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**THE CRYSTAL STRUCTURES OF THREE MINERALS
PHOSINAITE-(Ce), ABENAKIITE-(Ce) AND YOSHIMURAITE,
WITH REMARKS ON THE CRYSTAL CHEMISTRY
OF SILICOPHOSPHATES**

by

ANDREW MICHAEL McDONALD, B.Sc., M.Sc.

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of**

Doctor of Philosophy

Department of Earth Sciences

Carleton University

Ottawa, Ontario

September, 1992

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in partial fulfilment of the requirements
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ABSTRACT

Phosinaite-(Ce) $[\text{Na}_{13}\text{Ca}_2\text{REE}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4]$ from Mont Saint-Hilaire, Que., is orthorhombic, $P2_12_1$, a 12.297(2), b 14.660(3), c 7.245(1) Å, V 1306.1(1) Å³, $Z = 2$. Its structure ($R = 3.6\%$, 1868 reflections) is characterized by a (SiP)-layer (Si_4O_{12} rings cross-linked by Na octahedra to PO_4 tetrahedra) and a (P)-layer (PO_4 tetrahedra corner-linked to Na octahedra), stacked along a in a (SiP):(SiP):(P) manner. Bonding between layers occurs *via* corner-sharing, reinforced by edge- and face-sharing of Na, Ca and REE polyhedra.

Abenakiite-(Ce) $[\text{Na}_{26}\text{REE}_6(\text{SiO}_3)_6(\text{PO}_4)_6(\text{CO}_3)_6(\text{SO}_2)\text{O}]$, a new mineral from Mont Saint-Hilaire, Que., is rhombohedral, $R\bar{3}$, a 16.025(2), c 19.773(4) Å, V 4397.4(1) Å³, $Z = 3$. Its structure ($R = 3.1\%$, 2116 reflections) can be described as composite layers stacked along c , one layer consisting of Si_6O_{18} rings and six-membered NaO_7 rings joined *via* edge-sharing NaO_7 polyhedra, the other of both six-membered NaO_7 and $\text{NaO}_7\text{-REEO}_9$ rings, joined through edge- and corner-sharing PO_4 tetrahedra. The two composite layers are joined through edge- and face-sharing between rings and by edge- and corner-sharing between NaO_7 and PO_4 groups. The polyhedral rings define channels along c that are occupied by Na octahedra, CO_3 groups and disordered SO_2 groups.

Yoshimuraite, $\text{Ba}_2\text{Mn}_2(\text{Ti,Fe}^{3+})\text{O}(\text{Si}_2\text{O}_7)[(\text{P,S})\text{O}_4](\text{OH})$, from the Noda-Tamagawa mine, Honshu, Japan, is triclinic, $P\bar{1}$, a 5.386(1), b 6.999(1), c 14.748(3) Å, α 95.50(1), β 93.62(2), γ 89.98(2)°, V 552.3(1) Å³, $Z = 2$. Its structure ($R = 3.0\%$, 1842 reflections), is layered parallel to $\{001\}$, consisting of a brucite-type

Mn octahedral layer, a layer of TiO_5 polyhedra cross-linked by Si_2O_7 groups and a layer of edge-and face-sharing PO_4 tetrahedra and BaO_{11} polyhedra. The Mn octahedral layer is sandwiched between two $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers to form a composite layer, with the $[\text{Ba}_2(\text{PO}_4)]$ layer situated between composite layers.

The term silicophosphate is applied to minerals containing well-ordered Si and P. The crystal chemical features of the silicophosphates are: (1) SiO_4 tetrahedra may be polymerized, but PO_4 tetrahedra are not; (2) no sharing of tetrahedral elements between SiO_4 and PO_4 groups; (3) structures with distinct layered aspects; (4) high concentrations of large lithophile elements.

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CHAPTER 1

INTRODUCTION

Minerals which contain essential Si and P have often been loosely regarded as silicophosphates (*e.g.* Moore, 1980), a term that has never been formally defined. These silicophosphates are unusual in that they contain both SiO_4 and PO_4 anionic groups while most minerals develop as distinct silicate or phosphate species. They also appear to be quite rare, generally occurring in unusual geological environments. Furthermore, little is known about their crystal chemistry or the reasons for their existence.

There presently exists two distinct groups of so-called silicophosphate minerals. The first group consists of those minerals that contain disordered Si and P, and hence, exhibit highly variable Si:P compositions. Good examples of these include minerals belonging to the apatite-britholite group. The second group consists of minerals that contain well-ordered Si and P and so, exhibit relatively constant Si:P compositions. Good examples of these include lomonosovite and vuonnemite. Up until now, no attempt has been made to distinguish these two groups of Si- and P-bearing minerals.

The main objective of this study was to determine and describe the crystal structures of phosinaite-(Ce), abenakiite-(Ce) and yoshimuraite, three minerals with apparently well-ordered Si and P, using a combination of X-ray diffraction and electron microprobe analyses. Information obtained from this investigation would be used to: (1) establish or verify the chemical formulas of these minerals;

(2) confirm their crystallography; (3) determine the extent of Si-P ordering; (4) provide crystal chemical information on silicophosphate minerals. Such a study would lead to a suitable definition of the term silicophosphate, an explanation of some of the possible mechanisms controlling the ordering of Si and P and finally, would provide information on the paragenesis of these minerals.

CHAPTER 2

ANALYTICAL METHODS

2.1 Electron microprobe analyses

All minerals were chemically analyzed using a Cambridge Microscan MK5 electron microprobe operating in the wavelength dispersion mode. An operating voltage of 15 kV and an estimated beam current of 30 nA were used. For phosinaite-(Ce) and yoshimuraite, the electron beam was rastered over an area of 10 x 10 μm . For abenakiite-(Ce), the beam was rastered over an area of 60 x 60 μm , to minimize damage to the sample. Table 1 lists the standards used and the X-ray lines analyzed for those elements that were detected. X-ray intensities were converted to oxide concentrations using a modified version of EMPADR VII (Rucklidge and Gasparrini, 1969).

2.2 Optical characterization

The optical properties for the minerals involved were determined in sodium light ($\lambda = 589.3 \text{ nm}$) using a spindle stage and crystals previously oriented by X-ray goniometry. Refractive indices were measured at room temperature ($\approx 20^\circ \text{C}$) using Cargille immersion liquids and verified using a Bausch and Lomb Abbe 3L refractometer.

Table 1. Standards used and X-ray lines analyzed in electron microprobe analyses.

4

Element	Standard	X-ray line analyzed
Na	albite ^{a,p,y}	<i>Kα</i>
Al	Kakanui hornblende ^a	<i>Kα</i>
Si	Kakanui hornblende ^{a,p,y}	<i>Kα</i>
P	Durango fluorapatite ^{a,p,y}	<i>Kα</i>
S	celestine ^y	<i>Kα</i>
K	Kakanui hornblende ^y	<i>Kα</i>
Ca	Kakanui hornblende ^{a,p} anorthite ^y	<i>Kα</i>
Ti	Kakanui hornblende ^y	<i>Kα</i>
Mn	tephroite ^{p,y}	<i>Kα</i>
Fe	Kakanui hornblende ^y	<i>Kα</i>
Zn	willemite ^y	<i>Kα</i>
Sr	celestine ^a barite ^y	<i>Kα</i> <i>Kα</i>
Nb	synthetic NaNbO ₃ ^y	<i>Lα</i>
Ba	Ba, Zn, Si glass ^y (NBS standard K458)	<i>Lα</i>
La	REE glass ^{a,p}	<i>Kα</i>
Ce	REE glass ^{a,p}	<i>Kα</i>
Pr	REE glass ^{a,p}	<i>Lβ</i>
Nd	REE glass ^{a,p}	<i>Lβ</i>
Sm	REE glass ^{a,p}	<i>Lβ</i>
Th	Synthetic ThO ₂ ^{a,p}	<i>Mα</i>

Legend: a = abenakiite-(Ce); p = phosinaite-(Ce) and
y = yoshimuraite.

2.3 X-ray diffraction

The observed X-ray powder diffraction patterns provided for each mineral were obtained using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a 114.6 mm Gandolfi camera operating at 35 kV and 20 mA. Single-crystal X-ray precession photographs were taken with a Huber precession camera using Zr-filtered $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) operated at 50kV and 25 mA. Unit cell parameters, obtained from the single-crystal photographs, were refined by the least-squares program CELREF (Appleman and Evans, 1973) using X-ray powder diffraction data. Indexing was carried out using the intensities of reflections observed on the precession photographs as a guide.

2.4 X-ray intensity data collection

X-ray intensity data used in the determining the phosinaite-(Ce) and abenakiite-(Ce) crystal structures, were collected on an Enraf Nonius CAD 4 four-circle diffractometer using the NRCVAX package of computer programs (Gabe *et al.*, 1989). The operating conditions were 50 kV and 20 mA and graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.70932 \text{ \AA}$) was used. Cell parameters were refined by a least-squares method (Busing, 1970), using 24 reflections ($5^\circ < 2\theta < 42^\circ$) for phosinaite-(Ce) and 42 reflections ($15^\circ < 2\theta < 27^\circ$) for abenakiite-(Ce). These were permuted four ways ($\pm h$ at $\pm 2\theta$). Intensity data for both minerals [a hemisphere for phosinaite-(Ce) and a full sphere for abenakiite-(Ce)] were collected to $2\theta = 55^\circ$ using a $\theta:2\theta$ scanning mode and a scanning range of

1.6°(2 θ) performed over 48 steps. A constant scanning speed of 8°/min. in 2 θ was used in both cases. Backgrounds were measured for 20 seconds on either side of the reflections. Three intensity standards were remeasured every 10⁵ seconds and three orientation standards, every 400 reflections. No significant variations were noted. Intensities were reduced to structure factors using the NRCVAX set of computer programs (Gabe *et al.*, 1989). Data reduction included background, scaling and corrections for Lorentz and polarization effects. No absorption corrections were applied because of the small size of the crystals analyzed and the small linear absorption coefficients associated with them.

For yoshimuraite, a hemisphere of intensity data was collected on a Nicolet R3m four-circle diffractometer operating at 50 kV and 35 mA with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). A set of 25 reflections were used to orient the crystal and to refine the cell dimensions (by a least-squares method). The intensity data were collected in θ :2 θ scan mode, using 96 steps with a scan range of 2°(2 θ) and a variable scan-rate ranging from 4.0°/min. for weak diffractions to 29.3°/min. for intense diffractions. Backgrounds were measured for half the scan time at the beginning and end of each scan. Two standards were monitored every 58 reflections to check crystal orientation, crystal decrepitation and beam intensity. No significant variations were noted. The intensity data were reduced to structure factors using the SHELXTL package of programs (Sheldrick, 1990). Data reduction included background and scaling, along with Lorentz, polarization and absorption corrections. For the absorption correction, 11 intense

diffraction-maxima over the range of 10 to $53^\circ(2\theta)$ were selected for ψ -diffraction vector scans (ψ being the azimuthal angle corresponding to rotation of the crystal about its diffraction vector), using a modified version of the procedure outlined by North *et al.* (1968), available in the SHELXTL set of programs (Sheldrick, 1990). Intensity data were collected every 10° in a 360° rotation about the diffraction vector (ψ). The ψ -scan set data was then used to refine an ellipsoidal shape for the crystal (lengths and orientation of the semi-major axes). An ellipsoidal empirical absorption-correction was then calculated and applied to the ψ -scan data, reducing $R(\text{azimuthal})$ from 4.59% to 2.09%. This correction was then applied to the whole data set, resulting in minimum and maximum transmissions of 0.815 and 0.624, respectively.

Structure determinations and refinements for all the minerals were carried out with the SHELXTL set of programs (Sheldrick, 1990). Scattering curves for neutral atoms were taken from Cromer and Mann (1968) and anomalous dispersion coefficients from Cromer and Liberman (1970).

CHAPTER 3

REFINEMENT OF THE CRYSTAL STRUCTURE OF PHOSINAITE-(Ce)

3.1 OCCURRENCE AND PROPERTIES

Phosinaite-(Ce) $[\text{Na}_{13}\text{Ca}_2\text{REE}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4]$ is a rare silicophosphate mineral, previously known only from the Khibina and Lovozero massifs of Russia. It has recently been found at the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Quebec, where it was found in sodalite syenite xenoliths and tentatively designated UK64 (Chao *et al.*, 1990). The important minerals associated with it include: microcline, analcime, albite, natrolite, villiaumite, astrophyllite, thermonatrite, vitusite, revdite and vuonnemite. However, more than 72 different minerals have been found in this particular xenolith (Chao *et al.*, 1991).

The Mont Saint-Hilaire phosinaite-(Ce) occurs as anhedral, elongated grains (up to 2 mm) set in the groundmass and as euhedral, prismatic crystals (up to 2x1 mm) in small vugs and fractures in sodalite. Well-formed crystals are commonly bounded by the forms {100} and {010} and are elongate on [001]. Phosinaite-(Ce) varies from colourless to pale brown and is often coated with a brown film. Powder X-ray diffraction and energy dispersive spectroscopic analyses indicate this film to be an amorphous Ca, Na, K silicate. Phosinaite-(Ce) is quite brittle with perfect {001}, distinct {110} and good {010} cleavages. The measured density of $2.97(1) \text{ g/cm}^3$ was determined by flotation in bromoform diluted with acetone.

Optically, phosinaite-(Ce) is non-pleochroic with a very low birefringence. The observed interference figures were found to be extremely poor, so no $2V$ or dispersion determinations could be made. The refractive indices are: $\alpha = \beta = 1.568(1)$ and $\gamma = 1.572(1)$. The optical orientation is $X = b$, $Y = c$ and $Z = a$ and the mineral exhibits both positive and negative elongation.

A summary of the physical and optical properties for phosinaite-(Ce) from Mont Saint-Hilaire is presented and compared in Table 2 with those obtained for material from Khibina and Lovozero. These properties are generally in good agreement, although a significant range in measured densities is evident (2.62-3.00 g/cm³).

3.2 CHEMICAL COMPOSITION

Electron microprobe analyses of phosinaite-(Ce) from Mont Saint-Hilaire are given in Table 3. In addition to those elements listed, S, Zr, U and Fe were also sought for, but not detected. Overall, these results agree quite favourably in terms of both major and minor elements and there are no indications of significant compositional variations. Based on 8(Si+Al+P) atoms, the average composition given in Table 3 (Col. 5) gives the empirical formula:

(with $Z = 2$), which suggests the ideal formula, $\text{Na}_{13}\text{Ca}_2\text{Ce}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4$.

The density of phosinaite-(Ce) from Mont Saint-Hilaire, calculated from

TABLE 2. PHYSICAL PROPERTIES OF PHOSINAITE-(Ce)

	1	2	3	10
Habit	Anhedral aggregates	Columnar crystals up to 5x1 mm	Prismatic crystals up to 2x1 mm, elongated, anhedral grains up to 2 mm	
Colour	Colourless to pale rose	colourless, pale rose to brownish rose	colourless to pale brown	
Hardness (Mohs')	3.5	3.5	4	
Forms Observed	None	{110} predominant, also {100}, {010}, {001}	{100}, {010}, {001}	
Cleavage	{100} perfect, {010}, {110} imperfect	As in 1.	{001} perfect, {110} distinct, {010} good	
D _{meas} (g/cm ³)	2.62	3.00	2.97(1)	
D _{calc} (g/cm ³)	3.37*	3.36**	3.089	
Optics				
α	1.567	1.570	1.568(1)	
β	1.569	1.572	1.568(1)	
γ	1.570	1.573	1.572(1)	
2V _{meas} (°)	(+)68	(+)70	(+)†	
2V _{calc} (°)	70‡	70‡	0	
Elongation	(±)	(±)	(±)	
Orientation	X = b Y = c Z = a	X = b Y = c Z = a	X = b Y = c Z = a	

* - Calculated in this study for the formula:

** - Calculated in this study for the formula:

† - 2V could not be determined.

‡ - Calculated in this study.

1. Khibina massif, Kapustin *et al.* (1974).

2. Lovozero massif, " " ".

3. Mont Saint-Hilaire, this study.

**TABLE 3. CHEMICAL COMPOSITION OF PHOSINAITE-(Ce)
FROM MONT SAINT-HILAIRE, QUEBEC.**

	1	2	3	4	5 ¹
Na₂O wt.%	31.39	31.51	32.70	31.10	31.68
CaO	8.98	9.11	8.96	8.62	8.92
MnO	0.79	0.89	0.94	0.95	0.89
La₂O₃	4.12	4.34	4.29	3.99	4.18
Ce₂O₃	6.19	6.83	6.52	6.55	6.52
Nd₂O₃	1.03	0.90	1.08	0.96	0.99
Pr₂O₃	0.40	0.16	0.20	0.26	0.26
ThO₂	2.62	1.18	0.61	2.94	1.84
Al₂O₃	0.11	0.26	0.10	0.14	0.15
SiO₂	18.26	18.01	18.04	18.52	18.21
P₂O₅	24.25	22.93	23.62	23.96	23.69
TOTAL	98.14	96.12	97.06	97.99	97.33

1. Average of analyses 1-4 on one grain.

the empirical formula, is 3.089 g/cm^3 , slightly greater than the measured value of $2.97(1) \text{ g/cm}^3$, but reasonably close to the measured value of 3.00 g/cm^3 obtained for material from Lovozero (Table 2). The discrepancy between the D_{calc} and D_{meas} for Mont Saint-Hilaire phosinaite-(Ce) could be due to the material containing adsorbed water. Chemical analyses for phosinaite-(Ce) from Khibina and Lovozero have indicated the presence of H_2O in the range of 2 to 6 wt.% H_2O (Table 4). The water must be considered non-essential based on thermogravimetric analyses of the Khibina material, which showed a weight loss of only 1.23 % up to 1000°C (Krutik *et al.*, 1981), and refinement of the crystal structure in this study, for which bond valence sums for all the oxygen atoms are close to 2 v.u. (Table 11). Although no water analysis was performed on the Mont Saint-Hilaire material, the possibility of adsorbed water being present is supported both by the low D_{meas} and the low analytical totals (Table 3). The water may be the product of simple surface alteration or it may be related to partial metamictization of the material, as the Mont Saint-Hilaire phosinaite-(Ce) contains up to 3 wt. % ThO_2 (Table 3). The possibility of this particular material being partially metamict is also supported by the low birefringence and the poor interference figures observed for the mineral.

Table 4 gives the chemical composition of phosinaite-(Ce) from the three known localities. Overall, the major element compositions for this mineral agree reasonably well and are close to those calculated for $\text{Na}_{13}\text{Ca}_2\text{Ce}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4$. In terms of minor elements, the Mont Saint-Hilaire phosinaite-(Ce) appears to

TABLE 4. CHEMICAL COMPOSITION OF PHOSINAITE-(Ce)

	1	2	3	4	5
Na ₂ O wt.%	31.68	28.05	28.78	29.76	33.48
K ₂ O	-	0.72	0.47	0.50	-
CaO	8.92	12.10	5.39	8.90	9.32
MnO	0.89	-	1.90	0.16	-
Fe ₂ O ₃	-	-	0.49	0.45	-
REE ₂ O ₃	11.95	13.22	13.80	11.67	13.64
ThO ₂	1.84	-	-	-	-
SiO ₂	18.36	18.56	23.78	20.00	19.97
P ₂ O ₅	23.69	21.45	20.50	25.50	23.59
H ₂ O	-	5.87	4.41	2.38	-
TOTAL	97.33	99.97	99.52	99.32	100

1. This study; Mont St. Hilaire, Rouville Co., Quebec, Canada; SiO₂ includes Al₂O₃ 0.15 wt.%; For REE composition, see Table 3.
2. Kapustin *et al.* (1974); average of two analyses; Khibina, Russia; Spectrographic analysis gave La 16.8, Ce 53.9, Pr 4.4, Nd 19.5, Sm 3.0, Eu 0.5, Gd 0.7, Tb 0.3, Er 0.3, Y 0.6.
3. Kapustin *et al.* (1974); Mt. Karnasurt, Lovozero, Russia; Spectrographic analysis as above; Analysis also gave Li₂O 0.24 wt%.
4. Krutik *et al.* (1981); Khibina Massif, Russia; Analysis also gave MgO 0.28 and SrO 0.30 wt.% respectively.
5. Composition calculated for: Na₁₃Ca₂Ce(Si₄O₁₂)(PO₄)₄.

have a distinctive ThO_2 content when compared with that from Khibina and Lovozero.

3.3 CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE REFINEMENT

Single-crystal X-ray precession studies of phosinaite-(Ce) from Mont Saint-Hilaire confirmed that the mineral is orthorhombic, space group $P2_212_1$ (#18). The unit-cell parameters refined from the powder data are: a 12.297(2), b 14.660(3), c 7.245(1) Å, with V 1306.1(1) Å³ and $Z = 2$. These are in good agreement with those determined in previous studies (Table 5). The indexed powder patterns for phosinaite-(Ce) from Mont Saint-Hilaire, Lovozero (Kapustin *et al.*, 1974) and that calculated from the refined crystal structure (for $\text{CuK}\alpha$ radiation), are given in Table 6. Overall, agreement between visually-estimated and calculated intensities is good, despite minor discrepancies (which may be attributed to both inaccuracies in the visual estimates and the recording geometry of the Gandolfi camera). The 6.92 Å reflection reported by Kapustin *et al.*, (1974) is both unindexable on the cell adopted for phosinaite-(Ce) and inconsistent with the observed diffraction symmetry. This reflection, however, was not observed in analyses of Lovozero material carried out in the present study (using a 114.6 mm Gandolfi camera, $\text{CuK}\alpha$ radiation and 12 hour exposures). Therefore, it is believed to be either erroneous or perhaps caused by impurities included in some of the Lovozero phosinaite-(Ce).

Intensity-data were collected using a four-circle diffractometer following the

TABLE 5. CELL DIMENSIONS OF PHOSINAITTE-(Ce).

Space Group	1		2	3
	<i>P22₁2</i> or <i>P22₁2₁</i>		<i>P2₁2₁2</i>	<i>P22₁2₁</i>
	i	ii		
a(Å)	12.23(4)	12.24(4)	7.234(3)	12.297(2)
b	14.62(4)	14.59(4)	14.670(4)	14.660(3)
c	7.21(4)	7.20(4)	12.231(4)	7.245(1)
V(Å³)	1290(1)	1286(1)	1298(1)	1306.1(1)
Z	2	2	2	2

1. Kapustin *et al.* (1974); i) Khibina massif, Russia;
ii) Lovozero massif, Russia; $\text{H}_6\text{Na}_6(\text{Ca,Ce})_3(\text{SiO}_4)_3(\text{PO}_4)_3$.
2. Krutik *et al.* (1981); Khibina massif, Russia;
 $\text{Na}_{11}(\text{Na,Ca})_2\text{Ca}_2(\text{Ce},\square)_{\Sigma=0.67}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4$.
3. This study; Mont St. Hilaire, Que.;
 $\text{Na}_{13}\text{Ca}_2\text{REE}(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4$; dimensions refined from the X-ray powder diffraction pattern.

TABLE 6. X-RAY DIFFRACTION DATA FOR PHOSINAITE-(Ce)

1 Lovozero		2 Mont Saint-Hilaire		3 Calculated		<i>hkl</i>
<i>I</i> _{est} ¹	<i>d</i> _{meas} ¹	<i>I</i> _{est} ²	<i>d</i> _{meas} ²	<i>I</i> _{calc} ³	<i>d</i> _{calc} ³	
		70	9.420	75	9.421	110
55	7.44	20	7.338	24	7.330	020
50	6.92					
9	6.39	10	6.531	28	6.495	011
		40	6.265	39	6.296	120
				43	6.242	101
15	5.72	20	5.740	72	5.743	111
				14	5.670	210
12	4.71			16	4.752	121
		25	4.718	16	4.711	220
				52	4.688	201
		10	4.541	26	4.541	130
15	4.11	5	4.080	16	4.100	300
				13	4.051	031
		60	3.949	66	3.949	221
20	3.94			7	3.948	310
				17	3.848	131
		15	3.825	14	3.826	230
				9	3.665	040
30	3.62			10	3.622	002
40	3.51			0	3.512	140
		20	3.468	27	3.466	311
18	3.37	25	3.384	15	3.383	231
				16	3.381	112
				11	3.208	321
				26	3.160	141
20	3.13			7	3.148	240
				4	3.140	330
		30	3.141	28	3.140	122
		40	3.049	59	3.053	212
18	3.01			3	3.009	410
7	2.89	15	2.899	10	2.910	032
				13	2.887	241
7	2.82			0	2.852	150
				20	2.835	420
		10	2.819	9	2.830	401
100	2.74			100	2.732	340

TABLE 6. (continued)

1 Lovozero		2 Mont Saint-Hilaire		3 Calculated		<i>hkl</i>
I_{est}^1	d_{meas}^1	I_{est}^2	d_{meas}^2	I_{calc}^3	d_{calc}^3	
9	2.504	100	2.718	10	2.718	051
				86	2.714	302
				14	2.646	250
				87	2.576	042
		70	2.577	12	2.546	222
				2	2.522	142
				4	2.485	251
				10	2.449	431
		<5	2.486	14	2.396	160
				3	2.385	350
				1	2.344	402
				9	2.339	113
11	2.317	10	2.315	1	2.329	501
				1	2.315	061
				13	2.314	412
				3	2.279	052
		5	2.274	3	2.275	161
				2	2.271	260
				20	2.233	422
				15	2.197	530
		40	2.178	22	2.181	342
				13	2.137	252
18	2.038	20	2.050	4	2.065	170
				23	2.050	600
				11	2.036	451
				3	1.999	162
10	1.985	10	1.988	6	1.990	143
				12	1.966	541
				9	1.916	243
				1	1.914	615
7	1.907	30	1.913	5	1.913	460
				1	1.912	271
				1	1.884	550
				5	1.883	413
		10	1.883	6	1.843	153
				20	1.832	080
15	1.804	35	1.835	0	1.812	180

TABLE 6. (continued)

1 Lovozero		2 Mont Saint-Hilaire		3 Calculated		<i>hkl</i>
I_{est}^1	d_{meas}^1	I_{est}^2	d_{meas}^2	I_{calc}^3	d_{calc}^3	
		20	1.811	23	1.811	004
		15	1.800	5	1.798	014
		5	1.768	5	1.770	433
10	1.685	20	1.691	12	1.692	462
		15	1.674	0	1.673	380
10	1.659			1	1.663	721
		5	1.656	0	1.657	304
		5	1.635	1	1.635	082
				1	1.625	533
		5	1.618	0	1.616	324
				3	1.615	190
13	1.596	20	1.604	15	1.604	642
		5	1.576	2	1.576	191
				3	1.562	472
		10	1.561	1	1.560	404
		5	1.545	8	1.545	722
11	1.511	20	1.520	16	1.519	382
		15	1.507	11	1.510	750
Plus others						

1. Data from Kapustin *et al.* (1974) for a specimen from Mt. Karnasurt, Lovozero massif, Russia; The 6.92 Å line is not indexable on the cell reported by the authors.
2. Data from this study for a specimen from Mont Saint-Hilaire; 114.6 mm Gandolfi camera, CuK α radiation ($\lambda = 1.5418$ Å); I_{est} visually estimated; d_{calc} determined from the cell refined from the powder data: a 12.297, b 14.660, c 7.245 Å.
3. I_{calc} determined using the program DISPOW (Gabe *et al.*, 1989).

method outlined under *Experimental Methods*. For this collection, an optically clean, prismatic crystal was selected and mounted to rotate approximately about *c*. The cell parameters refined from the four-circle diffractometer data are presented in Table 7 and differ slightly from those refined from the X-ray powder-pattern. Of the 2158 unique reflections collected, 1868 were considered observed [$F > 6\sigma(F)$].

The crystal structure of phosinaite-(Ce) was determined independently of that by Krutik *et al.* (1981) using a sharpened Patterson synthesis and difference Fourier maps, from which all cation and oxygen positions were identified. Refinement of this model with isotropic thermal factors gave $R = 5.2\%$ and $wR = 5.9\%$. Refinement of site occupancies indicated that most were fully occupied, although those for rare-earths (assumed to be Ce) and one Na atom refined to values significantly less than one, suggesting deficiencies in the scattering powers at these sites. These particular sites were subsequently found to have mixed (Ce,Ca,Th) and (Na,Ca) compositions respectively. Further refinement of the model using anisotropic temperature factors and a weighting scheme [involving the term $1/\sigma^2(F_o)$] converged to $R = 3.6\%$ and $wR = 3.6\%$ for 227 parameters and 1868 observed reflections. No improvement in the final residual was noted when an extinction correction was included. The final difference map indicated no maxima greater than $1 \text{ e}^-/\text{\AA}^3$. Final positional and thermal parameters are given in Table 8, selected bond lengths and angles in Table 9 and the observed and calculated structure factors in Table 10.

**TABLE 7. MISCELLANEOUS DATA FOR THE REFINEMENT OF
THE CRYSTAL STRUCTURE OF PHOSINAITE-(Ce).**

Space Group	$P2_12_1$ (#18)	Diffractometer	Enraf-Nonius CAD4
a (Å)	12.270(1)*	Radiation	MoKα (50kV, 20 mA)
b	14.648(2)*	Monochromator	Graphite
c	7.231(1)*	Crystal Shape	Equant, Prismatic
V (Å³)	1299.6(1)	Crystal Size	0.25 x 0.06 x 0.04 mm
Z	2	μ(MoKα)	4.76 mm⁻¹
Chemical Formula		Na₁₃Ca₂REE(Si₄O₁₂)(PO₄)₄	
Intensity Data Collection		θ-2θ Scanning Mode	
2θ Limit		55°	
Intensity Standards		Three every 10,000 seconds	
Orientation Standards		Three every 400 reflections	
Number of Unique Reflections		2158	
Number of Observed Reflections		1868	
Criterion for Significance		$F > 6\sigma(F)$	
Weighting Scheme		$wR = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$, $w = 1/\sigma^2$	
Final R for all Observed Reflections		3.6%	
Final wR for all Observed Reflections		3.7%	

* Refined from four-circle diffractometer data.

TABLE 8. POSITIONAL AND THERMAL PARAMETERS FOR PHOSINAITE-(Ce).

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Si(1)	0.3320(2)	0.8891(1)	0.3095(3)	194(9)	108(8)	210(9)	-7(7)	-32(8)	18(7)	174(5)
Si(2)	0.3646(2)	0.9111(1)	0.7451(3)	127(7)	123(7)	171(8)	-6(7)	12(8)	2(6)	142(5)
P(1)	0.9734(2)	0.1253(1)	0.2299(3)	127(8)	194(8)	244(10)	-41(8)	-11(8)	-17(6)	188(5)
P(2)	0.3067(2)	0.6183(1)	0.7657(3)	121(7)	116(7)	162(8)	-1(7)	-10(7)	-18(6)	133(4)
Na(1)	0.1826(3)	0.7586(2)	0.5431(6)	332(18)	391(19)	414(26)	73(17)	26(16)	125(16)	379(12)
Na(2)	0.0028(3)	0.3490(3)	0.2239(6)	300(20)	613(26)	355(23)	-10(22)	20(18)	4(18)	422(14)
Na(3)	0.1717(3)	0.5	0.5	356(11)	356(11)	356(11)	0	0	0	356(11)
Na(4)	0.1610(4)	0.5	0	368(15)	368(15)	368(15)	0	0	0	368(15)
Na(5)	0.8764(4)	0.5	0	353(10)	353(10)	353(10)	0	0	0	353(10)
Na(6)	0.4509(4)	0.5	0	282(9)	282(9)	282(9)	0	0	0	282(9)
Na(7)	0.3309(2)	0.6402(2)	0.2632(5)	188(16)	133(12)	244(15)	10(12)	10(13)	-19(10)	195(8)
Na(8)	0.4558(4)	0.5	0.5	346(28)	407(25)	391(30)	22(36)	309(56)	26(131)	382(16)
(Na,Ca)	0.1903(2)	0.7661(2)	0.0242(4)	501(17)	207(11)	236(16)	-9(10)	-3(12)	-3(10)	314(8)

TABLE 8. (continued)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	0.4969(1)	0.7500(1)	0.5211(3)	178(6)	172(5)	233(9)	-3(1)	-1(1)	-4(1)	194(4)
REE	0.13595(5)	0	0	135(2)	135(2)	135(2)	0	0	0	135(2)
O(1)	0.6496(5)	0.8389(4)	0.0891(7)	265(27)	296(27)	208(25)	-49(22)	-4(25)	-49(25)	256(15)
O(2)	0.8125(4)	0.1478(4)	0.7070(9)	193(24)	251(26)	385(33)	22(25)	64(26)	-40(22)	276(16)
O(3)	0.6873(4)	0.0145(3)	0.7516(8)	308(23)	100(23)	312(27)	28(21)	-48(24)	-3(18)	240(14)
O(4)	0.3741(4)	0.7977(3)	0.2363(9)	320(28)	130(20)	465(34)	-35(25)	108(30)	29(21)	305(16)
O(5)	0.1444(4)	0.3426(4)	0.7199(9)	170(24)	492(36)	403(33)	-3(30)	-16(30)	80(28)	355(18)
O(6)	0.9810(5)	0.9820(4)	0.7583(11)	374(31)	336(34)	564(42)	81(32)	-108(35)	2(25)	425(21)
O(7)	0.3719(5)	0.3522(4)	0.0637(7)	345(30)	252(25)	186(22)	-33(20)	35(24)	120(25)	261(15)
O(8)	0.0333(5)	0.1475(4)	0.0488(8)	352(31)	355(31)	333(35)	80(26)	64(26)	111(28)	346(19)
O(9)	0.1964(4)	0.9038(4)	0.2615(8)	177(22)	268(25)	328(29)	7(25)	11(24)	5(25)	258(15)
O(10)	0.4727(4)	0.8579(4)	0.7913(10)	130(22)	208(23)	535(42)	45(27)	-12(26)	41(20)	291(17)
O(11)	0.3964(4)	0.9787(3)	0.2516(9)	207(22)	131(23)	401(32)	0(22)	70(24)	1(16)	246(15)

TABLE 8. (continued)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
O(12)	0.6705(8)	0.6151(4)	0.0354(8)	1330(80)	341(34)	228(34)	-24(27)	276(41)	-78(45)	633(31)
O(13)	0.2613(5)	0.1058(5)	0.1333(10)	352(33)	252(29)	582(42)	110(31)	-245(33)	-55(26)	396(20)
O(14)	0.0290(5)	0.3363(7)	0.8983(12)	434(44)	964(68)	523(49)	383(50)	68(39)	-204(47)	640(32)

Note: Anisotropic temperature factors have the form: $\exp. -2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} \dots + 2hka^* b^{*2} U_{12})$;
all U values are in $\text{\AA}^2 \times 10^4$; estimated standard deviations in parentheses.

TABLE 9. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) ²⁴
FOR PHOSINAITTE-(Ce).

Si(1) tetrahedron					
Si(1) - O(4)	1.576(6)	O(4) - Si(1) - O(9)	115.7(3)	O(4) - O(9)	2.688(8)
- O(9)	1.598(5)	- O(11)	111.4(3)	- O(11)	2.670(8)
- O(11)*	1.654(5)	- O(12)	106.3(4)	- O(12)	2.575(8)
- O(12)*	1.641(6)	O(9) - Si(1) - O(11)	111.8(3)	O(9) - O(11)	2.694(8)
Mean	1.617	- O(12)	106.0(4)	- O(12)	2.587(8)
		O(11) - Si(1) - O(12)	104.6(5)	O(11) - O(12)	2.617(8)
		Mean	109.3	Mean	2.637
Si(2) tetrahedron					
Si(2) - O(10)	1.577(5)	O(10) - Si(2) - O(11)	106.3(3)	O(10) - O(11)	2.592(8)
- O(11)*	1.662(5)	- O(12)	107.8(4)	- O(12)	2.588(8)
- O(12)*	1.625(7)	- O(13)	119.1(4)	- O(13)	2.709(8)
- O(13)	1.566(7)	O(11) - Si(2) - O(12)	107.8(3)	O(11) - O(12)	2.656(8)
Mean	1.608	- O(13)	109.6(3)	- O(13)	2.638(8)
		O(12) - Si(2) - O(13)	105.8(4)	O(12) - O(13)	2.546(8)
		Mean	109.4	Mean	2.622
P(1) tetrahedron					
P(1) - O(5)	1.525(6)	O(5) - P(1) - O(6)	111.4(4)	O(5) - C(6)	2.546(8)
- O(6)	1.554(6)	- O(8)	110.4(4)	- O(8)	2.516(8)
- O(8)	1.540(7)	- O(14)	110.7(4)	- O(14)	2.495(8)
- O(14)	1.507(9)	O(6) - P(1) - O(8)	103.3(4)	O(6) - O(8)	2.425(8)
Mean	1.532	- O(14)	107.5(5)	- O(14)	2.469(8)
		O(8) - P(1) - O(14)	113.2(4)	O(8) - O(14)	2.543(8)
		Mean	109.4	Mean	2.498
P(2) tetrahedron					
P(2) - O(1)	1.523(6)	O(1) - P(2) - O(2)	109.2(3)	O(1) - O(2)	2.497(8)
- O(2)	1.541(6)	- O(3)	108.9(3)	- O(3)	2.482(8)
- O(3)	1.529(5)	- O(7)	112.1(3)	- O(7)	2.537(8)
- O(7)	1.536(6)	O(2) - P(2) - O(3)	109.6(3)	O(2) - O(3)	2.509(8)
Mean	1.532	- O(7)	108.3(3)	- O(7)	2.494(8)
		O(3) - P(2) - O(7)	108.7(3)	O(3) - O(7)	2.491(8)
		Mean	109.5	Mean	2.502

TABLE 9. (continued)

Na(1) octahedron

Na(1) - O(1)	2.532(7)	O(1) - Na(1) - O(2)	60.4(2)	O(1) - O(2)	2.497(8)
- O(2)	2.433(7)	- O(5)	85.3(2)	- O(5)	3.381(8)
- O(5)	2.460(8)	- O(9)	116.8(2)	- O(9)	4.678(8)
- O(9)	2.953(7)	- O(12)	80.7(3)	- O(12)	3.314(8)
- O(12)	2.587(9)	O(2) - Na(1) - O(5)	100.3(2)	O(2) - O(5)	3.756(8)
- O(14)	2.247(9)	- O(12)	118.4(3)	- O(12)	4.314(8)
Mean	2.535	- O(14)	102.6(3)	- O(14)	3.654(8)
		O(5) - Na(1) - O(9)	84.9(2)	O(5) - O(9)	3.671(8)
		- O(14)	106.9(3)	- O(14)	3.785(8)
		O(9) - Na(1) - O(12)	55.2(2)	O(9) - O(12)	2.587(8)
		- O(14)	79.2(3)	- O(14)	3.360(8)
		O(12) - Na(1) - O(14)	103.2(3)	O(12) - O(14)	3.794(8)

Na(2) octahedron

Na(2) - O(2)	2.275(7)	O(2) - Na(2) - O(6)	84.6(3)	O(2) - O(6)	3.234(8)
- O(6)	2.521(8)	- O(8)	103.7(2)	- O(8)	3.675(8)
- O(8)	2.396(8)	- O(14)	96.4(3)	- O(14)	3.484(8)
- O(9)	2.579(6)	- O(14) [*]	86.2(2)	- O(14) [*]	3.654(8)
- O(14)	2.399(10)	O(6) - Na(2) - O(8)	84.1(3)	O(6) - O(8)	3.294(8)
- O(14) [*]	3.014(11)	- O(9)	76.3(2)	- O(9)	3.149(8)
Mean	2.531	- O(14)	100.8(3)	- O(14)	3.791(8)
		O(8) - Na(2) - O(9)	77.1(2)	O(8) - O(9)	3.165(8)
		- O(14) [*]	68.1(2)	- O(14) [*]	3.072(8)
		O(9) - Na(2) - O(14)	84.8(3)	O(9) - O(14)	3.360(8)
		- O(14) [*]	111.4(2)	- O(14) [*]	4.627(8)
		O(14) - Na(2) - O(14) [*]	111.1(3)	O(14) - O(14) [*]	4.476(8)

Na(3) octahedron

Na(3) - O(3)	2.508(6) x2	O(3) - Na(3) - O(3) [*]	92.5(3)	O(3) - O(3) [*]	3.624(8)
- O(5)	2.824(7) x2	- O(5)	114.7(2) x2	- O(5)	4.492(8)
- O(6)	2.583(8) x2	- O(5) [*]	75.3(2) x2	- O(5) [*]	3.268(8)
Mean	2.638	- O(6)	91.5(2) x2	- O(6) [*]	3.647(8)
		O(5) - Na(3) - O(6)	56.0(2) x2	O(5) - O(6)	2.546(8)
		- O(6) [*]	112.8(2) x2	- O(6) [*]	4.505(8)
		O(6) - Na(3) - O(6) [*]	86.8(4)	O(6) - O(6) [*]	3.549(8)

Na(4) octahedron					
Na(4) - O(2)	2.655(6) x2	O(2) - Na(4) - O(3)	111.9(2) x2	O(2) - O(3)	4.368(8)
- O(3)	2.617(7) x2	- O(3) [*]	56.8(2) x2	- O(3) [*]	2.509(8)
- O(6)	<u>2.576(8) x2</u>	- O(6)	113.7(2) x2	- O(6)	4.380(8)
Mean	2.616	- O(6) [*]	76.4(2) x2	- O(6) [*]	3.234(8)
		O(3) - Na(4) - O(3) [*]	89.1(3)	O(3) - O(3) [*]	3.671(8)
		- O(6)	89.2(2) x2	- O(6)	3.647(8)
		O(6) - Na(4) - O(6) [*]	96.4(4)	O(6) - O(6) [*]	3.549(8)
Na(5) octahedron					
Na(5) - O(6)	2.581(8) x2	O(6) - Na(5) - O(6) [*]	94.4(2)	O(6) - O(6) [*]	3.549(8)
- O(9)	2.403(6) x2	- O(9) [*]	78.3(2) x2	- O(9)	3.149(8)
- O(14)	<u>2.767(10)x2</u>	- O(14)	54.9(2) x2	- O(14)	3.791(8)
Mean	2.584	- O(14) [*]	90.2(2) x2	- O(14) [*]	4.607(8)
		O(9) - Na(5) - O(9) [*]	136.3(3)	O(9) - O(9) [*]	4.461(8)
		- O(14)	80.7(2) x2	- O(14)	3.360(8)
		O(14) - Na(5) - O(14) [*]	118.3(4) x2	O(14) - O(14) [*]	5.021(8)
Na(6) octahedron					
Na(6) - O(3)	2.501(6) x2	O(3) - Na(6) - O(3) [*]	94.4(3)	O(3) - O(3) [*]	3.671(8)
- O(7)	2.419(7) x2	- O(7)	86.7(2) x2	- O(7)	2.490(8)
- O(11)	<u>2.620(8) x2</u>	- O(7) [*]	60.8(2) x2	- O(7) [*]	3.379(8)
Mean	2.513	- O(11) [*]	88.6(2) x2	- O(11) [*]	3.579(8)
		O(7) - Na(6) - O(11)	92.9(2) x2	O(7) - O(11)	4.402(8)
		- O(11) [*]	121.7(2) x2	- O(11) [*]	3.654(8)
		O(11) - Na(6) - O(11) [*]	88.4(4)	O(11) - O(11) [*]	3.653(8)
Na(7) octahedron					
Na(7) - O(1)	2.393(6)	O(1) - Na(7) - O(3)	100.0(2)	O(1) - O(3)	3.580(8)
- O(3)	2.281(5)	- O(4)	86.2(2)	- O(4)	3.260(8)
- O(4)	2.378(6)	- O(5)	91.9(2)	- O(5)	3.381(8)
- O(5)	2.310(7)	- O(10)	79.3(2)	- O(10)	3.075(8)
- O(7)	2.424(6)	O(3) - Na(7) - O(5)	90.8(2)	O(3) - O(5)	3.268(8)
- O(10)	<u>2.424(6)</u>	- O(7)	91.7(2)	- O(7)	3.379(8)
Mean	2.368	- O(10)	96.4(4)	- O(10)	3.510(8)
		O(4) - Na(7) - O(5)	96.9(2)	O(4) - O(5)	3.509(8)
		- O(7)	80.1(2)	- O(7)	3.091(8)
		- O(10)	76.9(2)	- O(10)	2.985(8)
		O(5) - Na(7) - O(7)	104.7(2)	O(5) - O(7)	3.749(8)
		O(7) - Na(7) - O(10)	82.8(2)	O(7) - O(10)	3.205(8)

Na(8) polyhedron

Na(8) - O(1)	2.729(6) x2	O(1) - Na(8) - O(3)	85.0(2)	O(1) - O(3)	2.482(8)
- O(3)	2.525(6) x2	- O(3)'	55.7(2)	- O(3)'	3.580(8)
- O(10)	2.720(6) x2	- O(10)	68.1(2)	- O(10)	3.075(8)
- O(11)	<u>2.594</u> (7) x2	- O(11)	93.5(2)	- O(11)	4.789(8)
Mean	2.642	O(3) - Na(8) - O(3)'	91.7(3)	O(3) - O(3)'	3.624(8)
		- O(10)	83.9(2)	- O(10)	3.510(8)
		O(10) - Na(8) - O(11)	58.3(2)	O(10) - O(11)	2.592(8)
		- O(11)'	94.1(2)	- O(11)'	3.891(8)
		O(11) - Na(8) - O(11)'	91.0(2)	O(11) - O(11)'	3.699(8)

REE polyhedron

REE - O(6)	2.640(7) x2	O(6) - REE - O(6)'	84.6(2)	O(6) - O(6)'	3.549(8)
- O(8)	2.551(6) x2	- O(8)	55.7(2)	- O(8)	2.425(8)
- O(9)	2.463(6) x2	- O(8)'	78.8(2)	- O(8)'	3.294(8)
- O(13)	<u>2.362</u> (6) x2	- O(9)	76.2(2)	- O(9)	3.149(8)
Mean	2.504	- O(13)	97.2(2)	- O(13)	3.754(8)
		O(8) - REE - O(9)	76.5(2)	O(8) - O(9)	3.105(8)
		- O(13)	73.2(2)	- O(13)	2.934(8)
		O(9) - REE - O(13)	76.1(2)	O(9) - O(13)	3.205(8)
		- O(13)'	83.2(2)	- O(13)'	2.974(8)
		O(13) - REE - O(13)'	101.4(3)	O(13) - O(13)'	3.654(8)

(Na,Ca) polyhedron

(Na,Ca) - O(2)	2.411(6)	O(2) - (Na,Ca) - O(4)	121.1(2)	O(2) - O(4)	4.517(8)
- O(4)	2.772(7)	- O(5)	93.1(2)	- O(5)	3.571(8)
- O(5)	2.510(7)	- O(7)	55.1(2)	- O(7)	2.494(8)
- O(7)	2.899(6)	- O(8)	102.6(2)	- O(8)	3.729(8)
- O(8)	2.368(7)	- O(13)	104.0(2)	- O(13)	3.762(8)
- O(9)	2.653(6)	O(4) - (Na,Ca) - O(5)	83.1(2)	O(4) - O(5)	3.509(8)
- O(13)	<u>2.435</u> (7)	- O(7)	66.0(2)	- O(7)	3.091(8)
Mean	2.568	- O(9)	59.4(2)	- O(9)	2.688(8)
		- O(13)	80.4(2)	- O(13)	3.331(8)
		O(5) - (Na,Ca) - O(7)	87.5(2)	O(5) - O(7)	3.749(8)
		- O(8)	108.7(2)	- O(8)	3.966(8)
		- O(9)	90.6(2)	- O(9)	3.671(8)
		O(7) - (Na,Ca) - O(9)	125.2(2)	O(7) - O(9)	4.929(8)
		- O(13)	76.6(2)	- O(13)	3.893(8)
		O(8) - (Na,Ca) - O(9)	76.2(2)	O(8) - O(9)	3.105(8)
		- O(13)	94.8(2)	- O(13)	2.934(8)
		O(9) - (Na,Ca) - O(13)	72.4(2)	O(9) - O(13)	2.974(8)

Ca polyhedron									
Ca	- O(1)	2.278(6)	O(1) - Ca	- O(4)	82.5(2)	O(1)	- O(4)	3.260(8)	
	- O(4)	2.651(7)		- O(4)*	102.8(2)		- O(4)*	3.603(8)	
	- O(4)*	2.332(6)		- O(10)	95.6(2)		- O(10)	3.075(8)	
	- O(7)	2.285(6)		- O(10)*	83.8(2)		- O(10)*	3.568(8)	
	- O(10)	2.534(7)		- O(12)	79.5(2)		- O(12)	3.314(8)	
	- O(10)*	2.326(7)	O(4) - Ca	- O(7)	91.1(2)	O(4)	- O(7)	3.534(8)	
	- O(12)	2.856(9)		- O(10)	111.7(2)		- O(10)	2.985(8)	
	Mean	2.466		- O(10)*	73.4(2)		- O(10)*	4.292(8)	
		- O(12)		55.6(2)	- O(12)		2.575(8)		
		O(4)* - Ca	- O(7)	84.1(2)	O(4)*	- O(7)	3.091(8)		
			- O(10)	75.6(2)		- O(10)	3.555(8)		
			- O(10)*	99.5(2)		- O(10)*	2.985(8)		
			- O(12)	132.4(2)		- O(12)	4.751(8)		
		O(7) - Ca	- O(10)	83.2(2)	O(7)	- O(10)	3.487(8)		
			- O(10)*	98.0(2)		- O(10)*	3.205(8)		
			- O(12)	93.7(2)		- O(12)	3.772(8)		
		O(10) - Ca	- O(12)	57.0(2)	O(10)	- O(12)	4.659(8)		

Note: Estimated standard deviations in parentheses; * denotes symmetry equivalent atom;
+ denotes bridging oxygen.

TABLE 10. OBSERVED AND CALCULATED STRUCTURE FACTORS
FOR PHOSINAITE-(Ce).

h	k	l	10Fo	10Fc	10e	h	k	l	10Fo	10Fc	10e	h	k	l	10Fo	10Fc	10e	h	k	l	10Fo	10Fc	10e	h	k	l	10Fo	10Fc	10e
1	0	0	12	12	-46	9	5	0	276	266	4	3	11	0	345	349	4	6	18	0	102	51	-20	-7	4	1	288	287	5
2	0	0	93	93	7	10	5	0	533	518	4	4	11	0	593	600	4	7	18	0	653	629	5	-5	4	1	288	287	5
3	0	0	586	586	2	11	5	0	413	398	4	5	11	0	796	811	4	8	18	0	232	243	5	-5	4	1	1067	1072	4
4	0	0	456	456	2	12	5	0	445	438	4	6	11	0	93	33	-16	1	19	0	190	187	8	-2	4	1	164	130	7
5	0	0	438	438	2	13	5	0	229	193	6	7	11	0	285	286	5	2	19	0	205	194	8	-3	4	1	504	512	4
6	0	0	3603	3526	4	14	5	0	103	42	15	8	11	0	306	297	5	3	19	0	104	79	-18	-2	4	1	428	470	4
7	0	0	575	575	2	15	5	0	224	192	7	9	11	0	595	585	4	4	19	0	297	302	7	-1	4	1	678	671	4
8	0	0	330	315	4	16	5	0	254	220	7	10	11	0	435	439	5	5	19	0	173	170	7	-1	4	1	95	123	10
9	0	0	65	55	-20	0	6	0	1308	1333	2	11	11	0	64	1	9	6	19	0	259	263	7	-1	4	1	167	151	14
10	0	0	114	103	10	1	6	0	1199	1272	2	12	11	0	130	112	14	7	19	0	465	458	5	-1	4	1	264	248	10
11	0	0	429	414	4	2	6	0	460	715	2	13	11	0	333	333	6	8	19	0	124	106	16	-1	4	1	275	257	9
12	0	0	157	152	8	3	6	0	235	226	4	14	11	0	80	47	-25	9	19	0	527	527	5	-1	4	1	198	194	10
13	0	0	96	96	1	4	6	0	1078	1030	2	15	11	0	955	1003	4	10	19	0	214	225	8	-2	4	1	146	129	12
14	0	0	64	64	-26	5	6	0	183	215	3	16	11	0	74	22	-19	11	19	0	512	495	2	-2	4	1	486	500	6
15	0	0	64	64	-29	6	6	0	183	193	3	17	11	0	1435	1463	3	12	19	0	1026	1004	2	-2	4	1	413	415	6
16	0	0	414	395	5	7	6	0	1539	1567	3	18	11	0	494	524	4	13	19	0	155	152	5	-8	5	1	98	68	-17
1	1	0	609	574	2	8	6	0	357	362	4	19	11	0	74	21	-20	14	19	0	622	606	2	-7	5	1	339	319	5
2	1	0	461	454	2	9	6	0	453	507	4	20	11	0	468	474	4	15	19	0	207	205	4	-6	5	1	607	614	4
3	1	0	455	457	2	10	6	0	863	847	4	21	11	0	89	70	-16	16	19	0	305	288	4	-5	5	1	471	466	4
4	1	0	384	372	2	11	6	0	318	314	5	22	11	0	657	664	4	17	19	0	356	391	4	-4	5	1	878	878	4
5	1	0	697	719	2	12	6	0	302	323	5	23	11	0	321	321	5	18	19	0	570	539	3	-3	5	1	393	381	5
6	1	0	79	81	12	13	6	0	515	513	4	24	11	0	339	338	5	19	19	0	444	441	4	-2	5	1	435	432	4
7	1	0	1143	1133	2	14	6	0	64	57	-29	25	11	0	64	36	-28	20	19	0	104	85	11	-1	5	1	127	135	9
8	1	0	43	24	-29	15	6	0	498	521	5	26	11	0	67	8	-29	21	19	0	84	60	-17	0	5	1	946	937	2
9	1	0	613	615	2	16	6	0	319	317	6	27	11	0	148	172	13	22	19	0	337	303	5	-16	6	1	380	357	8
10	1	0	49	29	-29	17	6	0	1239	1226	2	28	11	0	608	596	5	23	19	0	514	506	4	-15	6	1	161	150	14
11	1	0	62	71	-24	18	6	0	1068	1061	2	29	11	0	240	213	5	24	19	0	61	8	-29	-14	6	1	83	84	-31
12	1	0	395	375	2	19	6	0	71	20	-16	30	11	0	795	790	4	25	19	0	137	114	11	-13	6	1	390	356	7
13	1	0	504	492	4	20	6	0	205	251	5	31	11	0	162	175	7	26	19	0	350	314	6	-12	6	1	459	448	6
14	1	0	130	118	14	21	6	0	985	989	3	32	11	0	150	130	8	27	19	0	337	329	9	-11	6	1	119	94	17
15	1	0	248	220	1	22	6	0	929	941	3	33	11	0	107	64	13	28	19	0	291	246	8	-10	6	1	459	451	6
16	1	0	551	575	2	23	6	0	357	353	4	34	11	0	146	132	8	29	19	0	300	316	8	-9	6	1	504	487	5
1	2	0	615	641	2	24	6	0	396	392	4	35	11	0	62	43	-26	30	19	0	196	211	10	-8	6	1	450	450	5
2	2	0	437	456	2	25	6	0	414	386	4	36	11	0	422	421	5	31	19	0	133	137	14	-7	6	1	264	274	6
3	2	0	341	290	12	26	6	0	139	148	9	37	11	0	338	327	5	32	19	0	327	325	6	-6	6	1	519	521	4
4	2	0	1350	1403	2	27	6	0	659	661	4	38	11	0	164	178	8	33	19	0	721	719	5	-5	6	1	590	598	4
5	2	0	352	355	3	28	6	0	276	266	6	39	11	0	363	340	5	34	19	0	167	177	8	-4	6	1	324	321	5
6	2	0	430	443	3	29	6	0	389	357	5	40	11	0	145	147	12	35	19	0	446	418	5	-3	6	1	454	455	4
7	2	0	1565	1564	2	30	6	0	191	187	8	41	11	0	299	274	7	36	19	0	521	504	4	-2	6	1	715	722	4
8	2	0	166	167	5	31	6	0	239	226	8	42	11	0	294	299	5	37	19	0	266	254	5	-1	6	1	522	477	4
9	2	0	461	482	4	32	6	0	370	370	2	43	11	0	533	528	4	38	19	0	333	303	4	0	6	1	320	343	3
10	2	0	546	551	5	33	6	0	56	117	-17	44	11	0	90	94	-17	39	19	0	308	307	4	-16	7	1	226	233	12
11	2	0	277	320	5	34	6	0	88	66	11	45	11	0	326	345	5	40	19	0	890	882	3	-15	7	1	215	221	11
12	2	0	469	492	4	35	6	0	705	703	3	46	11	0	874	685	4	41	19	0	233	237	4	-14	7	1	303	280	8
13	2	0	617	592	4	36	6	0	167	177	5	47	11	0	303	310	5	42	19	0	636	573	2	-13	7	1	319	309	8
14	2	0	73	55	24	37	6	0	639	616	3	48	11	0	79	10	-21	43	19	0	596	573	2	-12	7	1	185	193	12
15	2	0	323	352	26	38	6	0	1690	1689	3	49	11	0	495	497	4	44	19	0	518	495	7	-11	7	1	420	399	6
16	2	0	126	128	13	39	6	0	624	618	4	50	11	0	266	256	6	45	19	0	311	299	8	-10	7	1	577	581	5
1	3	0	73	73	1	40	6	0	156	159	7	51	11	0	118	119	14	46	19	0	20	91	-28	-9	7	1	123	87	17
2	3	0	653	653	1	41	6	0	52	75	-29	52	11	0	621	606	5	47	19	0	426	410	7	-8	7	1	326	326	6
3	3	0	152	150	2	42	6	0	157	179	8	53	11	0	100	84	-20	48	19	0	437	424	6	-7	7	1	735	748	5
4	3	0	1610	1579	2	43	6	0	774	776	4	54	11	0	354	348	6	49	19	0	240	228	7	-6	7	1	127	140	5
5	3	0	1610	1579	2	44	6	0	101	75	16	55	11	0	294	312	5	50	19	0	907	913	5	-5	7	1	287	272	5
6	3	0	343	345	3	45	6	0	62	43	-27	56	11	0	432	417	4	51	19	0	641	654	5	-4	7	1	334	318	5
7	3	0	732	720	3	46	6	0	65	55	-28	57	11	0	255	266	5	52	19	0	825	831	4	-3	7	1	441	434	4
8	3	0	425	425	3	47	6	0	88	18	-19	58	11	0	119	75	13	53	19	0	156	178	8	-2	7	1	371	368	4
9	3	0	453	453	3	48	6	0	1199	1179	3	59	11	0	309	296	5	54	19	0	654	678	4	-1	7	1	432	436	4
10	3	0	657	647	4	49	6	0																					

TABLE 10. (continued)

n	k	l	10Fe	10Fe	10e	n	k	l	10Fe	10Fe	10e	n	k	l	10Fe	10Fe	10e	n	k	l	10Fe	10Fe	10e	n	k	l	10Fe	10Fe	10e
0	9	1	471	432	3	4	16	1	93	94	-27	12	3	2	443	433	6	5	8	2	46	63	-43	1	14	2	435	451	6
14	10	1	133	99	22	3	16	1	309	311	3	11	3	2	130	124	16	4	8	2	711	711	5	0	14	2	305	337	5
13	10	1	365	372	3	2	16	1	323	299	7	10	3	2	194	195	8	3	8	2	2170	2178	5	11	15	2	70	81	-44
12	10	1	335	309	9	1	16	1	243	242	9	9	3	2	572	584	5	2	8	2	217	193	7	10	15	2	467	451	8
11	10	1	235	227	9	0	16	1	314	312	5	8	3	2	191	212	8	1	8	2	130	131	10	9	15	2	384	362	8
10	10	1	269	270	1	9	17	1	197	207	13	7	3	2	943	936	4	0	8	2	861	881	3	8	15	2	239	230	10
9	10	1	468	452	6	8	17	1	261	238	10	6	3	2	693	709	4	15	9	2	210	191	13	7	15	2	65	77	-40
8	10	1	378	382	7	7	17	1	217	219	12	5	3	2	741	751	4	14	9	2	68	52	-42	6	15	2	193	184	10
7	10	1	74	93	-29	6	12	1	257	253	10	4	3	2	394	395	4	13	9	2	258	230	10	5	15	2	450	437	7
6	10	1	506	504	5	5	17	1	144	138	19	3	3	2	264	242	5	12	9	2	278	262	8	4	15	2	383	402	7
5	10	1	350	351	5	4	17	1	275	271	8	2	3	2	353	359	4	11	9	2	297	295	8	3	15	2	305	312	7
4	10	1	359	607	5	3	17	1	416	422	7	1	3	2	160	182	7	10	9	2	407	405	7	2	15	2	149	169	12
3	10	1	286	278	6	2	17	1	85	99	-25	0	3	2	1169	1179	2	9	9	2	248	249	8	1	15	2	345	339	7
2	10	1	791	766	4	1	17	1	258	241	9	15	4	2	338	314	9	8	9	2	419	424	6	0	15	2	74	15	-22
1	10	1	651	641	4	0	17	1	296	286	6	14	4	2	98	37	-27	7	9	2	124	134	13	10	16	2	196	187	12
0	10	1	255	279	11	8	17	1	217	206	11	14	4	2	204	208	10	6	9	2	396	395	4	9	16	2	206	189	11
14	11	1	281	263	10	7	18	1	89	66	-33	13	4	2	68	59	-41	5	9	2	414	389	5	8	16	2	497	491	7
13	11	1	239	255	10	6	18	1	251	248	10	12	4	2	45	455	6	4	9	2	302	295	6	6	16	2	323	321	8
12	11	1	285	292	9	5	18	1	399	375	8	10	4	2	52	4	-41	2	9	2	610	600	5	5	16	2	88	91	-29
11	11	1	317	303	9	4	18	1	291	264	9	9	4	2	101	57	-18	1	9	2	551	519	4	4	16	2	439	432	7
10	11	1	273	271	8	3	18	1	143	132	18	8	4	2	134	142	12	0	9	2	98	127	11	3	16	2	819	829	6
9	11	1	294	325	8	2	18	1	424	423	9	7	4	2	449	421	5	14	10	2	148	104	17	2	16	2	181	182	11
8	11	1	337	329	7	1	18	1	347	330	9	6	4	2	2027	2038	4	13	10	2	351	304	8	1	16	2	256	159	13
7	11	1	377	366	6	0	18	1	64	65	-29	5	4	2	470	446	4	12	10	2	168	166	12	0	16	2	654	663	5
6	11	1	627	639	5	5	19	1	233	236	12	4	4	2	131	104	9	11	10	2	146	170	11	9	17	2	286	306	10
5	11	1	186	172	9	4	19	1	150	110	15	3	4	2	2025	1930	4	10	10	2	651	657	6	8	17	2	172	188	16
4	11	1	452	456	5	3	19	1	249	249	10	2	4	2	282	270	5	9	10	2	380	378	7	7	17	2	82	62	-31
3	11	1	558	568	5	2	19	1	333	310	9	1	4	2	465	475	4	8	10	2	56	104	-19	6	17	2	66	25	-41
2	11	1	126	178	8	1	19	1	67	53	-43	0	4	2	3855	3819	2	7	10	2	1122	1106	6	5	17	2	414	394	8
1	11	1	156	152	10	0	19	1	163	173	13	16	5	2	293	246	9	6	10	2	162	157	11	4	17	2	64	73	-43
14	12	1	289	288	4	0	20	1	169	159	10	15	5	2	161	149	16	5	10	2	119	104	15	3	17	2	229	228	10
13	12	1	332	314	3	3	20	1	454	447	8	14	5	2	403	380	7	4	10	2	489	497	5	2	17	2	98	122	-28
12	12	1	257	242	10	2	20	1	257	249	10	13	5	2	456	455	7	3	10	2	698	731	5	1	17	2	576	552	7
11	12	1	446	449	7	1	20	1	311	310	9	12	5	2	207	202	10	2	10	2	77	81	-25	0	17	2	62	90	-31
10	12	1	328	326	8	0	20	1	441	447	6	11	5	2	134	130	15	1	10	2	840	846	4	7	18	2	245	229	10
9	12	1	329	314	8	0	20	1	521	451	2	10	5	2	307	279	7	0	10	2	175	171	14	6	18	2	68	10	-42
8	12	1	511	503	6	2	0	2	245	239	4	9	5	2	449	449	5	14	11	2	325	299	8	5	18	2	265	280	9
7	12	1	70	50	-32	3	0	2	3645	3621	2	8	5	2	98	136	-20	13	11	2	574	557	7	4	18	2	564	578	7
6	12	1	37	370	7	4	0	2	390	384	3	7	5	2	325	319	5	12	11	2	169	168	13	3	18	2	164	159	16
5	12	1	618	615	5	5	0	2	486	482	3	6	5	2	413	422	5	11	11	2	261	245	8	2	18	2	109	102	23
4	12	1	266	231	9	6	0	2	39	84	-29	5	5	2	947	961	4	10	11	2	311	295	7	1	18	2	240	242	10
3	12	1	313	305	6	7	0	2	134	90	7	4	5	2	328	304	5	9	11	2	315	285	7	0	18	2	342	344	6
2	12	1	474	450	5	8	0	2	466	432	4	3	5	2	318	299	5	8	11	2	701	702	5	5	19	2	244	255	11
1	12	1	459	456	5	7	0	2	701	711	4	2	5	2	1098	1044	4	7	11	2	839	856	5	4	19	2	152	110	17
14	13	1	121	97	-15	10	0	2	539	523	4	1	5	2	623	620	4	6	11	2	236	235	8	3	19	2	159	171	16
13	13	1	204	198	13	11	0	2	247	235	5	0	5	2	920	894	2	5	11	2	157	139	10	2	19	2	254	238	10
12	13	1	359	350	8	12	0	2	84	76	-17	16	6	2	121	63	-22	4	11	2	182	172	9	1	19	2	101	66	-29
11	13	1	312	312	1	13	0	2	347	366	5	14	6	2	129	150	20	3	11	2	608	595	5	0	19	2	75	57	-24
10	13	1	312	312	1	14	0	2	579	556	4	13	6	2	243	217	10	2	11	2	519	510	5	2	20	2	237	214	11
9	13	1	83	19	-29	15	0	2	166	168	10	12	6	2	310	320	8	1	11	2	348	372	4	1	20	2	169	168	16
8	13	1	256	282	6	15	0	2	116	54	17	11	6	2	620	634	6	0	11	2	85	80	-35	0	20	2	539	534	5
7	13	1	444	419	5	16	1	2	331	315	8	10	6	2	87	45	-26	13	12	2	67	26	-42	1	9	2	626	652	3
6	13	1	234	245	9	15	1	2	258	240	9	9	6	2	1030	1001	5	12	12	2	629	629	7	2	0	2	460	651	3
5	13	1	432	475	6	14	1	2	115	127	-23	10	6	2	293	290	7	11	12	2	62	22	-40	3	0	2	497	493	3
4	13	1	316	295	5	13	1	2	229	222	9	8	6	2	257	271	7	10	12	2	183	186	13	4	0	2	82	123	13
3	13	1	342	354	6	12	1	2	382	369	6	7	6	2	615	598	5	9	12	2	59	88	-41	5	0	2	753	741	3
2	13	1	317	301	6	11	1	2	253	232	7	6	6	2	285	295	6	8	12	2	468	459	6	6	0	2	75	80	-14
1	13	1	611	607	4	10	1	2	1084	1088	5	5																	

TABLE 10. (continued)

n	k	L	10Fe	10Fe	10s	n	k	L	10Fe	10Fe	10s	n	k	L	10Fe	10Fe	10s	n	k	L	10Fe	10Fe	10s	n	k	L	10Fe	10Fe	10s
11	2	3	215	217	9	-3	7	3	395	394	5	0	13	3	356	358	5	-12	2	4	436	455	7	-1	7	4	524	520	5
10	2	3	277	274	5	-2	7	3	449	466	5	-11	14	3	143	135	19	-11	2	4	200	194	10	-0	7	4	782	850	3
9	2	3	525	487	5	-1	7	3	441	452	5	-10	14	3	110	92	-23	-10	2	4	659	655	5	-4	8	4	143	156	23
8	2	3	681	677	2	0	7	3	276	295	4	-9	14	3	399	386	8	-9	2	4	309	328	7	-13	8	4	145	127	19
7	2	3	548	546	2	-15	8	3	164	161	13	-8	14	3	325	322	8	-8	2	4	343	358	6	-12	8	4	65	34	-42
6	2	3	518	535	5	-14	8	3	168	160	-28	-7	14	3	230	216	10	-7	2	4	953	950	5	-11	8	4	585	593	7
5	2	3	522	527	4	-13	8	3	249	227	10	-6	14	3	258	247	9	-6	2	4	190	201	8	-10	8	4	132	145	14
4	2	3	747	753	4	-12	8	3	239	224	10	-5	14	3	320	312	8	-5	2	4	44	66	-42	-9	8	4	133	156	14
3	2	3	354	370	5	-11	8	3	211	220	9	-4	14	3	401	394	7	-4	2	4	1026	1045	4	-8	8	4	56	32	-43
2	2	3	627	608	4	-10	8	3	456	462	6	-3	14	3	249	253	8	-3	2	4	107	87	14	-7	8	4	620	619	5
1	2	3	537	553	4	-9	8	3	389	381	7	-2	14	3	461	444	6	-2	2	4	349	373	5	-6	5	4	1058	1080	5
0	2	3	55	118	10	-8	8	3	401	388	6	-1	14	3	425	413	6	-1	2	4	494	505	5	-5	8	4	421	415	6
-1	2	3	350	350	9	-7	8	3	75	82	-26	0	14	3	158	172	8	0	2	4	840	865	3	-4	8	4	103	24	-19
-2	2	3	333	234	10	-6	8	3	196	205	5	-15	15	3	224	227	12	-15	4	4	196	182	12	-3	8	4	545	536	5
-3	2	3	367	356	8	-5	8	3	646	662	5	-14	15	3	202	225	11	-14	4	4	232	219	10	-2	8	4	209	218	9
-4	2	3	347	325	8	-4	8	3	115	96	15	-13	15	3	312	294	9	-13	4	4	237	237	10	-1	8	4	458	487	5
-5	2	3	217	216	10	-3	8	3	275	270	6	-12	15	3	338	332	8	-12	4	4	384	380	7	0	8	4	2081	2091	3
-6	2	3	321	301	7	-2	8	3	559	543	5	-11	15	3	83	116	-32	-11	4	4	214	203	9	-13	9	4	396	355	6
-7	2	3	666	675	5	-1	8	3	422	461	5	-10	15	3	121	136	19	-10	4	4	647	652	7	-12	9	4	205	200	11
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-21	2	3	320	303	7	-2	9	3	260	257	7	-12	15	3	214	226	7	-12	4	4	332	312	7	-11	10	4	463	463	7
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-23	2	3	53	20	-41	0	9	3	137	138	20	-10	15	3	229	216	11	-10	4	4	459	459	6	-9	10	4	239	240	8
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-28	2	3	539	539	4	-9	10	3	301	273	8	-5	15	3	204	211	11	-5	4	4	413	424	5	-4	10	4	89	45	-25
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-32	2	3	641	653	4	-5	10	3	545	535	5	-1	15	3	368	355	8	-1	4	4	910	888	3	0	10	4	160	164	17
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-35	2	3	275	285	9	-2	10	3	713	700	5	-13	15	3	374	333	8	-13	4	4	218	204	10	-10	11	4	497	504	7
-36	2	3	62	41	-41	-1	10	3	691	694	5	-12	15	3	458	426	7	-12	4	4	455	440	7	-9	11	4	265	276	8
-37	2	3	271	292	10	0	10	3	269	261	5	-11	15	3	67	57	-30	-11	4	4	173	151	10	-8	11	4	176	201	12
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-40	2	3	515	515	5	-11	11	3	335	327	9	-8	15	3	71	43	-43	-8	4	4	545	548	5	-5	11	4	337	345	7
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-44	2	3	306	342	5	-7	11	3	312	299	7	-4	15	3	90	64	14	-4	4	4	217	200	8	-1	11	4	62	39	-26
-45	2	3	738	727	4	-6	11	3	447	455	6	-3	15	3	09	112	14	-3	4	4	630	603	5	-12	12	4	94	26	-31
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TABLE 10. (continued)

h k l 10Fe 10Fe 10s				h k l 10Fe 10Fe 10s				h k l 10Fe 10Fe 10s				h k l 10Fe 10Fe 10s			
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-2 14 4	173	177	11	-3 3 5	157	154	11	-12 10 5	362	329	8	11 0 6	404	392	5
-1 14 4	363	375	8	-2 3 5	687	683	5	-11 10 5	131	82	19	12 0 6	139	150	14
0 14 4	386	394	5	-1 3 5	415	401	5	-10 10 5	217	198	11	13 0 6	68	16	-31
1 14 4	281	279	10	0 3 5	469	485	4	-9 10 5	365	380	8	-13 1 6	229	218	11
2 14 4	260	243	10	-14 4 5	113	139	-29	-8 10 5	312	318	8	-12 1 6	414	412	8
3 14 4	365	361	8	-3 4 5	224	195	-10	-7 10 5	220	193	10	-11 1 6	97	83	-26
4 14 4	460	447	7	-2 4 5	160	187	11	-6 10 5	380	368	7	-10 1 6	662	656	7
5 14 4	252	257	9	-11 4 5	337	316	8	-5 10 5	332	331	7	-9 1 6	320	340	8
6 14 4	116	71	-23	-10 4 5	420	432	7	-4 10 5	289	300	8	-8 1 6	312	329	8
7 14 4	166	254	11	-9 4 5	371	380	7	-3 10 5	219	246	9	-7 1 6	374	393	7
8 14 4	404	373	7	-8 4 5	372	393	7	-2 10 5	462	470	5	-6 1 6	577	585	6
9 14 4	184	172	12	-7 4 5	203	202	9	-1 10 5	311	334	7	-5 1 6	447	455	6
10 14 4	320	349	5	-6 4 5	182	217	10	0 10 5	112	127	14	-4 1 6	549	517	6
11 14 4	72	134	-41	-5 4 5	651	657	5	-11 11 5	248	248	11	-3 1 6	690	689	5
12 14 4	407	435	8	-4 4 5	186	181	10	-10 11 5	167	196	17	-2 1 6	358	381	7
13 14 4	331	359	9	-3 4 5	224	316	7	-9 11 5	367	379	8	-1 1 6	566	578	5
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28 14 4	214	216	13	-3 5 5	513	513	5	-6 12 5	125	133	20	0 2 6	348	366	5
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37 0 5	73	92	-22	-8 6 5	159	161	14	-8 13 5	79	107	-38	-5 3 6	247	264	6
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39 0 5	180	194	7	-6 6 5	330	340	7	-6 13 5	301	303	8	-3 3 6	183	221	10
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45 0 5	112	114	17	0 6 5	329	318	5	0 13 5	531	534	5	-11 4 6	243	242	10
46 1 5	241	254	11	-13 7 5	155	119	16	-9 14 5	222	237	12	-10 4 6	202	210	11
47 1 5	79	108	-38	-12 7 5	257	264	10	-8 14 5	107	112	-22	-9 4 6	101	141	-22
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52 1 5	414	445	7	-7 7 5	307	325	8	-3 14 5	151	149	15	-4 4 6	283	311	8
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54 1 5	160	160	10	-5 7 5	340	352	7	-1 14 5	368	374	8	-2 4 6	105	119	-22
55 1 5	211	203	10	-4 7 5	342	365	7	0 14 5	62	26	-31	-1 4 6	281	296	9
56 1 5	298	318	7	-3 7 5	312	340	7	-15 15 5	221	203	11	0 4 6	1534	1532	4
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58 1 5	453	438	5	-1 7 5	339	347	7	-13 15 5	368	367	8	-12 5 6	80	69	-38
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62 2 5	342	313	8	-11 8 5	186	182	11	-9 15 5	65	29	-44	-8 5 6	59	54	-43
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64 2 5	160	137	14	-9 8 5	137	144	7	-7 15 5	435	425	5	-6 5 6	577	591	6
65 2 5	434	433	7	-8 8 5	358	348	7	-6 15 5	310	312	10	-5 5 6	531	544	6
66 2 5	438	432	7	-7 8 5	221	213	8	-5 15 5	290	275	10	-4 5 6	342	359	7
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68 2 5	263	243	7	-5 8 5	323	318	7	-3 15 5	78	73	-33	-2 5 6	584	591	5
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70 2 5	342	356	7	-3 8 5	317	306	7	-1 15 5	201	219	12	0 5 6	1071	1050	4
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72 2 5	402	414	6	-1 8 5	317	322	7	-4 17 5	210	194	13	-11 6 6	92	57	-32
73 2 5	516	519	5	0 8 5	51	57	-33	-3 17 5	394	394	8	-10 6 6	465	475	7
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75 2 5	228	200	6	-11 9 5	66	59	-44	-1 17 5	350	339	8	-8 6 6	243	266	9
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78 2 5	99	122	-29	-8 9 5	351	369	8	2 0 6	55	13	-34	-5 6 6	68	46	-52
79 2 5	203	241	10	-7 9 5	219	238	9	3 0 6	1695	1710	4	-4 6 6	502	507	6
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81 2 5	56	106	-34	-5 9 5	327	324	7	5 0 6	492	477	4	-2 6 6	323	347	7
82 2 5	148	160	-14	-4 9 5	236	248	8	6 0 6	54	57	-31	-1 6 6	224	261	7
83 2 5	343	348	7	-3 9 5	581	586	5	7 0 6	350	367	5	-17 7 6	203	216	13
84 2 5	363	363	7	-2 9 5	203	180	10	8 0 6	178	165	8	-17 7 6	115	112	-23
85 2 5	446														

TABLE 10. (continued)

h	k	l	10f _e	10f _e	10s	h	k	l	10f _e	10f _e	10s	h	k	l	10f _e	10f _e	10s	h	k	l	10f _e	10f _e	10s	h	k	l	10f _e	10f _e	10s
1	15	6	217	216	11	-9	5	7	229	118	21	-1	11	7	169	200	14	-4	4	8	267	284	10	4	0	9	127	128	17
2	15	6	113	87	-19	-8	5	7	256	270	10	-2	11	7	299	316	7	-3	4	8	320	341	7	5	0	9	265	277	8
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2	16	6	115	112	-28	-6	5	7	253	258	11	-6	12	7	255	279	11	-1	4	8	61	72	-52	7	0	9	49	14	-36
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1	0	7	421	451	5	-3	5	7	241	459	7	-3	12	7	160	135	16	-8	3	8	233	260	11	-6	1	9	159	209	16
2	0	7	420	446	5	-2	5	7	253	137	13	-2	12	7	229	242	11	-7	3	8	273	269	10	-5	1	9	112	68	-31
3	0	7	180	173	9	-1	5	7	375	392	7	-1	12	7	274	303	10	-6	3	8	360	377	8	-4	1	9	260	283	11
4	0	7	58	90	-34	0	5	7	139	147	12	0	12	7	118	68	19	-5	3	8	273	279	11	-3	1	9	205	216	17
5	0	7	359	387	5	-11	6	7	132	121	-25	-6	13	7	113	147	-26	-4	3	8	191	192	13	-2	1	9	164	158	17
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7	0	7	148	163	13	-9	6	7	300	305	9	-4	13	7	288	300	10	-2	3	8	264	276	11	0	1	9	163	276	8
8	0	7	263	248	7	-8	6	7	233	246	11	-3	13	7	303	306	10	-1	3	8	318	329	8	-7	1	9	186	160	15
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48	2	7	413	387	7	0	9	7	444	479	5	-3	0	8	548	549	5	-3	10	8	192	193	14	-3	7	9	131	164	-23
49	2	7	275	292	8	-9	10	7	302	291	10	-10	3	8	371	367	9	-2	10	8	97	108	-25	-2	7	9	293	287	11
50	2	7	272	290	6	-8	10	7	125	138	-24	-9	3	8	272	283	11	-1	10	8	193	202	14	-1	7	9	234	213	12
51	2	7	298	307	10	-7	10	7	67	45	-40	-8	3	8	228	264	11	0	10	8	478	466	5	0	7	9	269	302	8
52	2	7	68	111	-41	-6	10	7	165	201	14	-7	3	8	233	248	12	-4</											

As mentioned above, refinement of site occupancies indicated deficiencies in those assigned to one Na atom and Ce. Refinement of the scattering curves for these sites converged to $(\text{Na}_{0.64}\text{Ca}_{0.36})$ and $(\text{Ce}_{0.3}\text{Ca}_{0.2})$, respectively. The scattering curve for the rare-earth site was further refined to $(\text{Ce}_{0.15}\text{La}_{0.13}\text{Ca}_{0.18}\text{Th}_{0.04})$ using electron microprobe data (Table 3). The valence for the refined (Na,Ca) site, based on the refined site occupancies, is 1.36 v.u., close to the 1.199 v.u. value obtained from bond valence calculations (Table 11). The Ce site has a site valence of 2.56 v.u., which agrees well with that calculated from bond valence summations (2.704 v.u.; Table 11). In their determination of the structure of phosinaite-(Ce), Krutik *et al.* (1981) noted the partial occupancies of both of these particular sites. A (Na,Ca) composition was assigned to one Na site, but no attempt was made to refine the proportions of each element in the site. Krutik *et al.* (1981) also refined the Ce site and found it to be only two-thirds occupied, the remainder of which they attributed to a vacancy. However, such an occupation gives a site-valence of only 2.0 v.u., significantly lower than that calculated from bond valence summations (2.704 v.u.; Table 11). This suggests that additional cations must be located at this site, which have been demonstrated to be Ca and Th in this study.

Refinement of the enantiomorphous structure was also undertaken. This model gave a poorer *R*-factor ($R = wR = 5.0\%$), the Na(8) atom was found to have nonpositive temperature factors and all atoms were found to have greater *U*_{eq} factors, suggesting that such a model was incorrect.

TABLE 11. EMPIRICAL BOND VALENCES (v.u.) FOR PHOSNAITE-(Ce)*.

	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Na(7)	Na(8)	(Na,Ca)	Ca	REE	Si(1)	Si(2)	P(1)	P(2)	ΣV_c
O(1)	0.138					0.201	0.073 ^{1/2} ↓		0.431						1.245	2.088
O(2)	0.181	0.277		0.099 ^{1/2} ↓					0.231						1.186	1.974
O(3)			0.148 ^{1/2} ↓	0.110 ^{1/2} ↓		0.150 ^{1/2} ↓	0.273	0.141 ^{1/2} ↓							1.225	2.047
O(4)							0.210		0.087	0.157, 0.332		1.139				1.925
O(5)	0.168		0.063 ^{1/2} ↓				0.252		0.177					1.238		1.890
O(6)		0.142	0.120 ^{1/2} ↓	0.123 ^{1/2} ↓	0.121 ^{1/2} ↓						0.227 ^{1/2} ↓			1.145		1.878
O(7)						0.188 ^{1/2} ↓	0.185		0.062	0.423					1.219	2.077
O(8)		0.200							0.260		0.285 ^{1/2} ↓			1.189		1.934
O(9)	0.044	0.122			0.196 ^{1/2} ↓				0.120		0.363 ^{1/2} ↓	1.073				1.918
O(10)						0.185	0.083 ^{1/2} ↓			0.216, 0.379			1.135			1.998
O(11)						0.109 ^{1/2} ↓		0.117 ^{1/2} ↓				0.922	0.902			2.050
O(12)	0.119								0.090			0.955	0.997			2.161
O(13)									0.262		0.477 ^{1/2} ↓		1.170			1.909
O(14)	0.299	0.198, 0.038						0.073 ^{1/2} ↓						1.300		1.908
ΣV_o	0.949	0.977	0.662	0.664	0.780	0.894	1.306	0.828	1.199	2.028	2.704	4.089	4.204	4.872	4.875	

Note: Valences for the Na/Ca and REE sites were calculated using weighted averages ($\text{Na}_{0.64}\text{Ca}_{0.36}$) and ($\text{Ce}_{0.3}\text{Ca}_{0.7}$) respectively; + calculated using the constants of Brese and O'Keefe (1991).

3.4 DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The crystal structure of phosinaite-(Ce) was originally determined by Krutik *et al.* (1981), who refined their model to $R = 7.2\%$. The essential features of this model were confirmed in this study and are discussed below.

Phosinaite-(Ce) contains two independent SiO_4 tetrahedra which share corners to form four-membered silicate rings, an uncommon configuration. In an overall-analysis of silicate structures, Liebau (1985) lists seven known minerals and four synthetic phases with established four-membered silicate rings. In addition to these, phosinaite-(Ce), clinophosinaite (Khomyakov *et al.*, 1981) and the new mineral ashburtonite (Grice *et al.*, 1991) may also be included. The silicate rings in phosinaite-(Ce) have an unusual topology, where adjacent tetrahedra alternately point up and down. This results in an arrangement of apical directions that may be described as {UDUD}. These rings have point-group symmetry 2 and deviate considerably from the maximum symmetry of $4/mmm$ observed in baotite $[\text{Ba}_4(\text{Ti,Nb})_8\text{O}_{16}(\text{Si}_4\text{O}_{12})\text{O}_{16}\text{Cl}]$; Nekrasov *et al.*, 1970], where the Si atoms are coplanar. The mean Si-O bond distances of 1.617 Å (range: 1.576-1.654 Å) and 1.608 Å (range: 1.566-1.662 Å), are close to the overall average Si-O value of 1.62 Å observed in silicates (Liebau, 1985). The mean Si-O distances in phosinaite-(Ce) are smaller than those observed in clinophosinaite $[\text{Na}_3\text{Ca}(\text{SiO}_3)\text{PO}_4]$; 1.624, 1.620 Å; Krutik *et al.*, 1981] which has topologically-similar Si_4O_{12} rings, and considerably smaller than those in kainosite-(Y) $[\text{Ca}_2\text{Y}_2(\text{Si}_4\text{O}_{12})\text{CO}_3\cdot\text{H}_2\text{O}]$; 1.626, 1.633 Å] which possesses a four-membered silicate ring of point-group symmetry m

(Guiseppe *et al.*, 1989). The mean bridging Si-O bond distances for both of the SiO_4 tetrahedra in phosinaite-(Ce) are considerably longer (1.648, 1.646 Å) than the mean non-bridging distances (1.587, 1.572 Å). The range in O-Si-O bond angles is 104.6-115.7° (mean = 109.3°) and 105.8-119.1° (mean = 109.4°), with those of the bridging bonds being smaller (mean = 106.2°) than those of non-bridging bonds (mean = 110.0°). The Si-O-Si bridging angles are 154.6 and 159.8°, well within the range of 130-180° given for minerals containing Si_2O_7 groups and somewhat greater than the average unstrained value of 140° given for silicates (Liebau, 1985). Calculated bond valence sums are: Si(1) = 4.089 v.u. and Si(2) = 4.204 v.u. (Table 11).

According to Liebau (1985), because of the relatively stronger repulsive forces between adjacent SiO_4 tetrahedra, silicate ring structures are energetically less favourable than chain structures. As such, a silicate will preferentially form chains rather than rings, unless the size of the cation-oxygen polyhedra prohibits chain formation. Liebau (1985) notes that silicate rings may also be stabilized by a number of factors, which include: 1) the presence of highly electronegative cations (*e.g.* Pb, Cu, Sn *etc.*); 2) the presence of additional ligands [*e.g.* H_2O , CO_3 or (OH)] and 3) the absence of so-called "hard" cations (*e.g.* Mg, Fe, Al and Li). The first two factors effectively reduce the total negative charge occurring at each tetrahedron, hence minimizing the repulsive forces between adjacent tetrahedra. Ring structures are also stabilized by the absence of cations that tend to form rigid coordination-polyhedra ("hard" cations). This is because the SiO_4 tetrahedra do

not have to be rotated or distorted in order to accommodate these cations.

Although Liebau (1985) presents data (p.192) which suggests that the existence of four-membered rings in kainosite-(Y) and papagoite $[\text{Ca}_2\text{Cu}_2\text{Al}_2(\text{Si}_4\text{O}_{12})(\text{OH})_6]$ is due to the presence of CO_3 with H_2O and Cu with (OH), respectively, neither of these factors (*i.e.* the presence of highly electronegative cations or additional ligands) apply in phosinaite-(Ce). Alternatively, the existence of the silicate ring in phosinate-(Ce) may be due to the {UDUD} arrangement of the SiO_4 tetrahedra. Such an arrangement slightly increases the distance between adjacent Si atoms compared to, for example, the tetrahedra in kainosite-(Y), which are arranged in a {UUUU} fashion. An increase in the distance between Si atoms would reduce the repulsive forces acting between adjacent tetrahedra and this could enhance stabilization of the silicate ring.

Two distinct PO_4 tetrahedra are present, exhibiting ranges in bond distances of P(1)-O 1.507-1.554 Å (mean = 1.532 Å) and P(2)-O 1.523-1.541 Å (mean = 1.532 Å). These lie within the range of 1.45-1.56 Å given by Ondik and Smith (1968) and are close to the average P-O distance of 1.535 Å (Corbridge, 1978). The P(1) O_4 tetrahedron appears to be slightly more distorted than that of P(2) based on the wider variation in its P-O bond distances, O-O distances and O-P-O bond angles (Table 9). The PO_4 tetrahedra do not share corners with each other, nor with the SiO_4 tetrahedra present in the structure. The bond valence sums calculated for P(1) and P(2) are 4.872 and 4.875 v.u., close to ideal (Table 11).

Essential ordering of Si and P in the phosinaite-(Ce) structure is indicated by refinement of the scattering powers of the tetrahedral atoms [Si(1) 96(1)%; Si(2) 98(1)%; P(1) 99(1)%; P(2) 99(1)%], electron microprobe analyses, mean T-O bond distances and calculated bond valence sums (Table 11).

Seven of the independent Na atoms present in the structure are octahedrally-coordinated. Their mean Na-O bond distances range from 2.368 Å to 2.642 Å, with most Na-O bond distances falling in the range of 2.29-2.75 Å given by Ondik and Smith (1968) for six-coordinated Na. In their work, Krutik *et al.* (1981) described Na(1) and Na(2) as being in five-fold coordination. From this study it is apparent that each contains five short bonds [2.247-2.587 Å and 2.399-2.579 Å, respectively] and one relatively long bond [2.953 and 3.014 Å, respectively]. Although Na-O bonds approaching 3 Å are not common, they have been recognized in minerals such as cancrinite (2.966 Å; Hassan and Grundy, 1991), scapolite (2.945 Å; Lin and Burley, 1973) and petarasite (3.093 and 3.213 Å; Ghose *et al.*, 1980). On this basis, Na(1) and Na(2) are both considered to be in distorted octahedral coordination. The O-Na-O bond angles for the Na(5) octahedron are quite variable (54.9-136.3°), suggesting that it is highly distorted. Calculated bond valence sums for most of the octahedrally-coordinated Na atoms are reasonably close to one (Table 10), although those of Na(3) and Na(4) are notably less than one and that for Na(7), greater than one. Despite the fact that refinement of the Na(3) and Na(4) site occupancies indicated these sites to be fully occupied, the low bond valence sums may suggest that vacancies are present.

The high bond valence sum, short bond distance to O and low U_{eq} for Na(7) suggests that Ca may also be present in this site.

The sites assigned to Ca and (Na,Ca) are both seven-coordinated and the resulting polyhedra may be described as monocapped octahedra (Fig. 1). The (Na,Ca)-O bond distances are 2.368-2.899 Å (mean = 2.568 Å), close to the range of 2.29-2.75(5) Å (mean = 2.53 Å) given for seven-coordinated Na (Ondik and Smith, 1968). The Ca-O bond distances are 2.285-2.856 Å (mean = 2.466 Å), close to the range of 2.29-2.80(8) Å (mean = 2.46 Å) provided for seven-coordinated Ca (Ondik and Smith, 1968). Inspection of Table 8 indicates that the (Na,Ca)O₇ polyhedron is larger and slightly less distorted. In both coordination polyhedra, the shortest O-O distances correspond to shared edges with tetrahedra; (Na,Ca)O₇ with P(2)O₄ and CaO₇ with Si(1)O₄.

Na(8) and REE are each coordinated by eight oxygen atoms. The resulting polyhedra (composed of twelve triangular faces) may be described as the D_{2d} dodecahedron-polyhedra of Britton and Dunitz (1973). The REEO₈ polyhedron (Fig. 2) is smaller and slightly more distorted than the Na(8)O₈ polyhedron (Table 9). The coordination polyhedra of Na(8)O₈ and REEO₈ are very similar to the Ca and Y polyhedra in kainosite-(Y) (Guiseppe *et al.*, 1989).

The phosinaite-(Ce) structure may be most easily described as series of mixed tetrahedral-octahedral layers that are stacked along *a* (Fig. 3). Two different types of layers are present: a (SiP)-layer with a [Na(SiO₄)₂(PO₄)] composition and a (P)-layer with the composition [Na(PO₄)]. Three layers are

Fig. 1. The CaO_7 polyhedron in phosinaite-(Ce). Distances in Å.

Fig. 2. The REEO₈ polyhedron in phosinaite-(Ce). Distances in Å.

Fig. 3. The (SiO_4) - and (P) -layers in the phosinaite-(Ce) structure projected down c . The Na(2) octahedra are unshaded, the Na(7) octahedra are lightly-shaded, the PO_4 tetrahedra are moderately-shaded and the SiO_4 tetrahedra are heavily-shaded. The unit cell is outlined. The REE, Ca and Na atoms of the polyhedral chains have been omitted for clarity. Compare this with Fig. 7.

present in each repeat along **a**, stacked in a (SiP):(SiP):(P) arrangement.

The (SiP)-layer is composed of SiO_4 and PO_4 tetrahedra which are cross-linked by Na(7) octahedra (Fig. 4). There are two types of four-membered rings in this layer: Si_4O_{12} rings and mixed NaO_6/PO_4 rings. Both are centred about a two-fold inversion axis and alternate along **a**. These rings also form empty channels along **a**, the cores of which are occupied by REE polyhedra and both Na octahedra and Na polyhedra. The remaining Na, Ca and (Na,Ca) cations are positioned in the interstices between the rings.

The (P)-layer in the phosinaite-(Ce) structure is composed of PO_4 tetrahedra that are corner-linked to Na(2) octahedra (Fig. 5). Each PO_4 tetrahedra shares three of its corners with four Na(2) octahedra.

The (SiP)- and (P)-layers are joined along **a** through tetrahedral-octahedral corner-sharing linkages, reinforced by edge- and face-sharing Na, Ca and REE polyhedra.

The structure of phosinaite-(Ce) may be alternatively described in terms of sheets, composed of sinuous, polyhedral chains that lie in the (001) plane and are reinforced by columns of four-membered silicate rings and mixed NaO_6/PO_4 rings (Fig. 6). The polyhedral chains, which extend along **b**, are composed of edge-sharing NaO_6 octahedra with $(\text{Na,Ca})\text{O}_7$, CaO_7 and REEO_8 polyhedra. These chains contain two different types of "hinge" units; a $(\text{Na,Ca})\text{O}_7$ - REEO_8 - $(\text{Na,Ca})\text{O}_7$ polyhedral unit and a $\text{Na}(1)\text{O}_6$ - $\text{Na}(5)\text{O}_6$ - $\text{Na}(1)\text{O}_7$ unit, each alternately occupying the hinge position within the chain along **b**, the two linked together by

Fig. 4. The (SiP)-layer in phosinaite-(Ce) projected down *a*. The SiO_4 tetrahedra are heavily-shaded, the PO_4 tetrahedra are moderately-shaded and the Na(7) octahedra are lightly-shaded. The unit cell is outlined.

Fig. 5. The (P)-layer in phosinaite-(Ce) projected down **a**. The PO_4 tetrahedra are shaded and the Na(2) octahedra are unshaded. The unit cell is outlined.

Fig. 6. A polyhedral chain in phosinaite-(Ce) projected down c . The CaO_7 polyhedra are unshaded, NaO_6 octahedra are stippled, the Na(8)O_8 polyhedra are lightly shaded, the $(\text{Na,Ca})\text{O}_7$ polyhedra are moderately shaded, the REEO_8 polyhedra heavily shaded, the SiO_4 tetrahedra are ruled and the PO_4 tetrahedra are cross-hatched. The unit cell is outlined.

the central CaO_7 polyhedron. The silicate and NaO_6/PO_4 rings occupy columns formed between the chains limbs and serve to reinforce the chains through shared corners, as do Na octahedra and NaO_8 polyhedra, which also occupy the interlimb positions (Fig. 6). Individual polyhedral chains are joined *via* polyhedral edge-sharing across **a**, to form complex sheets which are stacked along **c** (Fig. 7). Two compositionally-identical sheets occur in each repeat along **c**, each being translated $c/2$ and rotated 180° , as a result of the two-fold inversion axis along **c**. Bonding between these sheets is primarily through polyhedral edge-sharing along **c**, and the weakness of such linkages may be responsible for the pronounced {001} cleavage observed in phosinaite-(Ce).

3.5 RELATED STRUCTURES

Phosinaite-(Ce) is chemically and structurally-related to clinophosinate (Krutik *et al.*, 1980). The cell dimensions of the two minerals are comparable (Table 12), although differences in their structures result in phosinaite-(Ce) being orthorhombic and clinophosinate being monoclinic.

Clinophosinate also has a layered structure similar to that of phosinaite-(Ce). One of the PO_4 tetrahedra in the (SiP)-layer of clinophosinate is disordered, assuming two possible orientations. The two PO_4 tetrahedra share one oxygen which is not disordered. This type of disorder (*i.e.* rotation of two possible PO_4 tetrahedra about a common apical oxygen) has also been observed

Fig. 7. The phosinaite-(Ce) structure showing linkages of polyhedral chains into sheets. Projected down c . A compositionally-identical sheet is found $c/2$ above, but rotated 180° . Shading is as in Fig. 6. The unit cell is outlined.

TABLE 12. CRYSTALLOGRAPHIC RELATIONSHIPS BETWEEN PHOSINAITE-(Ce), CLINOPHOSINAITE AND KAINOSITE-(Y).

	CLINOPHOSINAITE ¹	PHOSINAITE-(Ce) ²	KAINOSITE-(Y) ³
	Na_3Ca $(\text{SiO}_3)(\text{PO}_4)$	$\text{Na}_{13}\text{Ca}_2\text{REE}$ $(\text{Si}_4\text{O}_{12})(\text{PO}_4)_4$	Ca_2Y_2 $(\text{Si}_4\text{O}_{12})(\text{CO}_3)\cdot\text{H}_2\text{O}$
Space Group	<i>P 2/c</i>	<i>P22₁2₁</i>	<i>Pmnb</i>
a (Å)	7.303(2)	12.297(2)	13.011(1)
b	12.201(5)	14.660(3)	14.310(1)
c	14.715(4)	7.245(1)	6.757(1)
β (°)	91.93(3)	-	-
V (Å ³)	1310.4(1)	1306.1(1)	1258.1(1)
Z	8	2	4

1. Krutik *et al.* (1980).
2. This study.
3. Guiseppetti *et al.* (1989).

in the mineral lomonosovite $[\text{Na}_5\text{Ti}_2\text{O}_2(\text{Si}_2\text{O}_7)(\text{PO}_4)]$, where it is believed to be related to the process of hydration (Rastsvetaeva, 1989).

The (P)-layer of clinophosinaite, is a sheet of PO_4 tetrahedra cross-linked by NaO_5 polyhedra (Fig. 8). This sheet may be more appropriately described as a layer of chains or ribbons, composed of NaO_5 polyhedra and PO_4 tetrahedra, that extend parallel to **a** in the **ac** plane.

Differences in the structures of phosinaite-(Ce) and clinophosinaite may also be described in terms of the polyhedral sheets. While phosinaite-(Ce) contains two compositionally-identical polyhedral sheets along **c** that are related by a two-fold screw axis, clinophosinaite has two similar sheets along **a**: one composed of Na and Ca polyhedra (Fig. 9) and the other of only Na polyhedra (Fig. 10). However, because these two sheets are compositionally different in clinophosinaite, there is no screw axis along **a**. Hence, the $P22_12_1$ symmetry of phosinaite-(Ce) is reduced to $P2/c$ in clinophosinaite.

Chemically, phosinaite-(Ce) and clinophosinaite are related. As illustrated in Table 13, their SiO_2 , P_2O_5 and NaO_2 contents are very comparable, although there are marked differences in their respective CaO and total REE_2O_3 contents. Clinophosinate has a CaO content close to 16 wt. % and a total REE_2O_3 content of close to 0 wt%; phosinaite-(Ce) has a CaO content of close to 9 wt.% and a

Fig. 8. The (P)-layer in clinophosinaite projected on the *ac* plane. The PO_4 tetrahedra are shaded and the NaO_5 polyhedra are stippled. The unit cell is outlined. The sheet is separated into chains or ribbons (along *a*) due to the absence of cross-linkage.

Fig. 9. A Ca/Na polyhedral chain in clinophosinaite, projected on the bc plane. The NaO_8 polyhedra are stippled, the CaO_7 polyhedra moderately shaded, the CaO_8 polyhedra heavily shaded and the CaO_6 octahedra are unshaded. The unit cell is outlined.

Fig. 10. A Na polyhedral chain in clinophosinaite, projected on the bc plane. The unit cell is outlined.

TABLE 13. THE CHEMICAL COMPOSITIONS OF
PHOSINAITE-(Ce) AND CLINOPHOSINAITE.

	<u>PHOSINAITE-(Ce)</u>			<u>CLINOPHOSINAITE</u>	
	1	2	3	4	5
Na ₂ O wt.%	31.68	28.78	29.76	32.55	32.70
K ₂ O	-	0.47	0.50	0.09	0.05
CaO	8.92	5.39	8.90	15.65	16.45
SrO	-	-	0.30	3.08	1.91
MnO	0.89	1.90	0.16	0.60	0.54
Fe ₂ O ₃	-	0.49	0.45	-	-
REE ₂ O ₃	11.95	13.80	11.67	0.18	0.44
ThO ₂	1.84	-	-	-	-
SiO ₂	18.36	23.78	20.00	20.10	20.10
P ₂ O ₅	23.69	20.50	25.50	25.35	25.50
H ₂ O	-	4.41	2.38	-	-
TOTAL	97.33	99.52	99.62	97.60	97.69

1. Phosinaite-(Ce), this study; Mont St. Hilaire, Rouville Co., Quebec, Canada; SiO₂ includes Al₂O₃ 0.15 wt.%; For REE composition, see table 3.
2. Phosinaite-(Ce), Kapustin *et al.* (1974); Mt. Karnasurt, Lovozero, Russia; Analysis also gave Li₂O 0.24 wt%.
3. Phosinaite-(Ce), Krutik *et al.* (1981); Khibina Massif, Russia; Analysis also gave MgO 0.28 wt%.
4. Clinophosinate, Khomyakov *et al.* (1981); Mt. Koashva, Khibina massif, Russia; Traces of Ti, Fe, Mg, Al, Zr and Ba also present.
5. Clinophosinaite, Khomyakov *et al.* (1981); Mt. Yukspor, Lovozero massif, Russia; Traces of Ti, Fe, Mg, Al, Zr and Ba also present.

total REE_2O_3 content of about 13 wt.% (Table 13). Therefore, phosinaite-(Ce) is related to clinophosinaite by a $\text{REE} + \text{Na} \rightleftharpoons 2\text{Ca}$ substitution scheme.

Phosinaite-(Ce) and kainosite-(Y) (Guiseppe *et al.*, 1989) have a number of features in common, which include: 1) belonging to the same crystal system (orthorhombic); 2) similar cell dimensions (Table 12); 3) the presence of four-membered silicate rings in their structures and 4) mixed-oxyanionic compositions. However, the space-group symmetries for the two minerals are different (Table 12) and their structures are different. The crystal structure of kainosite-(Y) is composed of two polyhedral sheets, one of CaO_8 polyhedra and the other of YO_8 polyhedra, which are stacked in an alternating fashion along **b**. These sheets are joined together through shared edges and corners, and such linkages result in the formation of six-sided holes, which are occupied by Si_4O_{12} rings. Although four-membered silicate rings are present in both minerals, their topologies are slightly different. In kainosite-(Y), the apical oxygens of the SiO_4 tetrahedra are arranged {UUUU}, in contrast with those in phosinaite-(Ce), which are arranged {UDUD}. This results in the silicate rings having slightly different point-group symmetries: *m* in kainosite-(Y) and 2 in phosinaite-(Ce).

CHAPTER 4

DETERMINATION OF THE CRYSTAL STRUCTURE OF ABENAKIITE-(Ce)

4.1 OCCURRENCE

Abenakiite-(Ce), ideally $\text{Na}_{26}\text{REE}_6(\text{SiO}_3)_6(\text{PO}_4)_6(\text{CO}_3)_6(\text{SO}_2)\text{O}$, was discovered in a sodalite syenite xenolith found in nepheline syenite at the Poudrette Quarry, Mont Saint-Hilaire, Rouville Co., Quebec. The xenolith in which the mineral occurs is estimated to be 1-2 m in diameter and has been described by Chao *et al.* (1991).

Abenakiite-(Ce) occurs as a single ellipsoidal grain, approximately 2 x 1 mm, embedded in matrix. The grain is pale brown and surrounded by a yellow to white rim of an unidentified rhabdophane-group mineral $[(\text{REE})\text{PO}_4 \cdot \text{H}_2\text{O}]$, which may be an alteration product of abenakiite-(Ce). Although abenakiite-(Ce) is closely associated with aegirine, eudialyte, polyolithionite, steenstrupine-(Ce), terskite and ussingite, at least 72 different minerals have also been found in the same xenolith (Chao *et al.*, 1991).

4.2 PHYSICAL AND OPTICAL PROPERTIES

Abenakiite-(Ce) is predominantly pale brown, but appears colourless in places. It is transparent, has a vitreous lustre, a white streak and does not fluoresce under ultraviolet light. The Mohs' hardness is greater than four. The mineral is brittle with a conchoidal fracture and a poor {001} cleavage. A very

weak effervescence in 1:1 HCl was noted. The measured density, determined by flotation in a heavy liquid and a 10 mL pycnometer, is 3.21 (2) g/cm³.

Optically, abenakiite-(Ce) is uniaxial negative with ϵ 1.586(1) and ω 1.589(1) and is non-pleochroic.

4.3 CHEMICAL COMPOSITION

Results of electron microprobe analyses carried out on abenakiite-(Ce) are listed in Table 14. Also sought for but not detected were F, Ba, Ti, Fe, Mn, Zr, Y and Ca. Aluminum was not analyzed for, but a qualitative energy dispersive scan indicated less than 0.2 wt.% Al₂O₃.

The results given in Table 14 show a deficiency of 10-13 wt.%, which must be due to elements with atomic numbers less than seven or water that are not detectable by the electron microprobe. The missing constituent was identified as C from the crystal structure analysis, based on its electron density, the fact that it was bonded to three oxygens in a trigonal planar configuration with mean cation-to-oxygen distances of 1.30 Å and by its valence sum (3.826 v.u.; Table 19). Bond valence calculations also verified the absence of water in the mineral (Table 19) and determined that the valence state of S is 4+.

The average analysis from Table 14 (col. 5) corresponds to the empirical formula (calculated on the basis of 63 oxygen atoms as determined by crystal structure analysis):

TABLE 14. THE CHEMICAL COMPOSITION
OF ABENAKIITE-(Ce).

	1	2	3	4	5 ¹	6 ²
Na ₂ O Wt.%	25.04	25.33	25.52	25.37	25.32	27.67
Ce ₂ O ₃	15.50	15.36	15.24	15.15	15.31	16.91
La ₂ O ₃	6.08	5.86	6.11	5.69	5.94	5.60
Nd ₂ O ₃	8.04	8.07	7.59	7.41	7.78	11.56
Pr ₂ O ₃	1.91	2.43	1.95	1.77	2.02	-
Sm ₂ O ₃	0.88	0.78	0.59	0.70	0.74	-
ThO ₂	1.86	1.27	1.21	1.32	1.42	-
SrO	0.12	0.13	0.09	0.13	0.12	-
SiO ₂	13.71	13.35	13.00	13.14	13.30	12.39
P ₂ O ₅	14.60	14.09	13.70	14.05	14.11	14.62
SO ₂	2.34	2.34	2.18	2.28	2.28	2.20
CO ₂ ³	<u>(9.10)</u>	<u>(8.95)</u>	<u>(8.76)</u>	<u>(8.82)</u>	<u>(8.90)</u>	<u>9.05</u>
TOTAL	99.18	97.96	95.94	95.83	97.24	100

1. Average of analyses 1-4 on one grain;
2. Calculated for the formula,
Na₂₆(Ce₃Nd₂La₁)_{Σ=6}(SiO₃)₆(PO₄)₆(CO₃)₃(SO₂)O.
3. Calculated from stoichiometry.

with C taken to be in stoichiometric proportions. From the crystal structure analysis, the structural formula for abenakiite-(Ce) is,

$\text{Na}_{26}\text{REE}_6(\text{SiO}_3)_6(\text{PO}_4)_6(\text{CO}_3)_6(\text{SO}_2)\text{O}$, with $Z = 3$. The fact that the Na content of the empirical formula is slightly lower than ideal is attributed primarily to volatilization of the element under the electron beam and to a lesser extent, vacancies in the Na sites. The densities calculated from the empirical formula and ideal formula using the cell dimensions refined from powder data are 3.271 and 3.295 g/cm³ respectively, close to the measured density of 3.21(2) g/cm³.

Gladstone-Dale calculations using the measured density, indices of refraction and the constants given by Mandarino (1981) give $1-(K_p/K_c) = 0.034$ (excellent) or $1-(K_p/K_c) = 0.017$ (superior) using the calculated density.

4.4 X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE DETERMINATION

Single-crystal X-ray precession photographs show abenakiite-(Ce) to be rhombohedral, with possible space group choices $R\bar{3}$ and $R\bar{3}$. Results of crystal structure analysis indicate that $R\bar{3}$ is the correct space group. The refined cell parameters, obtained from single-crystal four-circle diffractometer data, are: a 16.025(2), c 19.773(4) Å and V 4397.4(1) Å³. These agree well with those refined from powder X-ray diffraction data: a 16.018(2), c 19.761(4) Å and V 4390.9(1) Å³. The observed X-ray powder diffraction pattern (CuKα) is presented

in Table 15 along with that calculated from the crystal structure. Despite some discrepancies, agreement between the two patterns is reasonably good.

X-ray intensity data were collected following the procedure outlined under *Analytical Methods*. A small, disc-shaped fragment was mounted to rotate approximately about *c*. The grain was optically homogeneous and gave a sharp, uniform extinction when viewed under crossed-polars. Important information regarding the data collection is presented in Table 16. Of the 2238 reflections collected, 2116 were considered observed [$F > 6\sigma(F)$].

The abenakiite-(Ce) crystal structure was solved using direct methods. Intensity distribution ($|E^2 - 1| = 0.927$) strongly suggested a centric space group and it was subsequently confirmed that $R\bar{3}$ is the correct choice. From the *E*-map, the positions of the rare-earths (assumed to be Ce), Si, P, two different Na atoms and an oxygen atom were identified. Difference-Fourier maps of this initial model revealed additional atomic sites to which the appropriate scattering curves for the other elements believed to be present in the mineral, were assigned. At $R = 7.3\%$, the rare-earth, Si, P, S, five crystallographically-distinct Na sites and 11 crystallographically-distinct O sites had been located. An examination of the difference map calculated at this stage, showed a positive maximum of approximately $8 \text{ e}^-/\text{\AA}^3$. The maximum was coordinated by three oxygens in a trigonal planar configuration, with a mean *X* - O distance of $1.302 \text{ \AA}$. Based on these data, the residual electron density was assigned to C, a conclusion also supported by the bond valence sum for the site

TABLE 15. X-RAY DIFFRACTION DATA
FOR ABENAKIITE-(Ce).

d_{meas}	I_{est}	d_{calc}	I_{calc}	hkl
11.414	75	11.3538	53	101
8.036	85	8.0478	61	012
		6.5870	25	003
6.554	85	6.5446	55	021
5.696	10	5.6769	9	202
5.066	60	5.0678	31	121
4.646	75	4.6539	27	104
		4.6314	5	122
		4.6240	13	030
3.994	1	4.0045	10	220
		3.7846	48	303
3.773	90	3.7765	47	131
		3.5956	26	214
3.591	80	3.5852	29	312
3.420	3	3.4218	6	223
3.150	70	3.1560	52	125
		3.0292	10	232
3.024	50	3.0271	10	410
2.844	5	2.8384	6	404
		2.7568	7	315
2.745	20	2.7506	12	143
2.674	100	2.6826	100	036
		2.6697	89	330
		2.6067	8	045
2.604	10	2.5988	4	241
2.532	15	2.5355	9	422
		2.5856	5	217
2.471	45	2.4742	11	333
		2.4719	14	511
2.414	5	2.4159	5	152
2.312	1	2.3157	7	244
		2.2760	7	137
2.272	15	2.2708	9	505
		2.2346	5	128
		2.2287	5	146
2.222	50	2.2213	12	520
		2.1957	10	009
		2.1846	8	425
2.181	50	2.1815	31	063
2.102	40	2.1048	9	523

TABLE 15. X-RAY DIFFRACTION DATA
FOR ABENAKIITE-(Ce).

d_{meas}	I_{est}	d_{calc}	I_{calc}	hkl
		2.1034	7	161
		2.0786	7	318
		2.0706	5	434
1.976	5	1.9834	9	039
		1.9473	6	164
1.943	10	1.9430	5	072
		1.9210	5	247
1.917	10	1.9157	2	621
1.890	45	1.8923	48	066
		1.8680	6	517
1.865	15	1.8651	15	615
1.838	5	1.8374	2	710
1.802	15	1.7816	11	01-11
		1.7698	10	173
		1.7578	5	13-10
		1.7541	7	158
		1.7040	7	339
		1.6893	7	363
1.688	25	1.6885	7	271
		1.6714	6	544
1.6701	15	1.6703	3	722
		1.6200	9	455
1.618	10	1.6096	1	05-10
1.604	5	1.6046	3	716
		1.5644	7	23-11
		1.5513	12	03-12
1.542	50	1.5438	19	366
plus others				

Note: d_{meas} obtained using a 114.6 mm Gandolfi camera with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$); I_{est} visually estimated; d_{calc} determined from the cell refined from powder data: a 16.018(2), c 19.761(6) $\text{\AA}$; I_{calc} calculated from the crystal structure.

**TABLE 16. MISCELLANEOUS DATA FOR DETERMINATION
OF THE CRYSTAL STRUCTURE OF ABENAKIITE-(Ce).**

Space Group	$R\bar{3}$ (#148)	Diffractometer	Enraf-Nonius CAD4
a (Å)	16.025(2)*	Radiation	MoK α (50kV, 20 mA)
c	19.773(4)*	Monochromator	Graphite
V (Å ³)	4390.9(1)	Crystal Shape	Flat, rounded
Z	3	Crystal Size	0.27 x 0.36 x 0.09 mm
		μ (MoK α)	4.91 mm ⁻¹
Chemical Formula		Na ₂₆ REE ₆ (SiO ₃) ₆ (PO ₄) ₆ (CO ₃) ₆ (SO ₂)O	
Intensity Data Collection		Θ -2 Θ scanning mode	
2 Θ Limit		55°	
Intensity Standards		Three every 10,000 seconds	
Orientation Standards		Three every 400 reflections	
Number of Unique Reflections		2238	
Number of Observed Reflections		2116	
Criterion for Observed		$F > 6\sigma(F)$	
Weighting Scheme		$wR = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2},$ $w = 1/\sigma^2$	
Final <i>R</i> for all Observed Reflections		3.1%	
Final <i>wR</i> for all Observed Reflections		3.0%	

* Values refined from four-circle diffractometer data.

(Table 19). Refinement of this model, which included conversion of temperature displacement factors to an anisotropic basis [except for S and O(11)], modification of the weighting scheme to one involving $1/\sigma^2(F_o)$ term and refinement of site occupancies, converged to $R = 3.1\%$ and $wR = 3.0\%$. An extinction correction was also included, but did not improve the refinement. The S and O(11) sites could not be refined anisotropically (as large negative temperature displacement factors resulted) and were therefore refined on an isotropic basis. Site occupancy refinement indicated most sites to be fully occupied, although partial occupancies were indicated for Na(4) [88(1) %] and O(11) [34(2) %]. The occupancy of O(11) was subsequently fixed at 1/3 to agree with the interpretation of a SO₂ group being present in the mineral.

Refinement of the acentric space group $R3$ was also undertaken. The final residuals for this model ($R = 4.1\%$ and $wR = 3.5\%$) were greater than those obtained for the $R\bar{3}$ model, a number of atoms [Si, Na(5), O(1),(3),(4),(5),(6),(9) and (10)] were found to have non-positive temperature factors, and all atoms were found to generally have greater U_{eq} factors. This strongly suggests that the non-centrosymmetric model is incorrect.

The final difference map was relatively smooth, with only one minor maximum, $\approx 1.7 \text{ e}^-/\text{\AA}^3$, associated with the rare-earth site. Since this site was refined using only a Ce scattering curve, this minor peak may be due to the presence of rare-earth elements heavier than Ce at the site.

Final positional and thermal parameters are given in Table 17, selected

TABLE 17. POSITIONAL AND THERMAL PARAMETERS FOR ABENAKITE-(Ce).

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Si	0.4299(1)	0.8652(1)	0.1271(1)	85(6)	95(6)	116(6)	7(5)	4(5)	48(5)	98(5)
P	0.3185(1)	0.0006(1)	0.0009(1)	144(6)	140(6)	201(6)	9(5)	12(5)	79(6)	158(5)
Na(1)	0.3480(2)	0.3483(2)	0.1712(1)	298(13)	475(16)	231(12)	-30(11)	-2(10)	310(13)	283(11)
Na(2)	0.5525(2)	0.1046(2)	0.7103(1)	182(12)	255(13)	330(13)	-89(10)	58(10)	2(10)	303(10)
Na(3)	1/3	2/3	0.0230(2)	124(11)	124(11)	332(21)	0	0	62(6)	193(10)
Na(4)	0.2088(2)	0.7850(2)	0.7378(2)	483(18)	260(14)	498(18)	104(13)	-151(14)	62(13)	468(13)
Na(5)	0.1121(2)	0.2089(3)	0.0975(2)	350(16)	769(23)	468(17)	438(17)	231(13)	409(16)	472(15)
REE	0.5355(2)	0.11288(2)	0.05834(1)	117(1)	76(1)	125(1)	6(1)	19(1)	48(1)	106(1)
C	0.2657(3)	0.7643(3)	0.8747(2)	110(21)	94(20)	82(19)	16(16)	-29(16)	-92(17)	159(16)
S	2/3	1/3	1/3	585(14)						
O(1)	0.4400(3)	0.8250(3)	0.0555(2)	184(19)	155(18)	125(17)	-6(14)	14(14)	86(16)	154(15)
O(2)	0.3141(3)	0.8141(3)	0.1462(2)	106(17)	263(21)	165(18)	46(16)	16(14)	59(17)	193(15)
O(3)	0.8377(3)	0.1914(3)	0.8014(2)	237(20)	249(21)	175(18)	-22(15)	-17(15)	182(18)	194(16)

TABLE 17. (continued).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
O(4)	0.5001(4)	0.8052(4)	0.8433(2)	604(33)	336(27)	241(22)	19(19)	33(21)	323(26)	355(23)
O(5)	0.3940(3)	0.9682(3)	0.9947(2)	248(21)	277(22)	272(21)	-49(17)	-16(17)	199(19)	235(18)
O(6)	0.6046(3)	0.9600(4)	0.7340(2)	258(24)	406(27)	256(23)	22(20)	86(18)	85(21)	342(20)
O(7)	0.6301(3)	0.9079(3)	0.9552(2)	193(21)	238(22)	440(26)	-105(19)	-30(19)	120(19)	285(18)
O(8)	0.7691(3)	0.0731(3)	0.9617(2)	268(24)	260(24)	443(27)	91(20)	129(21)	98(20)	339(20)
O(9)	0.3277(3)	0.8427(3)	0.8480(2)	307(24)	197(21)	300(23)	86(18)	2(19)	45(19)	304(18)
O(10)	0.4618(3)	0.7162(3)	0.9377(2)	230(21)	151(18)	232(20)	12(15)	98(16)	72(17)	214(16)
O(11)	0.5774(14)	0.2456(15)	0.3374(10)	588(48)						

Note: Anisotropic temperature factors have the form: $\exp. -2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} \dots + 2hka^* b^{*2} U_{12})$; all U values are in $\text{\AA}^2 \times 10^4$; estimated standard deviations in parentheses.

TABLE 18. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)
FOR ABENAKIITE-(Ce).

Si tetrahedron											
Si	- O(1)	1.607(4)	O(1) - Si	- O(2)	108.5(2)	O(1) - O(2)	2.638(8)				
	- O(2)*	1.655(4)		- O(2)*	110.5(3)		- O(2)*			2.670(8)	
	- O(2)*	1.664(5)		- O(3)	117.6(2)		- O(3)			2.741(8)	
	- O(3)	1.606(5)		O(2) - Si	- O(2)*		106.4(2)			O(2) - O(2)*	2.656(8)
	Mean	1.633		- O(3)	107.4(3)		- O(3)			2.628(8)	
			O(2)* - Si	- O(3)	105.8(2)	O(2)* - O(3)*	2.605(8)				
			Mean	109.4	Mean	2.656					
P tetrahedron											
P	- O(5)	1.541(6)	O(5) - P	- O(6)	110.5(3)	O(5) - O(6)	2.498(8)				
	- O(6)	1.506(5)		- O(7)	103.3(3)		- O(7)			2.416(8)	
	- O(7)	1.545(5)		- O(8)	110.9(3)		- O(8)			2.505(8)	
	- O(8)	1.503(4)		O(6) - P	- O(7)		111.7(3)			O(6) - O(7)	2.511(8)
	Mean	1.524		- O(8)	112.0(3)		- O(8)			2.432(8)	
			O(7) - P	- O(8)	108.1(3)	O(7) - O(8)	2.467(8)				
			Mean	109.4	Mean	2.480					
Na(1) polyhedron											
Na(1)	- O(2)	2.721(6)	O(2) - Na(1)	- O(3)	56.6(2)	O(2) - O(3)	2.608(8)				
	- O(3)	2.777(4)		- O(3)*	59.0(2)		- O(3)*			2.628(8)	
	- O(3)*	2.611(6)		- O(6)	103.1(2)		- O(6)			3.960(8)	
	- O(6)	2.342(5)		- O(7)	112.0(2)		- O(7)			4.547(8)	
	- O(7)	2.770(5)		- O(8)	78.7(2)		- O(8)			3.474(8)	
	- O(8)	2.761(5)		- O(9)	126.1(2)		- O(9)			4.572(8)	
	- O(9)	2.407(4)		O(3) - Na(1)	- O(3)*		114.5(2)			O(3) - O(3)*	4.529(8)
	Mean	2.627		- O(6)	100.9(2)		- O(6)			3.263(8)	
				- O(8)	80.9(1)		- O(8)			3.574(8)	
			- O(9)	71.2(2)	- O(9)	3.032(8)					
			O(3)* - Na(1)	- O(6)	82.2(2)	O(3)* - O(6)	3.247(8)				
			- O(7)	81.5(2)	- O(7)	3.513(8)					
			- O(8)	97.9(2)	- O(8)	4.045(8)					
			O(6) - Na(1)	- O(7)	125.1(2)	O(6) - O(7)	2.525(8)				
			- O(9)	98.7(2)	- O(9)	3.597(8)					
			O(7) - Na(1)	- O(8)	53.0(1)	O(7) - O(8)	2.467(8)				
			- O(9)	93.3(2)	- O(9)	3.757(8)					
			O(8) - Na(1)	- O(9)	81.0(2)	O(8) - O(9)	3.366(8)				

TABLE 18. (continued)

Na(2) octahedron					
Na(2) - O(1)	2.396(5)	O(1) - Na(2) - O(2)	87.9(1)	O(1) - O(2)	3.353(8)
- O(2)	2.445(5)	- O(6)	89.4(1)	- O(6)	3.719(8)
- O(5)	3.069(6)	- O(7)	85.5(2)	- O(7)	3.306(8)
- O(6)	2.866(8)	- O(10)	76.2(1)	- O(10)	3.031(8)
- O(7)	2.489(5)	O(2) - Na(2) - O(5)	83.4(2)	O(2) - O(5)	3.680(8)
- O(8)	2.251(4)	- O(6)	113.6(2)	- O(6)	4.448(8)
- O(10)	2.538(5)	- O(8)	95.3(2)	- O(8)	3.464(8)
Mean	2.579	- O(10)	117.5(2)	- O(10)	3.032(8)
		O(5) - Na(2) - O(6)	132.2(1)	O(5) - O(6)	2.498(8)
		- O(7)	108.6(2)	- O(7)	2.416(8)
		- O(8)	53.6(2)	- O(8)	2.505(8)
		- O(10)	71.2(1)	- O(10)	3.288(8)
		O(6) - Na(2) - O(7)	55.7(1)	O(6) - O(7)	2.511(8)
		- O(8)	79.7(2)	- O(8)	3.313(8)
		- O(10)	125.9(2)	- O(10)	4.805(8)
		O(7) - Na(2) - O(8)	89.4(2)	O(7) - O(8)	3.322(8)
		- O(10)	71.1(1)	- O(10)	2.922(8)
		O(8) - Na(2) - O(10)	111.1(2)	O(8) - O(10)	3.945(8)
Na(3) octahedron					
Na(3) - O(1)	2.331(4) x3	O(1) - Na(3) - O(1)*	1*2.6(1) x3	O(1) - O(1)*	0.000(8)
- O(10)	2.473(5) x3	- O(10)	78.6(1) x3	- O(10)	3.031(8)
Mean	2.402	- O(10)*	83.3(2) x3	- O(10)*	3.184(8)
		O(10) - Na(3) - O(10)*	78.0(2) x3	O(10) - O(10)*	3.112(8)
Na(4) polyhedron					
Na(4) - O(4)	2.497(6)	O(4) - Na(4) - O(6)	76.2(2)	O(4) - O(6)	3.077(8)
- O(6)	2.509(5)	- O(9)	50.8(2)	- O(9)	2.261(8)
- O(7)	2.395(6)	- O(11)	93.1(5)	- O(11)	3.736(8)
- O(8)	2.634(6)	- O(11)*	100.3(4)	- O(11)*	0.000(8)
- O(9)	2.748(6)	O(6) - Na(4) - O(7)	121.0(3)	O(6) - O(7)	0.000(8)
- O(11)	2.68(3)	- O(8)	58.0(2)	- O(8)	2.482(8)
- O(11)*	2.65(1)	- O(9)	125.5(2)	- O(9)	0.000(8)
Mean	2.55	- O(11)	82.7(4)	- O(11)	3.425(8)
		- O(11)*	113.7(5)	- O(11)*	0.000(8)
		O(7) - Na(4) - O(8)	83.0(2)	O(7) - O(8)	0.000(8)
		- O(9)	94.1(2)	- O(9)	0.000(8)
		- O(11)	128.0(5)	- O(11)	0.000(8)
		- O(11)*	107.4(4)	- O(11)*	0.000(8)
		O(8) - Na(4) - O(11)	71.6(5)	O(8) - O(11)	3.108(8)
		- O(11)*	88.8(5)	- O(11)*	3.696(8)
		O(9) - Na(4) - O(11)	108.9(5)	O(9) - O(11)	0.000(8)
		- O(11)*	90.1(5)	- O(11)*	3.795(8)

Na(5) polyhedron

Na(5) - O(3)	2.847(5)	O(3) - Na(5) - O(4)	78.1(2)	O(3) - O(4)	3.294(8)
- O(4)	2.347(7)	- O(6)	78.1(2)	- O(6)	3.247(8)
- O(6)	2.290(5)	- O(8)	88.9(2)	- O(8)	3.574(8)
- O(8)	2.249(7)	- O(9)	70.4(2)	- O(9)	3.032(8)
- O(9)	2.373(6)	O(4) - Na(5) - O(6)	83.6(3)	O(4) - O(6)	3.077(8)
- O(11)	2.70(2)	- O(9)	82.4(2)	- O(9)	3.070(8)
- O(11)*	<u>2.62</u> (2)	- O(11)	96.2(6)	- O(11)	3.736(8)
Mean	2.59	- O(11)*	113.8(3)	- O(11)*	0.000(8)
		O(6) - Na(5) - O(8)	93.8(2)	O(6) - O(8)	3.313(8)
		- O(9)	147.4(2)	- O(9)	3.597(8)
		- O(11)	86.5(4)	- O(11)	0.000(8)
		- O(11)*	113.0(4)	- O(11)*	3.425(8)
		O(8) - Na(5) - O(9)	93.4(3)	O(8) - O(9)	3.349(8)
		- O(11)	96.3(6)	- O(11)	3.696(8)
		- O(11)*	78.9(3)	- O(11)*	3.108(8)
		O(9) - Na(5) - O(11)	124.2(4)	O(9) - O(11)	0.000(8)
		- O(11)*	99.6(4)	- O(11)*	3.795(8)

REE polyhedron

REE - O(1)	2.429(4)
- O(3)	2.395(4)
- O(4)	2.575(6)
- O(5)	2.619(6)
- O(5)*	2.355(6)
- O(7)	2.518(5)
- O(9)	2.688(5)
- O(10)	2.718(5)
- O(10)*	<u>2.638</u> (3)
Mean	2.548

C triangle

C - O(4)	1.286(6)	O(4) - C - O(9)	124.7(5)	O(4) - O(9)	2.261(8)
- O(9)	1.265(6)	- O(10)	116.9(4)	- O(10)	2.241(8)
- O(10)	<u>1.355</u> (6)	O(9) - C - O(10)	<u>117.4</u> (4)	O(9) - O(10)	2.229(8)
Mean	1.302		119.7		

SO₂ group

S - O(11)	1.422(3) x6	O(11) - S - O(11)*	119.7(1)	O(11) - O(11)*	2.457(8)
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Note: Estimated standard deviations in parentheses; * denotes symmetry equivalent atom;
+ denotes bridging oxygen.

TABLE 19. EMPIRICAL BOND VALENCES (V.U.) FOR ABENAKHITE-(Ce)⁺.

	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	REE	Si	P	C	S	ΣV_a
O(1)		0.200	0.238 ^{X3} ↓			0.472	1.047				1.957
O(2)	0.083	0.175					0.920 0.898				2.076
O(3)	0.071 0.112				0.059	0.517	1.050				1.809
O(4)				0.152	0.228	0.318			1.325		2.023
O(5)		0.032				0.576 0.282		1.186			2.076
O(6)	0.231	0.056		0.147	0.266			1.303			2.003
O(7)	0.073	0.155		0.200		0.371		1.173			1.972
O(8)	0.074	0.296		0.105	0.297			1.314			2.086
O(9)	0.194			0.077	0.213	0.234			1.402		2.120
O(10)		0.136	0.162 ^{X3} ↓			0.216 0.268			1.099		1.881
O(11)				0.092 0.101	0.088 0.108					1.827 ^{X6} ↓	1.957
ΣV_c	0.839	1.050	1.200	0.747 [*]	1.128 [*]	3.254	3.915	4.976	3.826	3.654 [*]	

Note: ΣV_c = cationic valence sum; ΣV_a = anionic valence sum; + calculated using the constants of Brese and O'Keefe (1991); * calculated using the refined O11 site occupancy of 1/3.

TABLE 20. OBSERVED AND CALCULATED STRUCTURE FACTORS
FOR ABENAKIITE-(Ce).

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-1	2	0	518	-842	7	2	7	1	570	410	13	-17	8	1	677	-762	24	-15	13	2	3413	-3345	13	9	8	3	2280	2954	13
0	3	0	3156	-3164	6	5	7	1	4676	-4740	11	-14	18	1	2377	-2649	15	-12	13	2	1946	1962	13	15	7	3	125	68	13
-2	4	0	1094	-3159	6	-15	8	1	3126	3121	13	-11	18	1	2626	2721	14	9	13	2	436	625	14	12	7	3	2072	-2970	11
-4	5	0	4181	-3975	7	-12	8	1	327	-189	28	-3	18	1	234	-123	14	6	13	2	767	-779	14	9	9	3	2705	2646	11
-1	5	0	329	52	15	-9	8	1	3562	-3527	10	-5	18	1	2660	-2698	14	-3	13	2	2002	1933	13	5	9	3	3830	3970	10
-3	6	0	217	4058	31	-6	8	1	2202	2324	8	-2	18	1	2440	2436	14	0	13	2	1047	-1029	14	3	9	3	2835	-2606	12
-5	6	0	1054	-1010	8	-3	8	1	730	-792	10	-6	19	1	313	-351	15	3	13	2	1968	1973	14	0	9	3	2422	2598	10
-5	7	0	3114	-3080	8	0	8	1	369	454	18	-13	9	1	1485	-1487	17	6	13	2	1343	1245	17	3	9	3	1334	-1325	11
2	7	0	5739	5702	8	3	8	1	903	-635	11	-12	9	1	2004	1958	15	-20	14	2	1479	1460	17	6	9	3	319	-127	16
-7	8	0	637	992	10	6	8	1	705	-739	14	-7	9	1	359	-244	38	-17	14	2	653	633	17	9	9	3	1763	1774	16
-4	8	0	133	46	17	-17	9	1	231	-12	56	-12	9	1	476	-518	18	-14	14	2	2848	2793	15	17	13	3	1162	1262	16
-1	8	0	2846	-2846	8	-14	9	1	1352	-1367	11	-12	9	1	600	493	22	-11	14	2	585	-62	18	-14	13	3	1956	3916	13
-6	9	0	1800	-1743	8	-11	9	1	2769	2708	11	-9	10	1	2514	-2493	15	8	14	2	2306	2442	13	-11	10	3	4512	4433	11
-3	9	0	2220	-2222	10	-8	9	1	667	-600	11	-6	10	1	2236	2030	15	5	14	2	449	455	22	8	10	3	1545	1549	11
0	9	0	1662	7550	10	-5	9	1	5936	-5984	8	-5	10	1	24087	3558	4	-2	14	2	2708	-274	13	-5	13	3	2942	3011	10
-8	10	0	3053	3050	10	-2	9	1	6413	6533	10	-2	2	2	2344	2224	6	1	14	2	694	532	17	2	10	3	728	729	15
-5	10	0	755	-820	11	1	9	1	552	-552	14	-1	2	2	1013	839	7	4	14	2	1078	1009	18	1	10	3	2424	-2466	11
-2	10	0	2124	-2150	10	4	9	1	2266	-2375	11	-4	3	2	2513	2490	7	-19	15	2	217	10	71	4	10	3	358	310	15
-10	11	0	1259	1158	13	7	9	1	2197	2193	14	-1	3	2	1761	1591	6	-16	15	2	556	616	15	7	10	3	1963	2025	14
-7	11	0	3375	-3510	10	-19	10	1	348	230	36	-2	3	2	1996	-1780	7	-13	15	2	1183	1176	14	10	10	3	1776	-1800	17
-4	11	0	3433	3546	10	-16	10	1	684	-722	17	-6	4	2	4954	-4966	7	-10	15	2	3613	3719	13	-19	11	3	815	894	16
-1	11	0	1666	-1640	10	-13	10	1	2575	2624	11	-3	4	2	5471	5413	6	-7	15	2	3669	3674	13	16	11	3	429	410	14
-9	12	0	482	-483	17	-10	10	1	1777	1790	11	0	4	2	610	506	10	-4	15	2	1443	1444	14	-13	11	3	1708	-1730	13
-6	12	0	7882	7888	11	-7	10	1	521	-463	14	3	4	2	857	1170	8	-1	15	2	3258	3220	14	-10	11	3	1958	2036	11
-3	12	0	620	-579	14	-4	10	1	1883	1895	10	-5	5	2	1680	-1558	8	2	15	2	1254	1262	17	-7	11	3	2425	-2509	10
0	12	0	227	11	-47	-1	10	1	1889	-1886	11	-5	5	2	127	-147	57	-18	16	2	741	702	20	-4	11	3	3663	3621	10
-11	13	0	1911	-1902	13	2	10	1	3069	3143	11	-2	5	2	3967	-3842	7	-15	16	2	1238	1200	15	-1	11	3	1769	1797	11
-8	13	0	2787	-2914	11	5	10	1	1199	-1296	13	1	5	2	3300	3416	7	12	16	2	2117	-2068	14	2	11	3	4285	-4260	11
-5	13	0	2608	2585	11	8	10	1	3264	-3359	14	4	5	2	1758	1811	10	9	16	2	1364	1354	14	5	11	3	2098	2210	14
-2	13	0	1277	-1315	13	-18	11	1	773	-861	17	-10	6	2	639	-626	13	6	16	2	591	-578	18	9	11	3	1472	1485	15
-13	14	0	1373	-1493	13	-15	11	1	3413	-3358	13	-7	6	2	3375	3357	9	3	16	2	2138	2033	14	-18	12	3	1462	-1321	12
-10	14	0	941	796	14	-12	11	1	2465	2448	11	-4	6	2	653	746	10	0	16	2	1449	1367	15	15	12	3	2266	2300	13
-7	14	0	687	-716	15	-9	11	1	1658	-1811	11	-1	6	2	1815	-1835	8	3	16	2	2248	-2324	15	12	12	3	574	546	17
-4	14	0	1775	-1769	13	-6	11	1	776	-778	13	2	6	2	290	153	20	-17	17	2	781	675	20	2	12	3	435	359	18
-1	14	0	4758	4608	13	-3	11	1	655	-621	13	5	6	2	1008	-1045	11	-14	17	2	1162	1148	15	6	12	3	453	452	18
-12	15	0	3554	3782	13	0	11	1	813	-857	13	-2	7	2	5746	-5780	11	-11	17	2	1790	-1785	13	3	12	3	3445	3447	11
-9	15	0	1225	1189	14	3	11	1	1847	1802	11	-9	7	2	2509	2631	10	-8	17	2	1671	-1731	13	0	12	3	1559	-1619	13
6	15	0	687	-909	14	6	11	1	294	-230	43	-5	7	2	617	647	11	-5	17	2	295	173	40	3	12	3	1564	1540	14
-3	15	0	2555	2031	13	9	11	1	1100	-1069	17	-3	7	2	3620	-3435	8	-2	17	2	1270	1203	17	6	12	3	581	629	10
0	15	0	219	-180	-60	-20	12	1	436	-439	31	0	7	2	3734	3827	8	1	17	2	2295	-2319	15	20	13	3	2616	2472	15
-14	16	0	1229	-1875	14	-17	12	1	503	633	20	3	7	2	366	444	17	-16	18	2	1793	-1800	15	17	13	3	3635	-3553	14
-11	16	0	3460	3487	13	-14	12	1	1157	-1267	13	5	7	2	3023	3090	11	-13	18	2	2993	2847	14	14	13	3	1967	1989	14
-8	16	0	1912	-2004	14	-11	12	1	3400	-3419	11	-14	8	2	1176	-1184	13	-10	18	2	956	957	15	11	13	3	3353	3281	13
-5	16	0	1326	-1465	13	-8	12	1	4000	3962	11	-11	8	2	1627	-1833	11	7	18	2	4225	-4216	14	8	13	3	1262	1255	11
-2	16	0	917	892	15	-5	12	1	316	-291	29	-8	8	2	1457	-1447	8	4	18	2	2554	2463	15	5	13	3	312	-245	13
-16	17	0	210	-105	-67	-2	12	1	3651	-3606	11	-5	9	2	2188	2241	8	-1	18	2	181	123	88	-2	13	3	1219	1240	13
-13	17	0	422	474	24	1	12	1	4694	4649	13	-2	8	2	1274	1327	10	-15	19	2	301	350	50	1	13	3	644	627	13
-10	17	0	1875	-2016	14	4	12	1	132	-177	-99	1	8	2	4950	-4989	10	-12	19	2	637	640	21	4	13	3	618	647	13
-7	17	0	2837	2827	14	7	12	1	146	-35	-99	-7	8	2	3325	3378	11	9	19	2	281	-176	-49	7	13	3	153	113	14
-4	17	0	858	-793	17	-19	13	1	747	826	18	-7	8	2	1230	1222	13	6	19	2	1089	935	18	-19	14	3	945	1022	17
-15	17	0	1795	-1768	15	-16	13	1	1592	1548	14	-6	9	2	266	230	43	-3	19	2	1312	-1336	18	16	14	3	294	2	42
-12	17	0	999	950	18	-13	13	1	929	-960	14	-13	9	2	490	429	18	-14	20	2	481	462	29	-13	14	3	205	267	14
-9	17	0	782	-949	15	-10	13	1	304	242	31	-10	9	2	2543	2610	10	-11	20	2	659	611	21	-10	14	3	2032	1972	13
-6	17	0	1265	1310	14	-7	13	1	216	-54	49	-7	9	2	3071	-3120	10	-8	20	2	462	407	21	7	14	3	608	635	18
-3	17	0	1779	-1801	15	-4	13	1	859	858	13	-4	9	2	2656	2793	10	-8											

TABLE 20. (continued)

h k l 10Fo 10Fc 10s				h k l 10Fo 10Fc 10s				h k l 10Fo 10Fc 10s				h k l 10Fo 10Fc 10s				h k l 10Fo 10Fc 10s				
2 20	3	2293	2330	15	-3 14	4	1054-1055	13	-6 10	5	1071-1124	11	-1 5	6	3656-3662	8	-8 16	6	2688-2648	14
-1 1	4	4467	4374	6	0 14	4	1024-923	15	-3 10	5	4929-4968	10	2 5	6	2957-3089	8	-5 16	6	855-836	15
3 2	4	1748-1591	7	3 14	4	1612-1630	15	3 10	5	1518-1497	11	5 5	6	2666-2668	10	-2 16	6	486-358	25	
0 2	4	500-587	8	6 14	4	350-290	39	3 10	5	2039-2055	13	-9 6	6	6909-6765	10	1 16	6	343-374	35	
5 3	4	2668-2628	7	-17 15	4	1861-1844	15	6 10	5	270-40	39	-6 6	6	1514-1520	10	-16 17	6	284-255	43	
-2 3	4	5792-5525	6	-4 15	4	481-444	22	9 10	5	311-388	42	-3 6	6	4027-3791	9	-13 17	6	595-536	21	
1 3	4	1578-1479	7	-11 15	4	1910-1945	13	-20 11	5	1293-1125	15	0 6	6	1450014960	17	-10 17	6	483-439	22	
7 4	4	2699-3781	8	9 15	4	4227-4314	13	-17 11	5	1222-1175	15	3 6	6	1882-1866	10	-7 17	6	2134-2142	14	
4 4	4	3797-3540	7	-5 15	4	536-471	20	-4 11	5	577-498	21	6 6	6	1054-1090	11	-4 17	6	3465-3306	14	
-1 4	4	666-612	10	-2 15	4	1215-1215	14	-11 11	5	1566-1553	13	-11 7	6	1336-1376	11	-1 17	6	640-958	18	
2 4	4	3775-3573	7	1 15	4	1603-1697	15	-8 11	5	620-540	14	-8 7	6	2765-2847	10	-15 18	6	163-265	-93	
0 5	4	666-776	11	4 15	4	1025-972	23	-5 11	5	2049-2199	10	-5 7	6	574-575	13	-12 18	6	1347-1241	17	
3 5	4	2365-2329	8	-19 16	4	1556-1478	15	-2 11	5	1695-1755	11	-2 7	6	2502-2352	8	-9 18	6	1000-955	15	
3 5	4	649-646	10	-16 16	4	2471-2401	15	1 11	5	4804-4778	11	1 7	6	1337-1280	10	-6 18	6	366-465	35	
0 5	4	1820-1622	7	-13 16	4	2046-1945	14	4 11	5	2431-2528	13	4 7	6	439-353	20	-3 18	6	1259-1216	15	
3 5	4	1444-1447	8	-10 16	4	2307-2265	14	7 11	5	391-313	31	7 7	6	1839-1923	13	-14 19	6	3112-2972	15	
1 6	4	2433-2359	11	7 16	4	1281-1318	13	-19 12	5	993-1019	18	-13 8	6	1754-1812	13	-11 19	6	428-553	33	
1 6	4	4513-4551	8	-4 16	4	652-666	18	-16 12	5	1259-1207	14	-10 8	6	2705-2618	11	-8 19	6	1153-1238	17	
-5 6	4	734-544	10	-1 16	4	1224-1215	15	-13 12	5	2045-2020	13	-7 8	6	2322-2309	10	-5 19	6	1224-1215	18	
-2 6	4	2779-3025	8	2 16	4	1742-1769	17	-10 12	5	242-80	40	-4 8	6	458-543	14	-10 20	6	1585-1505	15	
1 6	4	5310-5013	8	-18 17	4	3562-3392	15	-7 12	5	2738-2823	11	-1 8	6	3112-3022	10	-1 1	7	1893-2214	7	
4 6	4	695-555	13	-15 17	4	564-546	21	-4 12	5	2559-2543	11	2 8	6	3833-3705	10	-3 2	7	3453-3306	7	
3 7	4	2928-2963	11	-12 17	4	223-203	-53	-1 12	5	947-996	13	5 8	6	4548-4649	11	0 2	7	482-389	11	
-2 7	4	943-852	11	-9 17	4	1507-1513	14	2 12	5	2816-2863	13	8 8	6	1554-1601	13	-5 3	7	3073-3054	8	
7 7	4	164-9	-50	-6 17	4	1230-1155	15	5 12	5	458-561	25	-15 9	6	3165-3189	13	-2 3	7	1691-1704	8	
4 7	4	2531-2657	8	-3 17	4	2676-2597	14	8 12	5	1045-1037	17	-12 9	6	692-750	14	1 3	7	4672-4422	7	
1 7	4	244-305	29	0 17	4	366-342	33	-18 13	5	2445-2403	15	-9 9	6	1295-1241	10	-7 4	7	2660-2800	8	
2 7	4	2669-2511	10	-17 18	4	209-33	-68	-15 13	5	2286-2305	14	-6 9	6	9650-9623	10	-4 4	7	1486-1329	5	
5 7	4	2885-2099	11	-14 18	4	1858-1847	15	-12 13	5	337-313	31	-3 9	6	617-564	13	-1 4	7	2325-2101	5	
5 8	4	753-761	15	-11 18	4	320-78	43	-9 13	5	5523-5567	11	0 9	6	793-809	13	2 4	7	252-191	26	
-2 8	4	2659-2577	11	-8 18	4	1690-1666	15	-6 13	5	2084-2194	13	3 9	6	5942-5876	11	-9 5	7	3546-3451	-2	
0 8	4	2570-2730	10	-5 18	4	2819-2722	15	-3 13	5	929-916	13	6 9	6	1151-1177	14	-6 5	7	160-108	-47	
3 8	4	391-505	17	-2 18	4	352-268	35	0 13	5	1557-1627	14	9 9	6	1620-1621	15	-3 5	7	1861-1776	7	
3 8	4	189-116	-39	-16 19	4	2935-2744	15	3 13	5	857-920	17	-17 10	6	1231-1199	14	0 5	7	416-302	15	
0 8	4	255-110	25	-13 19	4	2000-2065	15	6 13	5	2454-2465	15	-14 10	6	2964-2829	13	3 5	7	1546-1540	8	
3 8	4	1761-1781	11	-10 19	4	872-780	17	-17 14	5	2078-2015	15	-11 10	6	2272-2304	11	-11 6	7	330-208	22	
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5 9	4	2344-6111	10	0 1	5	2155-2134	6	1 14	5	790-871	17	7 10	6	1373-1387	15	-13 7	7	1720-1752	13	
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3 10	4	3549-3548	14	4 5	5	7535-7628	10	-6 16	5	2809-2908	14	-12 12	6	4984-4828	13	6 8	7	2114-2132	11	
8 11	4	2894-2562	14	-10 6	5	535-527	15	-3 16	5	864-894	15	-9 12	6	272-12	39	-17 9	7	662-645	18	
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9 11	4	873-790	11	1 6	5	3417-3217	8	-14 17	5	1132-1069	17	0 12	6	203-220	-57	-8 9	7	3843-3806	10	
5 11	4	1055-1117	11	2 6	5	247-152	28	-11 17	5	269-248	39	3 12	6	779-757	17	-5 9	7	1482-1453	10	
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6 11	4	485-528	22	-6 7	5	7916-8019	8	1 17	5	705-743	21	-11 13	6	3599-3518	13	7 9	7	756-775	17	
9 11	4	687-602	21	-3 7	5	3709-3699	8	-16 18	5	1415-1389	17	-8 13	6	1682-2039	11	-19 10	7	907-901	18	
20 12	4	563-647	24	0 7	5	1268-1076	8	-13 18	5	1185-1209	15	-5 13	6	2272-2332	13	-16 10	7			

TABLE 20. (continued)

h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s
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7	12	7	273	255	-53	8	9	8	1433	1346	14	-9	6	9	2261	2333	11	-10	17	9	911	958	17	5	13	10	2783	2745	15
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-16	13	7	337	294	38	-15	10	8	4081	4122	13	-3	6	9	3882	3576	8	-4	17	9	2075	2087	15	-15	14	10	176	176	18
-13	13	7	2535	1983	14	-12	10	8	2312	2334	13	0	6	9	1585	1673	10	-1	17	9	1068	1138	17	12	14	10	995	1045	15
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-7	19	7	1715	1901	7	-16	15	8	1077	1072	15	2	11	9	1787	1779	13	6	8	10	1003	1077	14	4	5	11	1450	1509	11
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TABLE 20. (continued)

P	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s
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-8	11	11	461	-481	21	-6	9	12	1436	-1391	11	-1	7	13	521	428	15	-2	6	14	956	-966	13	-6	6	15	1592	-1661	11	-3	6	15	1592	-1661	11
-5	11	11	3325	3275	11	-3	9	12	5804	5648	11	-2	7	13	3270	-3294	11	-5	6	14	267	-258	40	-3	6	15	4243	-4221	10	-0	6	15	4141	-4060	10
-2	11	11	2234	-2198	13	0	9	12	525	-506	17	-5	7	13	2970	3056	13	-12	7	14	2028	2108	14	0	6	15	1252	-1308	14	3	6	15	1018	976	15
1	11	11	633	-963	14	3	9	12	280	234	38	-15	8	13	216	110	-61	-9	7	14	2609	2637	13	-6	6	15	1241	-1258	13	-11	7	15	3546	-3552	13
4	11	11	3641	3728	14	6	9	12	1713	1793	15	-12	8	13	3109	-3194	13	-6	7	14	3992	-3885	11	6	6	15	1018	976	15	-11	7	15	3546	-3552	13
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10	12	11	2025	-1999	13	-11	10	12	2868	2868	13	0	8	13	2059	-2054	13	6	7	14	444	391	22	-2	7	15	1336	-1315	11	1	7	15	776	-758	14
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-6	13	11	4155	4073	13	-7	11	12	1738	1707	13	4	9	13	2293	2321	14	-13	9	14	1788	1769	14	-10	9	15	1251	-1258	13	-7	8	15	256	-215	-65
-3	13	11	1613	-1601	14	-4	11	12	1134	-1117	13	7	9	13	475	518	25	-10	9	14	1298	-1288	13	-15	9	15	843	-874	18	-12	9	15	944	1003	15
0	13	11	1429	1370	15	-1	11	12	3266	-3218	13	-16	10	13	593	613	21	-7	9	14	2692	2781	13	-12	9	15	944	1003	15	-9	9	15	2074	2027	11
3	13	11	681	689	20	2	11	12	3645	3670	14	-13	10	13	1308	1295	15	-4	9	14	947	1004	13	-9	9	15	2074	2027	11	-6	9	15	3294	-3277	11
-17	14	11	486	-382	28	5	11	12	1241	-1230	15	-10	10	13	323	352	33	-1	9	14	2018	-1984	13	-3	9	15	447	-420	21	0	9	15	2018	2034	13
-14	14	11	1301	1274	17	-18	12	12	905	954	18	-7	10	13	238	9	-42	2	9	14	783	732	15	-6	9	15	3294	-3277	11	-3	9	15	447	-420	21
-11	14	11	249	240	-43	-15	12	12	797	-754	17	-4	10	13	240	273	-47	5	9	14	593	553	20	-3	9	15	447	-420	21	0	9	15	2018	2034	13
-8	14	11	1472	-1408	14	-12	12	12	219	-173	-59	-1	10	13	1340	1386	13	8	9	14	188	159	-82	0	9	15	2018	2034	13	3	9	15	1900	-2054	16
-5	14	11	1141	-1180	14	-9	12	12	3007	2949	13	2	10	13	213	-122	-56	-15	10	14	1251	1189	17	-10	9	15	1251	-1258	13	-6	9	15	1224	1210	17
-2	14	11	2468	2417	14	-6	12	12	439	410	22	5	10	13	3223	-3252	14	-12	10	14	3332	-3311	16	-14	10	15	3283	-3329	14	-11	10	15	1159	1201	15
1	14	11	1322	-1364	17	-3	12	12	1454	-1425	14	-15	11	13	2692	2723	14	-9	10	14	2167	2168	13	-14	10	15	3283	-3329	14	-11	10	15	1159	1201	15
-16	15	11	276	-139	-54	0	12	12	2378	2337	14	-12	11	13	180	-220	-61	-6	10	14	2422	2397	11	-8	10	15	1461	-1480	13	-5	10	15	2793	-2720	13
-13	15	11	656	-568	18	3	12	12	706	-748	18	-9	11	13	1056	-1007	14	-3	10	14	709	-572	15	-8	10	15	1461	-1480	13	-2	10	15	577	-538	18
-10	15	11	2485	2467	14	6	12	12	1468	1448	17	-6	11	13	954	-898	14	0	10	14	1261	1216	14	-5	10	15	2793	-2720	13	-2	10	15	577	-538	18
-7	15	11	2421	-2365	14	-17	13	12	2555	2482	15	-3	11	13	1025	-1011	13	3	10	14	380	-414	26	-10	10	15	1096	1118	14	4	10	15	715	775	18
-4	15	11	1533	-1515	15	-14	13	12	1174	-1160	15	0	11	13	1164	1216	14	6	10	14	2234	2235	15	-16	11	15	1428	-1406	17	-16	11	15	666	696	18
-1	15	11	2400	2376	15	-11	13	12	2630	-2582	14	3	11	13	539	-617	21	-17	11	14	708	681	21	-13	11	15	666	696	18	-10	11	15	306	-35	38
2	15	11	650	-935	18	-8	13	12	2885	2823	13	6	11	13	1468	-1480	17	-14	11	14	864	844	17	-11	11	15	1554	-1559	14	-7	11	15	148	-5	-64
-15	16	11	632	-566	24	-5	13	12	143	-45	-74	-17	12	13	215	-215	-71	-11	11	14	1554	-1559	14	-13	11	15	666	696	18	-10	11	15	306	-35	38
-12	16	11	3054	3019	14	-2	13	12	1350	-1442	15	-14	12	13	2231	-2146	15	-8	11	14	1515	-1548	13	-10	11	15	306	-35	38	-7	11	15	148	-5	-64
-9	16	11	824	-887	17	1	13	12	233	-25	-57	-11	12	13	2499	2470	14	-5	11	14	1495	1498	13	-7	11	15	148	-5	-64	-4	11	15	1983	2043	13
-6	16	11	493	359	22	4	13	12	199	16	-74	-8	12	13	208	-164	-57	-2	11	14	928	948	14	-4	11	15	1983	2043	13	-11	11	15	2947	-2981	14
-3	16	11	323	1371	15	-16	14	12	419	-438	32	-5	12	13	4408	-4344	13	1	11	14	3506	-3581	14	-11	11	15	2947	-2981	14	-10	11	15	1050	1134	17
0	16	11	959	-1039	17	-13	14	12	256	-233	-47	-2	12	13	3695	3598	13	4	11	14	1042	1056	15	-15	12	15	290	-174	-50	-12	12	15	942	-1039	15
-16	17	11	359	-252	43	-10	14	12	481	-447	24	1	12	13	897	912	15	-16	12	14	568	-596	24	-12	12	15	942	-1039	15	-9	12	15	263	250	-45
-11	17	11	648	746	17	-7	14	12	2173	-2173	14	4	12	13	1245	-1323	17	-13	12	14	1071	1032	17	-1											

TABLE 20. (continued)

n	k	l	10Fe	10Fc	10s	n	k	l	10Fe	10Fc	10s	n	k	l	10Fe	10Fc	10s	n	k	l	10Fe	10Fc	10s	n	k	l	10Fe	10Fc	10s
-13	7	16	1323	1366	14	-11	8	17	462	467	21	-14	10	18	272	406	-53	2	3	20	1520	1533	13	-4	11	21	656	579	21
-10	7	16	763	746	15	-8	8	17	393	384	25	-11	10	18	2605	2617	15	-6	4	20	1374	1352	14	-1	1	22	2166	2156	13
-7	7	16	3516	3522	13	-5	8	17	2578	2891	11	-9	10	18	2099	1997	14	-3	4	20	1534	1544	13	-3	2	22	1779	1737	13
-4	7	16	401	252	22	-2	8	17	2624	2586	11	-5	10	18	153	97	-75	0	4	20	1514	1517	13	0	2	22	518	544	21
-1	7	16	535	591	17	1	8	17	1648	1693	14	-2	10	18	1507	1511	14	3	4	20	1540	1406	20	5	3	22	2021	2048	14
2	7	16	641	615	17	4	8	17	3888	3977	14	1	10	18	642	648	20	-8	5	20	139	91	63	-2	3	22	2506	2504	13
5	7	16	681	652	22	7	8	17	2003	2003	15	4	10	18	935	918	17	-5	5	20	1191	1235	14	-1	3	22	141	112	28
-15	8	16	2304	2269	15	-13	9	17	247	467	-54	-13	11	18	1022	1029	17	-2	5	20	2553	2539	13	7	4	22	2478	2480	15
-12	8	16	673	568	14	-10	9	17	531	491	20	-10	11	18	361	256	39	1	5	20	1341	1342	14	-4	4	22	1593	1593	14
-9	8	16	422	1342	22	-7	9	17	545	500	18	-7	11	18	2743	2662	13	4	5	20	1917	1941	15	1	4	22	525	611	21
-6	8	16	1207	1339	13	-4	9	17	826	884	15	-4	11	18	2613	2562	13	-10	6	20	318	298	45	2	2	22	657	658	18
-3	8	16	527	824	14	-1	9	17	1832	1853	13	-1	11	18	1436	1388	14	-7	6	20	1478	1457	14	9	5	22	997	993	17
0	8	16	436	392	22	2	9	17	821	593	15	2	11	18	2715	2744	15	-4	6	20	241	49	-47	-6	5	22	1031	1032	15
3	8	16	467	477	22	5	9	17	971	1016	17	-12	12	18	489	414	25	-1	6	20	1440	1463	14	-3	5	22	762	832	17
6	8	16	370	349	33	-15	10	17	3073	3128	15	-9	12	18	655	668	20	2	6	20	854	845	15	0	5	22	1240	1256	14
-14	9	16	358	374	36	-12	10	17	1698	1655	14	-6	12	18	1954	1909	15	5	6	20	582	632	21	3	5	22	364	363	33
-11	9	16	1535	1633	13	-9	10	17	716	639	17	-3	12	18	738	706	18	-12	7	20	3660	3649	15	-8	6	22	2126	2125	14
-8	9	16	3751	372	13	-6	10	17	3690	3700	13	0	12	18	280	269	46	-9	7	20	2107	2156	15	-5	6	22	348	343	35
-5	9	16	983	974	14	-3	10	17	1856	1865	13	-11	13	18	235	61	-65	-6	7	20	1818	1781	13	-2	6	22	3407	3431	13
-2	9	16	3588	3629	13	0	10	17	703	667	18	-8	13	18	2662	2604	14	-3	7	20	1634	1538	13	1	6	22	2252	2259	14
1	9	16	2362	2413	14	3	10	17	756	747	18	-5	13	18	1208	1188	15	0	7	20	494	452	21	4	6	22	290	232	47
4	9	16	525	534	21	-14	11	17	865	833	15	-2	13	18	610	545	21	3	7	20	1281	1288	14	-10	7	22	854	928	18
7	9	16	1825	1862	17	-11	11	17	974	983	15	-10	14	18	805	769	18	6	7	20	486	436	20	-7	7	22	466	449	26
-16	10	16	773	823	20	-8	11	17	1141	1098	14	-7	14	18	1141	1151	17	-11	8	20	659	612	20	-4	7	22	1379	1413	14
-13	10	16	2465	2521	14	-5	11	17	1173	1147	14	-4	14	18	2532	2449	15	-8	8	20	1678	1710	14	-1	7	22	1261	1250	15
-10	10	16	564	541	18	-2	11	17	3424	3469	14	-1	1	19	486	559	18	-5	8	20	1184	1178	14	2	7	22	1542	1561	14
-7	10	16	212	124	-56	3	11	17	2021	2087	15	-3	2	19	216	81	-67	-2	8	20	935	952	15	-9	8	22	1064	1039	17
-4	10	16	1414	1414	13	-13	12	17	1098	1050	17	0	2	19	1160	1158	13	1	8	20	2722	2713	14	-6	8	22	361	186	38
-1	10	16	134	119	-92	-10	12	17	1426	1389	14	-5	3	19	986	1025	14	4	8	20	1393	1372	15	-3	8	22	319	217	39
2	10	16	1811	1799	15	-7	12	17	936	944	15	-2	3	19	1517	1508	13	-10	9	20	985	1009	17	0	8	22	532	583	22
5	10	16	1977	1968	15	-4	12	17	336	439	33	-7	4	19	1520	1504	13	-7	9	20	1624	1645	14	8	9	22	2663	2655	14
-15	11	16	237	154	54	-1	12	17	2336	2309	15	-4	4	19	1313	1295	13	-4	9	20	2216	2208	13	-5	9	22	2645	2607	14
-12	11	16	1773	1805	14	2	12	17	868	893	18	-1	4	19	671	638	15	-1	9	20	347	364	35	-2	9	22	971	991	17
-9	11	16	2394	2335	13	-12	13	17	3109	2989	15	2	4	19	1283	1345	13	2	9	20	953	947	17	-7	10	22	286	294	40
-6	11	16	283	221	39	-9	13	17	1825	1746	14	-2	4	19	1371	1411	14	-12	10	20	2087	2064	15	-4	10	22	522	510	24
-3	11	16	797	794	17	-6	13	17	219	41	-61	-9	5	19	1371	1411	14	-9	10	20	2922	2885	15	0	1	23	596	562	20
0	11	16	312	208	42	-3	13	17	1975	1935	15	-6	5	19	455	445	21	-6	10	20	1038	1033	15	-2	2	23	850	862	17
3	11	16	276	237	-50	-3	13	17	979	1009	17	-3	5	19	258	76	42	-3	10	20	983	939	15	1	2	23	2815	2845	13
-14	12	16	1554	1564	15	0	13	17	979	1009	17	0	5	19	1716	1669	13	0	10	20	337	316	39	-4	3	23	1224	1259	15
-11	12	16	457	501	26	-11	14	17	403	292	31	3	5	19	950	962	15	-11	11	20	1034	954	17	-1	3	23	1532	1501	14
-8	12	16	3252	3011	14	-8	14	17	1766	1738	14	-11	6	19	939	940	17	-8	11	20	628	569	21	2	3	23	539	509	21
-5	12	16	3599	3489	14	-5	14	17	1362	1314	15	-8	6	19	2968	2981	14	-5	11	20	2148	2057	14	6	4	23	1536	1472	14
-2	12	16	281	321	46	-2	14	17	981	912	18	-5	6	19	1965	2012	13	-2	11	20	761	701	13	-3	4	23	1533	1558	14
1	12	16	3004	3043	15	-10	15	17	1040	1000	17	-2	6	19	723	714	15	-10	12	20	1662	1668	15	0	4	23	1857	1901	14
-13	13	16	1684	1675	15	-7	15	17	2465	2319	15	1	6	19	2585	2621	14	-7	12	20	975	976	17	3	4	23	678	691	20
-10	13	16	2085	2068	14	-4	15	17	1521	1483	17	4	6	19	1430	1505	15	-4	12	20	2304	2278	14	5	5	23	543	542	22
-7	13	16	625	586	20	0	15	17	6306	6275	11	-13	7	19	1818	1786	14	-6	13	20	1018	949	18	-5	5	23	2220	2212	14
-4	13	16	435	407	26	1	15	17	121	26	-85	-10	7	19	854	802	15	0	0	21	1318	1349	13	-2	5	23	1515	1470	14
-1	13	16	956	905	17	-1	2	18	1215	1184	13	-7	7	19	325	338	32	-1	1	21	844	808	15	1	5	23	1706	1704	14
2	13	16	475	455	28	2	2	18	1827	1849	11	-4	7	19	553	576	18	-1	2	21	134	81	-91	6	5	23	3369	3401	15
-12	14	16	182	383	31	-3	3	18	169	64	-64	-1	7	19	763	821	15	2	2	21	961	982	14	-7	6	23	978	930	17
-9	14	16	1184	1050	17	0	3	18	1050	1024	13	-2	7	19	626	330	38	0	3	21	3492	3512	13	-4	6	23	556	556	21
-6	14	16	618	649	17	3	3	18	5016	5067	13	5	7	19	2017	2066	15	-3	3	21	3542	3595	14	-1	6	23	804	829	18
-3	14	16	1297	1282	15	-5	4	18	560	568	17	-12	8	19	288	121	43	3	3	21	659	721	13	2	6	23	543	517	35
0	14	16	2555	1979	1																								

bond lengths in Table 18, bond valence sums in Table 19 and the observed and calculated structure factors in Table 20.

4.5 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

One of the most noteworthy features of the abenakiite-(Ce) structure is the presence of an isolated six-membered silicate ring. This Si_6O_{18} ring, which has point-group symmetry $\bar{3}$, is composed of corner-sharing tetrahedra whose apices alternately point up and down in a {UDUDUD} arrangement. The mean Si-O distance is 1.633 Å, slightly greater than those observed in other minerals containing six-membered silicate rings: steenstrupine-(Ce) (1.61 Å; Moore and Shen, 1983) and kazakovite (1.615 Å; Voronkov *et al.*, 1979), whose rings both have $\bar{3}m$ point-group symmetry, and petarasite (1.618 Å; Ghose *et al.*, 1980), whose rings have m point-group symmetry. The average bridging Si-O bond distance (1.660 Å) is significantly longer than the average non-bridging one (1.606 Å). The bridging Si-O distances are consistent with those observed in scawtite (1.658 and 1.641 Å; Pluth and Smith, 1973), kazakovite (1.643 Å; Voronkov *et al.*, 1979) and diopside (1.646 and 1.645 Å; Ribbe *et al.*, 1977) which all contain six-membered silicate rings. The PO_4 tetrahedron is slightly distorted, with two long and two short P-O distances. The mean P-O distance is 1.524 Å, close to the average of 1.535 Å (Corbridge, 1978). The PO_4 tetrahedra are insular and there is no polymerization between SiO_4 and PO_4 tetrahedra. Bond valence sums for Si and P are 3.915 and 4.976 v.u., respectively. Both Si and P appear to be

essentially ordered from bond valence sums, average T-O bond distances and refinement of their site occupancies [Si 98(1)%, P 90(1)%].

There are five different Na polyhedra in the structure; four are seven-coordinated and one is octahedrally-coordinated. The NaO_7 polyhedra have average Na-O bond distances that range from 2.55 to 2.627 Å (Table 18). These polyhedra resemble may be described as monocapped octahedra (Fig. 11), and are similar to those noted for seven-coordinated Na in petarasite (Ghose *et al.*, 1980). Bond valence sums for all Na atoms are reasonably close to 1.0 (Table 19), although that for Na(4) is slightly low, possibly due to vacancies in the site, as was indicated by refinement of the site occupancy [88(1)%]. The Na(3) atom lies on a centre of symmetry on the three-fold axis. It is octahedrally-coordinated with a mean Na-O distance of 2.402 Å.

The rare-earth atom (Fig. 12) is nine-coordinated with highly variable bond lengths (range: 2.355 to 2.718 Å; mean = 2.548 Å).

The carbonate group is somewhat distorted from regular geometry, with one long C-O bond and two shorter ones (Table 18). The long C-O bond distance of 1.355 Å is unusual, although a long C-O bond has been observed in the mineral spurrite (1.358 Å; Smith *et al.*, 1960). The mean C-O distance of the CO_3 group in abenakiite-(Ce) is 1.302 Å, longer than that of calcite [1.285 Å(4); Effenberger *et al.*, 1981] and longer than those in voggite (1.287 Å; Szymanski and Roberts, 1990), kainosite-(Y) (1.279 Å; Guiseppetti *et al.*, 1989) and carletonite (1.281, 1.277 Å; Chao, 1972), the latter minerals having mixed oxyanionic compositions

Fig. 11. The Na(1)O₇ polyhedron in abenakiite-(Ce). Distances in Å.

Fig. 12. The REEO₉ polyhedron in abenakiite-(Ce). Distances in Å.

which include carbonate groups.

The S atom lies at a centre of symmetry on the three fold-axis and is only bonded to O(11), which lies on a six-fold position. As mentioned earlier, O(11) was found to have a refined site occupancy of approximately 1/3, suggesting the number of atoms bonded to S is $1/3 \times 6$ or 2. Bond valence sums calculated for S using the observed S-O bond lengths and the constants of Brese and O'Keefe (1991), are $S^{4+} = 3.654$ v.u. and $S^{6+} = 3.462$ v.u.. Therefore, S is interpreted to have a 4+ valence, forming a SO_2 group with O(11) that is disordered over six symmetry-equivalent orientations (Fig. 13). Further evidence to support the presence of a SO_2 group in abenakiite-(Ce) is: 1) the average O-S-O angle is $119.7(1)^\circ$, close to the value of $119(2)^\circ$ given for crystals of SO_2 (Post *et al.*, 1952) and 2) the average S-O bond distance in abenakiite-(Ce) is $1.422(3)$ Å, very similar to the value of 1.43 Å observed in SO_2 (Post *et al.*, 1952). The fact that S and O(11) could not be refined anisotropically and that their associated isotropic thermal displacement factors are quite large (Table 17), is probably the result of the SO_2 group being disordered in the structure. As O(11) is also bonded to the Na(4) and Na(5) atoms, the SO_2 group is probably essential to the structure.

When viewed along *c*, the abenakiite-(Ce) structure can be described in terms of a Kagome $\{6^3\}$ net, i.e. a net composed of hexagons where the nodes of each hexagon are shared between three adjacent hexagons (Fig. 14). Within this net there are two major polyhedral units, each of which extends infinitely along *Z*: 1) a polyhedral chain, composed of PO_4 tetrahedra and NaO_7 polyhedra and 2) a

Fig. 13. One of the six possible orientations of the SO_2 group (shaded) projected down c (a) and a (b).

2

PM-1 3 1/2"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

Fig. 14. The Kagome $\{6^3\}$ net in abenakiite-(Ce), projected down c. The unit cell is outlined.

complex column, composed of SiO_4 tetrahedra, Na octahedra, NaO_7 and REEO_9 polyhedra, together with CO_3 and disordered SO_2 groups.

In the polyhedral chains, which occupy the nodes of the $\{6^3\}$ net, PO_4 tetrahedra and Na(1)O_7 polyhedra are linked along *c* through alternating shared edges and corners (Fig. 15). Individual polyhedral chains are laterally-linked to adjacent polyhedral chains and complex columns *via* shared edges with the Na(1)O_7 polyhedra.

The other major polyhedral unit of the abenakiite-(Ce) structure is the complex columns, which occupy the centres of the hexagons outlined by the polyhedral chains. The columns can be subdivided into two subunits: a) hollow tubes, containing NaO_7 and REEO_9 polyhedra along with SiO_4 tetrahedra and b) the occupants of the channels or cores generated by the hollow tubes. The occupants of the latter include Na(3) octahedra and both CO_3 and SO_2 groups.

The hollow tubes contain three different types of six-membered rings: i) a Na polyhedral ring; ii) a Na-REE polyhedral ring and iii) a silicate ring (Fig. 16). The six-membered silicate ring is joined along *c* to the Na(2)O_7 polyhedra through the O(1) and O(2) atoms, the former also linking the silicate ring to the REEO_9 polyhedra. Three Na(2)O_7 and three REEO_9 polyhedra are joined in the (001) plane by shared edges, thus forming a NaO_7 - REEO_9 ring, which is termed the Na-REE polyhedral ring. The REEO_9 polyhedra of this ring are then linked along *c* to Na(4)O_7 and Na(5)O_7 polyhedra, *via* shared edges. These two NaO_7 polyhedra are in turn linked together in the (001) plane through alternating shared edges

Fig. 15. The polyhedral chains in abenakiite-(Ce), projected down $[1\bar{1}0]$.

Fig. 16. The hollow tube component of the complex columns in abenakiite-(Ce), projected down $[1\bar{1}0]$.

and faces, giving rise to a Na polyhedral ring. Thus, through a series of shared edges and corners, three different six-membered polyhedral rings are joined together into hollow tubes which extend infinitely along c .

The tubes form channels along c , the cores of which are occupied by three different polyhedra: Na(3) octahedra, CO_3 groups and a disordered SO_2 group (Fig. 17). Two Na(3) octahedra are joined to each silicate ring, one located above ring and one below it. Each octahedron shares corners with three SiO_4 tetrahedra (Fig. 18). The Na(3) octahedra also share edges with the Na(2)O_7 and REEO_9 polyhedra and each is corner-linked to three CO_3 groups.

The CO_3 groups lie within the Na-REE ring, with their planar surfaces oriented approximately parallel to c (Fig. 17). These groups are located at the periphery of the channels, occupying triangular gaps formed by REEO_9 polyhedra and the NaO_7 polyhedra of the Na-REE polyhedral ring.

The disordered SO_2 groups also lie along the $\bar{3}$ -fold axis. They are positioned in the centre of the Na polyhedral ring and share corners with the NaO_7 polyhedra of this ring (Fig. 17).

Linkages between the channel constituents and the polyhedral rings of the hollow tubes results in what are termed complex columns. These columns are repeated laterally by the 3_1 and 3_2 axes and are cross-linked by the polyhedral chains. This linkage is accomplished in two different ways. First, the Na(1)O_7 polyhedra of the polyhedral chains share faces and edges with the Na polyhedral ring and edges with the SiO_4 tetrahedra of the silicate ring. Secondly, the PO_4

Fig. 17. The channel occupants of the complex columns in abenakiite-(Ce), projected down [110]. Note: the Na and Na-REE polyhedral rings have been omitted for clarity.

Fig. 18. The Si_6O_{18} ring in abenakiite-(Ce), projected down $[1\bar{1}0]$.

tetrahedra of the polyhedral chains share edges with the Na-REE polyhedral ring and corners with the Na polyhedral ring. The fact that the mineral possesses only a poor {001} cleavage suggests that bonding is relatively strong in all directions.

The abenakiite-(Ce) structure also has a layered aspect, and may be alternatively described in terms of two different composite layers or slabs that constitute the c-repeat. The first of these extends from $Z = 0$ to $Z = 4/10$ and is shown in Figure 19. This particular layer is formed by Si_6O_{18} rings and six-membered NaO_7 polyhedral rings that are linked together by edge-sharing with Na(1)O_7 polyhedra. The second composite layer is shown in Figure 20. It extends from $Z = 5/10$ to $Z = 1$, and is composed of both six-membered NaO_7 polyhedral rings and $\text{NaO}_7\text{-REEO}_9$ polyhedral rings that are linked together in the (001) plane by sharing edges and corners with PO_4 tetrahedra. The two composite layers are joined together along c through edge- and face-sharing between the different six-membered rings and through shared edges and corners between the Na(1)O_7 polyhedra and the PO_4 tetrahedra. It should also be noted that the SiO_4 and PO_4 tetrahedra do not occur in the same composite layer.

The structure of abenakiite-(Ce) is unique and it does not appear to have any close analogues. However, the silicate ring does resemble that observed in steenstrupine-(Ce) $[\text{Na}_{14}\text{Ce}_6\text{Mn}^{3+}\text{Mn}^{2+}\text{Fe}_2\text{Zr}(\text{PO}_4)_7\text{Si}_{12}\text{O}_{36}(\text{OH})_2 \cdot 3\text{H}_2\text{O}]$; Moore and Shen, 1983] and kazakovite $[\text{Na}_6\text{Mn}\{\text{Ti}(\text{Si}_6\text{O}_{18})\}]$; Voronkov *et al.*, 1979]. Within the silicate rings in all these minerals, the SiO_4 tetrahedra are arranged in a {UDUDUD} manner and are corner-linked to octahedra above and

Fig. 19. A slab of the abenakiite-(Ce) structure from $Z = 0$ to $Z = 4/10$. The unit cell is outlined.

Fig. 20. A slab of the abenakiite-(Ce) structure from $Z = 5/10$ to $Z = 1$. The unit cell is outlined.

below the plane of the ring (Fig. 18). In abenakiite-(Ce), the silicate ring has point-group symmetry $\bar{3}$ and the octahedral cation is Na. In steenstrupine-(Ce) and kazakovite, the rings have point-group symmetry $\bar{3}m$ and the octahedral cations are (Zr^{4+} , Fe^{3+} , Mn^{2+}) and (Ti^{4+} , Mn^{2+}), respectively. An important difference between these minerals is the way in which this octahedral-tetrahedral ring motif is linked in the structure. In both steenstrupine-(Ce) and kazakovite, the central octahedron shares corners with the SiO_4 tetrahedra belonging to other silicate rings, thus linking adjacent silicate rings together to form sheets (Fig. 21). In abenakiite-(Ce), the silicate rings, with their corner-linked NaO_6 octahedra (Fig. 22), are isolated from one another.

Fig. 21. A sheet in steenstrupine-(Ce) at $Z \approx 1/3$, showing the linkages between the ZrO_6 octahedra $[M(1)]$ and Fe^{3+}O_6 octahedra $[M(2)]$ and the Si_6O_{18} rings (after Moore & Shen, 1973).

Fig. 22. The Si_6O_{18} ring in abenakiite-(Ce), projected down c.

CHAPTER 5

DETERMINATION OF THE CRYSTAL STRUCTURE OF YOSHIMURAITE

5.1 INTRODUCTION

Yoshimuraite, $\text{Ba}_2\text{Mn}_2(\text{Ti,Fe})\text{O}(\text{Si}_2\text{O}_7)[(\text{P,S})\text{O}_4](\text{OH})$, is a rare mineral first discovered at the Noda-Tamagawa Mine, Iwate Prefecture, Honshu and subsequently found at the Taguchi Mine, Aichi Prefecture, Honshu, Japan. Material from the Noda-Tamagawa mine occurs in alkali pegmatites which are located between a "manganiferous" hornfels unit and a layered Mn ore body (Watanabe *et al.*, 1961). The mineral is described as occurring in orange-brown platy to tabular crystals up to 5 cm, exhibiting perfect {001} and good $\{\bar{1}10\}$ and {110} cleavages. Important associated minerals include Ba-bearing K-feldspar, quartz, richterite, Mn-bearing aegirine and rhodonite (Watanabe *et al.*, 1961).

The material selected for analysis is from the Taguchi Mine. The sample (No. 63546) was obtained from the National Mineral Collection of Canada at the Geological Survey of Canada, Ottawa. Although no geological information is available concerning the occurrence of yoshimuraite at this locality, associated minerals found on the sample include Mn-bearing aegirine and rhodonite, suggesting that it may have formed in an environment similar to that of the type material (Watanabe *et al.*, 1961).

5.2 CHEMICAL ANALYSIS

The results of seven electron microprobe analyses obtained from two different grains of yoshimuraite from the Taguchi Mine are given in Table 21 (columns 1 to 7). The grains were found in close proximity with one another on the sample. Along with those elements found, Na, K, Ca, Al, Nb, Cl and F were also sought for, but not detected. Although the results show an overall consistency in terms of both major and minor elements, it is interesting to note that the analyses from YOSH-1 have analytical totals 2-3 wt. % higher than those from YOSH-2. These differences may be a function of the orientation of the grain with respect to the electron beam; YOSH-1 was analyzed with the beam impinging on a surface perpendicular to the perfect {001} cleavage, while YOSH-2 was analyzed parallel to this cleavage.

The chemical analysis taken from Watanabe *et al.*, (1961) for yoshimuraite from the Noda-Tamagawa Mine, is also presented in Table 21 (column 9). Major elemental oxides were determined by wet-chemical methods (including Fe^{3+} and Fe^{2+}), with the alkali oxides obtained by flame photometry. Comparison of the analytical results of this study with those from Watanabe *et al.*, (1961) shows good agreement between the two. The material analyzed from the Taguchi Mine show elevated Fe_2O_3 , FeO and BaO values with correspondingly lower TiO_2 , MnO and SrO contents, when compared to those for material from the Noda-Tamagawa Mine. There is also a slight but significant difference in the P_2O_5 and SO_3 contents for yoshimuraite from the two different localities. Results from

Table 21. Chemical composition of yoshimuraitc.

OXIDE	1	2	3	4	5	6	7	8	9	10
SiO ₂	16.96	16.83	16.97	17.22	16.48	16.54	16.64	17.00	18.25	17.25
P ₂ O ₅	4.37	4.19	4.01	4.28	4.42	4.32	4.29	4.21	3.98	4.85
SO ₃	3.56	3.84	4.02	3.41	3.63	3.42	3.98	3.71	5.40	4.38
TiO ₂	8.46	8.27	7.88	7.86	7.85	7.84	7.43	8.12	10.00	7.65
Fe ₂ O ₃	1.85	2.06	2.49	2.49	2.34	2.22	2.88	2.27	1.32	3.27
MnO	15.27	15.11	15.01	15.22	14.66	14.70	14.55	15.15	17.64	15.52
FeO	5.40	5.30	5.22	5.01	5.11	5.00	5.26	5.19	1.47	3.93
MgO	0.13	0.12	0.24	0.22	0.25	0.18	0.32	0.18	0.56	-
ZnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	0.50	-
BaO	39.75	39.29	38.95	38.34	37.58	38.47	38.05	39.08	33.51	41.92
SrO	2.64	3.05	3.19	3.16	3.14	3.07	3.16	3.01	4.62	-
Na ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	0.16	-
K ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	0.03	-
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	0.41	-
H ₂ O	(1.17)	(1.16)	(1.17)	(1.17)	(1.15)	(1.14)	(1.16)	(1.17)	2.34	1.23
-Cl	-	-	-	-	-	-	-	-	-0.09	-
TOTAL	99.56	99.22	99.15	98.38	96.61	96.90	97.72	99.09	100.10	100

Table 21. (continued)

Cation proportions based on 3(Si+P+S).

CATION	1	2	3	4	5	6	7	8	9	10
Si	2.18	2.17	2.18	2.21	2.15	2.18	2.15	2.18	2.13	2.10
P	0.48	0.46	0.44	0.46	0.49	0.48	0.47	0.46	0.39	0.50
S	0.34	0.37	0.39	0.33	0.36	0.34	0.39	0.36	0.47	0.40
Ti	0.82	0.80	0.76	0.76	0.77	0.78	0.72	0.78	0.88	0.70
Fe ³⁺	0.18	0.20	0.24	0.23	0.23	0.22	0.28	0.22	0.12	0.30
Mn	1.66	1.65	1.63	1.65	1.62	1.64	1.59	1.65	1.75	1.60
Fe ²⁺	0.58	0.57	0.56	0.54	0.56	0.55	0.54	0.56	0.14	0.40
Mg	0.02	0.02	0.05	0.04	0.05	0.04	0.06	0.03	0.10	-
Zn	-	-	-	-	-	-	-	-	0.04	-
Ba	2.00	1.99	1.96	1.93	1.93	1.99	1.92	1.97	1.53	2.00
Sr	0.20	0.23	0.24	0.23	0.24	0.23	0.24	0.22	0.31	-
Na	-	-	-	-	-	-	-	-	0.02	-
Cl	-	-	-	-	-	-	-	-	0.08	-
H	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.28	1.00

Note: n.d. = not detected; () = calculated from stoichiometry; * total Fe from as Fe₂O₃ in this study, then partitioned into Fe³⁺ and Fe²⁺; 1-4, YOSH-1, Taguchi Mine, this study; 5-7 YOSH-2, Taguchi Mine, this study; 8, average of 1-4; 9, Watanabe *et al.*, (1961), Noda-Tamagawa Mine; 10, calculated for:
 $\text{Ba}_2(\text{Mn}_{10}\text{Fe}^{3+}_4)_2\text{O}_2(\text{Ti}_{10}\text{Fe}^{3+}_3)_2\text{O}_2[\text{P}_{10}\text{S}_2\text{Si}_6\text{O}_{12}(\text{OH})]$

Watanabe *et al.*, (1961) indicate a composition with $S > P$, while that from the Taguchi Mine (this study) indicates $P > S$. In both cases however, the calculated P and S cation proportions are quite close to being equivalent (Table 21), suggesting a significant amount of $P \leftrightarrow S$ substitution in the site.

The chemical formula for the average of four YOSH-1 analyses [based on $3(\text{Si} + \text{P} + \text{S})$; Table 21, column 8] is:

reasonably close to that calculated from the data of Watanabe *et al.*, (1961):

Both empirical formulas are consistent with the structural formula,

as determined from the refined crystal structure.

5.3 DETERMINATION OF THE STRUCTURE

The crystal selected for study was a dark-brown plate measuring 0.09 x 0.06 x 0.04 mm. Although all the crystals analyzed by Watanabe *et al.* (1961) exhibited polysynthetic twinning on {001} (twin law unknown), the crystal used in this study was found to be single, with no indication of twinning either optically or by X-ray precession studies. The X-ray precession photographs verified that the mineral is triclinic, with possible space groups $P1$ or $P\bar{1}$. Piezoelectric tests carried out on

the type material were found to be inconclusive (Watanabe *et al.*, 1961).

The cell parameters refined from the powder-diffraction data agree well with those refined from the four-circle diffractometer data and those given in JCPDS card #19-1421 (Table 22). The observed and calculated powder patterns are also in good agreement, and are presented in Table 23.

X-ray intensity data were collected in the manner described under *Analytical Methods* and important information regarding this collection is given in Table 24. A total of 2353 unique reflections were collected to $2\theta = 55^\circ$, with 1842 being considered as observed [$F > 6\sigma(F)$].

The phasing of a set of normalized structure factors gave a mean $|E^2 - 1|$ value of 0.968, suggesting that the crystal was likely centrosymmetric. Therefore, structure analysis was carried out assuming $P\bar{1}$ space-group symmetry for the mineral. A sharpened Patterson map was calculated, from which the positions of all Ba, Mn, Ti, Si, P and eleven oxygens were inferred. This model was refined to $R = 9.9\%$ and $wR = 10.7\%$. Subsequent difference Fourier maps revealed the positions of the two remaining oxygens. The final steps of the least-squares refinement involved conversion to anisotropic temperature factors, modification of the weighting scheme to one involving a $1/\sigma^2(F_o)$ term inclusion of an isotropic extinction correction and refinement of site-occupancies. The P site was initially assumed to be occupied only by P, but the scattering factor was subsequently modified to $(P_{0.5}S_{0.4}Si_{0.1})$ to agree with results from the chemical analyses. Least-squares refinement of the (Ti,Fe) site converged to Ti 69(3)% and Fe 31(3)%, in

**TABLE 22. CELL PARAMETERS FOR
YOSHIMURAITE**

	1	2	3
a (Å)	5.361(5)	5.386(1)	5.39
b	6.982(4)	6.999(1)	7.01
c	14.766(7)	14.748(3)	14.64
α (°)	95.60(3)	95.50(1)	95.4
β	93.58(3)	93.62(2)	93.7
γ	89.87(3)	89.98(2)	90.2
V (Å³)	550.0	552.3	556.8
Z	2	2	2

1. this study; refined from powder data;
2. this study; refined from four-circle diffractometer data;
3. JCPDS card #19-1421.

TABLE 23. X-RAY DIFFRACTION DATA FOR YOSHIMURAITE 103

This study ⁽¹⁾		JCPDS CARD #19-1421 ⁽²⁾		Calculated ⁽³⁾		
I_{exp}	d_{meas}	I	d_{meas}	I_{calc}	d_{calc}	hkl
		6	14.5	32	14.6506	001
70	4.88	50	4.85	43	4.8835	003
				6	4.8223	012
		10	4.26	14	4.2676	$\bar{1}10$
10	4.22			22	4.2439	$\bar{1}10$
				6	4.2000	$\bar{1}11$
				21	4.1926	$\bar{0}13$
20	4.07	10	4.09	53	4.0880	$\bar{1}11$
35	3.964	10	3.97	60	3.9630	$\bar{1}11$
30	3.840	2	3.85	15	3.8583	$\bar{1}12$
		10	3.72	19	3.7343	$\bar{1}03$
			3.69	46	3.7011	$\bar{1}12$
				27	3.6739	$\bar{1}12$
		10	3.64	3	3.6626	004
		20	3.49	37	3.5056	103
				30	3.4833	$\bar{0}20$
70	3.388	20	3.38	100	3.3907	$\bar{1}13$
		2	3.35	22	3.3783	014
60	3.309	20	3.32	88	3.3179	021
		2	3.27	20	3.2699	$\bar{0}22$
80	3.218	50	3.21	98	3.2271	$\bar{1}13$
		2	3.18	24	3.2000	$\bar{1}13$
60	3.120	20	3.11	22	3.1208	014
				49	3.1202	$\bar{1}04$
				58	3.0439	113
70	3.035	20	3.04	49	3.0348	$\bar{0}22$
10	2.975			20	2.9741	$\bar{0}23$
				36	2.9412	$\bar{1}04$
				26	2.9348	$\bar{1}14$
100	2.933	100	2.91	58	2.9301	005
				6	2.9156	120
					2.8998	$\bar{1}21$
50	2.835			5	2.8487	$\bar{1}21$
				14	2.8224	$\bar{1}22$
50	2.791	20	2.80	58	2.7987	$\bar{1}21$
50	2.764	30	2.76	55	2.7678	$\bar{1}14$

TABLE 23. (continued)

This study ⁽¹⁾		JCPDS CARD # 19-1421 ⁽²⁾		Calculated ⁽³⁾		
<i>I</i> _{est}	<i>d</i> _{meas}	<i>I</i> _{est}	<i>d</i> _{meas}	<i>I</i> _{calc}	<i>d</i> _{calc}	<i>hkl</i>
				89	2.7656	$\bar{1}\bar{2}2$
				40	2.6876	200
20	2.668	30	2.68	12	2.6788	$\bar{1}\bar{2}2$
				81	2.6737	$\bar{2}01$
		20		7	2.6441	$\bar{1}05$
5	2.642	20	2.63	30	2.6403	$\bar{1}\bar{2}3$
				28	2.6349	114
				7	2.6142	201
				10	2.6128	015
				9	2.6080	$\bar{1}\bar{2}2$
				11	2.5765	$\bar{2}02$
				7	2.4729	202
				6	2.4633	$\bar{1}\bar{2}3$
				13	2.4111	024
				5	2.3858	$\bar{1}\bar{2}3$
40	2.382	20	2.36	42	2.3767	016
				6	2.3565	025
				6	2.3418	$\bar{1}\bar{2}4$
				7	2.3169	$\bar{2}13$
				7	2.2775	032
40	2.236			38	2.2355	$\bar{2}04$
				13	2.2120	$\bar{2}13$
				7	2.1799	033
				5	2.1719	106
10	2.165	10	2.16	19	2.1633	$\bar{1}\bar{2}4$
				13	2.1627	$\bar{2}14$
				8	2.1472	213
				8	2.1432	025
				7	2.1399	$\bar{1}\bar{3}1$
				12	2.1332	$\bar{1}\bar{3}1$
				23	2.1220	220
				21	2.1218	$\bar{1}\bar{2}5$
				12	2.1141	$\bar{2}\bar{2}1$
				29	2.1090	$\bar{2}\bar{2}1$
		10	2.11	19	2.1077	$\bar{1}\bar{3}2$
				25	2.1041	204

TABLE 23. (continued)

This study ⁽¹⁾		JCPDS CARD #19-1421 ⁽²⁾		Calculated ⁽³⁾		
I_{est}	d_{meas}	I_{est}	d_{meas}	I_{calc}	d_{calc}	hkl
30	2.066	10	2.10 2.08	17	2.1000	$\overline{222}$
				13	2.0960	$\overline{214}$
				6	2.0951	$\overline{131}$
				2	2.0929	$\overline{007}$
		10	2.07	19	2.0865	$\overline{132}$
				11	2.0722	$\overline{131}$
				23	2.0684	$\overline{221}$
				22	2.0597	$\overline{017}$
		10	2.05	17	2.0533	$\overline{222}$
				14	2.0440	$\overline{222}$
				13	2.0364	$\overline{133}$
				12	2.0283	$\overline{223}$
				18	2.0259	$\overline{125}$
				20	2.0169	$\overline{132}$
30	1.991	10	1.981	9	1.9935	$\overline{107}$
				21	1.9876	$\overline{126}$
		10	1.981	20	1.9838	$\overline{132}$
				13	1.9818	$\overline{214}$
40	1.953	6	1.943	16	1.9534	$\overline{017}$
				8	1.9309	$\overline{215}$
				6	1.9133	$\overline{133}$
				20	1.9115	$\overline{035}$
				9	1.9098	$\overline{107}$
				5	1.8356	$\overline{216}$
				17	1.7744	$\overline{126}$
30	1.773	6	1.753	10	1.7697	$\overline{036}$
				6	1.7680	$\overline{108}$
				3	1.7554	$\overline{134}$
				41	1.7493	$\overline{041}$
30	1.733	6	1.733	19	1.7417	$\overline{127}$
				6	1.7404	$\overline{035}$
				12	1.7308	$\overline{018}$
				7	1.7298	$\overline{216}$
35	1.705	6	1.705	13	1.7045	$\overline{207}$
				8	1.6849	$\overline{217}$
				7	1.6788	$\overline{313}$

TABLE 23. (continued)

This study ⁽¹⁾		JCPDS CARD #19-1421 ⁽²⁾		Calculated ⁽³⁾		
<i>I</i> _{est}	<i>d</i> _{meas}	<i>I</i> _{est}	<i>d</i> _{meas}	<i>I</i> _{calc}	<i>d</i> _{calc}	<i>hkl</i>
40	1.592			9	1.6590	042
				8	1.6767	$\bar{3}12$
				5	1.6513	$\bar{3}04$
				5	1.6486	$\bar{3}03$
				7	1.6207	$\bar{3}14$
				7	1.6180	$\bar{3}13$
				10	1.6147	$\bar{1}27$
				7	1.5976	$\bar{3}21$
				7	1.5970	$\bar{3}20$
				9	1.5933	$\bar{3}14$
				9	1.5909	$\bar{3}13$
				7	1.5898	$\bar{3}21$
				8	1.5896	$\bar{3}20$
				9	1.5867	$\bar{3}22$
				9	1.5864	$\bar{1}28$
				9	1.5855	$\bar{3}21$
Plus others						

1. Sample from the Taguchi mine, Japan; data obtained with a 114.6 mm Gandolfi camera and $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$); I_{est} , visually estimated.
2. Sample from the Noda-Tamagawa mine, Japan; data obtained with a diffractometer using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$).
3. Sample from the Taguchi mine, Japan; I_{calc} from the refined crystal structure, d_{calc} determined from the cell refined from the four-circle data: $a = 5.386$, $b = 6.999$, $c = 14.748 \text{ (\AA)}$, $\alpha = 95.50$, $\beta = 93.62$ and $\gamma = 89.98^\circ$.

**TABLE 24. MISCELLANEOUS DATA FOR DETERMINATION
OF THE CRYSTAL STRUCTURE OF YOSHIMURAITE.**

Space Group	$P\bar{1}$ (#2)	Diffractometer	Nicolet <i>R3m</i>
a (Å)	5.386(1)[°]	Radiation	MoKα (50kV, 40 mA)
b	6.999(1)[°]	Monochromator	Graphite
c	14.748(3)[°]	Crystal Shape	Irregular plate
α	95.50(2)[°]	Crystal Size	0.09 x 0.06 x 0.04 mm
β	93.62(2)[°]	μ(MoKα)	10.94 mm⁻¹
γ	89.98(1)[°]	Z	2
V(Å³)	552.3		
Chemical Formula	Ba₂Mn₂(Ti,Fe)O(Si₂O₇)[(P,S)O₄](OH)		
Intensity Data Collection	Θ-2Θ scanning mode		
2Θ Limit	55°		
Intensity Standards	Two every 58 reflections		
Orientation Standards	Two every 58 reflections		
Number of Unique Reflections	2353		
Number of Observed Reflections	1842		
Criterion for Observed	$F > 6\sigma(F)$		
Weighting Scheme	$wR = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$, $w = 1/\sigma^2$		
Final R for all Observed Reflections	3.0%		
Final wR for all Observed Reflections	4.2%		

* Values refined from four-circle diffractometer data.

good agreement with electron microprobe results of this study. The final residual indices for this model are $R = 3.0\%$ and $wR = 4.2\%$. The final difference map was relatively smooth, although exhibiting one maximum of $2 \text{ e}^-/\text{\AA}^3$ and a number of maxima of $1 \text{ e}^-/\text{\AA}^3$, many of which were associated with the Ba sites. Although bond valence sums clearly indicate that O(11) is an OH group (Table 27), the location of the H atom could not be determined from the Fourier synthesis. The valence sums given in Table 27 also preclude the possibility of any H_2O molecules being present in yoshimuraite.

The crystal structure of yoshimuraite was also refined in the non-centrosymmetric space group $P1$, but no significant improvement was noted.

Final positional and thermal parameters are listed in Table 25, selected interatomic distances and angles in Table 26, calculated bond valence sums in Table 27 and observed and calculated structure factors in Table 28.

5.4 DESCRIPTION OF THE STRUCTURE

The crystal structure of yoshimuraite contains two independent SiO_4 tetrahedra that are corner-linked to form a discrete $[\text{Si}_2\text{O}_7]$ group. The mean Si-O distances are: $\text{Si}(1)\text{O}_4 = 1.622 \text{ \AA}$ and $\text{Si}(2)\text{O}_4 = 1.613 \text{ \AA}$. The $\text{Si}(2)\text{O}_4$ tetrahedron is slightly smaller but more distorted than the $\text{Si}(1)\text{O}_4$ tetrahedron. The mean O-Si-O angles for both tetrahedra are very close to ideal, with those involving the bridging oxygen, O(10), generally being smaller. The $\text{Si}(1)\text{-O}_{\text{bridging}}$

TABLE 25. POSITIONAL AND THERMAL PARAMETERS FOR YOSHIMURAITE.

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Si(1)	0.6948(3)	0.0644(1)	0.1881(1)	32(8)	24(8)	74(8)	-8(6)	-7(6)	-9(6)	44(5)
Si(2)	0.6955(3)	0.5130(2)	0.1852(1)	50(8)	26(8)	65(8)	-1(6)	6(6)	-6(6)	47(5)
(P,S)	0.2537(4)	0.7182(3)	0.5229(2)	129(12)	138(12)	197(14)	4(9)	2(9)	3(8)	156(8)
(Ti,Fe)	0.1990(2)	0.7948(2)	0.20281(8)	30(6)	74(6)	101(6)	1(4)	-1(4)	-3(4)	69(4)
Mn(1)	0	0	0	90(7)	95(8)	192(7)	-11(6)	46(6)	-18(5)	126(4)
Mn(2)	0.4993(2)	0.2482(1)	0.99516(8)	91(6)	76(5)	125(6)	114	4(4)	-5(4)	98(3)
Mn(3)	0	0	1/2	132(8)	163(8)	265(10)	83(7)	84(7)	42(6)	179(5)
Ba(1)	0.22065(9)	0.33664(7)	0.32839(4)	160(2)	166(2)	256(3)	97(2)	13(2)	8(2)	189(2)
Ba(2)	0.73074(8)	0.82198(6)	0.39244(3)	157(2)	112(2)	120(2)	5(2)	4(2)	-1(2)	131(1)
O(1)	0.2364(12)	0.6897(10)	0.4190(4)	233(32)	438(40)	210(34)	-62(22)	63(27)	-2(29)	297(21)
O(2)	0.4576(10)	0.6080(8)	0.2322(3)	107(24)	267(29)	63(24)	26(22)	34(19)	94(21)	144(15)
O(3)	0.9527(9)	0.9905(8)	0.2353(4)	88(24)	284(29)	108(26)	-54(23)	-73(20)	136(21)	168(16)
O(4)	0.4561(10)	0.9918(8)	0.2365(4)	158(27)	283(30)	65(25)	-17(22)	60(21)	-121(22)	169(16)
O(5)	0.9510(10)	0.6079(8)	0.2309(4)	98(24)	262(29)	125(27)	40(23)	-26(20)	-104(21)	162(16)

TABLE 25. (continued)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
O(6)	0.0376(10)	0.8286(8)	0.5536(4)	137(26)	263(30)	160(29)	25(24)	8(22)	-25(22)	186(17)
O(7)	0.5180(10)	0.1718(8)	0.4476(4)	151(27)	238(30)	145(28)	-9(23)	13(22)	38(22)	178(16)
O(8)	0.3254(9)	0.4886(7)	0.9247(3)	113(23)	91(22)	57(22)	8(18)	-41(18)	21(18)	89(13)
O(9)	0.1834(9)	0.7721(7)	0.0818(4)	59(22)	106(23)	133(24)	5(19)	7(18)	16(18)	100(14)
O(10)	0.6974(13)	0.2960(7)	0.2149(4)	505(39)	36(23)	114(27)	-4(20)	29(26)	-42(23)	218(18)
O(11)	0.1731(9)	0.2619(7)	0.0666(4)	121(24)	116(24)	169(27)	9(20)	21(21)	-25(19)	135(15)
O(12)	0.6736(8)	0.0174(7)	0.0782(43)	69(22)	109(22)	69(22)	-3(18)	6(18)	-14(17)	73(13)
O(13)	0.2624(14)	0.5396(10)	0.5703(6)	369(40)	204(33)	628(54)	169(34)	72(37)	-8(28)	390(25)

Note: Anisotropic temperature factors have the form: $\exp. -2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} \dots + 2hka^{*2} b^{*2} U_{12})$;
all U values are in $\text{\AA}^2 \times 10^4$; estimated standard deviations in parentheses.

TABLE 26. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) AND FOR YOSHIMURAITE

Si(1) tetrahedron					
Si(1) - O(3)	1.621(5)	O(3) - Si(1) - O(4)	111.4(3)	O(3) - O(4)	2.675(8)
- O(4)	1.615(5)	- O(10)	104.8(3)	- O(10)	2.576(8)
- O(10)	1.631(5)*	- O(12)	113.0(3)	- O(12)	2.702(8)
- O(12)	1.620(6)	O(4) - Si(1) - O(10)	103.6(3)	O(4) - O(10)	2.699(8)
Mean	1.622	- O(12)	113.1(3)	- O(12)	2.551(8)
		O(10) - Si(1) - O(12)	110.2(3)	O(10) - O(12)	2.666(8)
		Mean	109.4	Mean	2.645
Si(2) tetrahedron					
Si(2) - O(2)	1.610(5)	O(2) - Si(2) - O(5)	111.3(3)	O(2) - O(5)	2.730(8)
- O(5)	1.606(5)	- O(8)	112.9(3)	- O(8)	2.689(8)
- O(8)	1.616(5)	- O(10)	103.5(3)	- O(10)	2.537(8)
- O(10)	1.621(6)*	O(5) - Si(2) - O(8)	112.8(3)	O(5) - O(8)	2.684(8)
Mean	1.613	- O(10)	104.8(3)	- O(10)	2.557(8)
		O(8) - Si(2) - O(10)	110.8(4)	O(1) - O(10)	2.663(8)
		Mean	109.4	Mean	2.643
(P,S) tetrahedron					
(P,S) - O(1)	1.522(7)	O(1) - (P,S) - O(6)	108.7(4)	O(1) - O(6)	2.432(8)
- O(6)	1.468(6)	- O(7)	107.8(4)	- O(7)	2.422(8)
- O(7)	1.471(6)	- O(13)	116.3(4)	- O(13)	2.565(8)
- O(13)	1.488(8)	O(6) - (P,S) - O(7)	109.2(3)	O(6) - O(7)	2.394(8)
Mean	1.487	- O(13)	107.2(4)	- O(13)	2.381(8)
		O(7) - (P,S) - O(13)	107.4(4)	O(7) - O(13)	2.387(8)
		Mean	109.4	Mean	2.430
(Ti,Fe) polyhedron					
(Ti,Fe) - O(2)	1.968(5)	O(2) - (Ti,Fe) - O(4)	86.0(2)	O(2) - O(4)	2.680(8)
- O(3)	1.952(5)	- O(5)	87.9(2)	- O(5)	2.730(8)
- O(4)	1.960(5)	- O(9)	102.3(2)	- O(9)	2.915(8)
- O(5)	1.964(5)	O(3) - (Ti,Fe) - O(4)	87.8(2)	O(3) - O(4)	2.712(8)
- O(9)	1.772(5)	- O(5)	85.9(2)	- O(5)	2.669(8)
Mean	1.923	- O(9)	104.5(2)	- O(9)	2.947(8)
		O(4) - (Ti,Fe) - O(9)	103.7(2)	O(4) - O(9)	2.938(8)
		O(5) - (Ti,Fe) - O(9)	102.9(2)	O(5) - O(9)	2.925(8)

Mn(1) octahedron					
Mn(1) - O(9)	2.280(5) x2	O(9) - Mn(1) - O(11)	101.7(2) x2	O(1) - O(11)	3.457(8)
- O(11)	2.176(5) x2	- O(11)*	78.3(2) x2	- O(11)*	2.813(8)
- O(12)	<u>2.159(5)</u> x2	- O(12)	93.6(2) x2	- O(12)	3.237(8)
Mean	2.205	- O(12)*	86.4(2) x2	- O(12)*	3.040(8)
		O(11) - Mn(1) - O(12)	84.4(2) x2	O(11) - O(12)	3.210(8)
		- O(12)*	95.6(2) x2	- O(12)*	2.913(8)
Mn(2) octahedron					
Mn(2) - O(8)	2.238(5)	O(8) - Mn(2) - O(8)*	77.3(2)	O(8) - O(8)*	2.812(8)
- O(8)*	2.263(5)	- O(9)	95.4(2)	- O(9)	3.216(8)
- O(9)	2.109(5)	- O(11)	84.0(2)	- O(11)	2.907(8)
- O(11)	2.104(5)	- O(12)*	104.7(2)	- O(12)*	4.521(8)
- O(12)	2.287(5)	O(8)* - Mn(2) - O(9)	88.0(2)	O(8)* - O(9)	3.038(8)
- O(12)*	<u>2.231(5)</u>	- O(11)	94.4(2)	- O(11)	3.207(8)
Mean	2.205	- O(12)	99.1(4)	- O(12)	4.493(8)
		O(9) - Mn(2) - O(12)	87.4(2)	O(9) - O(12)	3.158(8)
		- O(12)*	93.3(2)	- O(12)*	3.040(8)
		O(11) - Mn(2) - O(12)	93.4(2)	O(11) - O(12)	2.913(8)
		- O(12)*	83.4(2)	- O(12)*	3.198(8)
		O(12) - Mn(2) - O(12)*	78.8(2)	O(12) - O(12)*	2.869(8)
Mn(3) octahedron					
Mn(3) - O(8)	2.131(5) x2	O(8) - Mn(3) - O(9)	85.5(2) x2	O(8) - O(9)	3.283(8)
- O(9)	2.338(5) x2	- O(9)*	94.5(2) x2	- O(9)*	3.038(8)
- O(11)	<u>2.195(5)</u> x2	- O(11)	84.4(2) x2	- O(11)	2.907(8)
Mean	2.221	- O(11)*	95.4(2) x2	- O(11)*	3.204(8)
		O(9) - Mn(3) - O(11)	103.3(2) x2	O(9) - O(11)	2.813(8)
		- O(11)*	58.3(2) x2	O(10) - O(11)*	3.557(8)
Ba(1) polyhedron			Ba(2) polyhedron		
Ba(1) - O(1)	2.699(7)		Ba(2) - O(1)	2.886(6)	
- O(2)	2.826(6)		- O(1)*	2.890(6)	
- O(3)	2.997(5)		- O(2)	2.977(5)	
- O(4)	2.977(5)		- O(3)	3.007(6)	
- O(5)	2.835(6)		- O(4)	2.997(5)	
- O(6)	2.645(6)		- O(5)	2.999(5)	
- O(7)	2.650(6)		- O(6)	2.804(5)	
- O(10)	3.149(7)		- O(6)*	2.772(6)	
- O(10)*	3.184(6)		- O(7)	2.776(6)	
- O(13)	3.154(7)		- O(7)*	2.782(6)	
- O(13)*	<u>3.156(7)</u>		- O(13)	<u>2.639(7)</u>	
Mean	2.934		Mean	2.865	

Note: Estimated standard deviations in parentheses; * denotes symmetry equivalent atom;
+ denotes bridging oxygen.

TABLE 27. EMPIRICAL BOND VALENCES (v.u.) FOR YOSHIMURAITE^a.

	Ba(1)	Ba(2)	Mn(1)	Mn(2)	Mn(3)	(Ti,Fe)	Si(1)	Si(2)	(P,S)	ΣV_e
O(1)	0.331	0.200 0.203							1.283	2.017
O(2)	0.235	0.156				0.633		1.039		2.093
O(3)	0.148	0.144				0.662	1.008			1.962
O(4)	0.156	0.148				0.643	1.025			1.972
O(5)	0.229	0.147				0.640		1.050		2.066
O(6)	0.383	0.249 0.272							1.484	2.388
O(7)	0.378	0.269 0.265							1.472	2.384
O(8)					0.398 [‡] 0.278			1.022		1.996
O(9)			0.266 [‡]	0.422	0.227 [‡]	1.086				2.001
O(10)	0.098 0.089						0.981	1.008		2.087
O(11)			0.352 [‡]	0.428	0.335 [‡]					1.115
O(12)			0.369 [‡]	0.261 0.304			1.011			1.945
O(13)	0.097 0.096	0.389							1.472	2.054
ΣV_e	2.240	2.442	1.974	1.991	1.920	3.664 [*]	4.025	4.119	5.645 [*]	

Note: ΣV_e = cationic valence sum; ΣV_a = anionic valence sum; + calculated using the constants of Brese and O'Keefe (1991); * calculated for $(Ti_6, Fe_{0.3})_{2.10}$ as determined by crystal structure analysis; † calculated for $(P_{0.5}S_{0.5}Si_{0.1})_{2.10}$.

TABLE 28. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR YOSHIMURAITE.

h	k	l	10Fe	10Fe	10a	h	k	l	10Fe	10Fe	10a	h	k	l	10Fe	10Fe	10a	h	k	l	10Fe	10Fe	10a	h	k	l	10Fe	10Fe	10a
1	0	0	100	-52	8	8	5	0	455	-471	11	-5	12	0	599	-590	10	-3	-15	1	376	-385	12	1	-8	1	182	-161	12
2	0	0	1149	-1087	6	-8	6	0	272	275	13	-4	12	0	357	-352	11	-2	-15	1	74	73	-74	2	-8	1	671	653	7
3	0	0	115	-125	12	-7	6	0	952	-936	10	-3	12	0	1087	-1042	10	-1	-15	1	542	555	10	3	-8	1	227	228	11
4	0	0	808	753	7	-6	6	0	176	-164	15	-2	12	0	822	837	9	0	-15	1	331	313	12	4	-8	1	930	982	9
5	0	0	374	349	6	-5	6	0	360	-370	9	-1	12	0	182	-185	16	1	-15	1	278	-231	13	5	-8	1	626	-638	8
6	0	0	1130	1109	7	-4	6	0	1121	1127	9	0	12	0	648	688	8	2	-15	1	382	372	12	6	-8	1	613	-630	9
7	0	0	438	-442	7	-3	6	0	1220	1244	10	-1	12	0	512	-519	9	4	-15	1	71	74	-71	7	-8	1	265	250	13
8	0	0	250	-220	13	-2	6	0	616	-588	6	2	12	0	426	-427	10	5	-15	1	847	832	10	8	-8	1	166	170	21
9	0	0	130	-134	-27	-1	6	0	1904	-1926	14	4	12	0	741	717	10	6	-15	1	313	302	15	-8	-7	1	318	-283	14
10	0	0	152	-144	17	0	6	0	351	409	6	5	12	0	38	15	-38	-5	-14	1	258	223	17	-7	-7	1	62	-41	-62
11	0	0	962	-971	10	1	6	0	690	642	7	6	12	0	163	-190	23	-4	-14	1	503	490	11	-6	-7	1	1397	1376	12
12	0	0	333	-331	8	2	6	0	316	324	8	-7	13	0	336	349	14	-3	-14	1	38	32	-38	-5	-7	1	663	651	9
13	0	0	2778	2695	15	-3	6	0	472	479	7	-6	13	0	333	301	13	-2	-14	1	329	336	12	-4	-7	1	783	-743	8
14	0	0	513	482	4	4	6	0	461	-444	8	-5	13	0	203	213	17	-1	-14	1	454	-496	9	-3	-7	1	237	-219	12
15	0	0	55	4	-43	5	6	0	1027	-1019	10	-4	13	0	888	878	10	0	-14	1	166	-167	15	-2	-7	1	531	514	8
16	0	0	111	-128	11	6	6	0	260	256	12	-2	13	0	817	-817	9	1	-14	1	996	1004	10	-1	-7	1	166	151	15
17	0	0	176	168	8	7	6	0	108	83	-29	-1	13	0	301	307	12	3	-14	1	537	-492	10	0	-7	1	1020	1056	6
18	0	0	2055	1936	10	8	6	0	239	259	17	0	13	0	690	749	6	4	-14	1	174	-145	20	1	-7	1	30	4	-30
19	0	0	63	-30	-38	-8	7	0	321	327	13	1	13	0	195	190	16	5	-14	1	530	-515	11	2	-7	1	711	-728	11
20	0	0	274	-240	10	-7	7	0	932	925	9	2	13	0	263	254	13	6	-14	1	182	173	20	3	-7	1	176	134	12
21	0	0	62	32	-62	-6	7	0	160	157	17	6	13	0	494	474	12	-4	-13	1	521	-517	11	4	-7	1	321	-317	9
22	0	0	358	-369	9	-5	7	0	901	-895	9	6	13	0	203	181	21	-3	-13	1	713	758	9	5	-7	1	182	193	14
23	0	0	126	-119	-22	-4	7	0	367	374	9	-6	14	0	645	-601	11	-2	-13	1	956	958	10	6	-7	1	1008	1042	10
24	0	0	946	927	-10	-3	7	0	195	-215	11	-5	14	0	541	556	10	0	-13	1	99	-111	-35	7	-7	1	85	-80	-41
25	0	0	38	1	-38	-2	7	0	136	141	13	-2	14	0	371	-310	11	1	-13	1	245	-227	9	8	-7	1	602	-625	10
26	0	0	559	546	9	3	7	0	527	-473	5	-1	14	0	370	-402	8	3	-13	1	653	-640	9	-8	-6	1	223	-270	17
27	0	0	78	-72	-34	4	7	0	95	121	-25	0	14	0	178	182	17	4	-13	1	792	789	9	-7	-6	1	192	162	16
28	0	0	86	70	-25	5	7	0	291	-298	10	2	14	0	101	-124	-34	5	-13	1	36	43	-36	-6	-6	1	35	-1	-35
29	0	0	264	249	8	4	7	0	99	98	-26	3	14	0	259	264	15	6	-13	1	401	-386	11	-5	-6	1	291	-199	14
30	0	0	918	-838	8	5	7	0	618	624	8	4	15	0	397	365	13	7	-13	1	120	140	-30	-4	-6	1	854	840	9
31	0	0	995	944	8	6	7	0	339	-352	11	-5	15	0	41	-5	-41	-6	-12	1	380	-342	13	-3	-6	1	547	545	7
32	0	0	54	51	-34	-8	7	0	148	120	23	-2	15	0	372	348	11	-3	-12	1	614	608	12	0	-6	1	452	-457	7
33	0	0	414	371	6	-6	7	0	156	186	23	0	15	0	336	-306	15	-1	-12	1	341	-365	12	1	-6	1	330	-345	7
34	0	0	1705	-1583	11	-8	8	0	35	-48	-35	-2	15	0	372	348	11	2	-12	1	503	-527	10	2	-6	1	1605	1687	12
35	0	0	700	-654	7	-7	8	0	123	-72	-22	0	15	0	1108	1107	8	-1	-12	1	695	712	9	3	-6	1	123	136	16
36	0	0	1342	1309	11	-5	8	0	1113	1112	10	1	15	0	37	73	-37	0	-12	1	304	309	8	4	-6	1	640	-643	8
37	0	0	73	-59	-35	-4	8	0	129	48	18	2	15	0	680	-693	10	3	-12	1	69	116	-69	5	-6	1	390	373	9
38	0	0	387	-344	9	-3	8	0	121	-106	19	3	15	0	161	-160	21	4	-12	1	444	-442	10	6	-6	1	166	143	16
39	0	0	324	302	10	-2	8	0	32	27	-32	4	15	0	482	447	12	5	-12	1	472	-465	10	7	-6	1	71	-73	-59
40	0	0	210	-223	16	0	8	0	176	-164	10	-4	16	0	1124	1078	11	6	-12	1	792	774	9	8	-5	1	725	730	10
41	0	0	35	63	-35	2	8	0	100	-82	-26	-3	16	0	281	284	14	7	-12	1	387	404	11	-8	-5	1	422	392	12
42	0	0	469	-459	9	3	8	0	526	-520	8	-2	16	0	427	-447	11	8	-12	1	38	-69	-38	-7	-5	1	331	342	11
43	0	0	580	588	8	4	8	0	432	417	9	-2	16	0	230	-242	15	-6	-11	1	383	-389	13	-6	-5	1	34	27	-34
44	0	0	453	427	8	5	8	0	79	29	-44	-5	11	0	230	-242	15	-5	-11	1	382	358	12	-5	-5	1	124	120	-21
45	0	0	28	37	-28	6	8	0	186	-173	17	0	16	0	336	352	10	-3	-11	1	61	-61	-61	-4	-5	1	608	-581	8
46	0	0	959	912	8	7	8	0	877	888	10	-2	16	0	292	302	13	2	-11	1	638	672	9	-3	-5	1	816	-818	8
47	0	0	1126	-1056	8	-8	9	0	378	335	12	3	16	0	825	852	10	-1	-11	1	510	-518	9	0	-5	1	750	-696	5
48	0	0	719	-774	7	-6	9	0	91	56	-31	4	16	0	419	-406	12	0	-11	1	993	-1004	7	1	-5	1	579	546	6
49	0	0	920	986	-6	-5	9	0	284	-292	12	4	16	0	316	-305	15	2	-11	1	959	998	10	2	-5	1	69	65	-30
50	0	0	29	80	-29	-4	9	0	395	-400	9	-3	17	0	158	168	26	3	-11	1	234	-203	13	3	-5	1	672	-674	7
51	0	0	77	-61	-25	-5	9	0	284	-292	12	-3	17	0	207	198	18	4	-11	1	573	564	10	4	-5	1	1097	1141	9
52	0	0	347	335	7	-4	9	0	395	-400	9	-2	17	0	841	834	10	5	-11	1	168	-128	18	5	-5	1	597	627	8
53	0	0	308	-290	8	-3	9	0	748	740	8	-1	17	0	38	59	-38	6	-11	1	71	53	-71	6	-5	1	114	57	-22
54	0	0	347	324	9	-2	9	0	211	230	13	0	17	0	97	134	-30	7	-11	1	352	347	12	7	-5	1	36	-118	-36
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56	0	0	349	337	10	0	9	0	816	799	6	2	17	0	146	25	24	-6	-10	1	667	634	10	-7	-4	1	285	-267	13
57	0	0	234	233	14	2	9	0	644	-680	7	3	17	0	86	104	-83	-5	-10	1	393	-365	11	-6	-4	1	688	667	8
58	0	0	265	272	13	3	9	0	2																				

TABLE 28. (continued)

h	k	l	10Fe	10Fc	10s	h	k	l	10Fe	10Fc	10s	h	k	l	10Fe	10Fc	10s	h	k	l	10Fe	10Fc	10s	h	k	l	10Fe	10Fc	10s
-6	-2	1	713	699	8	3	3	1	284	-287	8	2	9	1	571	548	8	-2	18	1	385	397	13	-4	-9	2	36	-50	-36
-5	-2	1	903	903	9	4	3	1	402	-384	7	3	9	1	34	49	-34	-1	18	1	740	705	10	-3	-9	2	1023	-1083	10
-4	-2	1	339	-322	8	5	3	1	845	852	8	4	9	1	1023	-1027	10	0	18	1	394	444	9	-2	-9	2	84	-111	-37
-3	-2	1	1635	-1611	11	6	3	1	718	694	8	5	9	1	88	60	-37	1	18	1	712	-692	11	-1	-9	2	1062	-1113	10
-2	-2	1	950	951	8	7	3	1	555	-558	9	6	9	1	349	330	12	-1	18	2	40	-23	-40	0	-9	2	240	234	8
-1	-2	1	1001	1013	8	8	3	1	214	-205	16	7	9	1	277	275	14	0	-18	2	54	7	-35	1	-9	2	64	-82	-64
0	-2	1	115	-23	9	-8	4	1	36	43	-34	-8	10	1	413	437	13	1	-18	2	67	6	-67	2	-9	2	122	87	20
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2	-2	1	894	-842	8	-6	4	1	190	-173	14	-6	10	1	410	-413	11	-2	-17	2	490	479	12	4	-9	2	705	722	8
3	-2	1	1407	-1448	11	-5	4	1	1013	1033	10	-5	10	1	98	-50	-31	-1	-17	2	384	383	12	5	-9	2	647	645	8
4	-2	1	659	691	7	-4	4	1	776	811	8	-4	10	1	244	-227	13	0	-17	2	766	759	7	6	-9	2	108	-103	-28
5	-2	1	706	728	8	-3	4	1	347	-340	7	-2	10	1	872	928	9	1	-17	2	300	-316	15	7	-9	2	273	261	13
6	-2	1	205	-178	13	-2	4	1	769	730	7	-1	10	1	307	344	10	4	-17	2	673	652	12	8	-9	2	144	197	-24
7	-2	1	267	287	12	0	4	1	1499	-1414	9	0	10	1	1208	-1232	16	-3	-16	2	107	119	-38	-7	-8	2	687	-667	11
8	-1	1	36	115	-34	1	4	1	1420	1403	10	2	10	1	262	265	13	-2	-16	2	797	801	10	-6	-8	2	67	-64	67
-7	-1	1	710	-713	9	2	4	1	1527	1440	11	3	10	1	113	-130	-27	-1	-16	2	108	-108	-34	-5	-8	2	322	337	12
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-4	-1	1	58	5	-49	5	4	1	33	44	-33	6	10	1	262	-249	15	3	-16	2	117	-72	-33	-1	-8	2	1153	-1185	10
-3	-1	1	817	834	7	6	4	1	89	96	-33	7	10	1	40	37	-40	4	-16	2	598	-582	11	0	-8	2	951	968	9
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-1	-1	1	1181	-1267	8	8	4	1	275	280	14	-6	11	1	376	383	12	-4	-15	2	255	234	16	2	-8	2	187	193	13
0	-1	1	30	-10	-22	-8	5	1	550	543	10	-5	11	1	410	403	11	-3	-15	2	34	11	-38	3	-8	2	686	663	8
1	-1	1	409	433	6	-7	5	1	35	9	-35	-4	11	1	564	-557	10	-2	-15	2	362	375	12	4	-8	2	970	990	9
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3	-1	1	897	884	7	-5	5	1	162	-164	14	-2	11	1	192	-186	15	0	-15	2	777	-774	11	6	-8	2	98	28	-29
4	-1	1	591	-616	7	-4	5	1	1073	-1110	9	-1	11	1	522	-547	9	2	-15	2	223	201	18	7	-8	2	283	290	13
5	-1	1	665	-676	8	-3	5	1	500	526	7	0	11	1	681	688	16	3	-15	2	200	175	18	8	-8	2	527	517	11
6	-1	1	878	892	9	0	5	1	280	247	9	2	11	1	204	-212	16	4	-15	2	612	574	11	7	-7	2	185	132	19
7	-1	1	398	384	10	1	5	1	235	-274	9	3	11	1	76	78	-61	5	-15	2	158	-108	24	-6	-7	2	290	298	13
-8	0	1	145	-173	22	2	5	1	239	-232	9	4	11	1	100	-113	-35	-5	-14	2	177	187	21	-5	-7	2	601	-594	9
-7	0	1	686	653	6	3	5	1	861	868	8	5	11	1	210	-224	16	-4	-14	2	330	-322	13	-3	-7	2	149	-137	17
-6	0	1	443	458	6	4	5	1	667	668	8	6	11	1	803	819	10	-3	-14	2	297	-305	13	-1	-7	2	926	951	8
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-3	0	1	338	328	5	-7	5	1	35	-8	-35	5	12	1	769	-754	10	0	-14	2	646	666	7	2	-7	2	431	-433	7
-2	0	1	64	115	-22	-8	6	1	427	-428	11	-2	12	1	519	533	9	2	-14	2	450	-443	11	3	-7	2	547	567	7
-1	0	1	590	624	4	-8	6	1	749	-761	10	-2	12	1	345	348	10	3	-14	2	128	-92	-26	4	-7	2	666	680	8
0	0	1	71	-43	12	-6	6	1	53	36	-53	0	12	1	35	-7	-35	4	-14	2	470	459	11	5	-7	2	342	321	10
1	0	1	750	-794	5	-6	6	1	841	854	9	1	12	1	316	-299	8	5	-14	2	218	-220	16	6	-7	2	49	20	-58
2	0	1	681	665	12	-5	6	1	302	-293	10	2	12	1	721	706	9	6	-14	2	448	444	12	7	-7	2	978	-979	10
3	0	1	77	68	-17	-4	6	1	279	287	10	3	12	1	301	-274	13	-5	-13	2	199	-168	19	8	-7	2	354	353	12
4	0	1	119	122	18	-3	6	1	31	-28	-31	5	12	1	409	-417	12	-4	-13	2	598	591	10	-8	-6	2	39	5	-39
5	0	1	1168	1165	7	0	6	1	735	725	5	6	12	1	41	9	-61	-3	-13	2	261	272	14	-7	-6	2	198	-191	17
6	0	1	329	322	9	1	6	1	54	-30	-54	7	13	1	419	401	13	-2	-13	2	179	-147	17	6	-6	2	116	-118	-27
7	0	1	673	-671	12	2	6	1	1736	1694	13	-6	13	1	278	275	15	-1	-13	2	65	70	-65	-5	-6	2	557	531	9
8	0	1	113	129	-29	3	6	1	233	-240	10	-5	13	1	108	105	-37	1	-13	2	549	-566	10	-4	-6	2	1418	1404	11
-7	1	1	122	-140	-22	4	6	1	903	-891	9	-5	13	1	871	-871	10	2	-13	2	893	895	9	-3	-6	2	870	-914	8
-6	1	1	310	-317	10	5	6	1	282	308	11	-2	13	1	739	761	9	3	-13	2	520	500	10	0	-6	2	198	189	11
-5	1	1	597	615	7	6	6	1	1132	1116	10	-1	13	1	932	1000	10	4	-13	2	183	-213	18	-1	-6	2	551	586	7
-4	1	1	640	652	7	7	6	1	103	-30	-31	0	13	1	120	87	-27	5	-13	2	223	-187	15	1	-6	2	846	857	7
-3	1	1	1102	-1136	9	8	6	1	69	58	-69	1	13	1	308	-312	12	6	-13	2	116	-55	-29	2	-6	2	30	40	-30
-2	1	1	597	575	6	-8	7	1	447	468	11	3	13	1	461	-437	11	-5	-12	2	97	85	-41	3	-6	2	1650	-1641	12
-1	1	1	178	-198	10	-7	7	1	138	122	21	4	13	1	587	568	11	4	-12	2	169	135	19	4	-6	2	235	217	11
0	1	1	86	-57	-17	-6	7	1	375	-385	10	5	13	1	346	333	14	-3	-12	2	373	-389	11	5	-4	2	186	399	9
1	1	1	1357	1396	10	-5	7	1	400	-410	9	-6	14	1	307	321	16	-2	-12	2	743	778	9	6	-6	2	71	-60	-53
2	1	1	1952	1934	11	-4	7	1	576	583	8	-4	14	1	158	129	21	-1	-12	2	650	646	9	7	-6	2	418	423	10
3	1	1	1134	-1163	9	-3	7	1	204	-176	13	-3	14	1	128	57	-25	1	-12</										

TABLE 28. (continued)

h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s	h	k	l	10Fe	10Fe	10s
8	4	2	354	375	12	1	2	2	231	203	8	-5	8	2	854	-870	10	0	16	2	159	-178	17	3	-9	3	457	444	9
8	3	3	103	91	-33	2	2	2	343	410	6	-3	8	2	822	825	9	1	16	2	250	-254	17	4	-9	3	920	928	9
7	3	3	154	-152	19	3	2	2	340	329	7	-2	8	2	125	-104	-21	2	16	2	723	-720	11	5	-9	3	307	-294	12
6	3	3	748	-743	9	4	2	2	522	-502	7	-1	8	2	123	129	-22	3	17	2	169	-169	22	6	-9	3	401	-410	11
5	3	3	327	335	10	5	2	2	212	-221	13	0	8	2	1252	1239	8	4	17	2	661	-660	11	7	-9	3	137	-148	-24
4	3	3	1643	1625	13	6	2	2	572	564	9	1	8	2	1049	1040	9	5	17	2	121	-116	-29	7	-8	3	160	-177	26
2	3	3	154	-143	13	7	2	2	101	-119	-31	2	8	2	371	367	9	6	17	2	531	544	8	8	-8	3	800	783	11
1	3	3	342	-341	6	8	2	2	525	559	11	3	8	2	763	775	8	7	17	2	197	228	21	9	-8	3	527	560	10
0	3	3	542	555	4	9	2	2	331	351	13	4	8	2	724	726	9	8	17	2	79	-98	-79	10	-8	3	252	-250	13
1	3	3	847	828	7	10	2	2	440	452	10	5	8	2	82	80	-42	9	17	2	134	132	21	11	-8	3	736	-727	8
2	3	3	1201	1187	9	11	2	2	514	527	9	6	8	2	684	-713	10	10	17	2	202	-223	21	12	-8	3	121	86	-21
3	3	3	919	915	8	12	2	2	959	962	9	7	8	2	684	-713	10	11	17	2	136	83	-26	13	-8	3	931	938	7
4	3	3	301	-303	10	13	2	2	707	725	8	8	8	2	261	258	15	12	17	2	388	348	14	14	-8	3	72	62	-44
5	3	3	378	-379	10	14	2	2	454	447	7	9	8	2	101	83	-33	13	17	2	404	386	12	15	-8	3	308	-315	10
6	3	3	454	454	10	15	2	2	1195	1173	5	10	8	2	213	207	16	14	17	2	299	299	14	16	-8	3	122	-149	-21
7	3	3	954	959	10	16	2	2	442	456	5	11	8	2	604	-621	8	15	17	2	692	651	12	17	-8	3	661	-653	8
8	3	3	720	730	10	17	2	2	935	929	8	12	8	2	228	237	12	16	17	2	734	-713	11	18	-8	3	605	597	9
9	3	3	384	-381	11	18	2	2	335	346	8	13	8	2	1491	1479	9	17	17	2	42	-29	-42	19	-8	3	1047	1045	10
10	3	3	180	143	17	19	2	2	1612	1407	11	14	8	2	675	698	8	18	17	2	412	390	12	20	-8	3	288	-294	13
11	3	3	166	-132	14	20	2	2	318	316	10	15	8	2	308	303	11	19	17	2	639	-622	11	21	-8	3	40	89	-40
12	3	3	245	-219	10	21	2	2	895	919	9	16	8	2	1259	-1263	11	20	17	2	607	554	11	22	-8	3	614	593	11
13	3	3	520	-477	7	22	2	2	561	-549	10	17	8	2	290	299	12	21	17	2	389	358	12	23	-8	3	733	742	9
14	3	3	1258	1290	9	23	2	2	327	326	13	18	8	2	761	785	9	22	17	2	41	62	-41	24	-8	3	342	335	11
15	3	3	42	47	-42	24	2	2	335	330	12	19	8	2	134	-131	-29	23	17	2	139	-129	-26	25	-8	3	103	-80	-25
16	3	3	978	979	6	25	2	2	715	727	9	20	8	2	413	-401	12	24	17	2	654	-632	11	26	-8	3	234	-245	11
17	3	3	69	-64	-29	26	2	2	263	278	12	21	8	2	639	-621	10	25	17	2	532	-525	11	27	-8	3	767	-760	6
18	3	3	1514	1439	11	27	2	2	1195	1212	10	22	8	2	205	190	17	26	17	2	394	305	12	28	-8	3	63	48	-63
19	3	3	107	69	18	28	2	2	296	289	10	23	8	2	840	817	9	27	17	2	537	511	11	29	-8	3	130	-106	19
20	3	3	1668	1695	14	29	2	2	31	34	-31	24	8	2	519	524	9	28	17	2	113	-45	-28	30	-8	3	84	-40	-33
21	3	3	333	-334	9	30	2	2	617	-610	6	25	8	2	795	834	9	29	17	2	769	-753	10	31	-8	3	100	99	-28
22	3	3	188	-176	14	31	2	2	1792	1751	10	26	8	2	294	-292	12	30	17	2	99	-28	-34	32	-8	3	158	-155	19
23	3	3	588	-590	9	32	2	2	1305	1311	10	27	8	2	570	554	9	31	17	2	596	582	10	33	-8	3	37	-33	-37
24	3	3	170	-155	20	33	2	2	303	-304	8	28	8	2	284	284	12	32	17	2	138	109	-24	34	-8	3	39	5	-39
25	3	3	292	-310	12	34	2	2	1012	-1004	8	29	8	2	332	339	11	33	17	2	277	284	15	35	-8	3	319	270	13
26	3	3	576	574	8	35	2	2	233	220	11	30	8	2	114	85	-27	34	17	2	339	353	14	36	-8	3	687	-690	9
27	3	3	114	-91	20	36	2	2	106	-90	-24	31	8	2	722	-727	9	35	17	2	335	324	13	37	-8	3	532	-549	9
28	3	3	1485	1464	12	37	2	2	642	649	9	32	8	2	208	-182	17	36	17	2	519	-546	11	38	-8	3	1341	1335	11
29	3	3	478	441	7	38	2	2	261	262	13	33	8	2	522	502	12	37	17	2	401	-380	11	39	-8	3	95	25	-23
30	3	3	1849	1825	13	39	2	2	431	-451	12	34	8	2	806	793	10	38	17	2	235	229	11	40	-8	3	174	180	10
31	3	3	158	-179	10	40	2	2	347	345	12	35	8	2	470	-451	10	39	17	2	455	458	11	41	-8	3	503	494	7
32	3	3	2324	2349	9	41	2	2	34	4	-56	36	8	2	384	382	10	40	17	2	489	497	10	42	-8	3	222	-204	11
33	3	3	356	-330	6	42	2	2	68	-11	-57	37	8	2	85	-100	-39	41	17	2	777	-739	9	43	-8	3	416	-404	8
34	3	3	80	-48	-22	43	2	2	675	-689	8	38	8	2	227	207	14	42	17	2	127	-134	-25	44	-8	3	763	770	10
35	3	3	570	-543	6	44	2	2	751	782	8	39	8	2	644	-646	9	43	17	2	656	661	10	45	-8	3	101	-51	-27
36	3	3	800	-783	8	45	2	2	1676	1711	13	40	8	2	896	-911	10	44	17	2	435	432	12	46	-8	3	437	429	10
37	3	3	92	94	-26	46	2	2	31	-30	-31	41	8	2	263	252	13	45	17	2	80	-104	-80	47	-8	3	35	14	-35
38	3	3	740	749	8	47	2	2	721	-693	7	42	8	2	401	414	11	46	17	2	38	1	-38	48	-8	3	618	-611	11
39	3	3	107	-108	-27	48	2	2	420	401	7	43	8	2	252	263	15	47	17	2	294	288	14	49	-8	3	305	-366	12
40	3	3	878	862	10	49	2	2	388	-387	7	44	8	2	144	-128	-26	48	17	2	744	-719	9	50	-8	3	545	545	10
41	3	3	369	369	7	50	2	2	584	584	7	45	8	2	223	-208	18	49	17	2	470	-444	7	51	-8	3	219	-198	15
42	3	3	875	-867	6	51	2	2	1085	1083	8	46	8	2	825	856	10	50	17	2	444	442	10	52	-8	3	339	328	11
43	3	3	116	105	15	52	2	2	399	-380	8	47	8	2	474	-494	10	51	17	2	778	755	9	53	-8	3	799	810	9
44	3	3	1190	1210	12	53	2	2	221	-223	13	48	8	2	870	-906	9	52	17	2	121	74	-26	54	-8	3	113	5	-20
45	3	3	514	497	5	54	2	2	104	-120	-27	49	8	2	399	419	10	53	17	2	479	471	10	55	-8	3	834	-863	8
46	3	3	541	543	5	55	2	2	128	132	-24	50	8	2	270	244	13	54	17	2	437	-432	11	56	-8	3	714	707	7
47	3	3	373	345	4	56	2	2	728	780	10	51	8	2	278	280	13	55	17	2	193	188	19	57	-8	3	63	-20	-45
48	3	3	1607	1599	8	57	2	2	161	134	20	52	8	2	376	-384	12	56	17										

TABLE 28. (continued)

h k l 10Fe 10Fc 10a				h k l 10Fe 10Fc 10a				h k l 10Fe 10Fc 10a				h k l 10Fe 10Fc 10a				h k l 10Fe 10Fc 10a				
4	461	453	8	3	212	229	12	3	36	69	36	4	381	381	12	3	4	109	112	26
4	490	508	9	3	711	690	7	4	670	665	9	4	358	363	12	4	4	313	301	10
4	491	627	9	4	1181	1191	9	5	87	39	67	5	548	573	12	5	4	257	269	10
4	493	429	11	5	1049	1009	11	6	88	70	48	6	425	480	12	6	4	300	313	7
4	515	504	11	6	1424	1400	11	7	71	87	71	7	297	295	12	7	4	583	601	8
4	89	98	44	7	742	727	8	8	225	210	14	8	396	392	11	8	4	512	523	8
4	506	491	10	8	168	169	14	9	36	83	36	9	164	123	13	9	4	375	381	9
4	64	21	64	9	140	136	18	10	243	232	14	10	689	681	9	10	4	647	657	8
4	262	247	12	10	347	337	10	11	1027	997	8	11	434	444	10	11	4	427	425	10
4	138	147	20	11	184	162	15	12	104	67	30	12	502	495	10	12	4	412	429	11
4	1103	1115	9	12	682	680	10	13	309	286	12	13	625	613	10	13	4	382	378	12
4	95	92	20	13	190	165	18	14	288	291	13	14	203	200	17	14	4	144	117	25
4	1104	1112	9	14	168	156	18	15	267	239	13	15	317	302	14	15	4	353	327	13
4	144	113	9	15	671	682	9	16	450	442	11	16	355	345	13	16	4	37	16	37
4	52	39	52	16	726	731	9	17	776	767	10	17	1089	1082	11	17	4	232	199	13
4	1434	1398	11	17	510	487	8	18	430	455	12	18	166	129	18	18	4	408	429	9
4	1036	1018	9	18	848	826	8	19	447	457	11	19	422	434	10	19	4	671	691	8
4	663	654	9	19	61	62	61	20	94	99	35	20	643	31	12	20	4	172	174	13
4	529	527	8	20	644	633	7	21	444	431	11	21	232	223	13	21	4	826	831	6
4	1139	1126	8	21	832	818	8	22	476	452	15	22	255	255	13	22	4	164	163	15
4	36	28	36	22	32	16	32	732	726	9	23	524	532	10	23	4	790	772	8	
4	65	116	65	23	860	841	8	24	1042	1014	10	24	940	990	10	24	4	448	444	8
4	688	692	9	24	354	341	9	25	349	344	12	25	112	35	27	25	4	313	303	18
4	537	532	9	25	198	179	14	26	67	63	67	26	39	14	39	26	26	61	56	61
4	1026	980	10	26	541	554	10	27	137	130	28	27	40	66	40	27	191	197	17	
4	126	133	21	27	330	348	12	28	405	405	13	28	528	537	10	28	4	365	376	12
4	333	344	8	28	632	629	11	29	597	628	11	29	35	7	35	29	231	226	16	
4	1290	1272	10	29	37	12	37	158	168	22	30	641	691	9	30	4	84	55	51	
4	855	863	7	30	473	454	10	31	779	791	9	31	978	1001	7	31	4	36	57	36
4	134	87	14	31	137	137	11	32	501	511	11	32	35	95	35	32	896	919	9	
4	543	529	6	32	715	725	22	33	247	210	10	33	35	33	35	33	32	32	15	32
4	1348	1275	10	33	416	397	9	34	218	197	16	34	304	279	12	34	4	1205	1218	10
4	424	405	8	34	267	229	11	35	454	437	11	35	383	375	10	35	4	76	12	33
4	439	449	8	35	505	493	7	36	539	550	11	36	680	671	10	36	4	423	434	6
4	742	734	8	36	217	222	8	37	328	319	14	37	38	28	38	37	32	59	32	32
4	241	231	13	37	91	71	27	38	339	353	14	38	41	110	41	38	235	226	12	
4	435	422	11	38	1371	1337	11	39	320	315	14	39	115	158	33	39	289	294	11	
4	128	91	26	39	531	545	8	40	226	110	27	40	690	683	10	40	4	870	876	9
4	449	443	9	40	718	712	9	41	554	544	10	41	36	27	36	41	193	204	16	
4	224	223	9	41	99	93	29	42	90	66	42	42	167	134	19	42	4	423	424	10
4	712	711	9	42	320	298	12	43	343	350	14	43	996	1025	9	43	4	318	310	13
4	431	441	6	43	38	12	38	483	470	11	44	812	818	8	44	4	270	286	15	
4	501	476	6	44	37	36	37	347	353	13	45	785	805	8	45	4	686	674	10	
4	1339	1276	7	45	191	199	18	46	586	546	11	46	70	54	60	46	137	133	21	
4	514	500	4	46	35	18	35	657	653	11	47	34	30	34	47	4	75	67	40	
4	69	48	15	47	106	73	26	48	127	134	28	48	198	174	15	48	4	32	37	32
4	885	881	6	48	1578	1527	12	49	96	122	41	49	782	765	9	49	4	773	789	8
4	1330	1308	12	49	84	52	30	50	349	314	13	50	116	99	28	50	4	56	79	36
4	336	342	6	50	792	791	6	51	570	538	11	51	287	292	15	51	4	1728	1746	13
4	106	113	21	51	235	225	11	52	486	475	12	52	750	761	10	52	4	33	50	33
4	952	949	7	52	33	27	33	434	425	13	53	775	783	10	53	4	365	376	9	
4	557	558	10	53	367	377	10	54	105	99	36	54	247	259	13	54	4	207	206	13
4	721	707	7	54	724	693	9	55	710	723	11	55	100	96	28	55	4	864	879	9
4	105	133	34	55	483	493	10	56	460	443	11	56	535	546	8	56	4	225	216	14
4	35	33	35	56	643	623	10	57	183	202	21	57	43	43	29	57	4	850	854	10
4	1109	1111	10	57	68	92	68	58	81	55	35	58	1171	1192	10	58	4	264	297	15
4	538	551	8	58	267	254	15	59	333	339	14	59	217	223	13	59	4	88	81	30
4	642	626	8	59	1029	1053	10	60	537	542	11	60	543	547	9	60	4	759	761	14
4	1039	1021	9	60	670	695	9	61	298	299	15	61	34	17	34	61	4	273	255	8
4	1433	1447	11	61	118	145	26	62	127	83	25	62	132	36	22	62	4	691	708	9
4	60	19	40	62	281	272	11	63	113	131	42	63	153	132	20	63	4	290	286	8
4	160	143	8	63	79	70	37	64	149	123	28	64	873	884	10	64	4	180	172	10
4	1111	1090	9	64	931	908	14	65	97	72	51	65	161	166	23	65	4	94	98	17
4	30	26	30	65	87	81	33	66	905	862	8	66	316	321	12	66	4	1892	1905	8
4	1179	1167	10	66	819	807	8	67	86	34	54	67	538	548	9	67	4	79	115	28
4	132	144	19	67	308	295	10	68	374	380	14	68	431	439	9	68	4	1065	1065	12
4	303	286	10	68	282	276	12	69	40	27	40	69	283	289	10	69	4	114	125	16
4	34	19	34	69	559	567	9	70	99	92	47	70	99	128	19	70	4	1043	1054	12
4	448	458	11	70	746	726	10	71	94	105	49	71	643	631	8	71	4	157	128	17
4	39	100	39	71	190	194	19	72	113	72	24	72	387	391	9	72	4	407	403	9
4	492	493	11	72	155	144	23	73	353	326	13	73	1240	1222	10	73	4	130	126	18
4	410	419	11	73	380	407	12	74	482	485	12	74	703	715	8	74	4	425	428	11
4	685	663	9	74	874	916	9	75	92	37	44	75	646	688	8	75	4	212	189	16
4	463	469	9	75	828	803	9	76	83	67	58	76	36	12	34	76	4	103	110	32
4	477	466	9	76	223	232	13	77	115	79	34	77	108	59	32	77	4	1194	1209	11
4	1020	1040	9	77	579	527	7	78	232	236	18	78	212	211	15	78	4	309	299	10
4	440	427	7	78	178	167	16	79	342	343	13	79	718	717	8	79	4	518	52	

TABLE 28. (continued)

n	k	l	10Fe	10Fe	10a	n	k	l	10Fe	10Fe	10a	n	k	l	10Fe	10Fe	10a	n	k	l	10Fe	10Fe	10a	n	k	l	10Fe	10Fe	10a
3	2	4	478	477	8	2	9	4	344	354	11	2	8	3	805	824	9	2	1	1	35	35	35	2	7	3	379	384	14
3	2	4	784	778	8	2	9	4	492	499	10	2	8	3	128	128	22	2	1	1	141	153	21	2	7	3	340	344	11
3	2	4	274	265	9	2	9	4	188	193	12	2	8	3	583	595	7	2	1	1	101	126	30	2	7	3	340	344	11
3	2	4	309	313	7	2	9	4	109	107	29	2	8	3	36	34	36	2	1	1	599	598	10	2	7	3	239	234	15
3	2	4	163	163	15	2	9	4	97	97	33	2	8	3	1046	1064	10	2	1	1	280	256	14	2	7	3	103	138	30
3	2	4	306	308	10	2	9	4	778	797	9	2	8	3	93	109	36	2	1	1	350	353	14	2	7	3	649	630	7
3	2	4	447	446	9	2	9	4	129	122	25	2	8	3	286	301	14	2	1	1	345	361	14	2	7	3	36	63	36
3	2	4	1014	1039	10	2	9	4	413	420	12	2	8	3	209	227	17	2	1	1	274	273	14	2	7	3	1254	1272	11
3	2	4	182	185	17	2	9	4	310	299	14	2	8	3	112	137	38	2	1	1	329	333	7	2	7	3	281	286	14
3	2	4	458	457	10	2	9	4	39	79	39	2	8	3	518	518	11	2	1	1	82	34	34	2	7	3	123	135	29
3	2	4	159	141	21	2	9	4	352	349	12	2	8	3	154	120	19	2	1	1	183	181	21	2	7	3	100	29	46
3	2	4	454	441	12	2	9	4	604	591	10	2	8	3	971	996	10	2	1	1	87	1	21	2	7	3	760	765	11
3	2	4	317	335	14	2	9	4	614	627	7	2	8	3	34	4	34	2	1	1	436	641	6	2	7	3	436	397	12
3	2	4	534	514	11	2	9	4	505	514	10	2	8	3	330	322	8	2	1	1	218	202	10	2	7	3	1401	1394	12
3	2	4	195	205	15	2	9	4	523	520	10	2	8	3	66	93	66	2	1	1	473	458	13	2	7	3	315	283	12
3	2	4	175	146	14	2	9	4	210	213	16	2	8	3	162	174	16	2	1	1	35	27	25	2	7	3	37	18	29
3	2	4	258	243	11	2	9	4	407	416	12	2	8	3	72	1	72	2	1	1	443	443	16	2	7	3	203	211	17
3	2	4	700	719	8	2	9	4	363	360	14	2	8	3	151	160	22	2	1	1	39	13	27	2	7	3	95	64	38
3	2	4	792	791	7	2	9	4	798	793	11	2	8	3	240	222	15	2	1	1	83	65	57	2	7	3	107	104	34
3	2	4	614	628	8	2	9	4	467	449	11	2	8	3	77	62	77	2	1	1	399	425	11	2	7	3	641	639	11
3	2	4	545	547	8	2	9	4	128	123	27	2	8	3	340	333	12	2	1	1	392	394	11	2	7	3	345	352	14
3	2	4	302	299	11	2	9	4	45	31	32	2	8	3	459	481	10	2	1	1	775	793	9	2	7	3	129	128	31
3	2	4	299	304	12	2	9	4	661	638	10	2	8	3	161	175	18	2	1	1	474	459	9	2	7	3	155	147	22
3	2	4	569	580	10	2	9	4	375	349	12	2	8	3	137	138	20	2	1	1	413	419	9	2	7	3	36	51	38
3	2	4	346	331	13	2	9	4	435	425	11	2	8	3	158	170	18	2	1	1	120	1	22	2	7	3	681	686	10
3	2	4	397	422	13	2	9	4	90	8	48	2	8	3	219	221	14	2	1	1	458	448	9	2	7	3	58	104	38
3	2	4	793	781	10	2	9	4	194	206	20	2	8	3	655	649	9	2	1	1	443	433	9	2	7	3	348	351	12
3	2	4	648	674	9	2	9	4	338	341	14	2	8	3	301	300	12	2	1	1	817	842	9	2	7	3	84	139	40
3	2	4	987	971	9	2	9	4	178	150	15	2	8	3	627	648	9	2	1	1	238	231	14	2	7	3	273	263	17
3	2	4	405	402	9	2	9	4	40	37	40	2	8	3	119	75	27	2	1	1	425	446	10	2	7	3	118	111	38
3	2	4	74	68	37	2	9	4	218	209	17	2	8	3	361	380	12	2	1	1	467	440	11	2	7	3	561	556	11
3	2	4	145	133	13	2	9	4	144	96	27	2	8	3	101	14	37	2	1	1	312	292	14	2	7	3	445	470	12
3	2	4	708	698	8	2	9	4	406	414	13	2	8	3	153	130	19	2	1	1	146	160	22	2	7	3	542	555	9
3	2	4	556	576	8	2	9	4	94	133	51	2	8	3	367	378	11	2	1	1	209	212	15	2	7	3	344	349	13
3	2	4	726	728	8	2	9	4	266	263	16	2	8	3	713	711	9	2	1	1	825	849	9	2	7	3	363	373	13
3	2	4	192	203	15	2	9	4	715	699	8	2	8	3	694	713	8	2	1	1	825	834	9	2	7	3	52	25	62
3	2	4	80	13	44	2	9	4	41	27	41	2	8	3	739	740	6	2	1	1	1066	1074	10	2	7	3	269	274	16
3	2	4	492	513	10	2	9	4	120	126	34	2	8	3	291	293	12	2	1	1	498	490	9	2	7	3	91	58	33
3	2	4	464	475	13	2	9	4	212	236	21	2	8	3	323	328	11	2	1	1	560	565	9	2	7	3	135	144	27
3	2	4	36	21	36	2	9	4	196	189	21	2	8	3	74	103	56	2	1	1	594	595	10	2	7	3	168	137	16
3	2	4	1078	1037	9	2	9	4	481	466	9	2	8	3	505	500	10	2	1	1	474	485	10	2	7	3	443	450	12
3	2	4	375	358	9	2	9	4	83	96	83	2	8	3	608	631	10	2	1	1	218	218	14	2	7	3	350	317	14
3	2	4	931	927	9	2	9	4	308	284	15	2	8	3	133	108	26	2	1	1	742	748	9	2	7	3	117	47	35
3	2	4	732	749	6	2	9	4	146	129	25	2	8	3	442	443	12	2	1	1	77	109	77	2	7	3	434	412	15
3	2	4	34	32	34	2	9	4	591	600	11	2	8	3	544	554	10	2	1	1	752	729	11	2	7	3	193	186	15
3	2	4	334	344	9	2	9	4	785	761	11	2	8	3	195	193	16	2	1	1	565	571	11	2	7	3	75	19	75
3	2	4	451	450	9	2	9	4	434	444	13	2	8	3	201	212	15	2	1	1	385	396	11	2	7	3	394	392	12
3	2	4	1154	1183	11	2	9	4	144	118	21	2	8	3	165	162	16	2	1	1	34	34	34	2	7	3	73	119	47
3	2	4	772	792	9	2	9	4	94	39	48	2	8	3	761	770	8	2	1	1	355	344	10	2	7	3	113	84	33
3	2	4	101	91	34	2	9	4	347	311	13	2	8	3	609	618	6	2	1	1	593	602	9	2	7	3	40	1	40
3	2	4	811	806	11	2	9	4	312	300	14	2	8	3	1037	1065	10	2	1	1	763	748	9	2	7	3	251	265	16
3	2	4	604	582	10	2	9	4	41	58	41	2	8	3	111	98	26	2	1	1	876	889	9	2	7	3	602	599	10
3	2	4	352	332	10	2	9	4	40	9	40	2	8	3	487	507	10	2	1	1	81	52	45	2	7	3	129	138	18
3	2	4	201	184	14	2	9	4	416	397	12	2	8	3	89	63	37	2	1	1	375	346	11	2	7	3	240	262	16
3	2	4	1226	1209	10	2	9	4	414	405	8	2	8	3	39	5	38	2	1	1	83	21	42	2	7	3	82	20	57
3	2	4	1145	1149	15	2	9	4	375	378	12	2	8	3	921	925	10	2	1	1	38	54	38	2	7	3	318	308	14
3	2	4	914	924	9	2	9	4	108	79	34	2	8	3	113	118	34	2	1	1	118	70	59	2	7	3	93	82	43
3	2	4	34	45	34	2	9	4	39	21	39	2	8	3	808	813	10	2	1	1	331	315	13	2	7	3	144	137	23
3	2	4	115	140	25																								

Si(2) angle is 150.3° which compares favourably with the mean value of 148.2° given for a number of phases containing $[\text{Si}_2\text{O}_7]$ groups (Liebau, 1985).

Refinement of site occupancies [Si(1) 99(1)%; Si(2) 102(1)%], average Si-O bond distances (Table 26), bond valence summations (Table 27) and results of electron microprobe analyses, all combine to suggest that Si is ideally ordered in the structure.

The tetrahedrally-coordinated (P,S) site is slightly distorted with two longer oxygen bonds and two shorter bonds (Table 26). The average (P,S)-O bond distance ($1.487 \text{ \AA}$) is significantly smaller than the average P-O distance of $1.53 \text{ \AA}$ (Corbridge, 1978), but close to the average S^{6+} -O distance of $1.49 \text{ \AA}$ (Ondik and Smith, 1968). The fact that substitutions occur in the site is also supported by calculated bond valence sums. Using the constants of Brese and O'Keefe (1991) and assuming the site to be completely occupied by P gives a site valence of 5.493 v.u., or 5.797 v.u. for S^{6+} . Considering results from the electron microprobe analyses which show a $\text{P}:\text{S}^{6+}:\text{Si}$ ratio of approximately 5:4:1, the valence sum for the site is 5.645 v.u. (Table 27). Assuming the site to be occupied only by P, the occupancy of the site refined to 88(1)%. Combining this with the observed bond distances, electron microprobe analyses and the calculated bond valence sum, suggests that the site is occupied by both P and S^{6+} . The $(\text{P,S})\text{O}_4$ tetrahedra do not share corners with either of the SiO_4 tetrahedra.

The (Ti,Fe) site is coordinated by five non-equivalent oxygen atoms in a tetragonal pyramid. Bond distances to the four O atoms which form a planar base

are quite regular (1.952-1.968 Å; mean = 1.961 Å) and consistent with the average Ti-O distance in rutile (1.958 Å; Meagher and Lager, 1979), while that to the apical O atom is considerably shortened (1.772 Å). Although unusual, this type of TiO_5 coordination polyhedron has been recognized in the minerals innelite (which contains two such polyhedra; Chernov *et al.*, 1971), lamprophyllite (Saf'yanov *et al.*, 1983) and fresnoite (Moore & Louisnathan, 1969; Fig. 23). The average $\text{Ti-O}_{\text{basal}}$ distances of innelite (2.03, 1.98 Å), lamprophyllite (1.96 Å) and fresnoite (2.00 Å) are comparable to that in yoshimuraite, but the $\text{Ti-O}_{\text{apical}}$ distance in yoshimuraite is considerably longer than those in innelite (1.62, 1.71 Å), lamprophyllite (1.68 Å) and fresnoite (1.63 Å). Zemmann (1963) in considering tetragonal pyramidal coordination polyhedra for transition metals using a point-charge model, calculated the $\text{O}_{\text{apical}}\text{-M-O}_{\text{basal}}$ angle to be 104.07° . This predicted angle is slightly larger than that in yoshimuraite (103.4°), innelite (105.8 and 102.2°) and lamprophyllite (104.1°), but considerably smaller than that in fresnoite (107.7°).

Three crystallographically-distinct Mn atoms are present in the structure. All are octahedrally-coordinated, with mean Mn-O distances ranging from 2.205 to 2.221 Å (Table 26), close to the average $[\text{Mn}^{2+}\text{-O}]$ distance of 2.21 Å given by Ondik and Smith (1968) and longer than the average Mn-O distance in pyrolusite (1.8868 Å; Baur, 1976).

Bond valence sums confirm that all the Mn atoms are divalent (Table 27) and indicate that the O(11) atom probably represents an hydroxyl group. The

Fig. 23. Comparison of the TiO_5 tetragonal pyramids in: (a) yoshimuraite; (b) innelite; (c) innelite; (d) lamprophyllite and (e) fresnoite. Distances are in Å. Average $\text{O}_{\text{apical}}\text{-Ti-O}_{\text{basal}}$ angles (°) are indicated.

O(11) atom is shared among all three Mn octahedra, but not with any other polyhedra in the structure.

The Ba atoms occupy two non-equivalent positions and are both eleven-coordinated (Figs. 24, 25). The Ba-O distances range from 2.645 to 3.184 Å for Ba(1)O₁₁ and 2.639 to 3.007 Å for Ba(2)O₁₁. Except for four long Ba(1)-O bonds, they are reasonably close to the range of 2.68-3.09(6) Å given for ten-coordinated Ba (Ondik and Smith, 1968). The mean Ba-O distances in yoshimuraite [Ba(1)-O = 2.934 Å; Ba(2)-O = 2.865 Å] are comparable to the those of the BaO₁₁ polyhedra in innelite (2.86 and 2.88 Å; Chernov *et al.*, 1971) and close to that of the BaO₁₂ polyhedron in barite (2.952 Å; Hill, 1977).

The structure of yoshimuraite consists of three distinct layers which are stacked along *c*: 1) a close-packed Mn octahedral layer; 2) a [Ti(Si₂O₇)] layer and 3) a [Ba₂(PO₄)] layer (Fig. 26).

The octahedral layer contains edge-sharing Mn octahedra which are linked into straight chains running parallel to *b*. Two different chains are present in the layer: a Mn(1)/Mn(3) octahedral chain and a Mn(2) octahedral chain (Fig. 27). Linking of the two octahedral chains occurs across *a*, *via* shared edges, resulting in the formation of closest-packed octahedral sheets, which resemble those found in brucite. These linkages are unlike those found in pyrolusite, where trioctahedral chains are joined laterally through shared corners (Baur, 1976).

The Mn octahedral layer is "sandwiched" between two [Ti(Si₂O₇)] layers along *c*, forming a composite layer that is reminiscent of those in octahedral micas

Fig. 24. The Ba(1)O₁₁ polyhedron in yoshimuraite. Distances are in Å.

Fig. 25. The Ba(2)O₁₁ polyhedron in yoshimuraite. Distances are in Å.

Fig. 26. The structure of yoshimuraite projected on the bc plane. The Ba(1) atoms are empty, the Ba(2) atoms are stippled, the MnO_6 octahedra are lightly-shaded, the TiO_5 tetragonal pyramids are moderately-shaded, the PO_4 tetrahedra are heavily-shaded and the SiO_4 tetrahedra are very heavily-shaded. The unit cell is outlined.

Fig. 27. The octahedral layer in yoshimuraite, projected on the *ab* plane. The $\text{Mn}(1)\text{O}_6$ octahedra are lightly-shaded, the $\text{Mn}(2)\text{O}_6$ octahedra are moderately-shaded and the $\text{Mn}(3)\text{O}_6$ octahedra are heavily-shaded.

(Fig. 26). The $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers are composed of TiO_5 polyhedra, cross-linked by Si_2O_7 clusters (Fig. 28). Linking of the polyhedral layer to the octahedral layer in yoshimuraite occurs through three different corner-sharing bonds (Fig. 29): 1) SiO_4 tetrahedra with the Mn(1) and Mn(3) octahedra; 2) SiO_4 tetrahedra with the Mn(1) and Mn(2) octahedra and 3) TiO_5 tetragonal pyramids, which are joined to all three Mn octahedra through the shared O(9) atom. The apices of the SiO_4 tetrahedra tilt slightly away from one another as a result of accommodating the octahedral layer.

The $[\text{Ba}_2(\text{PO}_4)]$ layer is situated between the composite layers (Fig. 26). It is composed of a layer of PO_4 tetrahedra linked to a layer of BaO_{11} polyhedra on either side. The $[\text{Ba}_2(\text{PO}_4)]$ layer is very similar to a portion of the barite structure, in which layers of SO_4 tetrahedra alternate with layers of BaO_{12} polyhedra (Hill, 1977). The Ba(1) atoms in yoshimuraite lie in the centres of six-sided holes formed by two Si_2O_7 groups and two TiO_5 tetragonal pyramids, whereas the Ba(2) atoms lie in the centres of four-sided holes formed by two SiO_4 tetrahedra and two TiO_5 tetragonal pyramids (Fig. 28). The two BaO_{11} polyhedra are joined along *c* by edge- and face-sharing with the PO_4 tetrahedra. The perfect {001} cleavage in yoshimuraite probably results from the breaking of bonds between this unit and the $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers.

5.5 RELATED STRUCTURES

Yoshimuraite is chemically and structurally-related to a number of

Fig. 28. Projection of the yoshimuraite structure on the ab plane showing the $[\text{Ti}(\text{Si}_2\text{O}_7)]$ polyhedral layer and the positioning of the Ba atoms. The TiO_5 tetragonal pyramids are moderately-shaded, the SiO_4 tetrahedra are heavily-shaded, the Ba(1) atoms are empty and the Ba(2) atoms are stippled. The unit cell is outlined.

Fig. 29. The yoshimuraite structure showing bonding between the MnO_6 octahedral layer and the $[\text{Ti}(\text{Si}_2\text{O}_7)]$ polyhedral layer. The $\text{Mn}(1)\text{O}_6$ octahedra are stippled, the $\text{Mn}(2)\text{O}_6$ octahedra are lightly-shaded, the $\text{Mn}(3)\text{O}_6$ octahedra are moderately-shaded, the TiO_5 tetragonal pyramids are heavily-shaded and the SiO_4 tetrahedra are very heavily-shaded.

titanosilicate minerals, including innelite, lamprophyllite, bafertisite and lomonosovite. These minerals all have comparable cell dimensions (Table 29) and their crystal structures, which exhibit a pronounced layering, contain distinctive structural units composed of closest-packed octahedral layers sandwiched on two sides by $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers. Differences between yoshimuraite and the minerals listed in Table 29 may be described in terms of the composition of the octahedral layer, coordination of Ti^{4+} in the $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layer and the cations or anionic groups that occupy the interlayer space.

There are strong chemical and structural similarities between yoshimuraite and innelite. Its crystal structure, solved in space group $P1$ and refined to an unweighted R value of 11.9% (Chernov *et al.*, 1971), is analogous to that of yoshimuraite. There are, however, two significant chemical differences between the two. First, the octahedral layer in innelite is occupied by Na, Ti and M octahedra [the M site possessing a mixed (Ca,Mg,Fe) composition]. The average Na- and M -O bond distances (mean Na-O = 2.36 Å; mean M -O = 2.36 Å) are slightly larger than the Mn-O bonds in yoshimuraite, possibly resulting in a longer b axis. Due to the nature of the mixed octahedral layer in innelite, together with a large variation in O bond distances (mean Ti-O = 2.01 Å, together with this listed above), the Si-O_{bridging}-Si angles are 132.6° and 139.6°, significantly smaller than that in yoshimuraite (150.4°). Secondly, the minerals also differ in terms of the tetrahedral component of the layers containing Ba. In innelite, this component is believed to be predominantly SO_4 , although the average SO_4

TABLE 29. CELL PARAMETERS OF YOSHIMURAITE AND RELATED MINERALS.

MINERAL	SPACE GROUP	Z	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	LAYERIN G
YOSHIMURAITE ¹ $\text{Ba}_2\text{Mn}_2(\text{Ti,Fe})\text{O}(\text{Si}_2\text{O}_7)[(\text{P,S})\text{O}_4](\text{OH})$	$P\bar{1}$	2	5.386	6.999	14.748	95.50	93.62	89.98	(001)
INNELITE ² $\text{Ba}_3(\text{Ba,K,Mn})\text{Na}_2(\text{Ca,Na})\text{Ti}(\text{TiO}_2)_2(\text{Si}_2\text{O}_7)_2(\text{SO}_4)_2$	$P1$	1	14.76	7.14	5.38	90	95	99	(100)
LAMPROPHYLLITE ³ $\text{Sr}_2(\text{Na,Ca})(\text{Na,Ca,Mn})_2(\text{Ti,Fe}^{3+})(\text{TiO})_2(\text{Si}_2\text{O}_7)(\text{O,OH,F})_2$	$C2/m$	2	19.431	7.086	5.392		96.75		(100)
BAFERTISITE ⁴ $\text{BaFe}_2^*\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH})_2$	Cm	2	10.60	13.64	12.47		119.5		(001)
LOMONOSOVITE ⁵ $\text{Na}_3\text{Ti}_2(\text{Si}_2\text{O}_7)(\text{PO}_4)\text{O}_2$	$P\bar{1}$	2	5.49	7.11	14.50	101	96	90	(001)

1. This study; refined from four-circled diffractometer data.
2. Chernov *et al.*, 1971.
3. Saf'yanov *et al.*, 1983.
4. Kuan *et al.*, 1963.
5. Belov *et al.*, 1977.

distances (1.52, 1.50 Å) are slightly longer than average (1.49 Å; Ondik and Smith, 1968), and longer than that in yoshimuraite (1.489 Å), in which P dominates the site.

Lamprophyllite is monoclinic (space group $C2/m$) and its crystal structure was refined to $R = 8.7\%$ by Saf'yanov *et al.* (1983). The topology of the $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layer is identical to that of yoshimuraite, including the presence of TiO_5 tetragonal pyramids, with layering occurring parallel to (100). The two minerals chemically-differ in terms of the occupants of the octahedral layer. In lamprophyllite, there are two different octahedral layers: one composed of Na and Ti octahedra, the other containing only M octahedra (M being predominantly Na, with lesser amounts of Mn, Ca and Fe). The presence of the additional octahedral layer in lamprophyllite results in an increase in c by $1/3$ compared to yoshimuraite. The $\text{Si-O}_{\text{bridging}}\text{-Si}$ angle (135.6°) is much smaller in lamprophyllite than in yoshimuraite, probably because of the large variation in the average bonding distances to O (range = 1.99 - 2.43 Å) for the octahedral constituents. Tetrahedrally-coordinated cations are absent from the "interlayer" space of lamprophyllite and although the Sr atoms within this layer are eleven-coordinated, their coordination polyhedra (which may be described as having six meridional oxygens with a quadrangular base and a single apical oxygen; Saf'yanov *et al.*, 1983) are unlike those of Ba in yoshimuraite.

The crystal structure of bafertisite was determined by Kuan *et al.* (1963) who verified that the mineral was monoclinic, crystallizing in space group Cm (Fig.

Fig. 30. The structure of bafertsite projected on the *ac* plane. The Ba atoms are stippled circles, the Fe octahedra are lightly-shaded, the Ti octahedra are moderately-shaded and the SiO_4 tetrahedra are very heavily-shaded (after Kuan *et al.*, 1963).

30). The structural relationship between the two minerals may be expressed as $2a_{\text{yosh}} \approx a_{\text{bafert}}$, $2b_{\text{yosh}} \approx b_{\text{bafert}}$ and $c_{\text{yosh}} \approx c_{\text{bafert}}$. The octahedral layer in the mineral is occupied by Fe^{2+} , comparable to the Mn^{2+} cations which compose the octahedral layer in yoshimuraite. The $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers are different in the two minerals. In bafertisite, Ti^{4+} is octahedrally-coordinated, in contrast with the five-coordinated Ti^{4+} in yoshimuraite. The additional apical oxygen coordinating Ti^{4+} in bafertisite penetrates considerably into the "interlayer space", resulting in the mineral having a poorer $\{001\}$ cleavage than is observed in yoshimuraite or micas (Povaranhykh, 1972). The occupants of the interlayer space in bafertisite are eight-, nine- and twelve-coordinated Na atoms, unlike the eleven-coordinated Ba atoms in yoshimuraite.

The crystal structure of lomonosovite (Fig. 31) was refined to $R = 14\%$ in the space group $P\bar{1}$ (Belov *et al.*, 1977). The octahedral layer contains both Na and Ti octahedra. The $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layer in lomonosovite is slightly different than that in yoshimuraite, as it includes Ti octahedra and NaO_8 polyhedra in addition to the SiO_4 tetrahedra. The interlayer in lomonosovite is also unique since it contains Na polyhedra in addition to PO_4 tetrahedra. These polyhedra are linked through shared edges to form a $[\text{Na}_3(\text{PO}_4)]$ unit and are corner-linked to the Ti octahedra. However, the $[\text{Na}_3(\text{PO}_4)]$ unit is quite easily removed from the structure and the mineral becomes readily hydrated (Belov *et al.*, 1977). In yoshimuraite, the $[\text{Ba}_2(\text{PO}_4)]$ layer is more tightly bonded between $[\text{Ti}(\text{Si}_2\text{O}_7)]$ layers, therefore it is not readily lost and the mineral is apparently more stable.

Fig. 31. The structure of lomonosovite projected down on the bc plane. The Na atoms are empty circles, the NaO_8 polyhedra are lightly-shaded, the PO_4 tetrahedra are moderately shaded, the TiO_6 octahedra are heavily-shaded and the SiO_4 tetrahedra are very heavily-shaded (after Belov *et al.*, 1977).

CHAPTER 6

SYSTEMATIC MINERALOGY

6.1 Systematics of the silicophosphate minerals

Minerals which contain significant quantities of both Si and P have often been loosely regarded as silicophosphates (Ronsbo, 1989; Sokolova *et al.*, 1987a; Moore, 1980; Yes'kova *et al.*, 1975). An analysis of these minerals reveals that they all fall into one of two distinct groups: (1) those containing highly disordered Si and P, with variable Si:P ratios and (2) those that contain well-ordered Si and P and have essentially constant Si:P ratios.

Minerals belonging to group (1) are typically members of solid-solutions or partial substitution series. Their crystal structures are characterized by having either isolated SiO_4 or PO_4 tetrahedra and since Si and P substitute for one another, they must be disordered. Group (1) minerals are perhaps best exemplified by cheralite, huttonite and brabantite of the monazite group and apatite-britholite series. For example, the coupled substitution, $\text{Ca}^{2+} + \text{P}^{5+} \leftrightarrow \text{REE}^{3+} + \text{Si}^{4+}$, occurs extensively in fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] and britholite-(Ce) [$\text{REE}_5(\text{SiO}_4)_3(\text{F},\text{OH})$], which are isostructural (space-group $P6_3/m$). Fluorapatite can contain up to 8.17 wt. % SiO_2 (Ronsbo, 1989) and britholite-(Ce) can contain up to 7.27 wt. % P_2O_5 (Mandarino and Anderson, 1989). Furthermore, experimental work by Ito (1968) demonstrated that a complete solid-solution exists between synthetic phases with the compositions

$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (hydroxyapatite) and $\text{Y}_3\text{Ca}_2(\text{SiO}_4)_3(\text{OH})$ (britholite). Such minerals should be classified according to the dominant anionic group present (*i.e.* silicates or phosphates), following the nomenclature proposed by Nickel (1992) for minerals belonging to solid-solution series. Therefore, in the apatite-britholite series, those members with $\text{Si} > \text{P}$ must be referred to as britholite, and be classified as silicates, and those with $\text{P} > \text{Si}$ would be called fluorapatite, and be classified as phosphates.

In this study, the term silicophosphate is applied only to those minerals which belong to Group (2) listed above (*i.e.* they contain well-ordered Si and P). Surprisingly, there are only thirteen minerals which are considered as silicophosphates. In order to compare the crystal-chemistry of these minerals, the space-groups and cell parameters of these minerals are tabulated in Table 30, their chemical compositions in Table 31 and their optical and physical properties in Table 32. Furthermore, descriptions of the occurrences, associated minerals and the crystal structures of those silicophosphate minerals not already described [*i.e.* abenakiite-(Ce), lomonosovite, phosinaite-(Ce), yoshimuraite], are presented below.

ATTAKOLITE

Attakolite, $(\text{Ca},\text{Sr})\text{Mn}(\text{Al},\text{Fe}^{3+})_4(\text{HSiO}_4)(\text{PO}_4)_3(\text{OH})_4$, was originally discovered as a large mass (8.5 kg) of highly pure material at the Vastana mine (iron), near Nasium, Kristiansted, Sweden. Here, it is associated with berlinite,

TABLE 30. KNOWN SILICOPHOSPHATE MINERALS.

MINERAL NAME	SPACE-GROUP	Z	a(Å)	b	c	$\alpha(^{\circ})$	β	γ	$V(\text{\AA}^3)$
ABENAKITE-(Ce) ¹ $\text{Na}_{28}\text{REE}(\text{SiO}_3)_6(\text{PO}_4)_6(\text{CO}_3)_6(\text{SO}_2)_2\text{O}$	$R\bar{3}$	3	16.025		19.773				4397.4
ATTAKOLITE ² $(\text{Ca},\text{Sr})\text{Mn}(\text{Al},\text{Fe}^{3+})_4(\text{HSiO}_4)(\text{PO}_4)_3(\text{OH})_4$	$C2/m$	4	17.188	11.477	7.322		113.83		1321.2
BORNEMANITE ³ $\text{BaNa}_2\text{Ti}_2\text{NbSi}_4\text{O}_{17}(\text{F},\text{OH})\text{Na}_3\text{PO}_4$	$Ibmm$ or $Ibm2$	4	5.48	7.10	48.2				1875.4
CLINOPHOSINATE ⁴ $\text{Na}_3\text{Ca}(\text{SiO}_3)(\text{PO}_4)$	$P2_1c$	8	7.303	12.201	14.715		91.93		1310.4
HARRISONITE ⁵ $\text{CaFe}_2^{2+}(\text{SiO}_4)_2(\text{PO}_4)_2$	$R\bar{3}m$	3	6.248		26.802				906.1
LOMONOSOVITE ⁶ $\text{Na}_3\text{Ti}_2\text{O}_2(\text{Si}_2\text{O}_7)(\text{PO}_4)$	$P\bar{1}$	2	5.49	7.11	14.50	101	96	90	579.2
PHOSINATE-(Ce) ¹ $\text{Na}_{13}\text{Ca}_2\text{REE}(\text{SiO}_3)_4(\text{PO}_4)_4$	$P2_2,2_1$	2	12.297	14.660	7.245				1306.1
POLYPHITE ⁷ $\text{Na}_{17}\text{Ca}_3\text{Mg}(\text{Ti},\text{Mn})_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_6\text{O}_2\text{F}_6$	$P1$	1	5.412	7.079	26.56	95.21	93.51	90.10	101.4
QUADRUPHITE ⁸ $\text{Na}_4\text{CaMgTi}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_4\text{O}_4\text{F}_2$	$P1$	1	5.415	7.081	20.34	86.85	94.40	89.94	776.4
SOBOLEVITE ⁹ $\text{Na}_4(\text{Na},\text{Ca})_2\text{Ti}_3\text{Mn}(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_4\text{O}_3\text{F}_3$	$P1$	2	7.078	5.4115	40.618	90.01	93.19	90.00	1553.5

TABLE 30. (continued).

MINERAL NAME	SPACE-GROUP	Z	a(Å)	b	c	$\alpha(^{\circ})$	β	γ	$V(\text{\AA}^3)$
STEENSTRUPINE-(Ce) ¹⁰ $\text{Na}_{14}\text{REE}_8\text{Mn}^{3+}\text{Mn}^{2+}\text{Fe}_2^{3+}\text{Zr}(\text{Si}_6\text{O}_{18})(\text{PO}_4)_7(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	$R\bar{3}m$	3	10.460		45.479				4309.3
VUONNEMITE ¹¹ $\text{Na}_3\text{Ti}^{3+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2\text{F}_2\text{O}_2 \cdot 2\text{Na}_3\text{PO}_4$	$P\bar{1}$	1	5.4984	7.161	14.450	92.60	95.30	90.60	565.9
YOSHIMURATE ¹ $\text{Ba}_2\text{Mn}_2(\text{Ti},\text{Fe}^{3+})\text{O}(\text{Si}_2\text{O}_7)[(\text{P},\text{S})\text{O}_4](\text{OH})$	$P\bar{1}$	2	5.386	6.999	14.748	95.50	93.62	89.98	552.3

1. This study.

4. Krutik *et al.* (1980).7. Sokolova *et al.* (1987a).10. Sokolova *et al.* (1988)

2. Grice and Dunn (1993).

5. Grice and Roberts (1993).

8. Sokolova *et al.* (1988)

11. Ercit and Hawthorne (1990).

3. Mensikov *et al.* (1975).6. Belov *et al.* (1977).

9. Moore and Shen (1983).

TABLE 31. CHEMICAL COMPOSITIONS OF KNOWN
SILICOPHOSPHATE MINERALS

	1	2	3	4	5	6	7	8	9
SiO ₂ wt. %	13.30	7.9	25.00	20.10	15.99	25.07	18.21	13.2	16.5
P ₂ O ₅	14.11	31.9	6.80	25.50	19.18	12.31	23.69	23.3	19.2
Al ₂ O ₃		26.7					0.15		
SO ₃	2.28								
Na ₂ O	25.32		20.00	32.70		25.51	31.68	28.0	28.1
K ₂ O			0.67	0.05		0.17			
CaO		7.8	0.77	16.45	7.65	1.84	8.92	8.3	5.3
MnO		10.5	2.48	0.54	0.11	1.73	0.89	5.6	4.3
FeO					52.27			0.2	0.3
SrO	0.12	1.1	0.68	1.91					
MgO			0.06		3.89	0.19		1.3	1.1
TiO ₂			18.00			21.83		12.0	13.7
Nb ₂ O ₅			8.86			4.61		2.7	3.8
ZrO ₂			0.25			1.97		1.6	4.1
Fe ₂ O ₃		2.6	0.30			2.16			
Ce ₂ O ₃	15.31			0.44			6.52		
La ₂ O ₃	5.94						4.18		
Nd ₂ O ₃	7.78						0.99		
Pr ₂ O ₃	2.02						0.26		
Sm ₂ O ₃	0.74								
ThO ₂	1.42						1.84		
BaO			13.00						
CO ₂	(8.90)								
H ₂ O		11.5	0.70			1.96			
F			1.64			0.17		5.1	3.4
Cl						0.07			
Less O=F+Cl			0.69			0.09		2.1	1.4
SUM	97.24	100	98.52	97.69	99.09	99.50	97.33	99.2	98.4

TABLE 31. (continued).

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	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>
SiO ₂ wt. %	17.1	27.52	22.32	17.00
P ₂ O ₅	19.9	11.19	13.24	4.21
Al ₂ O ₃		0.12	0.18	
SO ₃				3.71
Na ₂ O	29.7	3.62	30.26	
CaO	6.4	2.00	0.94	
MnO	4.0	2.40	0.97	15.15
FeO			0.19	5.19
SrO				3.01
MgO	0.6			0.18
TiO ₂	15.2	0.26	9.64	8.12
Nb ₂ O ₅	4.4		20.51	
ZrO ₂		1.73	0.01	
Fe ₂ O ₃	0.6	4.62		2.27
Mn ₂ O ₃		2.19		
Ce ₂ O ₃		33.86		
ThO ₂		4.83		
BaO				39.08
H ₂ O		(5.37)		(1.17)
F	0.7	0.29	1.45	
Cl			0.04	
Less				
O=F+Cl	0.3		0.62	
SUM	98.3	100	99.13	99.09

Note: * = by difference; () by stoichiometry.

1. abenakiite-(Ce); this study.
2. attakolite; Grice and Dunn (1992).
3. bornemanite; Men'shikov *et al.* (1975).
4. clinophosinaite; Khomyakov *et al.* (1981).
5. harrisonite; Roberts *et al.* (1993).
6. lomonosovite; Khomyakov (1990).
7. phosinaite-(Ce); this study.
8. polyphite; Sokolova *et al.* (1987b).
9. quadruphite; Sokolova *et al.* (1987a).
10. sobolevite; Sokolova *et al.* (1988).
11. steenstrupine-(Ce); Moore and Shen (1983).
12. vuonnemite; Mandarino and Anderson (1989).
13. yoshimuraite; this study.

TABLE 32. OPTICAL AND PHYSICAL PROPERTIES OF KNOWN SILICOPHOSPHATE MINERALS.

MINERAL	OPTIC SIGN	α (or ϵ)	β (or ω)	γ	$2V_{\text{meas}}(^{\circ})$	$2V_{\text{calc}}(^{\circ})$	DISPERSION
ABENAKITE-(Ce) ¹	(-)	1.586	1.589				
ATTAKOLITE ²	(+)	1.650	1.654	1.661	75	74	$r > v$, strong
BORNEMANITE ³	(+)	1.683	1.687	1.718	40	66	n.a.
CLINOPHOSINAITE ⁴	(+)	1.556	1.560	1.565	78	84	n.a.
HARRISONITE ⁵	(-)	1.759	1.770				
LOMONOSOVITE ⁶	(-)	1.681	1.748	1.771	55	59	n.a.
PHOSINAITE-(Ce) ¹	(+)	1.568	1.568	1.572	0	n.a.	n.a.
POLYPHITE ⁷	(-)	1.600	1.658	1.676	56	57	$r < v$, strong
QUADRUPHITE ⁷	(-)	1.630	1.678	1.697	62	63	$r < v$, strong
SOBOLEVITE ⁸	(-)	1.627	1.686	1.690	25	28	$r < v$, strong
STEENSTRUPINE-(Ce) ⁹	(-)	1.663	1.665				
VUONNEMITE ¹⁰	(+)	1.639	1.651	1.681	53	66	n.a.
YOSHIMURAITE ¹¹	(+)	1.763	1.777	1.785	88	84	$r > v$

TABLE 32. (continued).

MINERAL	ORIENTATION	PLEOCHROISM	CLEAVAGE	$D_{\text{meas}} (\text{g/cm}^3)$	$D_{\text{calc}} (\text{g/cm}^3)$
ABENAKITE-(Ce) ¹		none	{001}, poor	3.21	3.27
ATTAKOLITE ²	$Y=b, Z=c,$ $Xa=32^\circ$	none	none observed	3.23	3.34
BORNEMANITE ³	$Z=a, Y=b, X=c$	X, Y = colourless Z = brownish	{001}, perfect	n.a.	3.49
CLINOPHOSINAITE ⁴	n.a.	n.a.	n.a.	2.86	2.86
HARRISONITE ⁵		very slight pale yellows	very poor	4.02	4.03
LOMONOSOVITE ⁶	$P(001)\wedge X=39^\circ$ $P(001)\wedge Y=62^\circ$ $P(001)\wedge Z=64^\circ$	light cinnamon with a rose tinge to a cinnamon yellow	{001}, perfect	3.15	3.04
PHOSINAITE-(Ce) ¹	$X=b, Y=c, Z=a$	none	{001}, perfect {110}, distinct {010}, good	2.97	3.09
POLYPHITE ⁷	$P(001)\wedge X=30^\circ$ $P(001)\wedge Y=64^\circ$ $P(001)\wedge Z=70^\circ$	X = colourless Y, Z = yellow	{001}, perfect {110}, medium {110}, medium	3.11	2.89
QUADRUPHITE ⁷	$P(001)\wedge X=28^\circ$ $P(001)\wedge Y=71^\circ$ $P(001)\wedge Z=70^\circ$	X = nearly colourless Y, Z = yellowish-brown	{001}, perfect {110}, medium {110}, medium	3.12	3.14
SOBOLEVITE ⁸	$Xa=32^\circ$	n.a.	{001}, perfect {110}, distinct	3.00	3.03

TABLE 32. (continued).

MINERAL	ORIENTATION	PLEOCHROISM	CLEAVAGE	D _{meas} (g/cm ³)	D _{calc} (g/cm ³)
STEENSTRUPINE-(Ce) ⁹		n.a.	none	3.35	3.631
VUONNEMITE ¹⁰	$\gamma \quad c=4^\circ$	n.a.	{001}, very perfect two other perfect cleavages	3.13	3.13
YOSHIMURITE ¹¹	$\alpha' \approx \parallel a$ $\gamma' \approx \parallel c$	$X = \text{bright yellow}$ $Y = \text{orange-brown}$ $Z = \text{brown}$	{001}, perfect {110}, distinct {110}, distinct	4.13	4.21

Note: n.a. = not available.

1. This study.
2. Grice and Dunn (1992).
3. Men'shikov *et al.* (1975).
4. Khomyakov *et al.* (1981).
5. Roberts *et al.* (1993).
6. Khomyakov (1990).
7. Mandarino (1991).
8. Khomyakov *et al.* (1983).
9. Vlasov (1966).
10. Bussen *et al.* (1973).
11. Watanabe *et al.* (1961).

quartz, an apatite-group mineral and lazulite (Gabrielson and Geijer, 1965).

The mineral is monoclinic, crystallizing in space group $C2/m$. Electron microprobe analyses (Table 31) give the average chemical formula

(based on O=20). Structure analysis showed that Si is ordered into one specific site, although chemical analyses indicate that there is some Si-P substitution in this site.

The attakolite structure (Grice and Dunn, 1992) contains chains composed of edge-sharing $[\text{AlO}_4(\text{OH})_2]$ octahedra (Fig. 32). These chains are cross-linked by isolated $[\text{HSiO}_4]$ groups and PO_4 tetrahedra to form sheets which are stacked along *b*. Interstices within the sheets are occupied by Mn^{2+} in seven-fold coordination and Ca in ten-fold coordination.

BORNEMANITE.

Bornemanite is known from the nepheline and sodalite syenites of the Khibina and Lovozero massifs, C.I.S., where it is found as yellow platy aggregates on cleavages and crystal surfaces of lomonosovite and within natrolite.

Based on electron microprobe (Table 34) and differential thermal analyses, the ideal chemical formula $\text{BaNa}_4\text{Ti}_2\text{NbSi}_4\text{O}_{17}(\text{F},\text{OH})\cdot\text{Na}_3\text{PO}_4$ has been assigned to the mineral. However, as noted by the Men'shikov *et al.* (1975), this formula is only tentative and cannot be confirmed until its crystal structure has been

Fig. 32. The crystal structure of attakolite, projected on the *ab* plane. The empty circles are Ca, the filled circles are Mn, the SiO_4 tetrahedra are stippled, the PO_4 tetrahedra are lightly-shaded and the $\text{AlO}_4(\text{OH})_2$ octahedra are heavily-shaded. (from Grice and Dunn, 1992).

determined.

Bornemanite may be related to lomonosovite and the lomonosovite-like minerals (*e.g.* polyphite, quadruphite *etc.*), based on the similarity of their chemical compositions, unit cell parameters and optical properties (Tables 31, 32, 33).

A specimen of bornemanite from the Khibina massif (CU 4798) was analyzed in this study. However, the mineral was found to be complexly intergrown with lomonosovite and/or other unidentified phases, so no single crystals suitable for X-ray diffraction studies could be separated out.

HARRISONITE

Harrisonite, $\text{CaFe}_6^{2+}(\text{SiO}_4)_2(\text{PO}_4)_2$, is a new mineral recently discovered at Arcedeckne Island, Boothia Peninsula in Arctic Canada (Roberts *et al.*, 1993). The mineral occurs as both discrete grains and as rims around fluorapatite in a granulite facies rock. Associated minerals include quartz, almandine, ferrosilite, fayalite and others. Electron microprobe analyses (Table 31) give the empirical formula,

(based on O=16). This chemical formula indicates a high degree of Si-P ordering, which has been confirmed by structure analysis.

The harrisonite crystal structure is strongly layered, consisting of two FeO_6 layers, a SiO_4 layer and a $[\text{Ca}(\text{PO}_4)_2]$ slab (Fig. 33; Grice and Roberts, 1993). Iron is six-coordinated by O in a trigonal prism. These polyhedra are joined

Fig. 33. The crystal structure of harrisonite: (a) the $[\text{Ca}(\text{PO}_4)_2]$ layer composed of CaO_6 trigonal antiprisms connected by PO_4 tetrahedra; (b) the FeO_6 layer with SiO_4 tetrahedra capping the top of the holes in this layer (from Grice and Roberts, 1993).

through shared edges into a corundum-like sheet, in which one-quarter of the sites are vacant. The SiO_4 layer is composed of independent tetrahedra that are linked into sheets *via* shared corners with the FeO_6 polyhedra. The SiO_4 groups are positioned above or below the vacancies in the FeO_6 layer, alternating with CaO_6 trigonal antiprisms. The $[\text{Ca}(\text{PO}_4)_2]$ layer consists of PO_4 tetrahedra linked to CaO_6 polyhedra in such a way that adjacent tetrahedra alternately point up and down.

POLYPHITE, QUADRUPHITE AND SOBOLEVITE

Polyphite $[\text{Na}_{17}\text{Ca}_3\text{Mg}(\text{Ti},\text{Mn})_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_6\text{O}_2\text{F}_6]$; Sokolova *et al.*, 1987b], quadruphite $[\text{Na}_{14}\text{CaMgTi}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_4\text{O}_4\text{F}_2]$; Sokolova *et al.*, 1987a] and sobolevite $[\text{Na}_{14}\text{Ca}_2\text{Ti}_3\text{Mn}(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_4\text{O}_3\text{F}_3]$; Sokolova *et al.*, 1988] are relatively new minerals which have all been discovered at Mount Alluaiv in the Lovozero massif, Kola Peninsula, C.I.S. All three minerals develop in epitaxial intergrowths with one another and with lomonosovite. They are associated with a number of Na silicates (lomonosovite, makatite, ussingite, grumantite *etc*) and zircono- and titanosilicates (kazakovite, lorenzenite, lintisite, zirsinalite *etc.*). Despite being chemically and structurally complex, polyphite, quadruphite and sobolevite are all closely-related.

Polyphite, quadruphite and sobolevite are all structurally-related. Their crystal structures (Figs. 34, 35, 36) may be best described in terms of two distinct layers: 1) a lomonosovite-like block, of composition

Fig. 34. The crystal structure of quadruphite (after Sokolova *et al.*, 1987a). The lomonosovite-like and sulfosalite-like blocks are indicated.

Fig. 35. The crystal structure of polyphite (after Sokolova *et al.*, 1987b).

Fig. 36. The crystal structure of sobolevite (after Sokolova *et al.*, 1988).

$\text{Na}_4(\text{Ti,Mn})_4(\text{Si}_2\text{O}_7)_2\text{O}_4 \cdot 2\text{Na}_2(\text{Ca,Mg})(\text{PO}_4)_2$ and 2) a sulfohalite-like block, $(\text{Na,Ca})_6(\text{PO}_4)_2\text{F}_2$. These minerals all exhibit a perfect {001} cleavage, which corresponds well with the pronounced layering of their structures. The lomonosovite-like block consists of a close-packed layer of edge-sharing Na, Ti and Mn octahedra that is sandwiched between $[\text{NaTi}(\text{Si}_2\text{O}_7)]$ slabs. These slabs contain Si_2O_7 groups that are corner-linked to Ti octahedra and NaO_8 polyhedra. Various five- to seven-coordinated Na, Ca and Mg polyhedra share corners with the Ti octahedra and NaO_8 polyhedra. The sulfohalite-like blocks in these minerals are fragments of the sulfohalite structure $[\text{Na}_6(\text{SO}_4)_2(\text{F,Cl})]$. Such blocks are composed of infinite columns of edge-sharing Na, Ca and Mg octahedra (coordinated by one F and five O atoms) that are corner-linked to independent PO_4 tetrahedra.

The quadruphite structure (Fig. 34) contains one sulfohalite-like block, whereas there are two in polyphite (Fig. 35). Since this block has a thickness of $\approx 6 \text{ \AA}$, c increases from $20.3 \text{ \AA}$ in quadruphite to $26.6 \text{ \AA}$ in polyphite. Sobolevite also contains a single sulfohalite-like block (Fig. 36), similar to that in quadruphite. However, the c -axis of sobolevite is doubled, possibly resulting from the PO_4 tetrahedra having slightly different orientations in alternating sulfohalite-like blocks (Sokolova *et al.*, 1988). In quadruphite, the orientations of the PO_4 tetrahedra are apparently fixed and do not vary. Results from electron microprobe (Table 31) and crystal structure analyses indicate that Si and P are highly ordered in all three minerals.

STEENSTRUPINE-(Ce)

Steenstrupine-(Ce) has been discovered in nepheline and sodalite syenites at Mont Saint-Hilaire, Quebec, the Ilimaussaq intrusion in southern Greenland and the Khibina and Lovozero massifs, C.I.S. The mineral develops in platy subhedral crystals and as rounded anhedral masses.

Steenstrupine-(Ce) has a very complicated chemistry and a number of chemical formulas have been proposed for it (Makovicky and Karup-Møller, 1981). The most recent is: $\text{Na}_{14}\text{REE}_6\text{Mn}^{3+}\text{Mn}^{2+}\text{Fe}_2^{3+}\text{Zr}(\text{PO}_4)_7(\text{Si}_6\text{O}_{18})_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ as determined by crystal structure analysis (Moore and Shen, 1983). The chemical analysis for steenstrupine-(Ce) presented in Table 34, has been obtained through the use of numerous analytical techniques including the electron microprobe (major elements), Mössbauer spectroscopy (Fe oxidation state), thermal gravimetric analysis (water content) and X-ray fluorescence (Mn valence, rare-earth composition) (Makovicky and Karup-Møller, 1981).

The crystal structure of steenstrupine-(Ce) was refined to $R = 7.3\%$ by Moore and Shen (1983) using material from Greenland. It is based on a $\{(6\cdot3\cdot6\cdot3)^4\}$ Kagome net, with the chemical constituents being positioned on two different types of rods which extend along c . One rod contains Fe, Zr and Mn octahedra along with a highly disordered $(\text{P},\text{Si})\text{O}_4$ group, while the other contains eight-coordinated Na and rare-earth polyhedra and both SiO_4 and PO_4 groups.

Steenstrupine-(Ce) has been poorly-studied due to its metamict nature

[natural steenstrupine-(Ce) may contain up to 4.83 wt. % ThO_2]. Chemical analyses of steenstrupine-(Ce) can show highly variable SiO_2 (21.36-32.36 wt. %) and P_2O_5 contents (0.65-5.32 wt. %; Vlasov, 1966). There is also evidence from crystal structure analysis for disordering of Si and P in some of the tetrahedral sites (Moore and Shen, 1983).

VUONNEMITE

Vuonnemite $[\text{Na}_5\text{Ti}^{3+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2]$ is a rare mineral that was originally discovered at the Khibina massifs, C.I.S., where it was found as yellow plates in association with albite, microcline, nepheline, aegirine, lorenzenite, cancrinite, villiaumite and serandite (Bussen *et al.*, 1973). The mineral has subsequently been found at the Lovozero massif, C.I.S., Mont Saint-Hilaire, Quebec and the Ilimaussaq intrusion of southern Greenland.

The crystal structure of vuonnemite, recently solved by Ercit and Hawthorne (1990), is also very similar to that of lomonosovite. It consists of a close-packed layer of Na and Ti^{3+} octahedra, bounded by a layer of corner-linked Si_2O_7 groups and Nb octahedra. Between two $[\text{Nb}(\text{Si}_2\text{O}_7)_2]$ layers is a sheet composed of edge- and face-sharing Na polyhedra and PO_4 tetrahedra.

6.2 INADEQUATELY DESCRIBED Si- AND P-BEARING MINERALS

In addition to known silicophosphate minerals and Si-P disordered silicates and phosphates, there are also a number of minerals which have been poorly-

TABLE 33. INADEQUATELY DESCRIBED SI- AND P-BEARING MINERALS.

MINERAL NAME	Z	CRYSTAL SYSTEM	a(Å)	b	c
KARNASURTITE-(La) ¹ REE(Ti,Nb)Al(Si,P) ₂ O ₇ (OH) ₄ ·3H ₂ O	n.a.	Hex.(?)	n.a.		n.a.
LAPLANDITE-(Ce) ² Na ₄ REETiPSi ₇ O ₂₂ ·5H ₂ O	4	Ortho.	7.27	14.38	22.25
PERHAMITE ³ Ca ₃ Al ₇ (SiO ₄) ₃ (PO ₄)(OH) ₃ ·16.5H ₂ O	1	Hex.	7.02		20.21
SARYARKITE-(Y) ⁴ Al ₅ CaY(SiO ₄) ₂ [(P,S)O ₄] ₂ (OH) ₇ ·6H ₂ O	4	Tetrag.	8.213		6.55
VISEITE ⁵ Ca ₁₀ Al ₂₄ (PO ₄) ₁₄ (SiO ₄) ₆ O ₁₁ (F,OH) ₃ ·72H ₂ O	2	Cubic	13.65		

Note: n.a. = not available.

1. Kuz'menko and Kozhanov (1959).
2. Yes'kova *et al.* (1975).
3. Dunn and Appleman (1977).
4. Krol *et al.* (1964).
5. Dunn and Appleman (1977).

TABLE 34. CHEMICAL COMPOSITIONS OF
INADEQUATELY DESCRIBED
SI- AND P-BEARING MINERALS.

	1	2	3	4	5
SiO ₂ wt. %	24.91	40.94	13.64	14.24	7.97
P ₂ O ₅	6.81	9.62	21.90	12.18	21.54
Al ₂ O ₃	5.52	0.94	27.09	26.61	26.82
SO ₃				3.41	
Na ₂ O		9.81	0.02	0.75	0.02
K ₂ O		1.88		0.32	0.14
CaO	3.20	0.56	12.26	6.59	12.53
MnO		0.20			
FeO			0.26		0.74
SrO					0.01
MgO	0.60	1.02	0.02		0.12
TiO ₂	12.33	4.08	0.09		
Nb ₂ O ₅	2.20	1.88			
ZrO ₂	1.20				
Fe ₂ O ₃	1.07	0.64		2.21	
Ce ₂ O ₃	8.11	16.79		10.79	
La ₂ O ₃	8.55				
ThO ₂	6.04	1.32		9.07	
H ₂ O	19.58	9.33	24.62*	14.02	(28.82)
F			0.10		1.29
SUM	100.12	99.01	100	100.19	100

Note: * = by difference; () by stoichiometry.

1. karnasurtite-(La); Kuz'menko and Kozhanov (1959).
2. laplandite-(Ce); Yes'kova *et al.* (1975); X-ray fluorescence and differential thermal analyses.
3. perhamite; Dunn and Appleman (1977); electron microprobe analyses.
4. saryarkite-(Y); Krol *et al.* (1964); X-ray fluorescence and differential thermal analyses.
5. viseite; Dunn and Appleman (1977); electron microprobe analyses.

TABLE 35. OPTICAL AND PHYSICAL PROPERTIES OF INADEQUATELY DESCRIBED
Si- AND P-BEARING MINERALS.

MINERAL	OPTIC SIGN	α (or ϵ)	β (or ω)	γ	$2V_{\text{meas}}(^{\circ})$	$2V_{\text{calc}}(^{\circ})$	DISPERSION
KARNASURTITE-(La) ¹	(-)	1.595	1.617				
LAPLANDITE-(Ce) ²	(-)	1.585	1.584	1.568	n.a.	28	n.a.
PERHAMITE ³	(+)	1.577	1.564				
SARYARKITE-(Y) ⁴	(+)	1.620	1.606				
VISEITE ⁵	isotropic	1.553					

TABLE 35. (continued).

MINERAL	ORIENTATION	PLEOCHROISM	CLEAVAGE	D _{mess} (g/cm ³)
KARNASURTITE-(La) ¹		none	one, good	2.92
LAPLANDITE-(Ce) ²	X=c	n.a.	none	2.83
PERHAMITE ³		n.a.	{001}, perfect	2.64
SARYARKITE-(Y) ⁴		n.a.	n.a.	3.11
WISEITE ⁵		n.a.	none	3.12

Note: n.a. = not available.

1. Kuz'menko and Kozhanov (1959).
2. Yes'kova *et al.* (1975).
3. Dunn and Appleman (1977).
4. Krol *et al.* (1964).
5. Dunn and Appleman (1977).

defined or inadequately described, and hence, cannot be properly classified at present. These unclassified Si- and P-bearing minerals are listed in Table 33, their chemical compositions in Table 34 and their optical and physical properties in Table 35. A brief description of each is provided below, with the most comprehensive reference provided beside the mineral name.

KARNASURTITE-(La) (Kuz'menko and Kozhanov, 1959).

This mineral was discovered in the nepheline and sodalite syenites at the Lovozero massif, C.I.S. Karnasurtite-(La) occurs as platy yellow aggregates (up to 10x6x2 cm) and discrete hexagonal plates (up to 1 cm). Important associated minerals include ussingite, polyolithionite, natrolite and epididymite.

Karnasurtite-(La) was originally assigned the ideal chemical formula $\text{REE}(\text{Ti}, \text{Nb})(\text{Al}, \text{Fe})(\text{Si}, \text{P})_2\text{O}_7(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (Kuz'menko and Kozhanov, 1959). Khomyakov (1990) has also presented modified formula $\text{REE}_2\text{Al}_2\text{Ti}_2\text{Si}_4\text{P}_2\text{O}_{23} \cdot 10\text{H}_2\text{O}$ for the mineral (no chemical analysis provided). Chemical analyses reported by Kuz'menko and Kozhanov (1959) indicate large variations in SiO_2 (20.47-30.27 wt. %) and P_2O_5 contents (2.42-5.55 wt. %), probably due to the metamict nature of this mineral [Karnasurtite-(La) may contain up to 6 wt. % ThO_2 ; Kuz'menko and Kozhanov, 1959].

Most Karnasurtite-(La) is amorphous to X-rays (Kuz'menko and Kozhanov, 1959) and no material suitable for X-ray diffraction analyses was found in this study. Kuz'menko and Kozhanov (1959) report that most crystals of karnasurtite-

(La) are optically uniaxial negative, although they may be anomalously biaxial on occasion.

Vlasov (1966) notes that the mineral alters in air, changing from honey-yellow when fresh to pale yellow when altered. The mineral has also been noted to weather to rhabdophane-group minerals (Vlasov, 1966).

LAPLANDITE-(Ce) (Yes'kova *et al.*, 1975).

This mineral occurs in nepheline and sodalite syenites at the Lovozero massif, C.I.S., in association with nordite, serandite, thermonatrite, steenstrupine-(Ce) and others. It develops in fine-grained fibrous to platy clusters up to 1 cm.

The ideal formula for laplandite-(Ce) is $\text{Na}_4\text{REETiPSi}_7\text{O}_{22}\cdot 5\text{H}_2\text{O}$, based on X-ray fluorescence and differential thermal analyses.

Crystals of laplandite-(Ce) are very fine-grained and its cell parameters could only be determined using electron diffraction techniques. Material suitable for structure analysis has not yet been found.

PERHAMITE (Dunn and Appleman, 1977).

Perhamite was discovered in pegmatites at Newry Hill, Newry, Maine. Here it was found in association with siderite, wardite, amblygonite, esophorite and sphalerite. It develops in botryoidal clusters and spherulitic masses composed of intergrown hexagonal plates.

Major element analyses of perhamite were carried out using the electron

microprobe, while the ion microprobe mass spectrometer was used to search for elements lighter than F (none detected). These analyses revealed that the crystals were chemically-homogeneous and that there was no evidence for chemical zonation or the presence of impurities. The average of these chemical analyses (Table 34) yields the ideal formula $\text{Ca}_3\text{Al}_7(\text{SiO}_4)_3(\text{PO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$.

As perhamite crystals were found to diffract X-rays quite well and that they appeared to be chemically-homogeneous, an attempt was made to determine the crystal structure of this mineral in order to verify the ordering of Si and P. A sharp, hexagonal crystal, selected from a sample taken from the Emmons mine, Newry, Maine, was studied using the precession method. From this, there was no photographic evidence for the presence of twinning or multiple crystals. However, when this same crystal was optically examined under crossed-polars along the c-axis, an incomplete extinction was noted, together with the presence of three sets of fine striae which intersected with one another at angles of approximately 60° . An X-ray intensity data set was collected using this crystal. However, determination of the structure was not successful, and refinement would not converge below $R = 40\%$. Given the anomalous optical features exhibited by the crystal used in data collection, it is possible that it may have been twinned or composed of multiple crystals on a fine scale.

SARYARKITE-(Y) (Krol *et al.*, 1964)

Saryarkite-(Y) is a rare mineral known from acid effusives and altered

granitic rocks from an unknown locality in the former U.S.S.R. It was noted to have been found in association with huttonite, barite, molybdenite, pyrite, hematite and hydrous Fe oxides. No description of the crystals themselves has been given.

Chemical analyses (Table 34) indicate an ideal formula $\text{Al}_5\text{CaREE}(\text{SiO}_4)_2[(\text{P,S})\text{O}_4](\text{OH})_7 \cdot 6\text{H}_2\text{O}$, although Krol *et al.* (1964) note that other ways of writing this formula are possible.

The X-ray pattern of saryarkite-(Y) is close to that of rhabdophane-group minerals (Fleischer, 1964). However, saryarkite-(Y) differs from rhabdophane-group minerals in having a high Al_2O_3 content and apparent tetragonal symmetry.

WISEITE (Dunn and Appleman, 1977).

Viseite has been discovered as botryoidal clusters composed of oolitic aggregates of tiny spherulites and as chalky, massive material (Dunn and Appleman, 1977).

Recent electron microprobe analyses carried out on type material indicate the approximate formula $\text{Ca}_{10}\text{Al}_{24}(\text{SiO}_4)_6(\text{PO}_4)_{14}(\text{F,OH})_3\text{O}_{11} \cdot 72\text{H}_2\text{O}$. These analyses (Table 34) show significant differences in the SiO_2 , P_2O_5 and CaO contents when compared to earlier analyses (McConnell, 1952), suggesting that impurities may be present or that this mineral is actually a composite of more than one phase.

No single crystals of viseite are known and all the known material is massive. Furthermore, the X-ray diffraction pattern for the mineral is quite poor,

containing only a few weak, diffuse lines.

CHAPTER 7

DISCUSSION AND CONCLUSIONS

7.1 CRYSTAL CHEMICAL CHARACTERISTICS OF SILICOPHOSPHATE MINERALS

Considering the information provided for known silicophosphate minerals together with that presented in the discussions of phosinaite-(Ce), abenakiite-(Ce) and yoshimuraite, the crystal-chemical similarities of the silicophosphates can be summarized as follows:

1. Polymerization of SiO_4 tetrahedra but not PO_4 tetrahedra.

Although the SiO_4 tetrahedra in these silicophosphates have been found to polymerize into disilicate groups, along with four- and six-membered silicate rings, the PO_4 groups only occur as isolated tetrahedra. This is consistent with the observations of Liebau (1966) and Moore (1980) who have noted that no minerals are known to contain polymerized PO_4 tetrahedra, the main reason being that a P-O-P bond would result in an excessive positive charge on the bridging oxygen.

The fact that PO_4 tetrahedra do not readily polymerize in minerals may also be related to the charge and radius of P. According to Pauling's rule 4, polyhedra formed from cations of high charge and small radii tend not to share polyhedral elements. Since P has a valence of 5+ and a small ionic radius of 0.17 Å (Shannon, 1976), PO_4 tetrahedra do not share corners with one another, but instead occur as isolated tetrahedral groups (Jaffe, 1988).

The tetrahedral bond lengths and bond angles for known silicophosphates

are given in figures 37, 38, 39 and 40. Most of these fall within typical ranges for silicates ($d\langle\text{Si-O}\rangle = 1.57 - 1.72\text{\AA}$; O-Si-O angle = $98 - 122^\circ$; Liebau, 1985) and phosphates ($d\langle\text{P-O}\rangle = 1.45 - 1.56$; Ondik and Smith, 1968). Overall, SiO_4 tetrahedra show more scatter in terms of bond distances and angles than those associated with PO_4 tetrahedra. This is due to polymerization of the SiO_4 groups, which results in the bond angles and distances involving $\text{O}_{\text{bridging}}$ generally being shorter and smaller than those formed with $\text{O}_{\text{non-bridging}}$.

Despite the absence of minerals with polymerized PO_4 groups in nature, phases containing such units ("condensed polyphosphates") have been synthesized (Corbridge, 1978). Synthetic polyphosphates are formed by heating solutions containing acid orthophosphate groups, $\text{PO}_3(\text{OH})$. The heating causes the elimination of water between hydroxyl groups and results in the formation of a P-O-P bond between adjacent PO_4 tetrahedra. Such a process can lead to PO_4 tetrahedra being linked into chains ("linear polyphosphates"), rings ("metaphosphates") as well as sheet and framework structures ("ultraphosphates"). While such compounds are relatively stable to chemical attack (Corbridge, 1978), they hydrate very rapidly. The hydration process results in breaking of the P-O-P bonds which leads to a total collapse of the structure, the end products being discrete orthophosphate tetrahedra (Corbridge, 1978). The instability of such compounds in hydrous environments is probably another reason that minerals with polymerized PO_4 tetrahedra have not been observed in nature.

Fig. 37. Si-O bond distances in confirmed silicophosphate minerals.

Fig. 38. P-O bond distances in confirmed silicophosphate minerals.

Fig. 39. O-Si-O bond angles in confirmed silicophosphate minerals.

Fig. 40. O-P-O bond angles in confirmed silicophosphate minerals.

2. No sharing of tetrahedral oxygens between SiO_4 and PO_4 .

While many minerals are known to contain SiO_4 tetrahedra linked to other tetrahedral anionic groups (e.g. BO_4 , BeO_4 and AlO_4), none of the silicophosphate minerals examined in this study were found to contain SiO_4 and PO_4 tetrahedra linked together through shared oxygens. This is probably due to the high valence of P^{5+} (compared to B^{3+} , Be^{4+} or Al^{3+}), which would lead to the bridging oxygen in a Si-O-P bond being oversaturated with positive charge.

There are minerals however, that are known to contain a tetrahedrally-coordinated pentavalent cation linked to an SiO_4 group. A good example of this is tiragalloite $[\text{Mn}_4\{\text{As}^{5+}\text{Si}_3\text{O}_{12}(\text{OH})\}]$, a rare mineral discovered in veinlets cutting massive aggregates of braunite ($\text{Mn}_7\text{SiO}_{12}$) and quartz (Gramaccioli *et al.*, 1980). The structure of tiragalloite is quite unusual, as it contains AsO_4 tetrahedra joined to SiO_4 tetrahedra through shared-corners, thus forming chain fragments of the composition $[\text{AsSi}_3\text{O}_7(\text{OH})]$ (Gramaccioli *et al.*, 1980). The structure of this mineral is believed to be stabilized by a combination of a H-bond network, along with AsO_4 tetrahedra that are linked only to SiO_4 tetrahedra. The fact that the AsO_4 and SiO_4 tetrahedra are not further polymerized is important because it results in a structure that is intermediate between those of unstable polyarsenates (which hydrate rapidly) and very stable polysilicates (Gramaccioli *et al.*, 1980)

Under laboratory conditions, glasses containing SiO_4 groups polymerized with PO_4 groups have been synthesized (Corbridge, 1978). Compounds containing

Si-O-P bonds can be formed by condensation of orthosilicate and orthophosphate anions, but are found to be unstable in the presence of water, hydrating rapidly (Corbridge, 1978).

3. Strongly layered structures.

All of the silicophosphate minerals analyzed in this study were found to have a pronounced layered aspect. The tetrahedral layers are often weakly-bonded together by various cationic polyhedra, resulting in well-defined basal-type cleavages that are observed in many of the silicophosphate minerals.

4. High concentrations of large lithophile elements.

The silicophosphates have characteristically high concentrations of alkalis (principally Na), alkaline-earths (principally Ca, but also Ba, Mn) and rare-earth elements. The similarity in their chemical compositions with regard to these components, may be due to their development in similar geochemical environments. Alternatively, it could be explained by the fact that these cations characteristically occur in irregular, highly-coordinated polyhedra. Due to their flexibility in their coordination, these cations could be accommodated in a given crystallographic site much easier than those that occur in more regular coordination polyhedra (*e.g.* Mg, Al or Fe).

7.2 CAUSES OF Si- AND P-ORDERING IN SILICOPHOSPHATE MINERALS

One of the main factors controlling the ordering of Si and P in these silicophosphate minerals may be polymerization of the tetrahedral components. It

was earlier noted that SiO_4 tetrahedra readily polymerize in minerals, while PO_4 tetrahedra never share tetrahedral elements. As such, P may be excluded from Si sites simply because the cations in these sites are involved in tetrahedral polymerization. This would result in P being segregated into isolated tetrahedra.

There are also significant differences in ionic radii, with Si^{4+} being more than 50% larger than P^{5+} ($\text{Si}^{4+} = 0.26 \text{ \AA}$, $\text{P}^{5+} = 0.17 \text{ \AA}$; Shannon, 1976). This could also inhibit extensive Si-P substitution, particularly in polymerized structures.

The ordering of Si and P may also be weakly related to the charge difference between Si^{4+} and P^{5+} . Many of the silicates and phosphates which exhibit extensive Si-P substitution also accommodate other heterovalent substitutions in their structures in order to compensate for charge imbalance [e.g. $\text{Ca}^{2+} + \text{P}^{5+} \leftrightarrow \text{REE}^{3+} + \text{Si}^{4+}$ (apatite-britholite); $\text{Th}^{4+} + \text{Si}^{4+} \leftrightarrow \text{REE}^{3+} + \text{P}^{5+}$ (huttonite-monazite)]. If however, the environment of formation was deficient in cations suitable for a coupled substitution scheme involving Si and P, the amount of Si-P disordering could be severely restricted. This could lead to an apparent ordering of Si and P in a Si- and P-bearing mineral.

7.3 THE OCCURRENCES OF SILICOPHOSPHATE MINERALS AND THEIR GENESIS AT MONT SAINT-HILAIRE

Silicophosphate minerals are extremely rare and have only been recorded from a limited number of localities world-wide. Most are restricted to nepheline and sodalite syenites, such as those found at Mont Saint-Hilaire, Quebec, the Ilimaussaq intrusion of southern Greenland and the Khibina and Lovozero

massifs, C.I.S. At these localities, they are frequently associated with Na silicates such as ussingite, as well as numerous zircono- and titanosilicates such as eudialyte and members of the lovozerite group.

Geochemically, the syenites in which many of these silicophosphate minerals form are characterized by high alkalinities, low silica contents, and relatively high P_2O_5 contents. While the P_2O_5 of most igneous rocks range from 0.01 to 0.05 wt. %, those of syenitic rocks average 1.5 to 2 wt. % (Koritnig, 1978). The fact that most silicophosphates are restricted to syenites, which characteristically have high P_2O_5 contents, suggests that the availability of P may be critical to their development.

Mont Saint-Hilaire is a Cretaceous igneous plug that intruded the overlying Lorraine and Richmond group sediments (shales and limestones) about 125 million years ago (Currie *et al.*, 1986). Its geology has been discussed and summarized by numerous authors [e.g. Currie *et al.* (1986) and Gilbert and Foland (1986)]. Briefly, Mont Saint-Hilaire is composed of three suites of intrusive rock: the Sunrise suite (melagabbros and pyroxenites), the Pain du Sucre suite (nepheline gabbros, diorites and monzonites) and the East Hill suite (nepheline and sodalite syenites). Data from Currie *et al.* (1986) indicates that the Sunrise suite is the oldest (134 ± 6 Ma), while the Pain du Sucre and East Hill suites are both younger and contemporaneous (120 ± 6 Ma).

Four known silicophosphate minerals [abenakiite-(Ce), phosinaite-(Ce), vuonnemite and steenstrupine-(Ce)] have been discovered in the East Hill suite at

Mont Saint-Hilaire, all in a particular rock type known as sodalite syenite xenoliths (Mandarino and Anderson, 1989). The xenoliths are thought to be fragments of previously solidified sodalite syenite that became included in a nepheline syenite magma during its emplacement. They occur in blocks that are angular and irregular to oblong in shape, ranging in size from a few centimetres to about two metres and are composed predominantly of sodalite (up to 90 %) with lesser amounts of microcline and analcime.

Although the dominant mineralogy of these xenoliths is relatively simple, the accessory minerals that are present are very unusual and chemically quite complex (Table 36). In addition to the silicophosphate minerals, the sodalite syenite xenoliths are characterized by an abundance of Na-bearing phases, including relatively simple silicates (*e.g.* linitite, revdite, silinaite), complex silicates (*e.g.* eudialyte, lovozerite-group minerals, terskite), phosphates [*e.g.* natrophosphate, sidorenkite, vitusite-(Ce)], carbonates (*e.g.* natron, thermonatrite, trona), sulphides (*e.g.* erdite, rasvumite). Along with these are numerous F-bearing minerals (*e.g.* kogarkoite, polyolithionite, villiaumite), native elements (*e.g.* Bi, Pb, Sb) and many phases in which REE are essential constituents [*e.g.* phosinaite-(Ce), vitusite-(Ce), steenstrupine-(Ce)] (Horvath and Gault, 1990). Many of the minerals also contain either structurally-bound water or hydroxyl groups.

These sodalite syenite xenoliths are rare at Mont Saint-Hilaire. Most are found in small clusters, concentrated around the edges of a large hornfels unit

TABLE 36. MINERALS FOUND IN SODALITE SYENITE XENOLITHS AT MONT SAINT-HILAIRE.

ABENAKITE-(Ce)	DIGENITE	LOELLINGITE	PHILLIPSITE	STEENSTRUPINE-(Ce)
AEGIRINE	DJURELITE	LOPARITE-(Ce)	PHOSINAITE-(Ce)	TAENIOLITE
ALABANDITE	DORFMANITE	LORENZENITE	POLYLITHIONITE	TERSKITE
ALBITE	EPISTOLITE	LOVOZERITE group	POSNJAKITE	TETRAHEDRITE
ANALCIME	ERDITE	LUESHITE	PYROCHLORE	TETRANATROLITE
ANATASE	EUDIALYTE	MAKATITE	PYROPHANITE	THALCUSITE
ANCYLITE-(Ce)	FLUORAPATITE	MANGAN-NEPTUNITE	RAITE	THERMONATRITE
ANTIMONY	FLUORITE	MICROCLINE	RASVUMITE	THOROGUMMITE
ARSENOPYRITE	GALENA	MOLYBDENITE	REVDITE	TITANITE
ASTROPHYLLITE	GARRONITE	MOSANDRITE	RHABDOPHANE group	TRONA
BARITE	GMELINITE	NAIPOITE	ROUVILLEITE	TUGTUPITE
BARYTO- LAMPROPHYLLITE	GRAPHITE-2H	NALIPOITE	SAZHINITE-(Ce)	USSINGITE
BISMUTH	GRICEITE	NATRITE	SEARLESITE	VILLIAUMITE
BRITHOITE-(Ce)	HALITE	NATROLITE	SERANDITE	VINOGRADOVITE
BURBANKITE	HARMOTOME	NATRON	SHORTITE	VITUSITE-(Ce)
CALCITE	HYDROCERUSSITE	NATROPHOSPHATE	SIDORENKITE	VUONNEMITE
CANCRINIITE	KOGARKOITE	NEPHELINE	SILINAITE	WURTZITE-2H,4H,8H
CATAPLEITE	KUPLETSKITE	PARAKELDYSHITE	SMECTITE group	YOFORTIERITE
CHABAZITE	LAMPROPHYLLITE	PARANATROLITE	SODALITE	
CHALCOPYRITE	LANGITE	PARAUMBITE	SPERTINIITE	
CHKALOVITE	LEAD	PECTOLITE	SPHALERITE	
CRYOLITE	LINTISITE	PETARASITE	STEACYITE

Fig. 41. Horizontal and longitudinal sections through the hornfels unit (*after* Van Velthuisen, 1990). Note: the sodalite syenite xenoliths are termed sodalite inclusions in the legend.

(Fig. 41). This particular unit is thought to represent a large block of Ordovician sedimentary material that became trapped in the nepheline syenite during its emplacement, and was subsequently metamorphosed (Van Velthuisen, 1990). It is quite dense and composed predominantly of quartz (40%), cordierite (30%), biotite (15%), muscovite (10%) and andesine (5%), with the quartz content increasing from the core to the edge of the unit (Van Velthuisen, 1990). Based on the observed mineral assemblage, the hornfels unit is believed to have been metamorphosed at moderate temperatures ($>500^{\circ}\text{C}$) and pressures (1-4 kb; Van Velthuisen, 1990).

The sodalite syenite (including the xenoliths) at Mont Saint-Hilaire is believed to have been derived through the interaction of a Cl-rich brine with a magma at a relatively shallow depth in the earth's crust (Mandarino and Anderson, 1989). The fact that many of the accessory minerals in the sodalite syenite xenoliths are enriched in incompatible elements such as Zr, Ti and REE, and are predominantly found in vugs and cavities in these xenoliths, combine to suggest that they crystallized after the xenoliths had already formed, *i.e.* they are not contemporaneous with the formation of the sodalite xenoliths themselves. Many of the accessory minerals, including the silicophosphate minerals, are characterized by high Na, F, P, Si and S compositions. The high Na and F contents are particularly reminiscent of the late-stage fluids associated with carbonatites (Gittins, 1989). Such fluids are believed to be responsible for the fenites that often surround carbonatites. Considering this, the fluids from which

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the accessory minerals found in the xenoliths crystallized, could have also been late-stage products of a crystallizing magma, similar to the fenetization fluids associated with carbonatites.

Relatively little is known about the *P-T* conditions under which the silicophosphates formed. Ussingite [$\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$] is a mineral frequently encountered in the sodalite syenite xenoliths and one that is often found in association with the silicophosphates at Mont Saint-Hilaire. Work by Platt and Rose-Hansen (1975) suggests that ussingite is unstable at pressures of 1 kb in the presence of water. The mineral has a melting temperature of 400-450°C, above which it melts to albite+analcime+sodium disilicate+liquid. This implies that the silicophosphates found in the xenoliths crystallized at moderate to low temperatures (400-450°C) and pressures (1 kb).

Considering the above information, the following scenario is proposed for the paragenesis of the silicophosphates within the sodalite syenite xenoliths:

1. Intrusion of a nepheline syenite unit into, or very close to, a body of already-crystallized sodalite syenite. This resulted in blocks of the sodalite syenite being torn off and becoming trapped in the crystallizing magma. A large block of sedimentary material also became entrapped in the nepheline syenite during its emplacement. This block was subsequently metamorphosed to a very dense hornfels body;
2. As the temperature and pressure began to fall, the principal rock-forming minerals of the nepheline syenite (kaersutite, biotite, alkali feldspar, nepheline

etc.) began to crystallize. Chemical elements which could not be accommodated in the structures of these minerals (*e.g.* Na, Zr, Ti, REE, F, P *etc.*) were concentrated in the residual melt;

3. As the nepheline syenite solidified, residual fluids were forced out. These fluids became trapped in the vicinity of the hornfels block, due to its high impermeability;

4. As temperature and pressure continued to fall, minerals began to crystallize from the residual melt in whatever spaces were available; principally, the vugs and cavities present in the sodalite syenite xenoliths.

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