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ABENAKIITE-(Ce), A NEW SILICOPHOSPHATE CARBONATE MINERAL FROM MONT SAINT-HILAIRE, QUEBEC: DESCRIPTION AND STRUCTURE DETERMINATION

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ABSTRACT

Abenakiite-(Ce) is a new mineral species discovered at the Poudrette Quarry, Mont Saint-Hilaire, Quebec. It occurs as a single 2 × 1 mm pale brown ellipsoidal grain in association with aegirine, eudialyte, mangan-neptunite, polylithionite, serandite, and steenstrupine-(Ce). The streak is white, and the luster, vitreous. The mineral is brittle, with a conchoidal fracture and a poor {0001} cleavage. It displays no discernible fluorescence under long- or short-wave ultraviolet radiation, has a Mohs hardness greater than 4, and exhibits a very weak effervescence in 1:1 HCl. *D*(meas.) is 3.21, *D*(calc.) 3.27 g/cm^3 for the empirical formula. Abenakiite-(Ce) is uniaxial negative, ω 1.589(1) and ε 1.586(1). The average of four electron-microprobe analyses is Na_2O 25.32, Ce_2O_3 15.31, La_2O_3 5.94, Nd_2O_3 7.78, Pr_2O_3 2.02, Sm_2O_3 0.74, ThO_2 1.42, SrO 0.12, SiO_2 13.30, P_2O_5 14.11, SO_2 2.28, CO_2 8.90 (calc.), total 97.24 wt.%, corresponding to $Na_{24.23}(Ce_{2.77}Nd_{1.37}La_{1.08}Pr_{0.36}Th_{0.16}Sm_{0.13}Sr_{0.03})_{\Sigma 5.90}Si_{6.56}P_{5.90}C_6S_{1.06}O_{63}$ on the basis of O = 63 or, ideally, $Na_{26}REE_6(SiO_3)_6(PO_4)_6(CO_3)_6(S^{4+}O_2)O$ with $Z = 3$. It is rhombohedral, $R\bar{3}$, with *a* 16.018(2), *c* 19.761(4) Å, *V* 4390.9(1) Å^3. The strongest eight reflections in the X-ray powder pattern [*d* in Å(*I*)(*hkl*)] are 11.414(75)(101), 8.036(85)(012), 6.554(85)(021), 4.646(75)(104), 3.773(90)(131), 3.591(80)(312), 3.150(70)(125), 2.674(100)(036). The name honors the Abenaki Indian Tribe, which inhabited the area around Mont Saint-Hilaire. The crystal structure has been refined to *R* = 3.1%, w*R* = 3.0% for 2116 observed [$F > 6\sigma(F)$] reflections. The structure, when viewed along *c*, may be best described in terms of a {6^3} hexagonal net, with chains of NaO_7 polyhedra joined to PO_4 groups at the nodes of the net and columns of six-membered SiO_4, NaO_7, and NaO_7–$REEO_8$ polyhedral rings in the center. Within the columns are NaO_6 octahedra, CO_3 groups, and disordered SO_2 groups.

Keywords: abenakiite-(Ce), new mineral species, silicophosphate carbonate, X-ray data, chemical composition, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

L'abénakiïte-(Ce), nouvelle espèce minérale, provient de la carrière Poudrette, au mont Saint-Hilaire, Québec. Elle se présente en cristaux uniques ellipsoïdaux, brun pâle, mesurant 2 × 1 mm, en association avec aegyrine, eudialyte, mangan-neptunite, polylithionite, serandite et steenstrupine-(Ce). Sa rayure est blanche, et son éclat, vitreux. Il s'agit d'un minéral cassant ayant une surface conchoïdale et montrant un clivage {0001} de piètre qualité. L'abénakiïte-(Ce) ne montre aucune fluorescence en lumière ultra-violette (ondes longues ou courtes); sa dureté (échelle de Mohs) est inférieure à 4, et en présence de HCl (1:1), elle produit une très faible effervescence. La densité mesurée est égale à 3.21, et la densité calculée, 3.27 g/cm^3 pour la formule empirique. Elle est uniaxe négative, ω 1.589(1), ε 1.586(1). Quatre analyses à la microsonde électronique ont donné, en moyenne, Na_2O 25.32, Ce_2O_3 15.31, La_2O_3 5.94, Nd_2O_3 7.78, Pr_2O_3 2.02, Sm_2O_3 0.74, ThO_2 1.42, SrO 0.12, SiO_2 13.30, P_2O_5 14.11, SO_2 2.28, CO_2 8.90 (calc.), pour un total de 97.24% (poids), ce qui correspond à $Na_{24.23}(Ce_{2.77}Nd_{1.37}La_{1.08}Pr_{0.36}Th_{0.16}Sm_{0.13}Sr_{0.03})_{\Sigma 5.90}Si_{6.56}P_{5.90}C_6S_{1.06}O_{63}$ sur une base de 63 atomes d'oxygène ou, plus simplement, $Na_{26}TR_6(SiO_3)_6(PO_4)_6(CO_3)_6(S^{4+}O_2)O$, $Z = 3$ (*TR*: terres rares). C'est un minéral rhomboédrique, $R\bar{3}$, avec *a* 16.018(2), *c* 19.761(4) Å, *V* 4390.9(1) Å^3. Les huit raies les plus intenses du tracé de diffraction X [méthode des poudres, *d* in Å(*I*)(*hkl*)] sont: 11.414(75)(101), 8.036(85)(012), 6.554(85)(021), 4.646(75)(104), 3.773(90)(131), 3.591(80)(312), 3.150(70)(125), 2.674(100)(036). Le nom honore la tribu des Abénakis, qui peuplait autrefois la région du mont Saint-Hilaire. Nous avons résolu la structure cristalline jusqu'à un résidu *R* de 3.1% (*wR* 3.0%) en utilisant 2116 réflexions observées [$F > 6\sigma(F)$]. La structure, le long de *c*, décrit un réseau hexagonal {6^3}, avec des chaînes de polyèdres NaO_7 liés à des groupes PO_4 aux noeuds du réseau, et avec des colonnes d'anneaux à six membres (SiO_4, NaO_7, NaO_7–TRO_8) dans le centre. Dans ces colonnes se trouvent des octaèdres NaO_6, des groupes CO_3, et des groupes SO_2 désordonnés.

Mots-clés: abénakiïte-(Ce), nouvelle espèce minérale, silicophosphate carbonate, données de diffraction X, composition chimique, structure cristalline, mont Saint-Hilaire, Québec.

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INTRODUCTION

A single crystal of an unknown phase (UK85) was discovered in a xenolith of sodalite syenite in nepheline syenite at the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Québec. This phase has been recognized as the new mineral species abenakiite-(Ce), named after the Abenaki Indian tribe, which inhabited the area around Mont Saint-Hilaire. Both the mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names. The type specimen has been deposited at the Canadian Museum of Nature, Ottawa, Ontario (#81501).

OCCURRENCE AND ASSOCIATED MINERALS

Abenakiite-(Ce) occurs embedded in sodalite and is coated by an unidentified rhabdophane-group mineral, which may be a product of its alteration. It is closely associated with aegirine, eudialyte, mangan-neptunite, polylithionite, serandite, and steenstrupine-(Ce). In addition, more than 72 minerals have been recorded from the same xenolith (Chao *et al.* 1991). Abenakiite-(Ce) is a late-stage phase, possibly arising from a metasomatic event associated with emplacement of the nepheline syenite.

PHYSICAL AND OPTICAL PROPERTIES

Abenakiite-(Ce) occurs as a single, ellipsoidal crystal measuring approximately 2 × 1 mm. It is predominantly pale brown, transparent, has a vitreous luster, a white streak, and does not fluoresce under either long- or short-wave ultraviolet radiation. The Mohs hardness is greater than 4. The mineral is brittle with a conchoidal fracture and a poor {0001} cleavage. Abenakiite-(Ce) effervesces very weakly in 1:1 HCl. The measured density of abenakiite-(Ce) is 3.21(2) g/cm^3, as determined by flotation in a heavy liquid and a pycnometer. This agrees well with the calculated density of 3.27 g/cm^3, based on the empirical chemical formula and the cell dimensions refined from the powder data. Optically, abenakiite-(Ce) is uniaxial (–), with ω 1.589(1) and ε 1.586(1) (λ = 589 nm). It is not pleochroic.

CHEMICAL DATA

Electron-microprobe analyses were done on a Cambridge Microscan MK5 instrument using an operating voltage of 15 kV and an estimated beam-current of 30 nA. The electron beam was rastered over an area of 60 × 60 μm^2 to minimize damage to the sample. Wavelength-dispersion data were collected using the following standards: albite (Na), hornblende (Si), apatite (P), celestine (S, Sr), *REE* glasses (La, Ce, Pr, Nd, Sm), and ThO_2. These were reduced using a modified version of EMPADR VII (Rucklidge & Gasparrini 1969). Also sought but not detected were F, Ba, Ti, Fe, Mn, Zr, Y, and Ca. A qualitative energy-dispersion scan indicated less than 0.2 wt.% Al_2O_3.

TABLE 1. THE CHEMICAL COMPOSITION (WT.%) OF ABENAKIITE-(Ce)

	1	2	3	4	5[a]	6[b]
Na_2O	25.04	25.33	25.52	25.37	25.32	27.67
Ce_2O_3	15.50	15.36	15.24	15.15	15.31	16.91
La_2O_3	6.08	5.86	6.11	5.69	5.94	5.60
Nd_2O_3	8.04	8.07	7.59	7.41	7.78	11.56
Pr_2O_3	1.91	2.43	1.95	1.77	2.02	-
Sm_2O_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_2O_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[c]	(9.10)	(8.95)	(8.76)	(8.82)	(8.91)	9.05
TOTAL	99.18	97.96	95.94	95.83	97.24	100

a Average of analyses 1-4 on one grain.
b Calculated for the formula, $Na_{26}(Ce_3Nd_2La_1)_{\Sigma 6}(SiO_3)_6(PO_4)_6(CO_3)_3(SO_2)O$.
c Calculated from stoichiometry.

Results of these analyses are presented in Table 1. Deficiencies of 10–13 wt.% are evident; these are attributed to the presence of elements with an atomic number less than eight or to water, which are not detectable by the electron microprobe. The missing constituent was subsequently identified by crystal-structure analysis to be C in the form of a carbonate group, on the basis of its electron density, its trigonal planar coordination by oxygen, its mean cation-to-oxygen bond distances (1.302 Å), and its calculated bond-valence sum (3.826 *v.u.*). Bond-valence calculations were also used to verify the absence of water and to determine the 4+ valence of the S in the mineral.

The Na_2O concentrations given in Table 1 are systematically low, owing to volatilization of Na under the electron beam and possibly to vacancies in some Na sites of the structure. The average composition from Table 1 gives the empirical formula (based on O = 63 from results of the crystal-structure analysis): $Na_{24.23}(Ce_{2.77}Nd_{1.37}La_{1.08}Pr_{0.36}Th_{0.16}Sm_{0.13}Sr_{0.03})_{\Sigma 5.90}Si_{6.56}P_{5.90}C_6S_{1.06}O_{63}$, which is close to the structural formula $Na_{26}REE_6(SiO_3)_6(PO_4)_6(CO_3)_6(SO_2)O$, with $Z = 3$.

Gladstone–Dale constants (Mandarino 1981) were used to calculate a compatibility index of 0.017, indicating superior agreement among optical, physical and chemical data.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession camera photographs show abenakiite-(Ce) to be rhombohedral, with possible space-groups $R3$ and $R\bar{3}$. The observed X-ray powder pattern for

TABLE 2. 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
3.773	90	3.7846	48	303
		3.7765	47	131
3.591	80	3.5956	26	214
		3.5852	29	312
3.420	3	3.4218	6	223
3.150	70	3.1560	52	125
3.024	50	3.0292	10	232
		3.0271	10	410
2.844	5	2.8384	6	404
2.745	20	2.7568	7	315
		2.7506	12	143
2.674	100	2.6826	100	036
		2.6697	89	330
2.604	10	2.6067	8	045
		2.5988	4	241
2.532	15	2.5355	9	422
		2.4856	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
2.272	15	2.2760	7	137
		2.2708	9	505
		2.2346	5	128
2.222	50	2.2287	5	146
		2.2213	12	520
		2.1957	10	009
2.181	50	2.1846	8	425
		2.1815	31	063
2.102	40	2.1048	9	523
		2.1034	7	161
		2.0786	7	318
		2.0706	5	434
1.976	5	1.9834	9	039
1.943	10	1.9473	6	164
		1.9430	5	072
1.917	10	1.9210	5	247
		1.9157	2	621
1.890	45	1.8923	48	066
1.865	15	1.8680	6	517
		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
1.688	25	1.6893	7	363
		1.6885	7	271
1.670	15	1.6714	6	544
		1.6703	3	722
1.618	10	1.6200	9	455
		1.6096	10	5·10
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 Cu*K*α radiation (λ = 1.5418 Å); I_{est} visually estimated; d_{calc} determined from the cell refined from powder data: *a* = 16.018(2), *c* = 19.761(6) Å; I_{calc} calculated from the crystal structure.

abenakiite-(Ce) (Table 2) was obtained using a 114.6-mm Gandolfi camera and Ni-filtered Cu*K*α radiation (λ = 1.5418 Å). It agrees well with that calculated from the crystal structure using the SHELXTL PC package of programs (Sheldrick 1990). The unit-cell parameters, *a* 16.018(2), *c* 19.761(4) Å, with *V* 4390.9(1) Å^3 and *Z* = 3, were refined from the powder data using the program CELREF (Appleman & Evans 1973). Indexing was carried out using the intensities of reflections on the precession photographs as a guide.

X-ray intensity data were collected on an Enraf–Nonius CAD–4 diffractometer using a disc-shaped fragment of dimensions 0.27 × 0.36 × 0.09 mm, which was mounted to rotate about *c*. The grain was found to be optically homogeneous, with a sharp, uniform extinction under crossed polars. Data measurement and reduction (Lorentz, polarization, background, scaling) were done using the NRCVAX package of computer programs (Gabe *et al.* 1989). No absorption correction was applied because of the low linear absorption coefficient [μ(Mo*K*α) = 4.91 cm^{-1}] and the small size of the crystal used. A set of 42 reflections (15°<2θ<27°) permuted four ways (±*h* at ±2θ) was used to refine the cell dimensions, *a* 16.020(2), *c* 19.920(4) Å and *V* 4427.4(1) Å^3, which are in good agreement with those refined from the powder data. A full sphere of X-ray intensity data to 2θ = 55° was collected. Further information regarding data collection is presented in Table 3.

The crystal structure of abenakiite-(Ce) was solved using direct methods and refined in the space group $R\bar{3}$ using the SHELXTL PC package of programs (Sheldrick 1990). Scattering curves for neutral atoms and anomalous dispersion corrections were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. From the *E*-map, the positions of the rare-earth element (assumed to be entirely Ce), Si, P, two distinct Na atoms, and an O atom were identified. Difference-Fourier maps of this initial model

TABLE 3. MISCELLANEOUS DATA FOR DETERMINATION OF THE CRYSTAL STRUCTURE OF ABENAKIITE-(Ce)

Space Group	$R\bar{3}$ (#418)	Diffractometer	Enraf-Nonius CAD4
a (Å)	16.020(2)*	Radiation	MoKα (50 kV, 20 mA)
c	19.920(4)*	Monochromator	Graphite
V (Å^3)	4427.4(1)	Crystal Shape	Flat, rounded
Z	3	Crystal Size	0.27x0.36x0.09 mm
μ(Mo*K*α)	4.91 cm^{-1}		

Chemical Formula	$Na_{26}REE_6(SiO_3)_6(PO_4)_6(CO_3)_6(SO_2)O$
Intensity Data Collection	Θ-2Θ scanning mode
2Θ Limit	55°
Intensity Standards	Three every 10,000 seconds
Orientation Standards	Three every 400 reflections
No. of Unique Reflections	2238
No.of Observed Reflections	2116
Criterion for Observed	$F > 6\sigma(F)$
Weighting Scheme	$wR = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$, $w = 1/\sigma^2$
R, all Observed Reflections	3.1%
wR, all Observed Reflections	3.0%

* values refined from four-circle diffractometer data.

revealed additional atomic sites, to which the appropriate scattering curves for the elements believed to be present were assigned. At R = 7.3%, all of the expected atoms were located. An examination of another difference map calculated at this stage showed a positive maximum of approximately 8 $e^-/\text{Å}^3$. The maximum was coordinated by three O atoms in a trigonal planar configuration, with a mean X–O distance of 1.302 Å. On the basis of these data, the residual electron-density was assigned to C.

Refinement of this model, which included conversion to anisotropic displacement-factors, introduction of a weighting scheme based on $[1/\sigma^2(F)]$, and refinement of site occupancies, converged to R = 3.1% and wR = 3.0%. An extinction correction was applied but did not improve the refinement. The S and O(11) atoms were refined on an isotropic basis owing to the large displacement-factors encountered during attempts to refine them anisotropically. Refinement of site-occupancy factors indicated all sites to be fully occupied, except for the partial occupancies noted for Na(4) [88(1)%] and O(11) [34(2)%]. The occupancy of O(11) was subsequently fixed at one-third, to agree with the interpretation of an SO_2 group being present in abenakiite-(Ce). All maxima in a new difference-map calculated at this stage were found to be less than 1 $e^-/\text{Å}^3$, except for a minor maximum of 1.7 $e^-/\text{Å}^3$ associated with the rare-earth site. An attempt also was made to refine the structure in the space group $R3$. However, (1) the residuals for this model (R = 4.1%, wR = 3.5%) were greater than those obtained for the centrosymmetric model, (2) a number of atoms were found to have nonpositive anisotropic displacement-factors, and (3) all atoms were found to have relatively larger U_{eq} factors, suggesting that the noncentrosymmetric model is unlikely.

Final positional and thermal parameters are given in Table 4, selected bond-lengths and distances in Table 5 and the calculated bond-valences in Table 6. The observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

If viewed along c, the abenakiite-(Ce) structure may be most easily described in terms of a $\{6^3\}$ hexagonal net (Fig. 1). Within this net, there are two major polyhedral units, (1) polyhedral chains, and (2) complex columns, both of which extend infinitely along c.

The polyhedral chain component is composed of PO_4 tetrahedra and $Na(1)O_7$ polyhedra, which are linked along c through alternating shared edges and corners (Fig. 2). These polyhedral chains occupy the nodes of the $\{6^3\}$ net and are linked laterally to adjacent chains *via* edge-sharing $Na(1)O_7$ polyhedra.

TABLE 4. POSITIONAL AND THERMAL PARAMETERS FOR ABENAKIITE-(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	0.53552(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)
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 $[-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} \ldots + 2hka^{*2}b^{*2}U_{12})]$; all U values are in $\text{Å}^2 \times 10^4$; estimated standard deviations in parentheses.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR ABENAKIITE–(Ce)

SiO_4 tetrahedron

Si -O(3)	1.606(5)	O(3) -Si -O(1)	117.6(2)	O(3) -O(1)	2.747(8)
-O(1)	1.607(4)	-O(2)	107.4(3)	-O(2)	2.628(8)
-O(2)$^+$	1.655(4)	-O(2)*	105.8(2)	-O(2)*	2.607(8)
-O(2)*$^+$	1.664(5)	O(1) -Si -O(2)	108.5(2)	O(1) -O(2)	2.648(8)
<Si-O>	1.633	-O(2)*	110.5(3)	-O(2)*	2.689(8)
		O(2) -Si -O(2)*	106.4(2)	O(2) -O(2)*	2.658(8)
		<O -Si -O>	109.4	<O -O>Si	2.663

PO_4 tetrahedron

P -O(8)	1.503(4)	O(8) -P -O(6)	112.0(3)	O(8) -O(6)	2.496(8)
-O(6)	1.506(5)	-O(5)	110.9(3)	-O(5)	2.508(8)
-O(5)	1.541(6)	-O(7)	108.1(3)	-O(7)	2.467(8)
-O(7)	1.545(5)	O(6) -P -O(5)	110.5(3)	O(6) -O(5)	2.503(8)
<P-O>	1.524	-O(7)	111.7(3)	-O(7)	2.525(8)
		O(5) -P -O(7)	103.3(3)	O(5) -O(7)	2.419(8)
		<O -P -O>	109.4	<O -O>P	2.486

$Na(1)O_7$ polyhedron

Na(1)-O(6)	2.342(5)	O(6) -Na(1)-O(9)	126.1(2)	O(6) -O(9)	3.604(8)
-O(9)	2.407(2)	-O(3)*	82.2(2)	-O(3)*	3.263(8)
-O(3)*	2.611(6)	-O(2)	103.1(2)	-O(2)	3.972(8)
-O(2)	2.721(6)	-O(7)	125.1(2)	-O(7)	4.571(8)
-O(8)	2.761(5)	-O(3)	100.9(2)	-O(3)	3.956(8)
-O(7)	2.770(5)	O(9) -Na(1)-O(2)	126.2(2)	O(9) -O(2)	4.573(8)
-O(3)	2.777(4)	-O(8)	81.0(2)	-O(8)	3.366(8)
<Na(1)-O>	2.627	-O(7)	93.3(2)	-O(7)	3.773(8)
		-O(3)	71.2(2)	-O(3)	3.033(8)
		O(3)*-Na(1)-O(2)	59.0(2)	O(3)*-O(2)	2.628(8)
		-O(8)	97.9(2)	-O(8)	4.052(8)
		-O(7)	81.5(2)	-O(7)	3.514(8)
		-O(3)	114.5(2)	-O(3)	4.531(8)
		O(2) -Na(1)-O(8)	78.7(2)	O(2) -O(8)	3.474(8)
		-O(7)	112.0(2)	-O(7)	4.553(8)
		-O(3)	56.6(2)	-O(3)	2.608(8)
		O(8) -Na(1)-O(7)	53.0(1)	O(8) -O(7)	2.467(8)
		-O(3)	80.9(1)	-O(3)	3.594(8)

$Na(2)O_7$ polyhedron

Na(2)-O(8)	2.251(4)	O(8) -Na(2)-O(2)	95.3(2)	O(8) -O(2)	3.627(8)
-O(1)	2.396(5)	-O(7)	89.4(2)	-O(7)	3.339(8)
-O(2)	2.445(5)	-O(10)	111.1(2)	-O(10)	3.594(8)
-O(7)	2.489(5)	-O(6)	79.7(2)	-O(6)	3.313(8)
-O(10)	2.538(5)	-O(5)	53.6(2)	-O(5)	2.505(8)
-O(6)	2.866(8)	O(1) -Na(2)-O(2)	87.9(1)	O(1) -O(2)	3.361(8)
-O(5)	3.069(6)	-O(7)	85.5(2)	-O(7)	3.314(8)
<Na(2)-O>	2.579	-O(10)	76.2(1)	-O(10)	3.046(8)
		-O(6)	89.4(1)	-O(6)	3.720(8)
		O(2) -Na(2)-O(10)	117.5(2)	O(2) -O(10)	4.261(8)
		-O(6)	113.6(2)	-O(6)	4.453(8)
		-O(5)	83.4(2)	-O(5)	3.680(8)
		O(7) -Na(2)-O(10)	111.1(2)	O(7) -O(10)	2.922(8)
		-O(6)	55.7(1)	-O(6)	2.525(8)
		-O(5)	108.6(2)	-O(5)	2.416(8)
		O(10)-Na(2)-O(6)	125.9(2)	O(10)-O(6)	4.816(8)
		-O(5)	71.2(1)	-O(5)	3.288(8)
		O(6) -Na(2)-O(5)	132.2(1)	O(6) -O(5)	2.498(8)

$Na(3)O_6$ octahedron

Na(3)-O(1)	2.331(4) x3	O(1) -Na(3)-O(1)*	112.6(1)x3	O(1) -O(1)*	3.879(8)
-O(10)	2.473(5) x3	-O(10)	78.6(1)x3	-O(10)	3.046(8)
<Na(3)-O>	2.402	-O(10)*	83.3(2)x3	-O(10)*	3.194(8)
		O(10)-Na(3)-O(10)*	78.0(2)x3	O(10)-O(10)*	3.114(8)

$Na(4)O_7$ polyhedron

Na(4)-O(7)	2.395(6)	O(7) -Na(4)-O(6)	121.0(3)	O(7) -O(6)	4.264(8)
-O(4)	2.497(6)	-O(8)	83.0(2)	-O(8)	3.339(8)
-O(6)	2.509(5)	-O(11)*	107.4(4)	-O(11)*	4.070(8)
-O(8)	2.634(6)	-O(11)	128.0(5)	-O(11)	4.566(8)
-O(11)*	2.65(1)	-O(9)	94.1(2)	-O(9)	3.772(8)
-O(11)	2.68(3)	O(4) -Na(4)-O(6)	76.2(2)	O(4) -O(6)	3.089(8)
-O(9)	2.748(6)	-O(11)*	100.3(4)	-O(11)*	3.951(8)
<Na(4)-O>	2.55	-O(11)	93.1(5)	-O(11)	3.762(8)
		-O(9)	50.8(2)	-O(9)	2.260(8)
		O(6) -Na(4)-O(8)	58.0(2)	O(6) -O(8)	2.496(8)
		-O(11)*	113.7(5)	-O(11)*	4.319(8)
		-O(11)	82.7(4)	-O(11)	3.431(8)
		-O(9)	125.5(2)	-O(9)	4.674(8)
		O(8) -Na(4)-O(11)*	88.8(5)	O(8) -O(11)*	3.699(8)
		-O(11)	71.6(5)	-O(11)	3.109(8)
		O(11)*-Na(4)-O(9)	90.1(5)	O(11)*-O(9)	3.818(8)
		O(11)-Na(4)-O(9)	108.9(5)	O(11)-O(9)	4.417(8)

$Na(5)O_7$ polyhedron

Na(5)-O(8)	2.249(7)	O(8) -Na(5)-O(6)	93.8(2)	O(8) -O(6)	3.313(8)
-O(6)	2.290(5)	-O(9)	93.4(3)	-O(9)	3.365(8)
-O(4)	2.347(7)	-O(11)*	78.9(3)	-O(11)*	3.109(8)
-O(9)	2.373(6)	-O(11)	96.3(6)	-O(11)	3.699(8)
-O(11)*	2.62(2)	-O(3)	88.9(2)	-O(3)	3.594(8)
-O(11)	2.70(2)	O(6) -Na(5)-O(4)	83.6(3)	O(6) -O(4)	3.089(8)
-O(3)	2.847(5)	-O(9)	147.4(2)	-O(9)	4.476(8)
<Na(5)-O>	2.59	-O(11)*	113.0(4)	-O(11)*	4.101(8)
		-O(11)	86.5(4)	-O(11)	4.431(8)
		-O(3)	78.1(2)	-O(3)	3.263(8)
		O(4) -Na(5)-O(9)	82.4(2)	O(4) -O(9)	3.108(8)
		-O(11)*	113.8(3)	-O(11)*	4.166(8)
		-O(11)	96.2(6)	-O(11)	3.762(8)
		-O(3)	78.1(2)	-O(3)	3.297(8)
		O(9) -Na(5)-O(11)*	124.2(4)	O(9) -O(11)*	4.384(8)
		O(11)	99.6(4)	-O(11)	3.818(8)

CO_3 triangle

C -O(9)	1.265(6)	O(9) -C -O(4)	124.7(5)	O(9) -O(4)	2.261(8)
-O(4)	1.286(6)	-O(10)	117.4(4)	-O(10)	2.239(8)
-O(10)	1.355(6)	O(4) -C -O(10)	116.9(4)	O(4) -O(10)	2.252(8)
<C -O>	1.302	<O -C -O>	119.7	<O -O>C	2.254

SO_2 group

S -O(11)	1.422(3)x6	O(11)-S -O(11)*	119.7(1)	O(11)-O(11)*	2.457(8)

$REEO_9$ polyhedron

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

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

The other major polyhedral units in the structure are the complex columns that occupy the centers of the hexagons outlined by the polyhedral chains (Fig. 1). These complex columns may most clearly be described in terms of two subunits: (1) a hollow tube unit, and (2) the channel occupant unit. The hollow tube unit (Fig. 3) consists of three different types of six-membered rings: (i) a Na–O polyhedral ring, composed of edge-sharing $Na(4)O_7$ and $Na(5)O_7$ polyhedra, (ii) a Na–*REE*–O polyhedral ring, composed of edge-sharing $Na(2)O_7$ and *REE*O_9 polyhedra, and (iii) a silicate ring, composed of corner-sharing SiO_4

TABLE 6. EMPIRICAL BOND VALENCES (*v.u.*) FOR ABENAKIITE-(Ce)

	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	REE	Si	P	C	S	ΣV
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	0.839	1.050	1.200	0.747*	1.128*	3.254	3.915	4.976	3.826	3.654*	

Note: Bond-valence constants used in the calculations are from Brese and O'Keeffe (1991); * calculated using the refined O(11) site occupancy of 1/3.

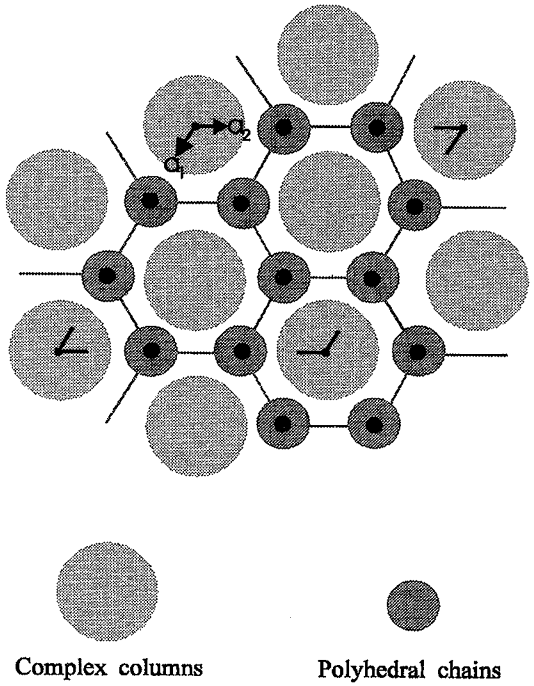

FIG. 1. The $\{6^3\}$ hexagonal net in abenakiite-(Ce) projected down *c*.

tetrahedra that are arranged in a {*UDUDUD*} manner to form a Si_6O_{18} ring. The three types of six-membered rings are joined along *c* through shared edges and corners, thus forming hollow tubes. The channel occupant unit (Fig. 4) consists of three different types of polyhedra that occupy the channels within the hollow tubes. These polyhedra include (i) a disordered SO_2 group, (ii) carbonate groups, and (iii) NaO_6 octahedra.

The disordered SO_2 group lies along the $\bar{3}$ axis and is positioned in the center of the Na polyhedral ring of the hollow tubes. The S atom is bonded only to the O(11) atoms, which lie on a six-fold equipoint. As the site-occupancy factor for O(11) refined to 34(2)%, it would seem that only two O(11) atoms are bonded to S ($\frac{1}{3} \times 6 = 2$). Bond-valence sums, calculated from the observed S–O bond distances and the constants of Brese & O'Keeffe (1991), are 3.654 *v.u.* assuming S^{4+} and 3.462 *v.u.* assuming S^{6+}. Therefore, S^{4+} is interpreted to form a SO_2 group with O(11). Further evidence to support the presence of SO_2 comes from (1) the average O–S–O angle in abenakiite-(Ce), which is 119.7(1)°, very close to the value of 119(2)° given for crystals of SO_2 (Post *et al.* 1952), and (2) the average S–O bond in abenakiite-(Ce), 1.422(3) Å, close to the value observed in SO_2, 1.43 Å (Post *et al.* 1952). Analysis of the environment around S on difference-Fourier maps failed to reveal any indication of additional O atoms being bonded to S. The SO_2 group is thus disordered over six orientations (Fig. 5), the

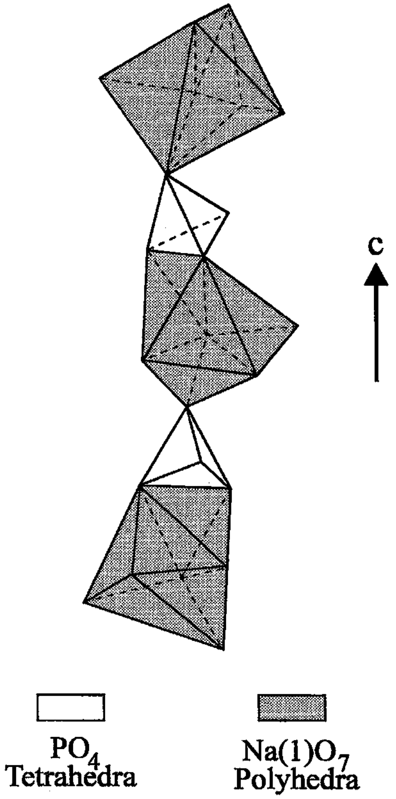

FIG. 2. The polyhedral chains in abenakiite-(Ce) projected down [1$\bar{1}$0].

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disordering being reflected in the large isotropic displacement-factors of S and O(11) and the fact that neither of these atoms could be refined anisotropically. Since O(11) is also bonded to Na(4) and Na(5), the SO_2 group probably is essential to the structure. Whereas the presence of an SO_2 group in abenakiite-(Ce) may be controversial, sulfur dioxide is an accepted ligand in certain synthetic compounds (Ryan *et al.* 1981, Cotton & Wilkinson 1988). One such compound is $[Mg(SO_2)(AsF_6)_2]_n$ whose structure has been solved by Hoppenheit *et al.* (1982). They observed that octahedrally coordinated Mg^{2+} cations had two *trans* Mg–O–S–O linkages with S–O bond distances in the range of 1.377(14) to 1.441(12) Å (average 1.412 Å) and O–S–O bond angles from 115.3(8) to 116.8(9)°.

FIG. 3. The hollow tube component of the complex columns in abenakiite-(Ce) projected down [1$\bar{1}$0].

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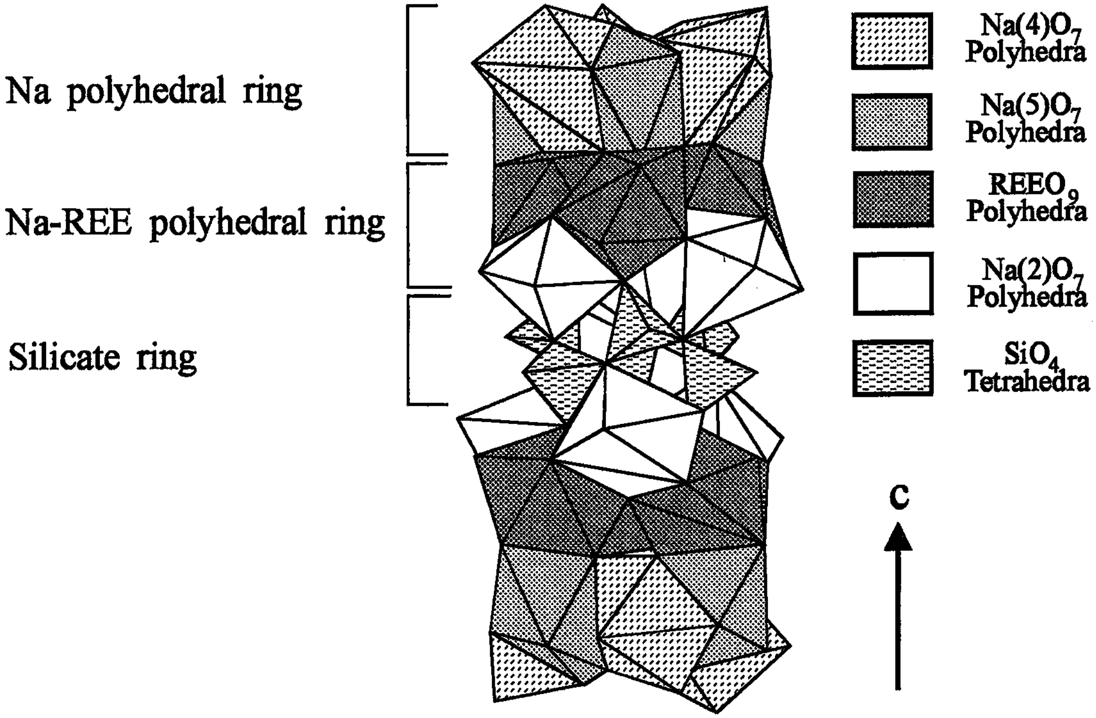
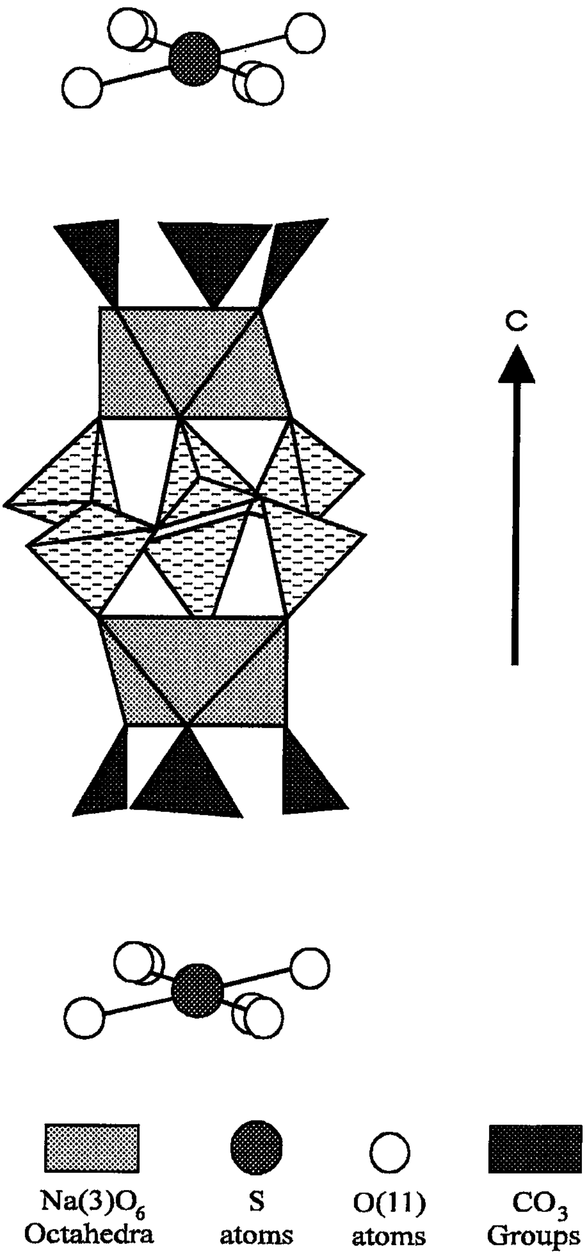


FIG. 4. The channel occupants of the complex columns in abenakiite-(Ce) projected down [1$\bar{1}$0]. The Na(4,5)O_7 and Na–*REE*–O polyhedral rings have been omitted for clarity.



Such linkages seem to be similar to the Na(4,5)–O–S–O linkages in abenakiite-(Ce), and the observed S–O bond distances and angles are in good agreement with those observed in abenakiite-(Ce). Complexes of the type $[M(SO_2)(AsF_6)_2]_n$ (M = Mg, Fe, Mn, Co, Ni, Zn) have been synthesized by the oxidation of pure metal by AsF_5 in liquid SO_2 through the reaction:

$$M + 3AsF_5 + SO_2 \rightarrow [M(SO_2)(AsF_6)_2]_n + AsF_3$$

(Hoppenheit *et al.* 1982). Such a reaction is quite interesting when one considers the geochemical features of the environment in which abenakiite-(Ce) crystallized. These include the presence of (1) numerous F-bearing species such as villiaumite

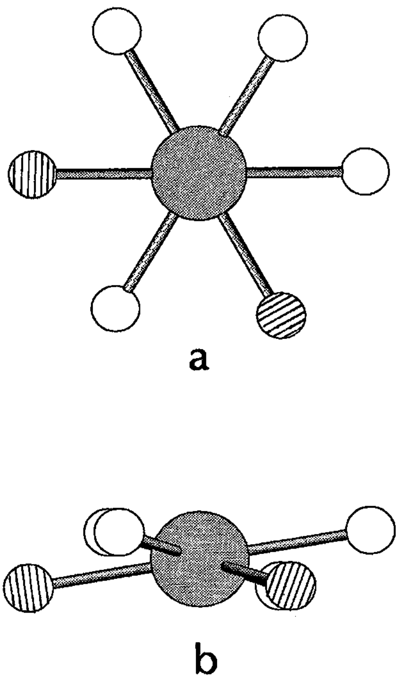


FIG. 5. One of six possible orientations of the SO_2 group (shaded) projected down *c* (a) and *a* (b).

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(NaF), kogarkoite [$Na_3(SO_4)_4F$] and vuonnemite [$Na_5Nb_2Ti(Si_2O_7)_2F_2{\cdot}2Na_3PO_4$], (2) As-bearing phases such as arsenopyrite (FeAsS) and löllingite ($FeAs_2$), and (3) native Sb and Bi (group-VB elements). Thus, many of the chemical constituents required to synthesize known SO_2-bearing compounds under laboratory conditions were apparently available in the sodalite syenite xenolith in which abenakiite-(Ce) formed. The second type of channel occupant is the carbonate

FIG. 6. Plan of the cations in the abenakiite-(Ce) structure from $z = 0$ to $z = 1/6$. Heights in *z* of atoms in the asymmetric unit are labeled. Circles are envelopes about the complex columns. P atoms of the polyhedral chains are located at the nodes of the $\{6^3\}$ net. The unit cell is indicated.

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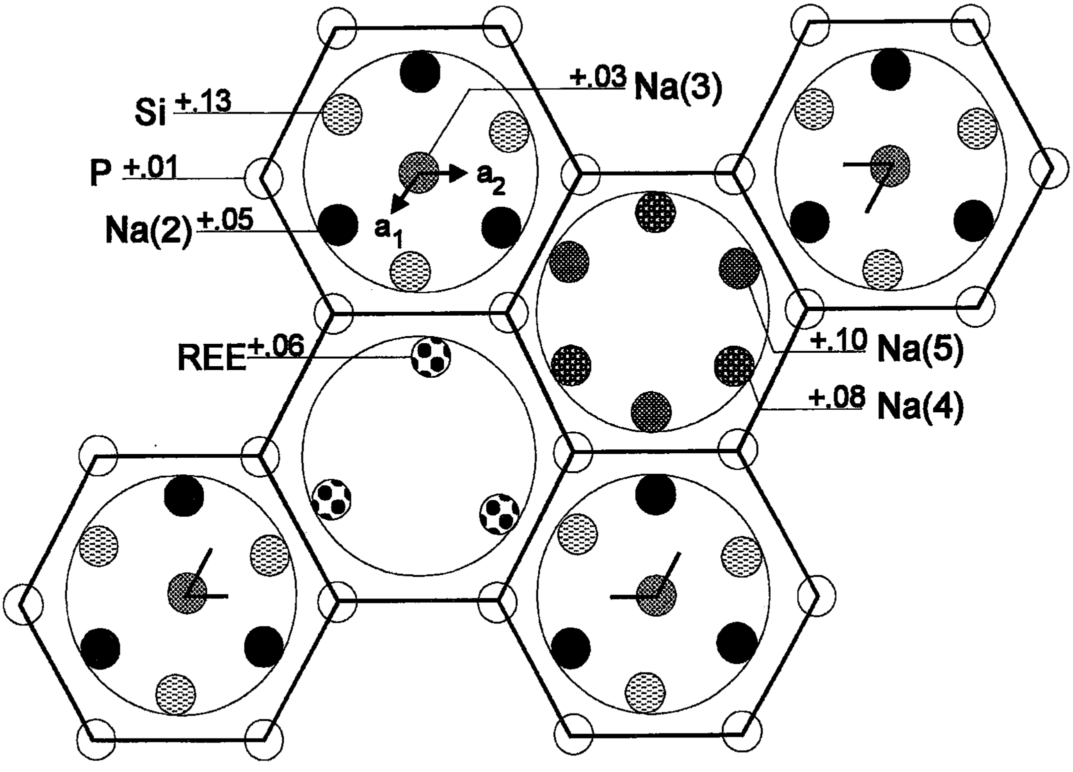

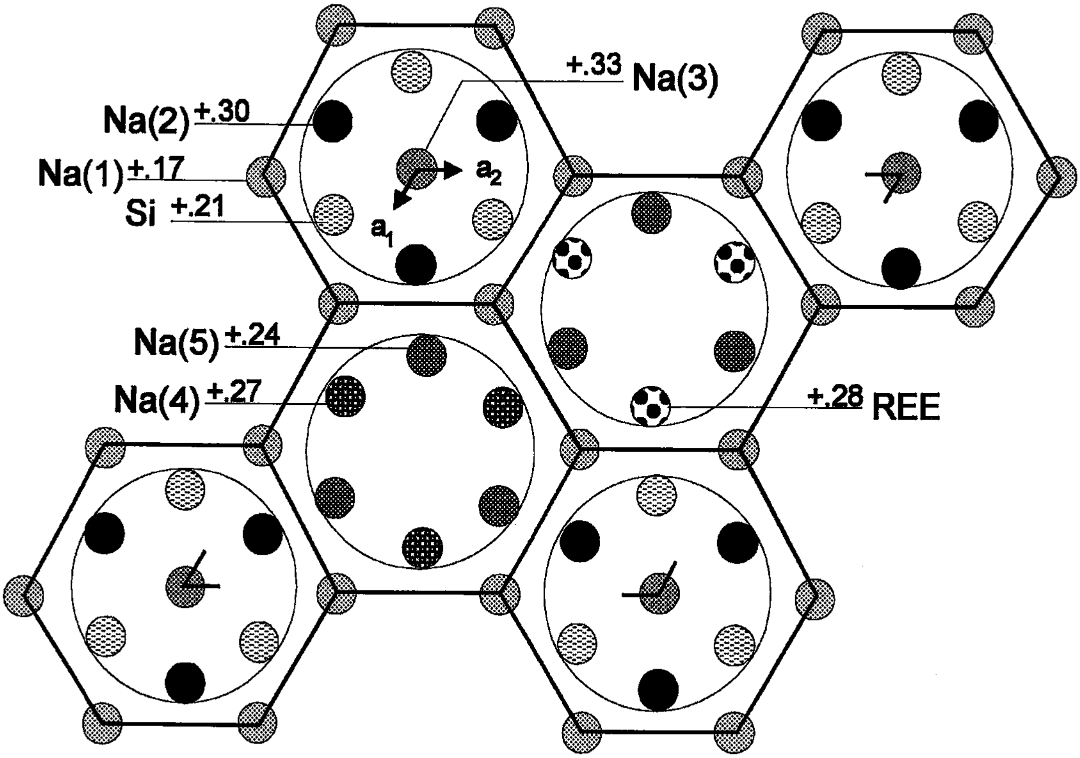

FIG. 7. Plan of the cations in the abenakiite-(Ce) structure from $z = 1/6$ to $z = 1/3$. Heights in z of the atoms in the asymmetric unit are labeled. Circles are envelopes about the complex columns. Na(1) atoms of the polyhedral chains are located at the nodes of the $\{6^3\}$ net. The unit cell is indicated.

group, which lies in the Na–*REE*–O polyhedral ring with its planar surface oriented approximately parallel to c. This group is located at the periphery of the channel, occupying triangular gaps formed between $REEO_9$ and NaO_7 polyhedra. The third type of channel occupant is $Na(3)O_6$ octahedron, which is bonded to two different Si_6O_{18} rings along c. The $Na(3)O_6$ octahedron shares oxygen atoms with three SiO_4 tetrahedra from the silicate ring above and with three SiO_4 tetrahedra from the silicate ring below.

The channel occupants and the polyhedral rings of the hollow tubes are bonded together to form complex columns that are repeated laterally by the 3_1 and 3_2 axes. The complex columns are in turn cross-linked to the polyhedral chains through two types of linkages; (1) the $Na(1)O_7$ polyhedra of the polyhedral chains are joined to the complex columns by sharing edges and faces with the $Na(4,5)O_7$ polyhedral ring and edges with the silicate ring, and (2) the PO_4 tetrahedra of the polyhedral chains are linked to the complex columns by shared edges with the Na–*REE*–O polyhedral ring and corners with the $Na(4,5)O_7$ polyhedral ring.

The abenakiite-(Ce) structure also has a distinct layered aspect and may be alternatively described in terms of two different composite layers along z (parallel to c). The first layer (Fig. 6) extends from $z = 0$ to $z = 1/6$, and the second from $z = 1/6$ to $z = 1/3$ (Fig. 7). The two composite layers are joined along c through shared edges and corners with the $Na(1)O_7$ polyhedra and PO_4 of the polyhedral chains. Lateral linkages are attained by (1) Si_6O_{18} rings and six-membered $Na(4,5)O_7$ polyhedral rings sharing edges with $Na(1)O_7$ polyhedra, and (2) the $Na(4,5)O_7$ and Na–*REE*–O polyhedral rings sharing edges and corners with the PO_4 tetrahedra.

The abenakiite-(Ce) structure appears to be unique in its topology. The six-membered silicate ring that is linked to a NaO_6 octahedron is somewhat reminiscent of that found in steenstrupine-(Ce), $Na_{14}Ce_6Mn^{3+}Mn^{2+}Fe_2Zr(Si_6O_{18})(PO_4)_7(OH)_2{\cdot}3H_2O$ (Moore & Shen 1983) and kazakovite, $Na_6Mn\{Ti(Si_6O_{18})\}$ (Voronkov *et al.* 1979), minerals that occur in highly alkaline, SiO_2-deficient rocks like that in which abenakiite-(Ce) was discovered. All three minerals contain six-membered silicate rings that are arranged in a {*UDUDUD*} manner and are corner-linked to octahedra above and below the plane of the ring. In abenakiite-(Ce), the silicate ring has point-group symmetry $\bar{3}$, and the octahedrally coordinated cation is Na. In steenstrupine-(Ce) and kazakovite, the rings have point-group symmetry $\bar{3}m$, and the octahedrally coordinated cations are (Zr^{4+}, Fe^{3+}, Mn^{2+}) and (Ti^{4+}, Mn^{2+}), respectively. An important difference among these minerals is the way in which this ring of octahedra and tetrahedra motif is linked in the structure. In both steenstrupine-(Ce) and kazakovite, the central octahedron links adjacent silicate rings together, forming sheets perpendicular to *c*. In abenakiite-(Ce), however, the silicate rings and NaO_6 octahedra are isolated from similar units in adjacent complex columns.

Certain Si- and P-bearing minerals like abenakiite-(Ce) contain essentially well-ordered Si and P. We propose that they be classified into their own unique chemical class, the *silicophosphates* (McDonald 1992). Currently, this group is known to include twelve minerals, including abenakiite-(Ce). There are also six additional minerals that are potential silicophosphates, but which require further work to study the degree of to which Si and P are ordered in their structures (McDonald 1992). Besides the high degree of Si–P order, silicophosphates are characterized by crystal-chemical similarities that include the absence of a SiO_4–PO_4 linkage through a common oxygen, unpolymerized to weakly polymerized SiO_4 groups, unpolymerized PO_4 groups, layered structures (most commonly with SiO_4 and PO_4 groups occurring in different layers, separated by layers of octahedra or of larger coordination polyhedra), highly coordinated cations and high concentrations of alkali or alkaline-earth metals (McDonald 1992).

Like abenakiite-(Ce), most of the known silicophosphates occur in strongly alkaline, agpaitic rocks such as those found at Mont Saint-Hilaire, Quebec, the Khibina and Lovozero massifs of Russia, and the Ilímaussaq intrusion of southwestern Greenland (McDonald 1992). The high degree of Si and P order is probably due to a combination of differences in charge and ionic radius between Si and P, along with presence of large cations, which tend to stabilize weak Lewis acids such as $[HSiO_4]^{3-}$ and $[HPO_4]^{-2}$, and H^+, which acts as network modifiers, suppressing silicate polymerization (McDonald 1992, Grice & McDonald 1993). These controls affecting development of the silicophosphates will be the focus of a forthcoming paper.

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