	0.0019(18)	-0.0039(17)	-0.0031(19)	0.0185(10)
O(17)	0.1439(9)	0.5665(13)	0.24806(14)	0.032(3)	0.036(3)	0.018(2)	-0.005(2)	0.009(2)	0.003(3)	0.0285(12)
O(18)	0.1328(7)	0.9289(11)	-0.12219(13)	0.014(2)	0.035(3)	0.012(2)	0.011(2)	-0.0024(16)	-0.001(2)	0.0204(10)
O(19)	-0.5478(9)	0.2160(12)	0.28499(13)	0.036(3)	0.035(3)	0.013(2)	-0.004(2)	0.0143(19)	0.009(2)	0.0274(12)
O(20)	0.1413(9)	0.1223(11)	-0.01050(15)	0.039(3)	0.017(2)	0.028(3)	-0.006(2)	0.005(2)	-0.005(2)	0.0277(12)
O(21)	0.1163(9)	0.4017(12)	0.13761(16)	0.029(3)	0.035(3)	0.039(3)	-0.016(3)	0.011(2)	-0.033(2)	0.0340(15)
O(22)	0.8112(10)	0.2993(17)	-0.15579(18)	0.033(3)	0.068(5)	0.040(3)	0.005(3)	0.009(3)	0.035(3)	0.047(2)
OF(23)	0.7483(8)	0.6789(10)	0.08908(14)	0.017(2)	0.016(2)	0.024(2)	-0.0016(19)	-0.0000(19)	-0.0018(17)	0.0191(10)
O(24)	-0.2339(7)	0.0962(10)	-0.02273(12)	0.021(2)	0.022(2)	0.013(2)	0.0092(18)	0.0053(17)	0.0117(19)	0.0185(10)
O(25)	-0.2344(7)	0.5879(9)	-0.02360(11)	0.024(2)	0.0122(19)	0.0094(17)	0.0024(15)	0.0075(15)	-0.0082(16)	0.0149(9)
O(26)	-0.4078(10)	0.1962(13)	0.22924(17)	0.037(3)	0.030(3)	0.042(3)	-0.004(3)	0.003(3)	0.008(3)	0.0360(14)
O(27)	0.2867(8)	0.3709(10)	0.04073(12)	0.029(2)	0.017(2)	0.013(2)	0.0069(17)	-0.0082(17)	-0.0073(18)	0.0201(10)
O(28)	-0.1952(10)	0.2096(12)	0.27935(15)	0.044(3)	0.028(3)	0.019(2)	0.005(2)	-0.012(2)	0.002(2)	0.0308(13)
O(29)	0.1513(9)	0.6080(12)	-0.01325(17)	0.021(3)	0.022(3)	0.050(3)	0.012(3)	0.012(2)	0.018(2)	0.0309(13)
O(30)	0.1089(8)	0.9843(10)	0.22244(14)	0.022(2)	0.020(2)	0.027(2)	0.0035(19)	0.017(2)	-0.0023(19)	0.0226(11)
O(31)	-0.0822(7)	0.6267(12)	0.20039(14)	0.0051(19)	0.037(3)	0.023(2)	0.004(2)	-0.0013(17)	-0.0043(19)	0.0217(11)
O(32)	0.2749(8)	0.6371(11)	0.19382(15)	0.027(3)	0.027(3)	0.022(3)	-0.004(2)	0.008(2)	0.002(2)	0.0252(12)
O(33)	-0.0630(7)	0.8481(9)	0.03138(11)	0.024(2)	0.016(2)	0.0037(18)	0.0023(15)	0.0018(17)	-0.0070(18)	0.0146(9)
O(34)	-0.3879(8)	0.8252(9)	0.26630(14)	0.020(2)	0.011(2)	0.028(3)	0.0101(17)	-0.0034(18)	0.0049(17)	0.0197(11)
F(1)	0.1321(8)	0.1001(9)	-0.19090(13)	0.034(2)	0.015(2)	0.038(3)	0.002(2)	0.013(2)	-0.0014(19)	0.0288(10)
F(2)	0.1353(6)	0.6007(8)	-0.18266(10)	0.0129(16)	0.0116(17)	0.0173(17)	0.0002(14)	-0.0006(13)	0.0002(14)	0.0140(7)

and 2.400 Å, respectively, and one Na(6) site coordinated by five O atoms with an <Na(6)-O> distance of 2.447 Å. The other layer also has two distinct Na sites, Na(2) and Na(5), tetrahedrally coordinated by O atoms

with <Na-O> 2.281 and 2.352 Å, respectively, and one Na(9) site octahedrally coordinated by six O atoms with an <Na(9)-O> distance of 2.471 Å. As with polyphite, the bond-valence sums incident at the Na sites of the I

layer (Table 10) indicate occupancy by Na rather than (Mg,Mn) as assigned in previous work.

On the basis of the SREF results and bond-valence calculations, the end-member formula of sobolevite is  $\text{Na}_{12}\text{Ca}(\text{NaCaMn}^{2+})\text{Ti}^{4+}_2(\text{Ti}^{4+}\text{Mn})[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_3\text{F}_3$ , space group  $Pc$ ,  $Z = 2$ .

#### Structure topology

The *TS* block occurs at  $z \approx 0.06$  and  $0.56$  (Fig. 5b). The O sheet at  $z \approx 0.06$  is a local close-packing of  $M(3,4)$  and  $Na(4,12)$  octahedra identical to the O

sheet in polyphite (Figs. 2a, b). The *Na* octahedra and  $M(3,4)$  octahedra form two types of *brookite* chains within the O sheet. As we have shown for polyphite and quadruphite (Sokolova & Hawthorne 2001), the size of a regular *M* octahedron is less than the size of an irregular *Na* octahedron, and in sobolevite, substitution of Mg and  $\text{Mn}^{2+}$  ( $r^{[6]}\text{Mg} = 0.72$  and  $r^{[6]}\text{Mn}^{2+} = 0.83 \text{ \AA}$ ) (Table 9) for Na ( $r^{[6]}\text{Na} = 1.02 \text{ \AA}$ ) (Shannon 1976) promotes linkage between the two compositionally different types of *brookite* chains. In sobolevite, the total content of (Mg +  $\text{Mn}^{2+}$ ) at the  $M(3)$  and  $M(4)$  sites of the O sheet is  $1.68 \text{ apfu}$ . In polyphite, it is  $0.30 \text{ apfu}$  at

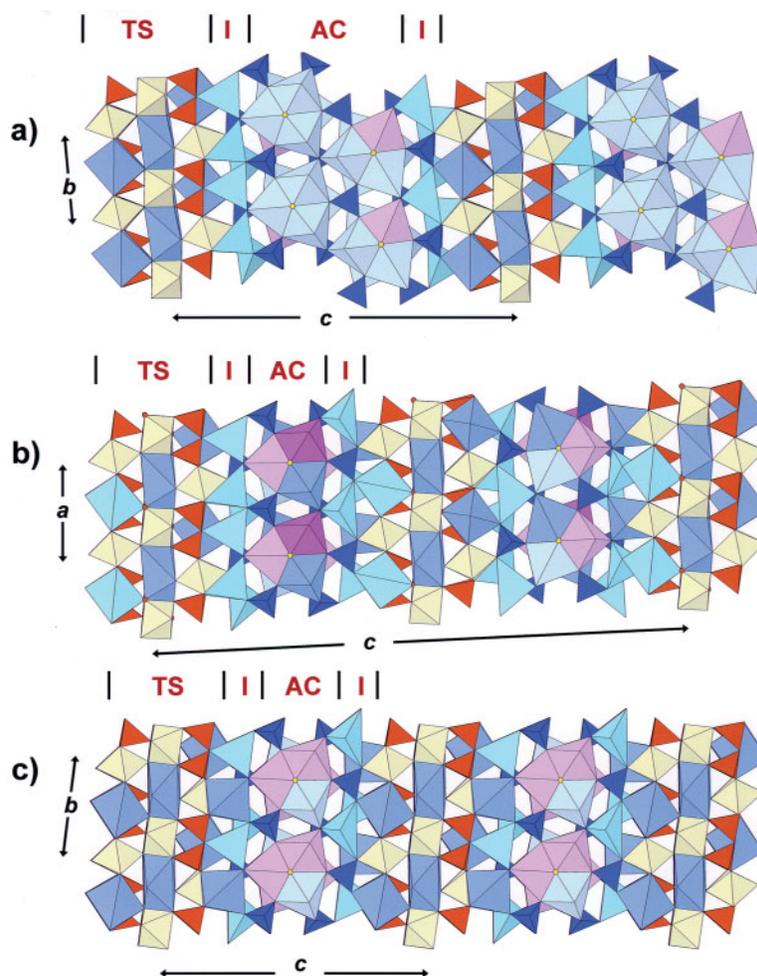


FIG. 5. The crystal structures of (a) polyphite projected along [100]; (b) sobolevite projected along [010], and (c) quadruphite projected along [100]. The Na-dominant and  $M^{2+}$ -dominant A-octahedra of the AC block are blue and pink, the [6–8]-coordinated Na polyhedra of the *TS* and AC blocks and intermediate layers are light navy-blue, the Ca octahedra of the AC block are dark pink, the [4–5]-coordinated Na polyhedra of *I* layers and *TS* block are greenish blue, the *P* tetrahedra are purple, the Si tetrahedra are orange, F atoms are shown as yellow circles, OF sites are shown as orange circles.

the  $M(2)$  site, about 2.5 times less in terms of a  $M$  site of the O sheet. In sobolevite, increase in  $M^{2+}$  at the  $M$  sites results in partial substitution of  $O^{2-}$  for  $F^-$  in the O sheet. In accord with the bond-valence requirements of the two sites, OF(2) and OF(23) are occupied by O and F atoms:  $(O_{0.5}F_{0.5})$  (Table 10). Each site receives bond valence from two  $M$  sites and one Na site of the O sheet and one Na site of the adjacent H sheet. These two OF sites form a common edge in a brookite chain of  $M$  octahedra. In each of the two unique H sheets (located at  $z \approx 0$  and 0.14),  $[\text{Si}_2\text{O}_7]$  groups share common edges with  $M(1)$  and  $M(2)$  octahedra, giving rise to the voids that incorporate the [5]-coordinated  $Na(10)$  polyhedra or  $Na(8)$  octahedra (Fig. 5b). The central O sheet and adjacent H sheets link to each other through common

vertices of  $(\text{SiO}_4)$  tetrahedra,  $M(1,2)$  octahedra and  $Na(8,10)$  polyhedra of an H sheet and  $M(1,2)$  and  $Na(4,12)$  octahedra of an O sheet.

The thickness of the AC block in sobolevite is about 6 Å along the  $c$  axis, *i.e.*, twice as small as in polyphite (Figs. 3a, 6a). The topologies of the AC block in sobolevite, polyphite and quadruphite (Sokolova & Hawthorne 2001) are identical (Figs. 5a–c). There are three A sites, two Na sites and one Ca site within the AC block, corresponding to two unique trimeric clusters. These trimeric clusters link to form a convoluted chain of octahedra (Fig. 6b) that extends in the  $b$  direction. Combination of two clusters corresponds to a sequence of two  $[\text{F}(1)–\text{F}(2)]$  edges of 2.722 and 2.729 Å, with an  $\angle\text{F}–\text{F}–\text{F} = 165.9^\circ$  (sum = 5.451 Å), defining the  $b$  repeat

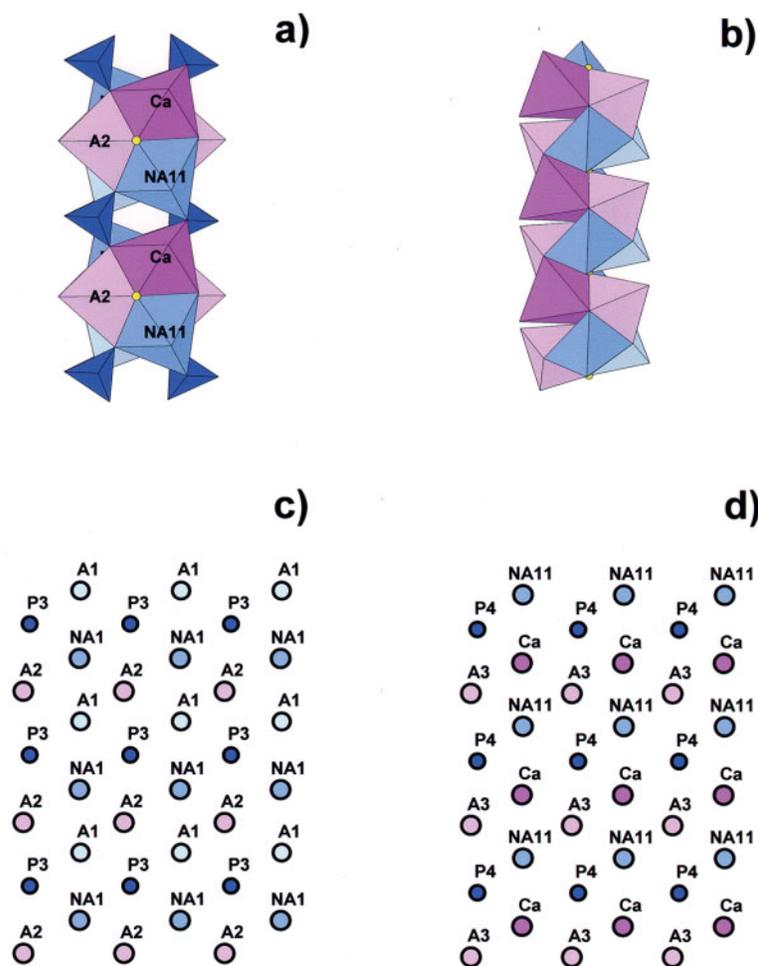


FIG. 6. The crystal structure of sobolevite: (a) the AC block viewed down [010]; (b) the infinite chain of trimeric clusters; (c) and (d) close-packed layers of P, Ca, Na and A cations at  $z \approx 0.28$  and 0.35. Legend as in Figure 5.

and giving a *b* unit-cell parameter of 5.4106(4) Å. The ratio of divalent to monovalent cations is 0.61, close to the corresponding value of 0.60 in polyphite.

In sobolevite, the *I* layer is characterized by *Na* sites with coordination numbers [4], [5] and [6] (Table 8, Figs. 4c, d). In spite of irregularity of the *I* layer, its topology is identical in polyphite (Fig. 4b), sobolevite and quadruphite (Figs. 4e, f). Its composition is also very simple, and the only cations involved are Na and P, the only difference being the coordination numbers

of the Na atoms. In accord with bond-valence requirements, they change from structure to structure for better articulation of the *TS* and *AC* blocks.

#### COMPARISON WITH PREVIOUS RESULTS

##### Polyphite

(1) The space group has been changed from *P1* to  $\bar{P}1$ .

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SOBOLEVITE

M(1)–O(1)	1.828(6)	M(2)–O(14)	2.209(5)	M(3)–O(1)	1.946(6)	M(4)–OF(2)	1.972(5)
M(1)–O(3)	2.030(5)	M(2)–O(20)	1.946(6)	M(3)–OF(2)	1.951(5)	M(4)–O(11)	2.140(5)
M(1)–O(6)	1.976(5)	M(2)–O(24)	1.963(5)	M(3)–O(11)	2.193(5)	M(4)–O(12)	2.152(6)
M(1)–O(9)	1.932(6)	M(2)–O(25)	2.019(5)	M(3)–O(12)	2.170(5)	M(4)–O(13)	1.998(5)
M(1)–O(21)	1.923(5)	M(2)–O(29)	1.864(5)	M(3)–OF(23)	1.973(5)	M(4)–OF(23)	1.988(5)
M(1)–O(32)	2.191(6)	M(2)–O(33)	1.790(4)	M(3)–O(27)	2.103(5)	M(4)–O(33)	2.006(5)
<M(1)–O>	1.98	<M(2)–O>	1.965	<M(3)–OF>	2.056	<M(4)–OF>	2.043
A(1)–O(8)	2.313(6)	A(2)–O(17)	2.253(7)	A(3)–O(4)	2.271(7)	Ca–O(7)	2.338(6)
A(1)–O(17)	2.378(7)	A(2)–O(19)	2.325(7)	A(3)–O(8)	2.345(6)	Ca–O(18)	2.325(5)
A(1)–O(19)	2.375(7)	A(2)–O(28)	2.392(8)	A(3)–O(18)	2.311(6)	Ca–O(22)	2.485(8)
A(1)–O(34)	2.284(6)	A(2)–O(30)	2.157(6)	A(3)–O(22)	2.371(8)	Ca–O(28)	2.400(6)
A(1)–F(1)	2.342(6)	A(2)–F(1)	2.237(6)	A(3)–F(1)	2.344(6)	Ca–F(1)	2.409(5)
A(1)–F(2)	2.388(5)	A(2)–F(2)	2.303(5)	A(3)–F(2)	2.212(5)	Ca–F(2)	2.338(4)
<A(1)–OF>	2.346	<A(2)–OF>	2.278	<A(3)–OF>	2.309	<Ca–OF>	2.383
[6]-coordinated Na-sites							
Na(1)–O(17)	2.507(7)	Na(4)–O(1)	2.605(7)	Na(8)–O(3)	2.552(6)	Na(9)–O(4)	2.239(8)
Na(1)–O(22)	2.427(8)	Na(4)–O(11)	2.709(7)	Na(8)–O(9)	2.511(8)	Na(9)–O(5)	2.289(5)
Na(1)–O(28)	2.437(7)	Na(4)–O(13)	2.283(6)	Na(8)–O(16)b	2.652(6)	Na(9)–O(14)a	2.532(6)
Na(1)–O(34)	2.312(6)	Na(4)–OF(23)	2.357(6)	Na(8)–O(21)	2.544(8)	Na(9)–O(24)	2.618(7)
Na(1)–F(1)	2.348(6)	Na(4)–O(27)	2.335(7)	Na(8)–O(23)	2.362(6)	Na(9)–O(25)	2.643(6)
Na(1)–F(2)	2.458(5)	Na(4)–O(33)	2.369(6)	Na(8)–OF(31)	2.266(6)	Na(9)–O(29)	2.504(8)
<Na(1)–OF>	2.415	<Na(4)–OF>	2.443	<Na(8)–O>	2.482	<Na(9)–O>	2.471
Na(11)–O(7)	2.389(7)	Na(12)–O(1)	2.351(7)				
Na(11)–O(8)	2.484(7)	Na(12)–OF(2)	2.401(6)				
Na(11)–O(18)	2.392(7)	Na(12)–O(12)	2.608(6)				
Na(11)–O(19)	2.414(6)	Na(12)–O(13)	2.399(5)				
Na(11)–F(1)	2.504(7)	Na(12)–O(27)	2.222(6)				
Na(11)–F(2)	2.427(5)	Na(12)–O(33)	2.684(7)				
<Na(11)–O>	2.435	<Na(12)–OF>	2.444				
[4]-coordinated Na-sites							
Na(2)–O(4)	2.196(8)	Na(3)–O(16)	2.328(6)	Na(5)–O(5)	2.416(6)	Na(7)–O(26)	2.519(8)
Na(2)–O(5)	2.209(6)	Na(3)–O(26)	2.262(8)	Na(5)–O(7)	2.291(7)	Na(7)–O(31)	2.408(7)
Na(2)–O(10)	2.333(7)	Na(3)–O(30)	2.238(7)	Na(5)–O(10)	2.339(6)	Na(7)–O(32)	2.337(7)
Na(2)–O(15)	2.386(7)	Na(3)–O(31)	2.372(7)	Na(5)–O(14)	2.362(5)	Na(7)–O(34)	2.336(8)
<Na(2)–O>	2.281	<Na(3)–O>	2.3	<Na(5)–O>	2.352	<Na(7)–O>	2.4
[5]-coordinated Na-sites							
Na(6)–O(3)	2.468(7)	Na(10)–OF(2)	2.330(5)				
Na(6)–O(6)	2.552(7)	Na(10)–O(10)	2.309(6)				
Na(6)–O(26)	2.388(8)	Na(10)–O(24)	2.618(7)				
Na(6)–O(30)	2.306(6)	Na(10)–O(25)	2.643(6)				
Na(6)–O(32)	2.523(7)	Na(10)–O(29)	2.504(8)				
<Na(6)–O>	2.447	<Na(10)–OF>	2.481				
Si(1)–O(9)	1.575(5)	Si(2)–O(11)	1.643(5)	Si(3)–O(3)	1.619(5)	Si(4)–O(15)	1.638(5)
Si(1)–O(13)	1.603(5)	Si(2)–O(15)	1.655(5)	Si(3)–O(6)	1.587(6)	Si(4)–O(20)	1.588(6)
Si(1)–O(16)	1.659(6)	Si(2)–O(24)	1.620(5)	Si(3)–O(12)	1.617(5)	Si(4)–O(27)	1.608(5)
Si(1)–O(21)	1.608(6)	Si(2)–O(25)	1.630(5)	Si(3)–O(16)	1.646(6)	Si(4)–O(29)	1.628(6)
<Si(1)–O>	1.611	<Si(2)–O>	1.637	<Si(3)–O>	1.617	<Si(4)–O>	1.616
Si(2)–O(15)–Si(4)		137.2(3)					
Si(1)–O(16)–Si(3)		137.1(3)					
P(1)–O(17)	1.528(6)	P(2)–O(4)	1.526(6)	P(3)–O(19)	1.599(6)	P(4)–O(5)	1.571(4)
P(1)–O(30)	1.551(6)	P(2)–O(10)	1.564(5)	P(3)–O(26)	1.465(7)	P(4)–O(7)	1.529(6)
P(1)–O(31)	1.487(5)	P(2)–O(14)	1.569(5)	P(3)–O(28)	1.543(7)	P(4)–O(8)	1.540(5)
P(1)–O(32)	1.566(6)	P(2)–O(18)	1.538(5)	P(3)–O(34)	1.551(5)	P(4)–O(22)	1.463(7)
<P(1)–O>	1.533	<P(2)–O>	1.549	<P(3)–O>	1.54	<P(4)–O>	1.526

a: x, y – 1, z; b: x + 1, y, z.

(2) The chemical formula has been changed from  $\text{Na}_{17} \text{Ca}_3 \text{Mg} (\text{Ti}^{4+}, \text{Mn})_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_6 \text{O}_2 \text{F}_6$  and  $Z = 1$  to  $\text{Na}_5 (\text{Na}_4 \text{Ca}_2) \text{Ti}^{4+}_2 [\text{Si}_2\text{O}_7] (\text{PO}_4)_3 \text{O}_2 \text{F}_2$  and  $Z = 2$ . There are differences in the content of Na (17 versus 18), Ca (3 versus 4), O (2 versus 4) and F (6 versus 4 *apfu*).

(3) The [4]-coordinated cation sites of the intermediate layer were originally assigned as partly occupied by Mg and Mn; here, they are assigned as completely occupied by Na, as indicated by the bond-valence incident at these sites (Table 6).

#### Sobolovite

(1) The space group has been changed from *P1* to *Pc*.

(2) The chemical formula has been rearranged from  $\text{Na}_{11} (\text{Na}, \text{Ca}) (\text{Mg}, \text{Mn}) \text{Ti}^{4+}_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_3 \text{F}_3$  and  $Z = 2$  to  $\text{Na}_{12} \text{Ca} (\text{Na}, \text{Ca}, \text{Mn}) \text{Ti}^{4+}_2 (\text{Ti}^{4+}, \text{Mn}) [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_3 \text{F}_3$  and  $Z = 2$ , with changes in Na (12 versus 13), Ca (1 versus 2) and Ti (4 versus 3 *apfu*).

(3) The [4]-coordinated cation sites of the intermediate layer were originally assigned as partly occupied by Mg and Mn; here, they are assigned as completely occupied by Na, as indicated by the bond-valences incident at these sites (Table 10).

#### CLOSE PACKING OF CATION LAYERS IN POLYPHITE AND SOBOLEVITE

The O sheet in both polyphite and sobolovite has the form  $[\text{MO}_2]$  (Fig. 2a); this sheet is close packed in the plane, and hence the layer of cations (designated 1 in Fig. 1) (Na and  $\text{Ti}^{4+}$ ) are close packed in that they occur at the vertices of a  $3^6$  net (Fig. 2b). The next layer of cations in the H sheet (layer 2 in Fig. 1) lies at the *Si*(1), *Si*(2), *M*(1) and *Na*(3) sites, and these are also arranged in accord with a  $3^6$  net (Fig. 2d). Next is the *I* layer (Figs. 1, 4), which contain phosphate tetrahedra and Na in [4]-, [5]- and [6]-coordination. Despite the unusual appearance of the polyhedron sheets in this layer (Figs. 4b–f), the P and Na cations are at the vertices of a  $3^6$  net

(Fig. 4a). Adjacent to the *I* layer is the AC block with two symmetrically distinct cation-layers (Fig. 1, layers 4 and 5). The AC block in sobolovite is shown in Figure 6a. There are two layers of cations within this block (compare Fig. 1 and Figs. 5a, b), and these are shown in Figures 6c, d. Again, the cations, (Na,Ca) and P, lie at the vertices of a  $3^6$  net, even though the coordination numbers of the Na cations here are very different from the coordination numbers of Na in the *I* layer.

All these cation layers in polyphite are shown in Figure 7, and all are characterized by a plane unit-cell of approximately  $5.4 \times 7 \text{ \AA}$  with  $\gamma \approx 90^\circ$ . Although each layer of cations is close-packed (that is, they lie at the vertices of a  $3^6$  net), inspection of the cation configurations in layers adjacent in the *c* direction (orthogonal to the plane of the figure) relative to the plane unit-cell shows that adjacent layers are *not* close packed, that is, they do not stack in a cubic or hexagonal close-packed arrangement. The reason for this involves the interleaving anion-layers. The anions within the O sheet form close-packed layers. However, the first layer of anions within the heteropolyhedral sheet deviates significantly from plane close-packing (*i.e.*, they do not lie at the vertices of a  $3^6$  net), and the ensuing anion-layers deviate further and further from close packing. These deviations are sufficient to prevent three-dimensional close-packing of all ions within the structure.

This type of relation between close packing of cations and non-close-packing of anions is characteristic also of sobolovite and quadruphite, and inspection of a few of the thirty or so related structures containing the *TS* block suggests that planar close-packing of cations is a common feature in these minerals. It seems likely that this feature plays an important role in the crystal chemistry of these structures, and a detailed examination of these minerals is currently in progress.

#### SUMMARY

(1) Based on the SREF results and bond-valence calculations, the end-member formulae of polyphite and sobolovite are as follows:

TABLE 9. REFINED OCTAHEDRAL-SITE SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR SOBOLEVITE

Scattering species	SREF value ( <i>epfu</i> )	Site population ( <i>apfu</i> )	Predicted site-scattering ( <i>epfu</i> )	$\langle X-\Phi \rangle_{\text{calc}}^*$ (Å)	$\langle X-\Phi \rangle_{\text{obs}}$ (Å)
<i>M</i> (1)	Nb, Ti 51.6(1)	1.50 Ti + 0.10 Fe <sup>3+</sup> + 0.09 Zr + 0.27 Nb + 0.04 Mg	50.8	1.999	1.98
<i>M</i> (2)	Nb, Ti 49.8(1)	1.60 Ti + 0.10 Fe <sup>3+</sup> + 0.26 Nb + 0.04 Mg	48.9	1.994	1.965
<i>M</i> (3)	Nb, Ti 46.2(1)	0.80 Ti + 0.49 Mn + 0.42 Mg + 0.20 Nb + 0.09 Zr	46.7	2.073	2.056
<i>M</i> (4)	Nb, Ti 46.0(1)	0.94 Ti + 0.45 Mn + 0.32 Mg + 0.29 Nb	47.7	2.059	2.043
<i>A</i> (1)	Ca, Na 26.0(1)	1.54 Na + 0.40 Ca + 0.06 Sr	27.2	2.4	2.346
<i>A</i> (2)	Ca, Na 27.2(1)	0.78 Na + 0.56 Mn + 0.32 Ca + 0.34 □	29	2.332	2.278
<i>A</i> (3)	Ca, Na 32.0(1)	0.92 Na + 0.54 Ca + 0.54 Mn	34.4	2.343	2.309

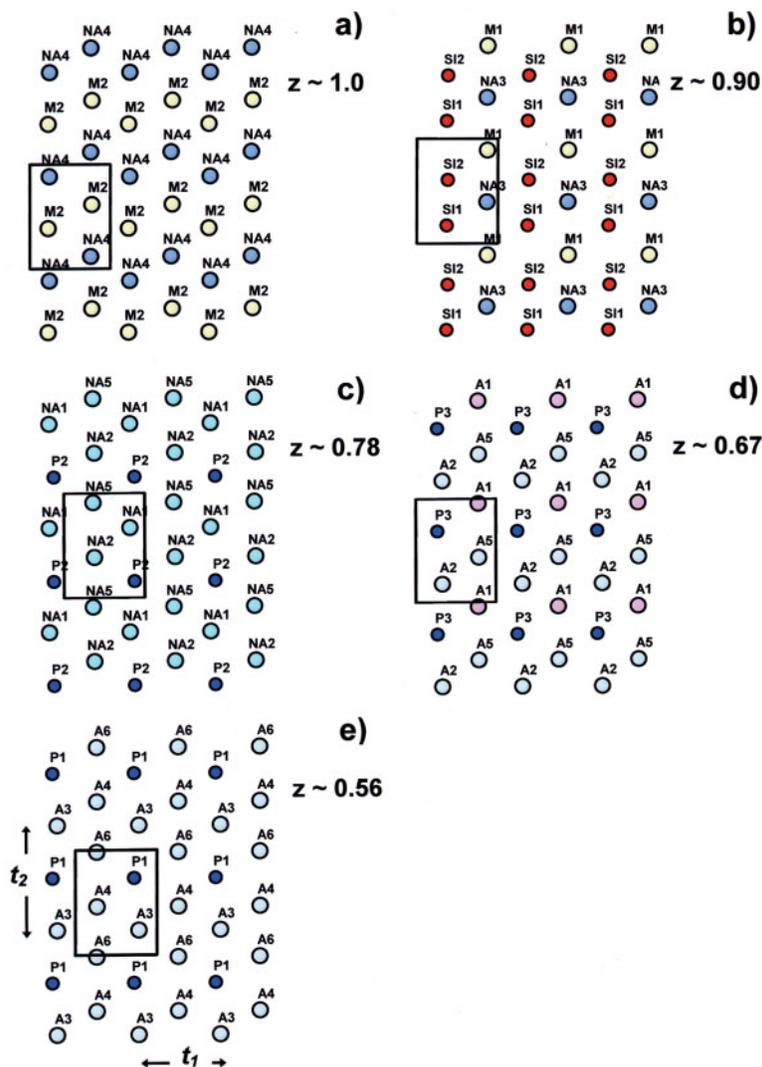


FIG. 7. "Close-packed" cation layers in the crystal structure of polyphite formed by (a)  $M(2)$  and  $Na(4)$  at  $z \approx 1.0$ , line labeled 1 in Figure 1; (b)  $M(1)$ ,  $Na(3)$ ,  $Si(1)$  and  $Si(2)$  at  $z \approx 0.90$ , line labeled 2 in Figure 1; (c)  $Na(1)$ ,  $Na(2)$ ,  $Na(5)$  and  $P(2)$  at  $z \approx 0.78$ , line labeled 3 in Figure 1; (d)  $A(1)$ ,  $A(2)$ ,  $A(5)$  and  $P(3)$  at  $z \approx 0.67$ , line labeled 4 in Figure 1; (e)  $A(3)$ ,  $A(4)$ ,  $A(6)$  and  $P(1)$  at  $z \approx 0.56$ , line labeled 5 in Figure 1.

polyphite  $Na_5 (Na_4Ca_2) Ti_2 [Si_2O_7] (PO_4)_3 O_2 F_2$

sobolevite  $Na_{12} Ca (Na Ca Mn) Ti_2 (Ti Mn) [Si_2O_7]_2 (PO_4)_4 O_3 F_3$ .

(2) Polyphite is triclinic,  $P\bar{1}$ ,  $Z = 2$ . Sobolevite is monoclinic,  $Pc$ ,  $Z = 2$ .

(3) There is a close relation among the structures of polyphite, sobolevite and quadruphite,  $Na_{14} Ca_2 Ti_4$

$[Si_2O_7]_2 (PO_4)_4 O_4 F_2$ . This type of structure consists of two structural blocks, Ti-silicate ( $TS$ ) and alkali-cation ( $AC$ ), stacked along  $[001]$ . The  $TS$  block has a three-layered structure consisting of a central sheet of octahedra (the  $O$  sheet) and two adjacent heteropolyhedral sheets (the  $H$  sheets). The  $AC$  block can be described in terms of nacaphite-like trimeric clusters; as in nacaphite, these trimeric clusters link along  $[100]$  to form an infinite chain. The  $TS$  and  $AC$  blocks join together



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