THE CRYSTAL STRUCTURE
OF SHOMIOKITE-(Y)

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ABSTRACT

The crystal structure of shomiokite-(Y), $Na_3(Y,REE)(CO_3)_3 \cdot 3H_2O$, has been determined and refined to indices $R = 5.3$ and $R_w = 4.7\%$. A sample from the Poudrette Quarry, Mont Saint-Hilaire, Quebec, gave the following average electron-microprobe-determined composition: Na_2O 23.25, Y_2O_3 19.05, La_2O_3 0.20, Ce_2O_3 1.81, Pr_2O_3 0.52, Nd_2O_3 2.79, Sm_2O_3 0.95, Gd_2O_3 1.05, Tb_2O_3 0.36, Dy_2O_3 2.81, Ho_2O_3 0.73, Er_2O_3 2.13, Eu_2O_3 0.00, Yb_2O_3 1.55, Tm_2O_3 0.40, Lu_2O_3 0.26, CO_2 33.36 and H_2O 13.66, total 104.88 wt.% (with proportion of CO_2 and H_2O determined by stoichiometry from results of crystal-structure analysis). This yields the empirical formula $Na_{2.97}(Y_{0.67}La_{0.01}Ce_{0.04}Pr_{0.01}Nd_{0.07}Sm_{0.02}Gd_{0.02}Tb_{0.01}Dy_{0.06}Ho_{0.02}Er_{0.04}Tm_{0.01}Yb_{0.03}Lu_{0.01})_{\Sigma 1.02}(CO_3)_3 \cdot 3H_2O$ and the simplified formula $Na_3(Y,REE)(CO_3)_3 \cdot 3H_2O$. The structure is orthorhombic, $Pbn2_1$, with refined unit-cell parameters a 10.035(6), b 17.32(1), c 5.937(3) Å, V 1031.7(7) Å^3, and $Z = 4$. An indexed X-ray powder-diffraction pattern is given. The structure analysis was essential in determining the number of C atoms and H_2O groups in the formula. The correct orientation for the polarity of the structure was determined. The crystal structure is layered on (001), with $Na(CO_3) \cdot H_2O$ layers being cross-linked by Y atoms in [9]-coordination. The $Na(CO_3) \cdot H_2O$ layer of shomiokite-(Y) is comparable to a layer of similar composition, $(Na,Y)(CO_3) \cdot H_2O$, in donnayite-(Y), but its Sr interlayer includes an additional (CO_3) group.

Keywords: shomiokite-(Y), crystal structure, carbonate, rare-earth element, Mont Saint-Hilaire, Quebec.

SOMMAIRE

Dans ce travail, on traite de la structure cristalline de la shomiokite-(Y), $Na_3(Y,REE)(CO_3)_3 \cdot 3H_2O$, affinée jusqu'à un résidu R de 5.3 ($R_w = 4.7\%$). Le cristal, provenant de la carrière Poudrette, mont Saint-Hilaire, Québec, a une composition comme suit (moyenne des données obtenues à la microsonde électronique): Na_2O 23.25, Y_2O_3 19.05, La_2O_3 0.20, Ce_2O_3 1.81, Pr_2O_3 0.52, Nd_2O_3 2.79, Sm_2O_3 0.95, Gd_2O_3 1.05, Tb_2O_3 0.36, Dy_2O_3 2.81, Ho_2O_3 0.73, Er_2O_3 2.13, Eu_2O_3 0.00, Yb_2O_3 1.55, Tm_2O_3 0.40, Lu_2O_3 0.26, CO_2 33.36 et H_2O 13.66, total 104.88 % (avec proportions de CO_2 et de H_2O déterminées par stoechiométrie à partir des résultats de l'affinement). Ceci mène à la formule empirique $Na_{2.97}(Y_{0.67}La_{0.01}Ce_{0.04}Pr_{0.01}Nd_{0.07}Sm_{0.02}Gd_{0.02}Tb_{0.01}Dy_{0.06}Ho_{0.02}Er_{0.04}Tm_{0.01}Yb_{0.03}Lu_{0.01})_{\Sigma 1.02}(CO_3)_3 \cdot 3H_2O$ et la formule simplifiée $Na_3(Y,REE)(CO_3)_3 \cdot 3H_2O$. La structure est orthorhombique, $Pbn2_1$, a 10.035(6), b 17.32(1), c 5.937(3) Å, V 1031.7(7) Å^3, et $Z = 4$. On présente un spectre indexé des raies obtenues par diffraction X (méthode des poudres). L'ébauche de la structure s'est avérée essentielle pour fixer la proportion d'atomes C et de groupes H_2O dans la formule. L'orientation de la polarité de la structure a été déterminée. La structure est faite de feuillets (001) de stoechiométrie $Na(CO_3) \cdot H_2O$ interliés par des atomes Y à coordinence [9]. Le feuillet $Na(CO_3) \cdot H_2O$ de la shomiokite-(Y) est comparable au feuillet $(Na,Y)(CO_3) \cdot H_2O$ de la donnayite-(Y), mais dans ce cas, le Sr entre les feuillets possède un groupe (CO_3) additionnel.

(Traduit par la Rédaction)

Keywords: shomiokite-(Y), structure cristalline, carbonate, terre rare, mont Saint-Hilaire, Québec.

INTRODUCTION

At Mont Saint-Hilaire, Quebec, 37 carbonate minerals have been identified, as well as several unknowns (Horváth & Gault 1990). Of the carbonates identified, 16 contain rare-earth elements (*REE*) as essential constituents: abenakiite-(Ce) (McDonald *et al.* 1994), ancylite-(Ce), bastnäsite-(Ce), calcio-ancylite-(Ce), cordylite-(Ce), daqingshanite-(Ce), donnayite-(Y), kainosite-(Y), mckelveyite-(Y), parisite-(Ce), petersenite-(Ce) (Grice *et al.* 1994), reederite-(Y) (Grice *et al.* 1995), remondite-(Ce), synchysite-(Ce), shomiokite-(Y) (this study), and tundrite-(Ce).

Shomiokite-(Y) was originally described by Khomyakov *et al.* (1992) from the hyperagpaitic nepheline syenite pegmatite of Mount Alluaiv near the Shomiok River, in the northwestern part of the Lovozero alkaline massif, Kola Peninsula, Russia. This material, which was described as irregular grains and

short, prismatic crystals, proved to be unsuitable for good X-ray-diffraction studies, and hence the space group was not determined. The shomiokite-(Y) described herein, from the Poudrette Quarry, Mont Saint-Hilaire, Quebec, occurs in crystals of suitable quality for crystal-structure analysis. The mineral occurs in late-stage syenitic pegmatite rocks as pale-yellow, striated, short, prismatic crystals to cleavable masses associated with microcline, aegirine, analcime, and albite, as well as minor amounts of rhodochrosite, eudialyte, catapleiite, sphalerite, and petersenite-(Ce). Shomiokite-(Y) commonly is partially altered to a silky white REE carbonate not yet described in the literature (UK91).

EXPERIMENTAL

Chemical analysis was performed on a JEOL 733 electron microprobe in wavelength-dispersion mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with a conventional ZAF routine in the Tracor Northern TASK series of programs. The operating voltage was 15 kV, and the beam current was 0.20 μA. The beam diameter was 50 μm; five spots were analyzed after first checking the sample for chemical homogeneity using back-scattered electron images. A 100-s energy-dispersion scan indicated no elements with $Z > 8$ other than those reported here. Standards used were: synthetic $Na_3La_2(CO_3)_4F$ ($NaK\alpha$), synthetic yttrium iron garnet (YIG) ($YL\alpha$), and synthetic REE_2PO_4 set ($LaL\alpha$, $CeL\alpha$, $PrL\beta$, $NdL\alpha$, $SmL\alpha$, $GdL\alpha$, $TbL\alpha$, $DyL\beta$, $HoL\beta$, $ErL\alpha$, $TmL\alpha$, $TbL\alpha$, $LuL\alpha$). REE results were corrected for overlaps. The average result of the electron-microprobe analyses gave Na_2O 23.25, Y_2O_3 19.05, La_2O_3 0.20, Ce_2O_3 1.81, Pr_2O_3 0.52, Nd_2O_3 2.79, Sm_2O_3 0.95, Gd_2O_3 1.05, Tb_2O_3 0.36, Dy_2O_3 2.81, Ho_2O_3 0.73, Er_2O_3 2.13, Eu_2O_3 0.00, Yb_2O_3 1.55, Tm_2O_3 0.40, Lu_2O_3 0.26, CO_2 33.36, and H_2O 13.66 total 104.88 wt.% (the proportions of CO_2 and H_2O were determined by stoichiometry from results of crystal-structure analysis). This yields the empirical formula $Na_{2.97}(Y_{0.67}La_{0.01}Ce_{0.04}Pr_{0.01}Nd_{0.07}Sm_{0.02}Gd_{0.02}Tb_{0.01}Dy_{0.06}Ho_{0.02}Er_{0.04}Tm_{0.01}Yb_{0.03}Lu_{0.01})_{\Sigma 1.02}(CO_3)_3 \cdot 3H_2O$ (calculated on the basis of 12 O atoms) and the simplified formula: $Na_3(Y,REE)(CO_3)_3 \cdot 3H_2O$. The small amount of pure material available precluded standard chemical analytical techniques capable of determining the amounts of H_2O and CO_2, but these were subsequently determined by the structure-analysis method (Hawthorne & Grice 1990). A combination of sample burn-up and statistical error, where approximately 45% of the oxide weight percent must be calculated by stoichiometry, is responsible for the high analytical totals.

As the original description of shomiokite-(Y) (Khomyakov et al. 1992) contains indexed X-ray

powder-diffraction data based only on a primitive orthorhombic cell without any space-group information, an indexed pattern for the Mont Saint-Hilaire material is given in Table 1.

The single crystal of shomiokite-(Y) used for the collection of X-ray diffraction-intensity data (catalogue number CMNMI 81527) is a roughly equant cleavage fragment that measures 0.10 × 0.10 × 0.25 mm. Precession photographs indicated the orthorhombic space-groups $Pbn2_1$ (33) or $Pbnm$ (62), on the basis of systematic absences of reflections. The cell orientation is consistent with the convention $c < a < b$ [the original cell given by Khomyakov et al. (1992)], which leads to a nonconventional space-group for this set of systematic absences. Intensity data were collected on a fully automated Nicolet P3 four-circle diffractometer operated at 50 kV and 40 mA, with graphite-monochromated $MoK\alpha$ radiation.

A set of 25 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Only

TABLE 1. SHOMIOKITE-(Y): X-RAY POWDER DIFFRACTION DATA

I	d_{obs} (Å)	$d_{calc}*$ (Å)	hkl	I	d_{obs} (Å)	$d_{calc}*$ (Å)	hkl
2	8.66	8.68	110	3	1.932	1.929	023
		8.66	020	<1	1.891	1.890	511
5	6.56	6.56	120	<1	1.867	1.869	352
5	5.11	5.11	101	<1	1.819	1.821	540
		4.90	111			1.806	531
10	4.89	4.90	021	<1	1.801	1.804	461
		4.82	210			1.801	191
5	4.34	4.34	220	<1	1.778	1.777	272
		4.33	040			1.772	143
<1	3.98	3.98	140	<1	1.759	1.754	233
2	3.75	3.74	211	2	1.723	1.723	182
3	3.50	3.504	221			1.720	291
		3.498	041	1	1.695	1.695	313
2	3.30	3.303	141			1.694	243
1	3.19	3.193	231	1	1.671	1.673	600
<1	3.121	3.120	320			1.668	390
<1	2.970	2.969	002	1	1.652	1.652	512
		2.874	311			1.653	372
10	2.862	2.870	241	1	1.633	1.634	333
		2.851	250			1.633	522
<1	2.805	2.808	022	<1	1.613	1.611	163
3	2.705	2.704	122	<1	1.597	1.598	532
3	2.593	2.602	331	<1	1.581	1.583	621
		2.596	061	<1	1.580	1.559	640
3	2.518	2.513	161			1.560	570
<1	2.479	2.483	410	<1	1.549	1.551	631
1	2.378	2.379	142	<1	1.529	1.528	353
1	2.294	2.301	430	<1	1.506	1.509	641
		2.291	411			1.500	433
3	2.230	2.230	351	<1	1.481	1.484	004
		2.227	171	<1	1.456	1.454	392
<1	2.201	2.200	242	<1	1.448	1.447	660
2	2.146	2.145	431			1.448	124
<1	2.113	2.116	180	<1	1.428	1.429	581
10	2.073	2.072	332			1.423	204
		2.070	062	<1	1.418	1.419	214
2	2.033	2.034	081			1.414	720
		2.032	450	<1	1.404	1.405	513
<1	1.994	1.993	181			1.403	373
		1.993	510	1	1.389	1.389	1121
<1	1.976	1.976	342			1.389	590
1	1.939	1.942	103				

Plus 30 lines to d = 0.937 Å with $I < .5$
114.6 mm Debye-Scherrer powder camera, $CuK\alpha$ radiation
*Based on a refined cell of a 10.035(6), b 17.32(1), c 5.937(3) Å

TABLE 2. DATA-COLLECTION INFORMATION FOR SHOMIOKITE-(Y)

Space Group	$Pbn2_1$ (33)	Measured unique reflections	2979
a (Å)	10.042(3)	Observed reflections [$>6\sigma(F)$]	2272
b (Å)	17.349(4)	Minimum transmission	0.179
c (Å)	5.948(1)	Maximum transmission	0.284
V (Å^3)	1036.2(4)	R/R_w (%)	5.3/4.7
Unit-cell contents	4[Na$_3$(Y,REE)(CO$_3$)$_3$•3H$_2$O]		
μ (mm^{-1})	5.84	$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w{F_o}^2]^{\frac{1}{4}}$	$w=[\sigma^2(F_o)]^{-1}$

TABLE 4. INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SHOMIOKITE-(Y)

Na1 polyhedron				Na2 polyhedron			
Na1-O3a	2.355(10)	O3a-O5a	95.5(4)	Na2-O1a	2.705(9)	O1a-O3b	51.5(3)
Na1-O5a	2.371(11)	O3a-O7	95.5(3)	Na2-O3b	2.424(10)	O1a-O4a	103.0(3)
Na1-O7	2.376(8)	O3a-O7a	162.9(4)	Na2-O4a	2.301(8)	O1a-O6	138.7(3)
Na1-O7a	2.490(9)	O3a-O9a	92.7(3)	Na2-O6	2.364(10)	O1a-O6a	82.5(3)
Na1-O9a	2.416(9)	O3a-O11b	80.0(3)	Na2-O6a	2.336(8)	O1a-O12a	124.3(3)
Na1-O11	2.933(11)	O5a-O7	107.1(3)	Na2-O12a	2.655(10)	O3b-O4a	86.5(3)
		O5a-O7a	70.8(3)			O3b-O6	94.6(3)
⟨Na1-O⟩	2.490	O5a-O9a	102.4(3)	⟨Na2-O⟩	2.464	O3b-O6a	113.7(3)
		O5a-O11	174.6(3)			O3b-O12a	159.1(4)
		O7-O7a	98.4(2)			O4a-O6	96.5(3)
		O7-O9a	148.4(3)			O4a-O6a	156.6(4)
		O7-O11	70.6(3)			O4a-O12a	74.3(3)
		O7a-O9a	80.7(3)			O6-O6a	93.7(3)
		O7a-O11	114.1(3)			O6-O12a	95.8(3)
		O9a-O11	80.9(3)			O6a-O12a	83.8(3)

Na3 polyhedron				Y polyhedron			
Na3-O1b	2.322(8)	O1b-O3c	151.8(4)	Y-O1b	2.440(7)	Y-O10	2.438(9)
Na3-O3c	2.369(9)	O1b-O4b	105.0(3)	Y-O2	2.362(8)	Y-O11	2.456(9)
Na3-O4b	2.473(9)	O1b-O6b	88.7(3)	Y-O4	2.433(8)	Y-O12	2.430(9)
Na3-O6b	2.451(10)	O1b-O9b	93.1(3)	Y-O5	2.381(9)		
Na3-O9b	2.431(9)	O1b-O10	70.2(3)	Y-O7	2.508(7)	⟨Y-O⟩	2.423
Na3-O10	2.913(11)	O3c-O4b	84.0(3)	Y-O8a	2.357(7)		
		O3c-O6b	117.4(3)				
⟨Na3-O⟩	2.493	O3c-O9b	91.5(3)	**C1 triangle**			
		O3c-O10	83.0(3)	C1-O1	1.312(11)	O1-O2a	114.2(9)
		O4b-O6b	54.6(3)	C1-O2a	1.300(14)	O1-O3	121.6(9)
		O4b-O9b	149.8(4)	C1-O3	1.256(13)	O2a-O3	124.1(9)
		O4b-O10	127.2(3)				
		O6b-O9b	103.0(3)	⟨C1-O⟩	1.289	⟨O-O⟩	120.0
		O6b-O10	158.7(3)				
		O9b-O10	81.5(3)				

C2 triangle				C3 triangle			
C2-O4	1.337(13)	O4-O5	115(1)	C3-O7	1.295(12)	O7-O8	116.4(9)
C2-O5	1.297(15)	O4-O6	120(1)	C3-O8	1.302(13)	O7-O9a	120.7(9)
C2-O6	1.262(14)	O5-O6	124(1)	C3-O9a	1.285(13)	O8-O9a	122.8(9)
⟨C2-O⟩	1.299	⟨O-O⟩	120.0	⟨C3-O⟩	1.294	⟨O-O⟩	120.0

O10, O11, and O12 are H$_2$O groups

one asymmetric unit of intensity data was collected (for the acentric space-group) up to $2\theta = 60°$ using a $\theta:2\theta$ scan mode, with scan speeds inversely proportional to intensity at rates of 4 to 29.3°/minute. Additional data pertinent to the collection of intensity data are given in Table 2.

Reduction of the intensity data, structure determination, and structure refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included a correction for background, scaling, Lorentz, polarization, and absorption effects. For the ellipsoidal absorption correction, 11 intense diffraction-maxima in the range 8 to 57° 2θ were chosen for ψ diffraction-vector scans after the method of North *et al.* (1968). The merging R for the ψ-scan data set (396 reflections) decreased from 3.6% before the absorption correction to 2.4% after this correction.

CRYSTAL-STRUCTURE ANALYSIS

The structure was solved using direct methods. The mean value of $|E^2 - 1|$ was 0.822, suggesting an

TABLE 3. POSITIONAL AND THERMAL PARAMETERS (X10^4, Å^2) FOR SHOMIOKITE-(Y)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Y	0.32164(8)	0.16175(4)	0	115(2)	140(2)	75(2)	8(7)	5(6)	3(4)	110(1)
Na1	0.6262(5)	0.0472(3)	0.2782(8)	416(25)	347(23)	23(19)	-14(19)	-26(22)		291(13)
Na2	-0.0155(5)	-0.0810(3)	-0.2227(7)	371(25)	389(24)	125(18)	-47(19)	-14(20)	-9(22)	295(13)
Na3	0.3611(5)	0.3627(3)	0.2871(8)	260(22)	512(26)	124(17)	-5(19)	-30(18)	-24(22)	299(13)
C1	-0.195(1)	0.1941(6)	0.274(1)	195(36)	283(34)	88(26)	-25(30)	27(32)	-78(34)	189(19)
C2	0.121(1)	0.0777(6)	-0.230(2)	382(37)	174(34)	143(32)	41(32)	-68(33)	-56(35)	233(20)
C3	0.561(1)	0.1016(6)	-0.222(2)	223(35)	296(36)	88(29)	-42(32)	-66(31)	-21(34)	202(19)
O1	-0.1167(8)	0.2033(4)	0.450(1)	356(31)	311(30)	135(31)	45(24)	-108(24)	-11(28)	267(18)
O2	0.2314(9)	0.2464(5)	-0.271(1)	325(33)	306(33)	107(27)	-26(27)	-36(27)	-67(30)	246(18)
O3	-0.2008(8)	0.1311(5)	0.171(1)	182(32)	277(32)	340(33)	-42(29)	28(29)	-23(29)	267(18)
O4	0.0902(8)	0.1264(4)	-0.084(1)	235(29)	309(30)	252(31)	-33(26)	78(25)	-61(29)	265(17)
O5	0.2474(8)	0.0874(5)	-0.263(1)	157(30)	409(35)	130(28)	-25(28)	-3(28)	21(31)	232(18)
O6	0.0303(8)	0.0460(5)	-0.344(1)	229(31)	418(34)	153(28)	-50(28)	-50(27)	-81(31)	267(18)
O7	0.5002(7)	0.0626(4)	-0.057(1)	194(29)	361(31)	162(29)	101(24)	32(23)	-6(27)	239(17)
O8	-0.0044(8)	0.3322(5)	0.234(1)	254(30)	282(31)	75(25)	-85(27)	57(24)	-20(30)	203(16)
O9	0.6537(8)	0.0766(5)	-0.327(1)	176(32)	355(34)	236(30)	3(28)	-9(26)	80(29)	255(18)
O10*	0.1915(9)	0.2265(5)	0.290(1)	416(35)	472(36)	134(26)	-11(29)	43(31)	178(33)	340(19)
O11*	0.4842(9)	0.1949(6)	0.293(1)	410(35)	675(38)	104(27)	-70(32)	-26(30)	-132(36)	396(19)
O12*	0.2784(9)	0.0648(5)	0.286(1)	463(37)	306(33)	166(28)	74(30)	-8(30)	27(31)	311(19)

*O10, O11 and O12 are H$_2$O groups

Temperature factors are of the form: exp $[-2\pi^2(U_{11}a^{*2} + U_{22}k^2b^{*2} + ... 2U_{12}hka^*b^*)]$

acentric space-group. The structure was therefore solved and refined in the space group $Pbn2_1$ (standard setting $Pna2_1$). The largest peaks in the E-map were assigned to scattering curves, one Y, three Na, and ten O atoms being thus located. This structure model refined to $R = 15.5\%$. The difference-Fourier maps of subsequent refinements required a rearrangement of some of the sites previously assigned to O and Na and the addition of new atomic sites. With all of the atomic sites assigned to the correct scattering curves, the model, with isotropic displacement-factors, refined to $R = 9.5\%$. By inverting the polarity of the structure along the Z axis, the residual dropped to $R = 7.5\%$, indicating the correct orientation of the crystal.

In the final least-squares refinement, all atomic positions were refined with anisotropic displacement-factors to final residuals of $R = 5.3\%$ and $R_w = 4.7\%$. The weighting scheme used weights inversely proportional to $\sigma^2(F)$. The addition of an isotropic extinction-correction did not improve the results. Refinement in the noncentrosymmetric space-group $P2_1$ also did not improve the R values, nor did it indicate in any way that lower symmetry was justified when tested by MISSYM (Le Page 1987). The final positional and thermal parameters are given in Table 3, and selected bond-lengths and angles, in Table 4. A table listing the observed and calculated structure-factors has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURE

In the crystal structure of shomiokite-(Y), each of the three Na atoms has [6]-coordination, to one H_2O group and five O atoms arranged in a very distorted octahedron. For each $[NaO_5(H_2O)]$ polyhedron, the H_2O group and three O ligands lie within the (001) plane. The other two O ligands of the polyhedron, which approximately parallel [001], reinforce the cross-layer linkages between carbonate slabs. The $[(Y,REE)O_6(H_2O)_3]$ polyhedron is a nearly regular trigonal prism with each of the three H_2O groups centering a face of the prism at the base, three O atoms in the edges of the prism at the equatorial plane, and three additional O atoms above the H_2O groups forming the top of the prism (Fig. 1). The polarity of the Y polyhedron is exemplified by the H_2O groups at one end of the prism and three O atoms at the other end. The effects of polarity were clearly demonstrated in the structure refinement when the structure was inverted and the R index dropped by 2%. This improvement in R is attributable to location of the correct absolute configuration of the crystal structure. The large anomalous dispersion-factors associated with Y when the crystal is subjected to Mo-radiation make these effects quite dramatic.

The crystal structure of shomiokite-(Y) is layered on (001) (Fig. 2). The layering in REE carbonates is described in detail by Grice *et al.* (1994). In shomiokite-(Y), there are two layers of differing
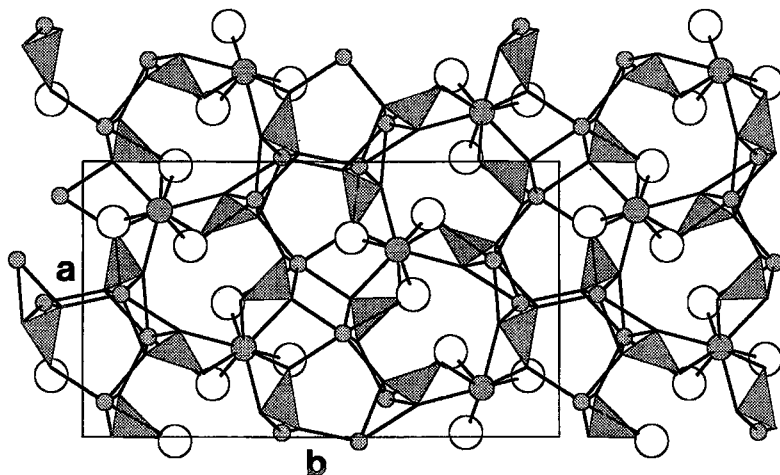

FIG. 1. The crystal structure of shomiokite-(Y) projected on (001). The carbonate groups are shaded triangles, H_2O groups are large open circles, (Y,*REE*) atoms are large shaded circles, and Na atoms are small shaded circles.
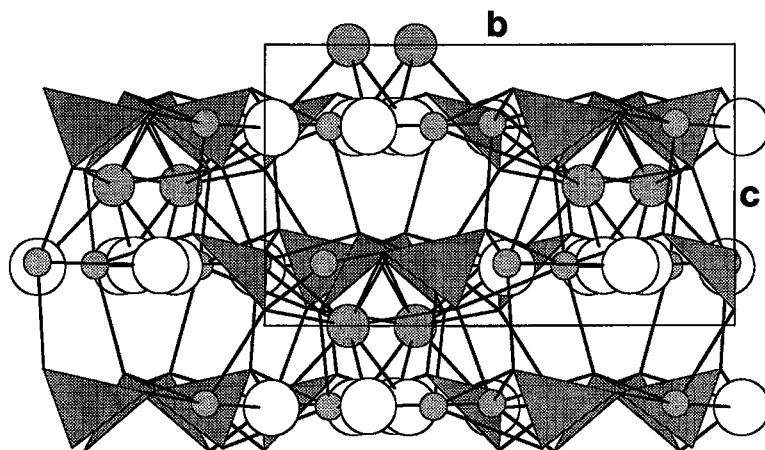
FIG. 2. The crystal structure of shomiokite-(Y) projected on (100). The carbonate groups are shaded triangles, H_2O groups are large open circles, (Y,REE) atoms are large shaded circles, and Na atoms are small shaded circles.

composition. The $Na(CO_3) \cdot H_2O$ layers are cross-linked through the layers of Y polyhedra. Grice *et al.* (1994) described the former type as a "mixed" carbonate layer, wherein the (CO_3) triangles are tilted within the layer, allowing the H_2O groups and Na octahedra to share the slab with the (CO_3) polyhedra. The crystal structure of donnayite-(Y) (Pobedimskaya *et al.* 1992) has a $(Na,Y)CO_3 \cdot H_2O$ layer (Fig. 3) comparable to the

$Na(CO_3) \cdot H_2O$ layer of shomiokite-(Y). The Sr atoms in donnayite-(Y) have [9]-coordination similar to that of the Y atoms in shomiokite-(Y), but with an extra layer of "flat-lying" carbonate groups (Grice *et al.* 1994) associated with the Sr sites, which are not present in the shomiokite-(Y) structure. The (001) projection of the donnayite-(Y) (Fig. 4) structure has topological similarities to that of the (001) projection of
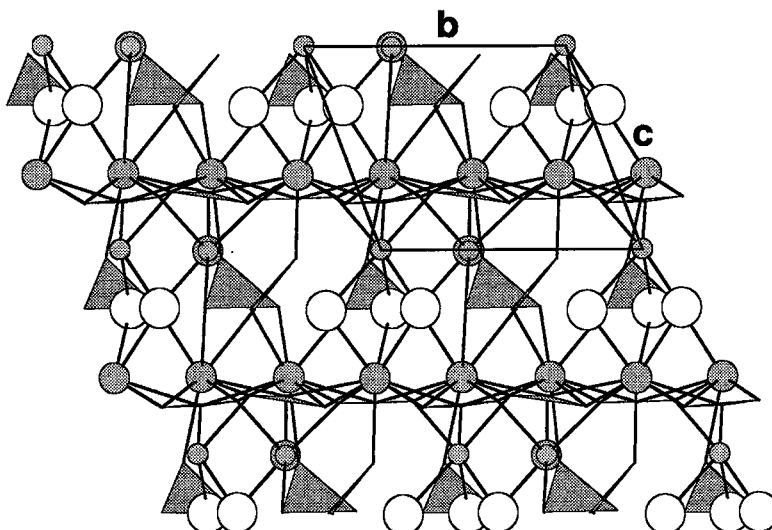

FIG. 3. The crystal structure of donnayite-(Y) projected on (100). The carbonate groups are shaded triangles, H_2O groups are large open circles, Sr and Y atoms are large shaded circles, and Na atoms are small shaded circles.
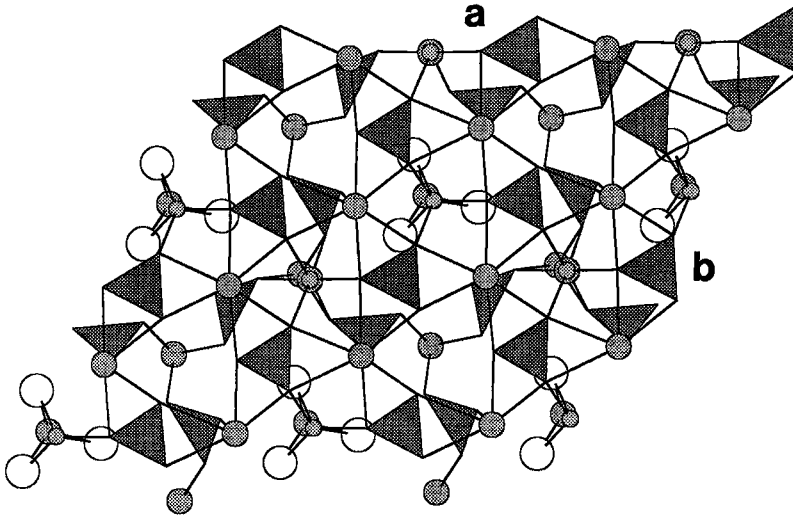
FIG. 4. The crystal structure of donnayite-(Y) projected on (001). The carbonate groups are shaded triangles, H_2O groups are large open circles, Sr and Y atoms are large shaded circles, and Na atoms are small shaded circles.

shomiokite-(Y) (Fig. 1), with pseudo-3-fold axes through the [9]-coordinated sites of Sr and Y, respectively. In the structure of these *REE* carbonates, the effects of H-bonding are negligible. This is in contrast to the Na carbonates, which are commonly associated with these *REE* carbonates in alkaline, highly agpaitic rocks. The Na bicarbonate minerals nahcolite (Sass & Scheuerman 1962), trona (Pertlik 1986), and wegscheiderite (Fernandes *et al.* 1990) all have H-bonded carbonate layers that are cross-linked by layers of Na-polyhedra. In the hydrated Na-carbonate minerals natron (Taga 1969) and thermonatrite (Wu & Brown 1975), the carbonate layer is again cross-linked by the layer of Na-polyhedra, but the H-bonding is not between two carbonate groups but between a carbonate group and an H_2O group, which in turn is bonded to a Na atom.

During crystallization of the nepheline syenite, the alkalinity increased until the very last stage, at which point the alkalinity dropped abruptly, owing to decreasing temperature, which caused an increase in H activity (Khomyakov 1995). The increase in alkalinity is exemplified by increasing amounts of Na silicates, Na carbonates and light-*REE* minerals. During the last stage of crystallization, in the more acidic conditions, minerals formed with increasing amounts of H_2O, and *REE* minerals rich in Y and the heavy lanthanides appeared. At Mont Saint-Hilaire, the late stages of crystallization are found in the pegmatite and altered pegmatite rocks, miarolitic cavities, breccia infilling and sodalite xenoliths. It is in these occurrences that natrite, natron, trona, and thermonatrite are found,

commonly coexisting with *REE* carbonates. These minerals would certainly correspond to Khomyakov's (1995) maximum alkalinity stage. The final acidic phase that Khomyakov (1995) documented in the Khibina and Lovozero massifs, Kola Peninsula, are not clearly observed at Mont Saint-Hilaire. The highly hydrated carbonates of Y of Mont Saint-Hilaire (listed in the Introduction) are certainly very late in the crystallization sequence, being most commonly found in the pegmatite or altered pegmatite, but the Ce carbonates and the basic Na carbonates are not excluded from this occurrence. Thus there is no marked segregation among carbonate minerals to differentiate the stages of maximum and declining alkalinity at Mont Saint-Hilaire, as noted in Khibina and Lovozero.

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