

PHOSINAITE-(Ce) FROM MONT SAINT-HILAIRE, QUEBEC: NEW DATA AND STRUCTURE REFINEMENT

ANDREW M. McDONALD* AND GEORGE Y. CHAO

Ottawa-Carleton Geoscience Centre, Department of Earth Sciences, Carleton University, Ottawa, Ontario K1S 5B6

JOEL D. GRICE

Mineral Sciences Section, Earth Sciences Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

ABSTRACT

Phosinaite-(Ce), ideally $\text{Na}_{13}\text{Ca}_2\text{REE}[\text{Si}_4\text{O}_{12}](\text{PO}_4)_4$, has been found in sodalite syenite xenoliths at the Poudrette Quarry, Mont Saint-Hilaire, Quebec. The mineral occurs as colorless to pale brown anhedral, elongate grains up to 2 mm set in the groundmass, and euhedral prismatic crystals up to 2×1 mm in vugs in sodalite. Crystals commonly are coated in a brown film of an amorphous Na-Ca-K silicate, previously believed to be a hydrocarbon. Important associated phases include microcline, analcime, albite, villiaumite, astrophyllite, thermonatrite, vitusite, revdite and vuonnemite. Average results of electron-microprobe analyses ($n = 4$) gave Na_2O 31.68, CaO 8.92, MnO 0.89, La_2O_3 4.18, Ce_2O_3 6.52, Nd_2O_3 0.99, Pr_2O_3 0.26, ThO_2 1.84, Al_2O_3 0.11, SiO_2 18.36 and P_2O_5 23.69 wt.%, corresponding to $(\text{Na}_{12.72}\text{Ca}_{0.14})_{\Sigma 12.86}(\text{Ce}_{1.84}\text{Mn}_{0.16})_{\Sigma 2.00}(\text{Ce}_{0.49}\text{La}_{0.32}\text{Th}_{0.09}\text{Nd}_{0.07}\text{Pr}_{0.02})_{\Sigma 0.99}[(\text{Si}_{3.77}\text{P}_{0.15}\text{Al}_{0.04})_{\Sigma 3.96}\text{O}_{12}](\text{PO}_4)_4$, based on 28 oxygen atoms. Phosinaite-(Ce) from Mont Saint-Hilaire is found to have a distinctive concentration of Th compared to that from the Khibina and Lovozero massifs, Russia. Single-crystal study showed it to be orthorhombic, $P22_12_1$, with a 12.297(2), b 14.660(3), c 7.245(1) Å, V 1306.1(1) Å³ and $Z = 2$. The observed powder-pattern is consistent with that previously published; the reflection reported at 6.92 Å was not observed in our material. The crystal structure was refined using single-crystal X-ray-diffraction data to $R = 3.1\%$ and $wR^2 = 7.99\%$. In addition to confirmation of the basic features of the structure originally proposed for the mineral, site-occupancy refinement for one octahedrally coordinated site gave $(\text{Na}_{0.66}\text{Ca}_{0.34})$. A high degree of order of Si and P was established on the basis of results from electron-microprobe analyses, site-occupancy refinement, mean T-O bond distances and calculated bond-valence sums, suggesting that the mineral be classified as a silicophosphate.

Keywords: phosinaite-(Ce), new occurrence, silicophosphate, Mont Saint-Hilaire, Quebec, X-ray data, chemical composition, crystal structure.

SOMMAIRE

Nous avons trouvé la phosinaïte-(Ce), de composition idéale $\text{Na}_{13}\text{Ca}_2\text{TR}[\text{Si}_4\text{O}_{12}](\text{PO}_4)_4$ (TR: terres rares) dans des xénolithes de syénite à sodalite dans la carrière Poudrette, mont Saint-Hilaire, Québec. Il s'agit d'un minéral incolore à brun pâle, se présentant en grains xénomorphes, allongés, jusqu'à 2 mm en longueur dans la pâte, et en grains idiomorphes atteignant 2×1 mm dans des cavités dans la sodalite. Les cristaux sont en général recouverts d'une pellicule brune d'un silicate amorphe de Na-Ca-K, que l'on avait auparavant considéré comme un hydrocarbure. Sont associés à la phosinaïte-(Ce) microcline, analcime, albite, villiaumite, astrophyllite, thermonatrite, vitusite, revdite et vuonnemite. Les analyses ($n = 4$) à la microsonde électronique ont donné Na_2O 31.68, CaO 8.92, MnO 0.89, La_2O_3 4.18, Ce_2O_3 6.52, Nd_2O_3 0.99, Pr_2O_3 0.26, ThO_2 1.84, Al_2O_3 0.11, SiO_2 18.36 et P_2O_5 23.69% (en poids), ce qui, sur une base de 28 atomes d'oxygène, correspond à $(\text{Na}_{12.72}\text{Ca}_{0.14})_{\Sigma 12.86}(\text{Ce}_{1.84}\text{Mn}_{0.16})_{\Sigma 2.00}(\text{Ce}_{0.49}\text{La}_{0.32}\text{Th}_{0.09}\text{Nd}_{0.07}\text{Pr}_{0.02})_{\Sigma 0.99}[(\text{Si}_{3.77}\text{P}_{0.15}\text{Al}_{0.04})_{\Sigma 3.96}\text{O}_{12}](\text{PO}_4)_4$. La phosinaïte-(Ce) du mont Saint-Hilaire possède une concentration distinctive en Th que les échantillons des massifs de Khibina et de Lovozero (Russie) ne montrent pas. Une étude sur cristal unique montre qu'elle est orthorhombique, $P22_12_1$, avec a 12.297(2), b 14.660(3), c 7.245(1) Å, V 1306.1(1) Å³ et $Z = 2$. Le spectre de diffraction X obtenu sur poudre concorde avec celui qui est déjà dans la littérature, exception faite de la réflexion à $d = 6.92\text{Å}$, qui n'a pas été observée dans nos échantillons. Nous avons affiné la structure sur cristal unique jusqu'à un résidu R de 3.1% ($wR = 7.99\%$). En plus de confirmer les grandes lignes de la structure déjà connues, nos résultats ont permis d'affiner l'occupation d'un des sites octaédriques: $(\text{Na}_{0.66}\text{Ca}_{0.34})$. Une distribution essentiellement ordonnée des atomes Si et P, établie par nos résultats d'analyses à la microsonde électronique, nos affinements de l'occupation des sites, les longueurs moyennes des liaisons T-O, et les valences de liaison, font penser qu'il s'agit d'un silicophosphate.

(Traduit par la Rédaction)

Mots-clés: phosinaïte-(Ce), nouvel exemple, silicophosphate, mont Saint-Hilaire, Québec, données de diffraction X, composition chimique, structure cristalline.

* Present address: Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3A 2E6.

INTRODUCTION

During the course of a mineralogical investigation of sodalite syenite xenoliths found in the Poudrette Quarry, Mont Saint-Hilaire, Québec, an unidentified mineral was encountered and temporarily designated UK64 (Chao *et al.* 1990). It was studied by optical, chemical and crystal-structure analyses, and subsequently found to be the rare species phosinaite-(Ce), which had previously been recorded only from the Khibina and Lovozero massifs of Russia (Kapustin *et al.* 1974). The occurrence of new material has therefore provided an opportunity to compare the physicochemical characteristics of phosinaite-(Ce) from all three localities and to investigate the extent of Si and P order in the structure.

OCCURRENCE AND PROPERTIES

The Canadian phosinaite-(Ce) is a late-stage phase that occurs as anhedral, elongate grains up to 2 mm set in the groundmass, as well as euhedral, prismatic crystals up to 2×1 mm in small vugs and fractures in colorless sodalite. Although more than 72 minerals have been found in these xenoliths (Chao *et al.* 1991), the most important phases associated with phosinaite-(Ce) include microcline, analcime, albite, villiaumite,

astrophyllite, thermonatrite, vitusite, revdite and vuonnemite.

The euhedral crystals of phosinaite-(Ce) are elongate on {001} and are commonly bounded by the forms {100}, {010} and {001}. The mineral is colorless to pale brown and commonly is coated with a brown film previously believed to be a hydrocarbon. However, a powder X-ray-diffraction pattern and results of an energy-dispersion analysis indicate that this film is actually an amorphous Ca-Na-K silicate. Phosinaite-(Ce) is quite brittle, with perfect {001}, distinct {110} and good {010} cleavages. The measured density was found to be 2.97 g/cm^3 , as determined by flotation in bromoform diluted with acetone.

Optically, the Mont Saint-Hilaire material is non-pleochroic with a very low birefringence. The observed interference figures were found to be quite poor, and no measurements of $2V$ or dispersion could be made. The indices of refraction are: $\alpha = \beta = 1.568(1)$ and $\gamma = 1.572(1)$, as determined in Na light ($\lambda = 589.3 \text{ nm}$), and the optical orientation is $X = b$, $Y = c$, $Z = a$, with a variable sign of elongation, all of which are consistent with those observed in the Russian material. A summary of the optical and physical properties of phosinaite-(Ce) from the three localities is provided in Table 1.

CHEMICAL COMPOSITION

TABLE 1. PHYSICAL PROPERTIES OF PHOSINAITE-(Ce)

Habit	1 Anhedral aggregates	2 Columnar crystals up to 5x1 mm	3 Prismatic crystals up to 2x1 mm, elongate, anhedral grains up to 2 mm
Colour	Colorless to pale rose	colorless, pale rose to brownish rose	colorless 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)	3.17*	3.21**	3.09
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)
$2V_{\text{meas}}(^{\circ})$	(+) 68	(+) 70	(+) †
$2V_{\text{calc}}(^{\circ})$	70^{\ddagger}	70^{\ddagger}	0
Elongation	(\pm)	(\pm)	(\pm)
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:

$(\text{Na}_{2.97}\text{K}_{0.03})_{23.02}(\text{Ca}_{0.71}\text{Ce}_{0.29})_{23.97}\text{Si}_{10}\text{P}_{0.56}\text{O}_{7.10}$

** - Calculated in this study for the formula:

$(\text{Na}_{3.04}\text{K}_{0.04})_{23.07}(\text{Ca}_{0.51}\text{Ce}_{0.28}\text{Mn}_{0.09})_{23.06}\text{Si}_{10}\text{P}_{0.95}\text{O}_{7.33}$

\dagger - $2V$ could not be determined.

\ddagger - Calculated in this study.

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

2. Lovozero massif,

3. Mont Saint-Hilaire, this study.

Electron-microprobe analyses were carried out on the Mont Saint-Hilaire phosinaite-(Ce) using a Cambridge Microscan MK5 instrument. The operating conditions were 15 kV, 30 nA (estimated), with the beam rastered over an area of $10 \times 10 \mu\text{m}^2$. Wavelength-dispersion data were collected using the following standards: albite (Na), Kakanui hornblende (Al, Si, Ca), Durango fluorapatite (P), tephroite (Mn), REE-bearing glasses (La, Ce, Pr, Nd, Sm) and synthetic ThO_2 (Th); the data were reduced using a modified version of EMPADR VII (Rucklidge & Gasparri 1969). In addition to the elements listed above, S, Zr, U and Fe were sought but not detected.

Results of these analyses indicate that the material is chemically homogeneous. The average of these analyses (Table 2) gives the empirical formula [based on 28 atoms of oxygen as determined from crystal-structure analysis]: $(\text{Na}_{12.72}\text{Ca}_{0.14})_{\Sigma 12.86}(\text{Ca}_{1.84}\text{Mn}_{0.16})_{\Sigma 2.00}(\text{Ce}_{0.49}\text{La}_{0.32}\text{Th}_{0.09}\text{Nd}_{0.07}\text{Pr}_{0.02})_{\Sigma 0.99}[(\text{Si}_{3.77}\text{P}_{0.15}\text{Al}_{0.04})_{\Sigma 3.96}\text{O}_{12}](\text{PO}_4)_4$ with $Z = 2$ or, ideally, $\text{Na}_{13}\text{Ca}_2\text{REE}[\text{Si}_4\text{O}_{12}](\text{PO}_4)_4$.

There is good agreement between the major-element content of phosinaite-(Ce) from all three localities and that calculated for the ideal composition (Table 2). In terms of minor elements, the Mont Saint-Hilaire material exhibits a distinctly high Th concentration. The Russian phosinaite-(Ce) contains water in the range of 2 to 6 wt.% (Table 2). However, it is now considered to

TABLE 2. 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., Québec; SiO₂ includes Al₂O₃ 0.15 wt.%; REE₂O₃ includes La₂O₃ 4.18, Ce₂O₃ 6.52, Nd₂O₃ 0.99 and Pr₂O₃ 0.26 wt. %.
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.

TABLE 3. CELL DIMENSIONS OF PHOSINAITE-(Ce)

Space Group	1 P2 ₂ ,2 or P2 ₂ ,2 ₁		2 P2 ₁ ,2 ₁ ,2	3 P2 ₂ ,2 ₁
	i	ii		
<i>a</i> (Å)	12.23(4)	12.24(4)	7.234(3)	12.297(2)
<i>b</i>	14.62(4)	14.59(4)	14.670(4)	14.660(3)
<i>c</i>	7.21(4)	7.20(4)	12.231(4)	7.245(1)
<i>V</i> (Å ³)	1289(1)	1286(1)	1298(1)	1306.1(1)
<i>Z</i>	2	2	2	2

1. Kapustin *et al.* (1974); i) Khibina massif, Russia; ii) Lovozero massif, Russia
2. Krutik *et al.* (1981); Khibina massif, Russia
3. This study; Mont St. Hilaire, Québec; dimensions refined from the X-ray powder-diffraction pattern.

phosinaite-(Ce) and inconsistent with the observed diffraction-symmetry. A 12-hour powder pattern of Lovozero phosinaite-(Ce) was made in the context of this study, but failed to reveal any indication of this enigmatic reflection. Therefore, it is believed to be

TABLE 4. 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> _{est} ¹	<i>I</i> _{est} ²	<i>d</i> _{est} ²	<i>I</i> _{est} ³	<i>d</i> _{est} 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
					66	3.949	221
20	3.94		60	3.949	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
					0	2.852	150
7	2.82				20	2.835	420
					9	2.830	401
100	2.74		10	2.819	100	2.732	340
					10	2.718	051
			100	2.718	86	2.714	302
					14	2.645	250
			70	2.577	87	2.576	042

be nonessential on the basis of results of a thermogravimetric analysis (Krutik *et al.* 1981) and refinement of the crystal structure, reported below. The water is most likely adsorbed, possibly resulting from supergene alteration, as commonly occurs in minerals from peralkaline rocks (Krutik *et al.* 1981).

X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

Single-crystal X-ray precession photographs of phosinaite-(Ce) from Mont Saint-Hilaire confirmed that the mineral is orthorhombic and belongs to the unique space-group P2₂,2₁ (#18). X-ray powder-diffraction data were collected using Ni-filtered CuK α radiation ($\lambda = 1.5418$ Å) and a 114.6-mm Gandolfi camera. The unit-cell parameters refined from these data using the program CELREF (Appelman & Evans 1973) are: *a* 12.297(2), *b* 14.660(3), *c* 7.245(1) Å, with a *V* of 1306.1(1) Å³ and *Z* = 2, in good agreement with those determined from previous studies (Table 3). The indexed powder-patterns of phosinaite-(Ce) from Mont Saint-Hilaire, the Russian localities and that calculated from the refined crystal-structure are presented in Table 4. Agreement between estimated and calculated intensities is good, with minor discrepancies owing to errors in the visual estimates and the recording geometry of the Gandolfi camera. The 6.92 Å reflection originally reported by Kapustin *et al.* (1974) is both unindexable on the cell adopted for

TABLE 4. X-RAY-DIFFRACTION DATA FOR PHOSINAITE-(Ce) — *Cont'd.*

1		2		3		<i>hkl</i>
<i>I</i> _{int} ¹	<i>d</i> _{meas} ¹	<i>I</i> _{int} ²	<i>d</i> _{meas} ²	<i>I</i> _{obs} ³	<i>d</i> _{calc} ³	
9	2.504	<5	2.486	12	2.546	222
				2	2.522	142
				4	2.485	251
				10	2.449	431
11	2.317	10	2.390	14	2.396	160
				3	2.385	350
				1	2.344	402
				9	2.339	113
20	2.172	5	2.346	1	2.329	501
				1	2.315	061
				13	2.314	412
				3	2.279	052
18	2.038	10	2.050	3	2.275	161
				2	2.271	260
				20	2.232	422
				15	2.197	530
10	1.985	10	1.988	22	2.181	342
				10	2.138	252
				4	2.065	170
				23	2.050	600
7	1.907	10	1.965	11	2.036	451
				3	1.999	162
				6	1.990	143
				12	1.966	541
17	1.832	30	1.913	9	1.916	243
				1	1.914	615
				5	1.913	460
				1	1.912	271
15	1.804	20	1.811	1	1.884	550
				5	1.883	413
				6	1.843	153
				20	1.832	080
10	1.685	5	1.768	0	1.812	180
				23	1.811	004
				5	1.798	014
				5	1.770	433
10	1.659	5	1.635	12	1.692	462
				0	1.673	380
				1	1.663	721
				0	1.657	304
13	1.596	20	1.604	1	1.635	082
				1	1.625	533
				0	1.616	324
				3	1.615	190
11	1.511	15	1.507	15	1.604	642
				2	1.576	191
				3	1.562	472
				1	1.560	404
				5	1.545	722
				8	1.545	722
				16	1.519	382
				11	1.510	750

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*_{int} 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).

either erroneous or perhaps caused by impurities trapped in some of the Lovozero material.

X-ray intensity data were collected on an automated four-circle diffractometer using an optically clean, prismatic crystal mounted so as to rotate about *c*. The cell dimensions given in Table 5 were derived by a

TABLE 5. MISCELLANEOUS DATA FOR THE REFINEMENT OF THE CRYSTAL STRUCTURE OF PHOSINAITE-(Ce)

Space Group	<i>P</i> 2 ₁ 2 ₁ (#18)	Diffractometer	Enraf-Nonius CAD4
<i>a</i> (Å)	12.270(1)*	Radiation	MoK α (50kV, 20 mA)
<i>b</i>	14.648(2)*	Monochromator	Graphite
<i>c</i>	7.231(1)*	Crystal Shape	Equant, Prismatic
<i>V</i> (Å ³)	1299.6(1)	Crystal Size	0.25 x 0.06 x 0.04 mm
<i>Z</i>	2	μ (MoK α)	4.76 mm ⁻¹
Chemical Formula	Na ₁₃ Ce ₂ REE(Si ₃ O ₁₂)(PO ₄) ₄		
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	2158		
Number of Observed Reflections	1868		
Criterion for Significance	$F > 6\sigma(F)$		
Final <i>R</i> for all Observed Reflections	3.1%		
Final <i>wR</i> ² for all Observed Reflections	7.99%		

* - refined from four-circle diffractometer data.

least-squares method (Busing 1970) using 24 automatically aligned reflections in the range 5° < 2 θ < 42° permuted four ways ($\pm h$ at $\pm 2\theta$). A total of 2158 reflections were collected to 2 θ = 55° (a hemisphere of data), of which 1868 were classified as observed [$F > 6\sigma(F)$]. Pertinent information regarding data collection is presented in Table 5.

Data measurement and reduction (Lorentz, polarization, background, scaling) were done using the NRC-VAX package of computer programs (Gabe *et al.* 1989). No absorption correction was applied owing to the low linear absorption-factor of the mineral and the small size of the crystal used.

The crystal structure of phosinaite-(Ce) was determined independently of that by Krutik *et al.* (1981) using the SHELXTL PC package of programs (Sheldrick 1990) and subsequently refined using SHELXL-93 (Sheldrick, in prep.). Scattering curves for neutral atoms and anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. A sharpened Patterson synthesis and subsequent difference-Fourier maps were used to identify all of the cation and anion positions. Refinement of this model with isotropic thermal factors gave an *R* of 5.2%. Site-occupancy refinement revealed that only those sites assigned to rare-earth elements (REE), and assumed to be Ce, and one Na atom were significantly less than ideal, suggesting deficiencies in the scattering powers at these sites. These results are consistent with those of Krutik *et al.* (1981), who assigned a (Na,Ca) occupancy to the Na site and a refined partial occupancy of Ce_{0.67} to the REE site (the remainder of which was attributed to a partial vacancy). Refinement of the site occupancy for the (Na,Ca) site in this study converged to Na 0.66(1) and Ca 0.34(1). This gives a valence of 1.34 *vu*, in good agreement with the value of 1.204 *vu* obtained from bond-valence calculations (Table 6). Refinement of the REE site, which lies on a

TABLE 6. EMPIRICAL BOND-VALENCES (*v.u.*) IN PHOSINAITE-(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
O(1)	0.137						0.200	0.073 ^{x2}		0.433					1.235	2.078
O(2)	0.185	0.278		0.098 ^{x2}					0.230						1.195	1.986
O(3)			0.146 ^{x2}	0.109 ^{x2}		0.153 ^{x2}	0.278	0.139 ^{x2}							1.218	2.047
O(4)							0.207		0.087	0.157, 0.337		1.129				1.917
O(5)	0.165		0.062 ^{x2}				0.251		0.177					1.238		1.893
O(6)		0.144	0.121 ^{x2}	0.124 ^{x2}	0.124 ^{x2}						0.272 ^{x2}			1.120		1.905
O(7)						0.189 ^{x2}	0.184		0.062	0.426					1.199	2.060
O(8)		0.199							0.263		0.339 ^{x2}			1.199		2.000
O(9)	0.044	0.121			0.194 ^{x2}				0.120		0.431 ^{x2}	1.067				1.977
O(10)							0.185	0.083 ^{x2}		0.217, 0.382			1.126			1.993
O(11)						0.107 ^{x2}		0.118 ^{x2}				0.917	0.907			2.049
O(12)	0.120									0.090		0.950	1.011			2.109
O(13)									0.262		0.570 ^{x2}		1.154			1.989
O(14)	0.298	0.201, 0.037			0.074 ^{x2}									1.293		1.903
ΣV	0.949	0.980	0.658	0.662	0.784	0.898	1.305	0.826	1.204	2.042	3.224	4.063	4.198	4.850	4.847	

Valence for the (Na,Ca) site was calculated using the weighted average ($\text{Na}_{0.66}\text{Ca}_{0.34}$); + calculated using the constants of Brese & O'Keeffe (1991).

special position and has an ideal site-occupancy factor of 0.5, converged to Ce 0.42(1). Attempts to refine the site incorporating the scattering curve of Th were not successful. The site was subsequently assumed to fully occupied by Ce, in accordance with results from the electron-microprobe analyses. This gives a calculated valence of 3 *vu*, close to the value of 3.224 *vu* determined from bond-valence summations and much more reasonable than the calculated value of 2.0 *vu*

given by Krutik *et al.* (1981). Calculated bond-valence sums for all the oxygen atoms present gave values all close to 2 (Table 6), indicating the absence of hydroxyl and water.

A further refinement of this model using anisotropic displacement factors and a weighting scheme converged to $R = 3.1\%$ and $wR^2 = 7.99\%$, a significant improvement over the value of $R = 7.2\%$ reported by Krutik *et al.* (1981). No improvement in the final

TABLE 7. 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)	0.3220(1)	0.8891(1)	0.3098(2)	204(8)	115(7)	191(8)	-8(6)	-36(7)	14(6)	170(3)
Si(2)	0.3646(1)	0.9111(1)	0.7449(2)	136(6)	152(7)	118(6)	1(6)	5(7)	9(6)	135(3)
P(1)	0.9736(2)	0.1255(1)	0.2295(3)	138(7)	198(7)	229(9)	-37(7)	-1(6)	-21(5)	189(4)
P(2)	0.3064(1)	0.6183(1)	0.7658(2)	124(6)	129(6)	139(7)	1(6)	-4(6)	-14(5)	131(3)
Na(1)	0.1829(3)	0.7588(2)	0.5440(5)	376(16)	370(16)	410(22)	80(14)	18(14)	129(13)	386(8)
Na(2)	0.0030(3)	0.3491(3)	0.2237(5)	306(18)	637(23)	371(20)	1(19)	11(16)	28(16)	439(9)
Na(3)	0.1714(3)	0.5	0.5	198(17)	566(24)	339(20)	0	0	0	358(10)
Na(4)	0.1604(4)	0.5	0	278(21)	390(20)	393(20)	0	0	0	353(9)
Na(5)	0.8772(3)	0.5	0	331(21)	492(23)	280(19)	0	0	0	368(9)
Na(6)	0.4504(3)	0.5	0	258(7)	296(17)	289(19)	0	0	0	281(8)
Na(7)	0.3307(2)	0.6398(2)	0.2635(4)	181(13)	143(10)	228(13)	-1(10)	21(10)	-23(9)	184(6)
Na(8)	0.4561(3)	0.5	0.5	306(19)	394(20)	247(19)	14(22)	0	0	316(9)
(Na,Ca)	0.1902(2)	0.7662(1)	0.0240(3)	481(13)	203(9)	222(13)	-15(8)	7(10)	-20(8)	302(8)
Ca	0.4971(1)	0.7500(1)	0.5210(3)	181(5)	166(4)	224(8)	-32(5)	-3(5)	-45(3)	191(3)
REE	0.13955(5)	0	0	120(2)	130(2)	118(2)	0	0	0	142(1)
O(1)	0.6492(4)	0.8390(3)	0.0896(6)	275(23)	305(22)	186(21)	-37(18)	-11(21)	-49(25)	255(10)
O(2)	0.8124(4)	0.1480(3)	0.7076(7)	176(20)	258(21)	392(29)	14(22)	55(21)	-42(19)	275(10)
O(3)	0.6873(4)	0.0144(2)	0.7513(6)	318(20)	100(20)	284(22)	21(17)	-45(20)	-7(15)	239(9)
O(4)	0.3741(4)	0.7976(3)	0.2360(8)	304(22)	132(17)	445(28)	40(20)	104(24)	20(17)	240(10)
O(5)	0.1442(4)	0.3424(4)	0.7200(8)	168(20)	481(29)	433(29)	-16(26)	-6(26)	78(23)	361(12)
O(6)	0.9812(4)	0.9808(3)	0.7585(9)	418(27)	322(28)	534(36)	86(26)	-122(29)	-8(22)	424(14)
O(7)	0.3720(4)	0.3522(3)	0.0636(6)	361(25)	268(21)	167(18)	-29(17)	39(20)	132(21)	266(10)
O(8)	0.0335(4)	0.1476(4)	0.0487(7)	362(26)	335(25)	343(31)	90(22)	74(22)	86(23)	346(12)
O(9)	0.1963(3)	0.9039(3)	0.2614(7)	154(18)	277(21)	322(25)	30(21)	7(20)	20(17)	251(10)
O(10)	0.4728(3)	0.8576(3)	0.7912(8)	149(19)	207(19)	506(34)	55(23)	-7(22)	39(17)	287(11)
O(11)	0.3962(3)	0.9789(2)	0.2514(7)	216(19)	132(19)	392(27)	-1(18)	62(20)	-6(14)	247(10)
O(12)	0.6704(7)	0.6152(4)	0.0359(7)	1335(68)	338(28)	214(28)	-10(22)	271(34)	-91(37)	629(22)
O(13)	0.2610(4)	0.1058(3)	0.1330(9)	366(28)	255(24)	582(36)	94(26)	-258(28)	-36(22)	401(14)
O(14)	0.9712(5)	0.3363(5)	0.8987(9)	424(35)	895(53)	476(39)	348(39)	53(30)	-192(37)	598(20)

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

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR PHOSINATE-(Ce)

Table with multiple columns listing interatomic distances and bond angles for various polyhedra: Si(1)O4 tetrahedron, Si(2)O4 tetrahedron, P(1)O4 tetrahedron, P(2)O4 tetrahedron, Na(1)O6 octahedron, Na(2)O6 octahedron, Na(3)O6 octahedron, Na(4)O6 octahedron, Na(5)O6 octahedron, Na(6)O6 octahedron. Each entry includes atom identifiers and numerical values.

TABLE 8. — Cont'd

Continuation of Table 8, listing distances and angles for Na(7)O6 octahedron, Na(8)O6 polyhedron, REEO3 polyhedron, (Na,Ca)O6 polyhedron, CaO6 polyhedron, and CaO6 polyhedron. Each entry includes atom identifiers and numerical values.

Estimated standard deviations in parentheses; * denotes symmetry-equivalent atom; † denotes bridging oxygen.

residual was noted when an extinction condition was included, and the final difference-map showed no maxima greater than 1 e- / Å³.

Final positional and thermal parameters are presented in Table 7, and selected bond-lengths and angles, in Table 8. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The structure of phosinaite-(Ce) may be best described as a series of mixed layers of tetrahedra and octahedra that are stacked along a (Fig. 1). Two different types of layers are present: a (SiP) layer with the composition $[\text{Na}(\text{SiO}_4)_2(\text{PO}_4)]$, and a (NaP) layer with the composition $[\text{Na}(\text{PO}_4)]$; there are two (SiP) layers on each side of a central (NaP) layer.

The (SiP) layer has SiO_4 and PO_4 tetrahedra that are cross-linked by $\text{Na}(7)\text{O}_6$ octahedra. Within the layer, two types of four-membered rings are present: Si_4O_{12} rings and mixed $\text{Na}(2)\text{O}_6\text{-PO}_4$ rings, which are both centered about a $\bar{2}$ axis and alternate along a . These rings form channels along a , the cores of which are occupied by REEO_8 and $\text{Na}(8)\text{O}_8$ polyhedra. The remaining NaO_6 octahedra and both CaO_7 and $(\text{Na,Ca})\text{O}_7$ polyhedra are positioned in the interstices between the rings. The (NaP) layer consists of PO_4 tetrahedra corner-linked to $\text{Na}(2)\text{O}_6$ octahedra, each PO_4 group sharing three of its corners with four $\text{Na}(2)\text{O}_6$ octahedra. Linking of the (SiP) and (NaP)

layers along a is accomplished among corner-sharing tetrahedra and octahedra, reinforced by edge- and face-sharing Na , Ca and REE polyhedra. Essential ordering of Si and P is indicated by refinement of their scattering powers [$\text{Si}(1)$ 96(1)%, $\text{Si}(2)$ 98(1)%, $\text{P}(1)$ 99(1)%, and $\text{P}(2)$ 99(1)%], as constrained by results of electron-microprobe analyses (Table 2), calculated bond-valence sums (Table 7) and mean $T\text{-O}$ bond distances (Table 8), and is most likely driven by considerations of charge and polymerization (McDonald 1992). The fact that Si and P are well ordered in phosinaite-(Ce) suggests that it should be classified as a *silicophosphate* (McDonald 1992, McDonald *et al.* 1994) rather than a disordered silicate or phosphate. A more in-depth discussion of the crystal chemistry of silicophosphates will be presented in a forthcoming paper. Although phosinaite-(Ce) exhibits the strong layering typical of all silicophosphates, it is only the second one known to contain both SiO_4 and PO_4 tetrahedra in the same layer [the other being clinophosinaite, $\text{Na}_3\text{Ca}(\text{SiO}_3)(\text{PO}_4)$; McDonald 1992].

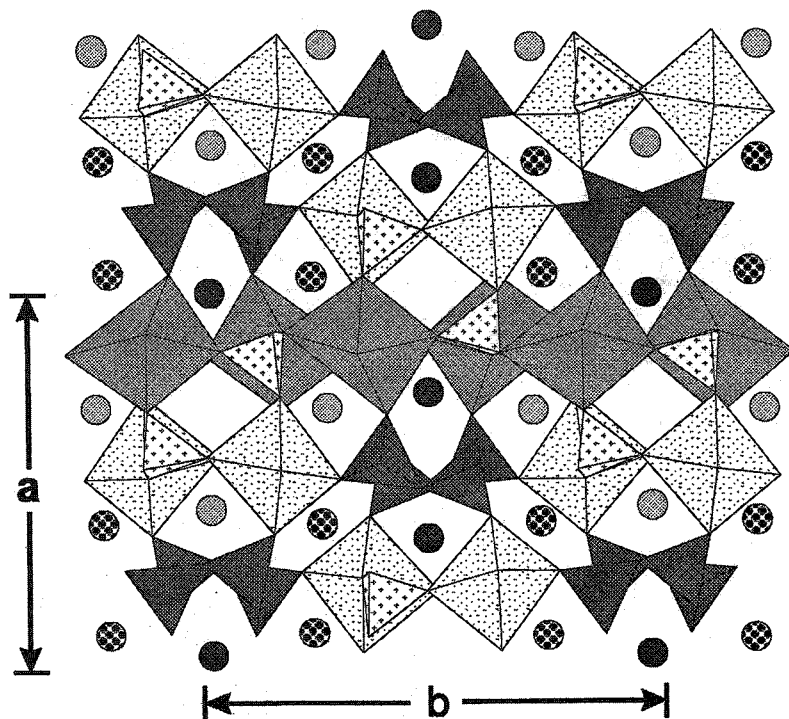


FIG. 1. The crystal structure of phosinaite-(Ce) projected down c . The (NaP) and (SiP) layers are stacked parallel to a . The SiO_4 tetrahedra are heavily shaded, the PO_4 tetrahedra are filled with crosses, the $\text{Na}(2)\text{O}_6$ octahedra are moderately shaded and the $\text{Na}(7)\text{O}_6$ octahedra are lightly stippled. Calcium ions are lightly stippled circles, Na ions filled with large dots, and REE ions heavily shaded.

The four-membered silicate rings present in phosinaite-(Ce) are composed of two independent SiO₄ tetrahedra whose apical directions alternately point up and down in a {UDUD} manner. They have point symmetry 2, deviating considerably from the maximum 4/*mmm* symmetry observed in the four-membered silicate rings in baotite [Ba₄Ti₈O₁₆(Si₄O₁₂)Cl; Nekrasov *et al.* 1970], where the Si atoms are all coplanar. Silicate rings are, in general, energetically less favorable than comparable chain motifs, because of the repulsive forces acting on adjacent tetrahedra (Liebau 1985). As such, silicate rings will develop only if a stabilizing factor, capable of reducing the net repulsive forces acting on the tetrahedra, is present. Such factors typically include the presence of highly electronegative cations (*e.g.*, Pb, Cu, Sn), additional ligands [*e.g.*, H₂O, CO₃, (OH)], and the absence of cations that tend to form rigid coordination polyhedra (*e.g.* Mg, Fe, Al, Li; Liebau 1985). Since none of these features can be called upon to explain the presence of the Si₄O₁₂ rings in phosinaite, we instead postulate that the {UDUD} topology of these rings slightly increases the distance between adjacent Si atoms, thus reducing the associated repulsive forces and stabilizing the ring configuration.

ACKNOWLEDGEMENTS

We thank the following for their cooperation and support: J.T. Szymański of the Canada Centre for Mineral and Energy Technology, Ottawa, for the use of and assistance with the single-crystal diffractometer; P.C. Jones for the electron-microprobe analyses, and Les and Elsa Horváth for donation of the specimens used. The comments of Dr. Peter Bayliss, an anonymous referee and Dr. R.F. Martin improved the manuscript and are appreciated. This work was partially supported by NSERC operating grant A5113 to GYC.

REFERENCES

- APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: indexing and least squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20** (NTIS Doc. PB2-16188).
- BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BUSING, W.R. (1970): Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. In *Crystallographic Computing* (F.R. Ahmed, ed.). Munksgaard, Copenhagen, Denmark.
- CHAO, G.Y., CONLON, R.P. & VAN VELTHUIZEN, J. (1990): Mont Saint-Hilaire unknowns. *Mineral. Rec.* **21**, 363-368.
- , GRICE, J.D. & GAULT, R.A. (1991): Silinaite, a new sodium lithium silicate hydrate mineral from Mont Saint-Hilaire, Quebec. *Can. Mineral.* **29**, 359-362.
- CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.
- & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.
- GABE, E.J., LEPAGE, Y., CHARLAND, J.-P., LEE, F.L. & WHITE, P.S. (1989): NRCVAX – an interactive program system for structure analysis. *J. Appl. Crystallogr.* **22**, 384-387.
- KAPUSTIN, YU.L., KHOMYAKOV, A.P., SEMENOV, E.M., ES'KOVA, A.V., BYKOVA, A.V. & PUDOVKINA, Y. (1974): Phosinaite, a new rare-earth mineral. *Zap. Vses. Mineral. Obshchest.* **103**, 567-570 (in Russ.).
- KRUTIK, V.M., PUSHCHAROVSKII, D.YU., KHOMYAKOV, A.P., POBEDIMSKAYA, E.A. & BELOV, N.V. (1981): Crystal structure and typtomorphism of phosinaite. *Sov. Phys. Crystallogr.* **26**(6), 679-682.
- LIEBAU, F. (1985): *Structural Chemistry of Silicates: Structure, Bonding and Classification*. Springer-Verlag, Berlin, Germany.
- MCDONALD, A.M. (1992): *The Crystal Structures of Three Minerals, Phosinaite-(Ce), Abenakiite-(Ce) and Yoshimuraitite, with Remarks on the Crystal Chemistry of Silicophosphates*. Ph.D. thesis, Ottawa-Carleton Geoscience Centre, Ottawa, Ontario.
- , CHAO, G.Y. & GRICE, J.D. (1994): Abenakiite-(Ce), a new silicophosphate carbonate mineral from Mont Saint-Hilaire, Québec: description and structure determination. *Can. Mineral.* **32**, 843-854.
- NEKRASOV, YU.V., PONOMAREV, V.I. SIMONOV, V.I. & KHEIKER, D.M. (1970): Refinement of the atomic structure of baotite and the isomorphic relationships in this mineral. *Sov. Phys. Crystallogr.* **14**, 508-514.
- RUCKLIDGE, J.C. & GASPARRINI, E. (1969): *Electron Microprobe Analytical Data Reduction EMPADR VII*. Dep. Geol., Univ. Toronto, Toronto, Ontario.
- SHELDRIK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.

Received January 16, 1995, revised manuscript accepted October 17, 1995.