The Canadian Mineralogist
Vol. 32, pp. 405-414 (1994)

PETERSENITE-(Ce), A NEW MINERAL FROM MONT SAINT-HILAIRE, AND ITS STRUCTURAL RELATIONSHIP TO OTHER REE CARBONATES

JOEL D. GRICE, JERRY VAN VELTHUIZEN AND ROBERT A. GAULT

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

ABSTRACT

Petersenite-(Ce) is a newly discovered rare-earth-element carbonate from the Poudrette Quarry, Mont Saint-Hilaire, Quebec. It is grey, with a slight pink tint, forming striated prisms up to 7 mm in length. It has a vitreous luster and is translucent to transparent. Petersenite-(Ce) is relatively soft (Mohs hardness ~3) and very brittle, having a conchoidal fracture. Optical properties are biaxial, with moderate dispersion, no absorption, and indices of refraction α 1.623(1), β 1.636(1), γ 1.649(1), $2V_{meas.}$ = 89.7(5)° and $2V_{calc.}$ = 89.8°, and an optical orientation of $X = b$, $Y \wedge c = 30°$ and $Z = a$. Electron-microprobe analyses gave Na_2O 17.38, CaO 1.32, BaO 0.32, SrO 1.70, La_2O_3 14.49, Ce_2O_3 23.66, Pr_2O_3 2.00, Nd_2O_3 5.82, Sm_2O_3 0.60 and CO_2 (from crystal-structure analysis) 32.92, total 100.21 wt.%, which yields the empirical formula $(Na_{3.75}Ca_{0.16})(Ce_{0.96}La_{0.59}Nd_{0.23}Sr_{0.11}Pr_{0.08}Sm_{0.02}Ba_{0.01})(CO_3)_5$ or, ideally, $Na_4(REE)_2(CO_3)_5$ for $Z = 4$, with $D_{calc.}$ = 3.67 g/cm^3 and $D_{meas.}$ = 3.69 g/cm^3. Crystal-structure analysis shows the mineral to be monoclinic, space group $P2_1$, with a 20.872(4), b 6.367(1), c 10.601(2) Å and β 120.50(3)°. The strongest lines in the X-ray powder pattern [d in Å(I)(hkl)] are 9.13(3)($\bar{2}$01,001), 5.22(5)($\bar{2}$11,011,201,$\bar{4}$01), 4.13(3)($\bar{5}$01,301), 3.70(4)($\bar{4}$12,012), 2.607(10)(402,$\bar{8}$02,420), 2.148(3)($\bar{8}$14,014) and 1.921(3)($\bar{4}$32,032,430). The crystal structure has the subcell of burbankite and remondite-(Ce), but the supercell changes the ratio of [8]-coordinated to [10]-coordinated cations. The layered structure is compared to that of other *REE* carbonates.

Keywords: petersenite-(Ce), new mineral species, rare-earth element, carbonate, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La petersenite-(Ce) est un carbonate à terres rares (TR) nouvellement découvert à la carrière Poudrette, au mont Saint-Hilaire, Québec. Il s'agit d'un minéral gris, avec une teinte rosâtre, se présentant en prismes striés translucides à transparents, à éclat vitreux et jusqu'à 7 mm en longueur. Sa dureté de Mohs est environ 3; elle est très cassante, et la fracture est concoïdale. C'est un minéral biaxe, ayant une dispersion moyenne, aucune absorption, et les indices de réfraction suivants: α 1.623(1), β 1.636(1), γ 1.649(1), $2V_{meas.}$ = 89.7(5)° et $2V_{calc.}$ = 89.8°. L'orientation optique donne $X = b$, $Y \wedge c = 30°$, et $Z = a$. Une analyse à la microsonde électronique démontre la présence de: Na_2O 17.38, CaO 1.32, BaO 0.32, SrO 1.70, La_2O_3 14.49, Ce_2O_3 23.66, Pr_2O_3 2.00, Nd_2O_3 5.82, Sm_2O_3 0.60 et CO_2 (des résultats de l'analyse de la structure cristalline) 32.92, pour un total de 100.21% (en poids), ce qui mène à la formula empirique $(Na_{3.75}Ca_{0.16})(Ce_{0.96}La_{0.59}Nd_{0.23}Sr_{0.11}Pr_{0.08}Sm_{0.02}Ba_{0.01})(CO_3)_5$ ou, plus simplement, $Na_4(TR)_2(CO_3)_5$ pour $Z = 4$, avec $D_{calc.}$ = 3.67 g/cm^3 et $D_{meas.}$ = 3.69 g/cm^3. Une analyse de la structure cristalline montre qu'il s'agit d'un minéral monoclinique, groupe spatial $P2_1$, avec a 20.872(4), b 6.367(1), c 10.601(2) Å et β 120.50(3)°. Le cliché de diffraction X (méthode des poudres) possède les raies les plus intenses suivantes [d en Å(I)(hkl)]: 9.13(3)($\bar{2}$01, 001), 5.22(5)($\bar{2}$11,011,201,$\bar{4}$01), 4.13(3)($\bar{5}$01,301), 3.70(4)($\bar{4}$12,012), 2.607(10)(402,$\bar{8}$02,420), 2.148(3)($\bar{8}$14,014) et 1.921(3)($\bar{4}$32,032,430). La structure contient la sous-maille de burbankite et remondite-(Ce), mais la super-maille change le rapport des cations à coordinence [8] à [10]. La structure en feuillets est comparée à celle d'autres carbonates à terres rares.

(Traduit par la Rédaction)

Mots-clés: petersenite-(Ce), nouvelle espèce minérale, terres rares, carbonate, structure cristalline, mont Saint-Hilaire, Québec.

Introduction

At Mont Saint-Hilaire, Quebec, 34 carbonate mineral species have been identified, as well as several unknowns (Horvath & Gault 1990). Of the identified carbonates, eleven contain essential amounts of rare-earth elements (*REE*). At the Canadian Museum of Nature, we have been routinely studying this interesting crystal-chemical class.

The new mineral described here, petersenite-(Ce), becomes the fourth member of the burbankite group, which also includes remondite-(Ce) and khanneshite. Petersenite-(Ce), found originally in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, is named in honor of Dr. Ole V. Petersen, Geologisk Museum, Copenhagen, Denmark, in recognition of his significant contributions to the understanding of the mineralogy and genesis of alkaline rocks. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Canadian Museum of Nature under catalog no. 81511.

Occurrence

Mont Saint-Hilaire is one of the ten Monteregian Hills rising above the Saint Lawrence Lowlands. This almost linear arrangement of monadnocks stretches for almost 150 km eastward from Oka to Megantic. The Hills are alkaline intrusive complexes. Horvath & Gault (1990) briefly described the geology, gave detailed descriptions of the minerals, and have compiled a very complete list of references for the Mont Saint-Hilaire locality.

In the spring of 1991, J.V.V. collected samples that later became the cotype specimens for petersenite-(Ce), in the Poudrette quarry, from a late-stage pegmatitic phase of the nepheline–sodalite syenite, near the contact with the hornfels unit. Petersenite-(Ce) is associated with the following minerals: a member of the astrophyllite group, aegirine, albite, analcime, biotite, calcite, catapleiite, a member of the chlorite group, epididymite, eudialyte, fluorite, galena, microcline, polylithionite, rhodochrosite, serandite and sphalerite. At present, we must consider petersenite-(Ce) a rare mineral since only ten specimens are known, each with only a few milligrams of the new mineral.

Subsequent to the initial discovery of the cotype samples, petersenite-(Ce) has been identified from two other associations at Mont Saint-Hilaire. It also occurs as yellow, transparent, acicular crystals attaining several millimeters in length, embedded in trona, from a sodalite-rich inclusion in nepheline syenite, and as mauve, acicular crystals up to 1 mm in length in a pegmatite phase in nepheline syenite associated with microcline, albite, aegirine and shomyokite-(Y).

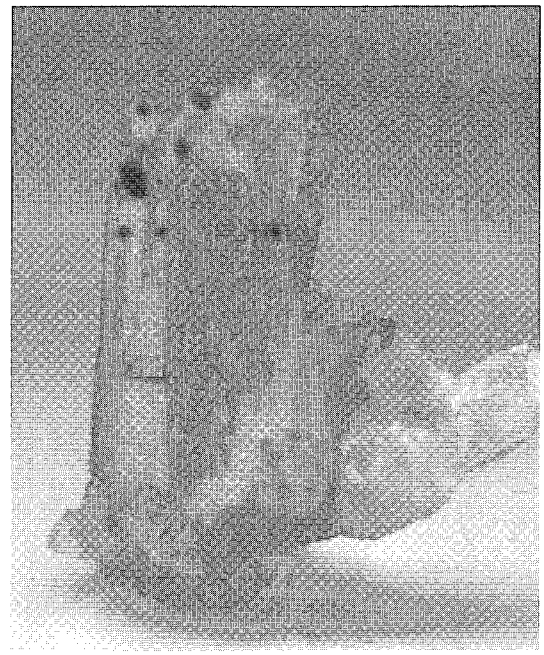

FIG. 1. Petersenite-(Ce) crystal with a dark coating, 7 mm in length, on albite.

Physical and Optical Properties

Petersenite-(Ce) forms striated prisms, owing to parallel growth, up to 7 mm in length (Fig. 1). The type material is grey with a slight pinkish tint and a vitreous luster. It has a white streak and is translucent to transparent in thin splinters. It shows no fluorescence with either long-wave or short-wave ultraviolet light. Petersenite-(Ce) is relatively soft (Mohs hardness about 3), very brittle, with no apparent cleavage, and a conchoidal fracture. The density, measured by suspension in Clerici solution, is 3.69 ± 0.03 g/cm^3, which agrees well with the calculated density of 3.67 g/cm^3.

Petersenite-(Ce) is biaxial, with indices of refraction α 1.623(1), β 1.636(1) and γ 1.649(1) (for λ = 590 mm); $2V_{meas.}$ = 89.7(5)° (extinction curves), $2V_{obs.}$ = 90 ± 5° (optic axis), and $2V_{calc.}$ = 89.8°; moderate dispersion; no pleochroism. As the $2V$ is close to 90°, neither the sign nor the dispersion formula could be determined. These optical properties are significantly different from those of remondite-(Ce), which is biaxial positive, with indices of refraction α = 1.632(2), β = 1.633(2), γ = 1.638(2) and $2V_{meas.}$ = 40(6)°. The optical orientation of petersenite-(Ce) is $X = b$, $Y \wedge c = 30°$, and $Z = a$.

CHEMICAL COMPOSITION

Chemical analysis was performed on a JEOL 733 Superprobe using Tracor–Northern 5600 automation. The wavelength-dispersion scan (WDS) mode was used; data reduction was done with the Tracor–Northern Task series of programs using a conventional ZAF correction routine. The operating voltage was 15 kV, and the beam current was 0.020 μA.

To prevent burn-up of the sample, the electron beam was defocused to 50 μm, and two different spots on the sample were used for each analysis after the area was checked for chemical homogeneity using the back-scattered electron detector. Each sample was analyzed for sodium first. Data for sodium were collected for 10 s to minimize burn-up. For all other elements in the samples, data were collected for 25 s or 0.50% precision, whichever was attained first. Data for standards were collected for 50 s or 0.25% precision, whichever was attained first.

Three analyses were performed on three grains. These analyses gave totals ranging from 99.87 to 100.63 wt. % (Table 1). A 100-s energy-dispersion spectrometer scan indicated no other elements with Z greater than 9 other than those reported here to be present. In addition, using WDS, the elements Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th were sought but not detected. Concentrations of the *REE* were corrected for overlaps. The following standards were used: albite (Na), calcite (Ca), sanbornite (Ba), celestine (Sr), $LaPO_4$ (La), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd) and $SmPO_4$ (Sm). CO_2 was calculated by stoichiometry from the results of the crystal-structure analysis.

TABLE 1. PETERSENITE-(Ce): CHEMICAL COMPOSITION

	1	2	3
Na_2O	17.38	16.81	17.16
CaO	1.32	1.31	10.54
BaO	0.32	0.22	-
SrO	1.70	1.66	3.98
La_2O_3	14.49	14.96	11.60
Ce_2O_3	23.66	24.40	14.99
Pr_2O_3	2.00	2.16	1.49
Nd_2O_3	5.82	5.89	3.34
Sm_2O_3	0.60	0.51	0.50
CO_2	32.92*	32.08	35.24
Total	100.21	100.00	99.25
	Atomic proportions based on 15 oxygens		
Na	3.75	3.72	3.47
Ca	0.16	0.16	1.18
Ba	0.01	0.01	-
Sr	0.11	0.11	0.24
La	0.59	0.63	0.45
Ce	0.96	1.02	0.57
Pr	0.08	0.09	0.06
Nd	0.23	0.24	0.12
Sm	0.02	0.02	0.02
C	5.00	5.00	5.00
Sum	10.91	11.00	11.11

* Determined from crystal-structure analysis.

1. Composition of petersenite-(Ce), results of three analyses averaged
2. Calculated composition of petersenite-(Ce)
3. Composition of remondite-(Ce) (Cesbron *et al.* 1988); total includes Eu_2O_3 0.09, Gd_2O_3 0.24, Dy_2O_3 0.07, Ho_2O_3 0.01, Er_2O_3 0.03, Y_2O_3 0.03, Lu_2O_3 0.004, Y_2O_3 0.024 wt. %.

The empirical formula for petersenite-(Ce) based on 15 atoms of oxygen, as determined in the crystal-structure analysis, is $(Na_{3.75}Ca_{0.16})_{\Sigma 3.91}(Ce_{0.96}La_{0.59}Nd_{0.23}Sr_{0.11}Pr_{0.08}Sm_{0.02}Ba_{0.01})_{\Sigma 2.00}(CO_3)_5$ or, ideally, $Na_4(REE)_2(CO_3)_5$ for $Z = 4$. The ideal formula of burbankite is $(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5$ with $Z = 2$, and that of remondite-(Ce) is $Na_3(Ca,Ce,La,Na,Sr)_3(CO_3)_5$ with $Z = 2$.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray precession photographs show petersenite-(Ce) to be monoclinic with possible space-groups $P2_1$ and $P2_1/m$. Although the precession photographs show a strong hexagonal subcell related to burbankite and remondite-(Ce), the monoclinic supercell is so pronounced that a standard monoclinic setting, b axis unique, was chosen for the cell. X-ray powder-diffraction (XRPD) data obtained with a 114.6-mm-diameter Debye–Scherrer camera with Cu$K\alpha$ (Ni-filtered) radiation are given in Table 2, with refined unit-cell parameters and volume. For comparison, the X-ray powder-diffraction data for burbankite and remondite-(Ce) also are given in Table 2. The pronounced supercell of petersenite-(Ce) serves to easily differentiate it from either of the other two minerals and from the fourth member of the group, khanneshite, which is the Ba-analogue of burbankite and has virtually the same XRPD pattern. The strongest, differentiating lines in the petersenite-(Ce) pattern [d in Å] are: 6.84, 5.47, 4.13 and 3.18. In order to save space in Table 2, the d_{calc} for all overlapping hkl reflections are averaged. Whether or not an hkl plane contributed to a reflection was determined from an XRPD pattern calculated from the crystal-structure refinement.

For the intensity-data measurements, a crystal fragment of petersenite-(Ce) from the cotype material (CMN # 81511) was ground to a sphere measuring 0.175 mm in diameter. Intensity data were collected on a fully automated Nicolet $R3m$ four-circle diffractometer using the method of Grice & Ercit (1986). The data relevant to the structure determination are given in Table 3. There was no appreciable decrepitation of the crystal due to X-ray damage throughout the experiment. It is significant that most of the superlattice reflections are observed and quite intense.

The structure was solved using direct methods, and the refinement was done with the SHELXTL PC (Sheldrick 1990) package of programs. Scattering curves for neutral atoms and anomalous dispersion

TABLE 2. PETERSENITE-(Ce): X-RAY POWDER-DIFFRACTION DATA

Petersenite-(Ce)				Remondite-(Ce)[1]				Burbankite[2]			
I obs	*d*,Å obs	*d*,Å calc	*hkl*	*I* obs	*d*,Å obs	*d*,Å calc	*hkl*	*I* obs	*d*,Å obs	*d*,Å calc	*hkl*
3	9.13	9.13	001	2	9.04	9.04	101	2	9.103	9.105	100
2	6.84	6.86	101								
2	5.47	5.46	-111								
5	5.22	5.22	011	3	5.21	5.23	101	5	5.276	5.301	101
				4	5.17	5.18	011				
>1	4.62	4.66	-311,111								
>1	4.54	4.57	-402	2	4.52	4.53	002	2	4.533	4.533	200
3	4.13	4.14	-501								
>1	3.96	3.97	-112								
4	3.70	3.71	-412	2	3.681	3.680	012	4	3.732	3.713	201
				3	3.673	3.675	212				
>1	3.46	3.47	-403								
								2	3.444	3.441	210
				10	3.416	3.418	203				
>1	3.28	3.29	-503								
								3	3.258	3.260	002
2	3.18	3.18	020								
				3	3.157	3.156	020				
2	3.04	3.04	-413					8	3.041	3.043	211
				4	3.010	3.011	112				
2	2.99	3.00	411	7	3.006	3.008	113				
>1	2.889	2.887	121								
								4	2.754	2.752	301
				2	2.724	2.724	013				
1	2.715	2.718	221								
				2	2.703	2.703	121				
>1	2.649	2.650	-404					8	2.651	2.651	202
		2.611	-422	5	2.617	2.17	202	10	2.631	2.628	220
10	2.607	2.609	402	7	2.609	2.611	204				
				10	2.589	2.590	022				
>1	2.525	2.523	321								
>1	2.343	2.343	-423,-223	2	2.330	2.333	411	1	2.354	2.355	311
>1	2.283	2.287	-523,303	1	2.26	2.265	004	>1	2.278	2.276	400
>1	2.198	2.200	-623,023					>1	2.220	2.221	302
				2	2.180	2.182	023				
								5	2.150	2.149	401
3	2.148	2.148	-913,313	7	2.132	2.132	014				
				5	2.127	2.128	414				
1	2.116	2.119	810					>1	2.112	2.114	103
1	2.066	2.067	-10.02,-230								
				3	2.049	2.050	031	3	2.046	2.046	222
>1	2.032	2.037	-424								
2	2.018	2.017	-822,422	2	2.015	2.014	222				
				3	2.012	2.012	224				
				1	1.977	1.977	104	2	1.989	1.987	410
				2	1.971	1.972	215				
1	1.965	1.965	-10.12,621	1	1.962	1.963	324	2	1.960	1.961	203
3	1.921	1.924	-430,-432								
				4	1.908	1.908	032				
>1	1.854	1.855	-923,024					2	1.867	1.866	402
>1	1.831	1.836	-115,-915	2	1.840	1.840	024	>1	1.837	1.838	213
>1	1.807	1.809	-921,721								
1	1.755	1.755	-425,-625					3	1.756	1.759	322
>1	1.733	1.740	-10.22,622								
>1	1.694	1.693	920,-225					>1	1.698	1.697	412
1	1.672	1.673	821,-10.21					>1	1.664	1.664	421
1	1.653	1.655	-12.14,414								
1	1.644	1.645	812,-12.12								
>1	1.619	1.617	631,-831								
>1	1.589	1.592	040,-13.04					>1	1.586	1.586	511
>1	1.555	1.556	333,-933					>1	1.570	1.572	403
>1	1.545	1.543	830					>1	1.537	1.535	204
1	1.500										
>1	1.484										
>1	1.467							>1	1.460	1.459	431
>1	1.446										
>1	1.415										
>1	1.405										
>1	1.387										
>1	1.370										
1	1.358										
>1	1.344										
>1	1.322										

114.6 mm Debye-Scherrer camera, CuKα radiation, visually estimated intensities. Indexed with the aid of intensity data collected with a single-crystal diffractometer, on a cell having *a* 20.84(2), *b* 6.374(4), *c* 10.578(4) Å, β 120.43(8)°. Data from the literature: 1. Cesbron *et al.* (1988), 2. Chao & Chen (1974).

TABLE 3. PETERSENITE-(Ce): STRUCTURE-REFINEMENT DATA

Ideal formula:	$Na_4REE_2(CO_3)_5$	*a* 20.872(4) Å
Space group:	$P2_1$	*b* 6.367(1) Å
Z:	4	*c* 10.601(2) Å
Crystal size:	Sphere d = 0.175 mm	β 120.50(1)°
		V 1213.9(4) Å^3
Rad./Mon:	Mo/graphite	Total no. $\|F_o\|$: 3845
μ:	6.32 mm^{-1}	No$\|F_o\| > 4\delta$: 3506
Min transmission	0.441	Final *R* (obs): 3.5%
Max transmission	0.467	Final R_w (obs): 3.0%

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1$

TABLE 4. PETERSENITE-(Ce): ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT COEFFICIENTS (x10^3, Å^2)

Atom	*x*	*y*	*z*	*U*(eq)
Na1	0.5812(2)	0.4996(16)	0.3247(3)	15(1)
Na2	0.9187(2)	0.9940(16)	0.1620(4)	15(1)
Na3	0.2332(3)	0.8037(8)	0.0356(4)	15(2)
Na4	0.7562(3)	0.3159(8)	0.5245(4)	15(2)
Na5	0.9776(2)	0.3071(8)	0.9731(4)	16(2)
Na6	0.5225(2)	0.8085(8)	0.0187(4)	15(2)
Na7	0.2667(3)	0.3030(8)	0.5694(4)	14(2)
Na8	0.2562(2)	0.3164(8)	0.9880(4)	13(2)
Ce1	0.6583(1)	0.0000	0.6419(1)	8(1)
Ce2	0.9206(1)	0.9968(3)	0.6556(1)	7(1)
Ce3	0.8417(1)	0.4975(3)	0.3254(1)	9(1)
Ce4	0.5794(1)	0.4979(3)	0.8144(1)	7(1)
C1	0.3293(5)	-.0197(22)	-.1470(8)	9(2)
C2	0.8291(5)	-.0208(22)	0.8080(9)	10(2)
C3	0.6966(5)	0.5334(16)	0.6840(8)	6(2)
C4	-.0979(5)	0.5358(15)	0.0942(8)	5(2)
C5	0.1002(5)	0.0344(16)	0.3141(8)	7(2)
C6	0.8027(5)	0.0299(18)	0.2900(9)	9(2)
C7	0.5975(5)	0.0313(16)	0.2907(8)	6(2)
C8	0.0010(7)	0.8277(18)	0.5080(12)	12(2)
C9	0.5999(5)	0.0323(17)	0.8865(9)	8(2)
C10	0.5029(7)	0.8275(17)	0.4978(11)	9(2)
O1	0.2945(3)	-.0192(18)	-.0760(6)	13(1)
O2	0.4005(4)	-.0275(14)	-.0767(6)	11(1)
O3	0.7086(4)	-.5257(15)	0.2899(6)	13(2)
O4	0.9010(4)	-.0258(15)	0.8795(6)	12(2)
O5	0.7949(3)	-.0155(20)	0.6663(6)	12(1)
O6	0.7914(4)	-.0260(15)	0.8716(6)	13(2)
O7	0.7213(4)	0.3480(13)	0.7046(7)	10(1)
O8	0.6841(4)	-.3626(13)	0.5699(7)	13(1)
O9	0.6843(4)	-.3752(12)	0.7805(7)	12(1)
O10	0.0366(4)	0.1279(13)	0.8708(7)	13(1)
O11	0.1437(4)	0.1258(13)	0.8782(7)	13(2)
O12	0.1106(5)	0.8518(15)	0.9613(8)	21(2)
O13	0.9562(4)	-.3650(13)	0.7764(7)	15(2)
O14	0.8870(4)	0.3451(12)	0.7105(7)	11(1)
O15	0.8522(4)	-.3742(12)	0.5644(7)	12(1)
O16	0.8169(4)	0.1360(13)	0.2020(7)	12(1)
O17	0.7783(4)	-.1499(13)	0.2634(7)	11(1)
O18	0.8156(4)	0.1242(12)	0.4111(7)	13(1)
O19	0.3893(5)	0.3502(14)	0.7401(8)	20(2)
O20	0.5354(4)	0.1291(13)	0.2011(8)	15(2)
O21	0.3555(4)	0.6248(12)	0.5889(7)	12(1)
O22	0.9586(4)	0.3084(14)	0.5517(8)	17(2)
O23	0.0343(4)	-.1241(13)	0.6439(7)	14(2)
O24	0.0677(4)	0.3068(14)	0.5599(8)	17(2)
O25	0.6479(4)	0.1255(12)	0.8597(7)	11(1)
O26	0.3879(4)	0.3458(12)	0.0646(7)	9(1)
O27	0.4560(4)	-.3637(13)	0.1361(7)	16(2)
O28	0.5678(4)	0.3075(14)	0.5742(8)	17(2)
O29	0.5346(4)	0.8760(13)	0.4250(8)	17(2)
O30	0.4589(4)	0.3100(13)	0.3667(7)	14(2)

corrections were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. From the *E*-map, the positions of the nine atomic sites with the highest scattering power were chosen and refined to $R = 17\%$. The difference-Fourier maps of subsequent refinements showed additional atomic sites.

Table 4 contains the final positional and isotropic displacement parameters for the petersenite-(Ce)

TABLE 5. PETERSENITE-(Ce): SELECTED BOND-LENGTHS (Å)

Na1-02B	2.847(9)	Na5-04	2.534(10)
Na1-03A	2.869(10)	Na5-010	2.313(11)
Na1-08A	2.544(7)	Na5-014	2.458(7)
Na1-019B	2.504(14)	Na5-04C	2.444(8)
Na1-020A	2.631(12)	Na5-010C	2.738(10)
Na1-021B	2.656(12)	Na5-012B	2.292(13)
Na1-027A	2.506(8)	Na5-013A	2.822(10)
Na1-029A	2.978(13)	Na5-013C	2.537(8)
Na2-04A	2.829(8)	Na6-020	2.730(10)
Na2-06A	2.872(6)	Na6-02A	2.446(9)
Na2-010B	2.599(13)	Na6-02C	2.555(10)
Na2-011B	2.610(13)	Na6-019C	2.284(7)
Na2-012A	2.542(13)	Na6-020B	2.310(8)
Na2-013B	2.514(10)	Na6-026B	2.451(11)
Na2-016A	2.534(11)	Na6-027B	2.537(12)
Na2-023C	3.010(12)	Na6-027C	2.828(11)
Na3-011	2.705(9)	Na7-03B	2.468(10)
Na3-012	2.284(11)	Na7-05B	2.443(9)
Na3-01A	2.418(11)	Na7-08B	2.425(11)
Na3-06C	2.481(11)	Na7-015B	2.423(9)
Na3-07B	2.431(8)	Na7-017B	2.410(11)
Na3-09B	2.746(8)	Na7-018C	2.746(10)
Na3-016C	2.429(8)	Na7-019A	2.282(8)
Na3-025B	2.425(9)	Na7-021A	2.698(10)
Na4-05	2.476(12)	Na8-01B	2.493(12)
Na4-07	2.373(11)	Na8-06C	2.390(10)
Na4-014	2.431(8)	Na8-09C	2.441(8)
Na4-018	2.446(11)	Na8-011A	2.359(9)
Na4-03A	2.383(8)	Na8-016C	2.722(8)
Na4-08A	2.724(11)	Na8-017C	2.392(9)
Na4-015A	2.688(10)	Na8-025B	2.684(8)
Na4-021B	2.349(9)	Na8-026A	2.446(10)
Ce1-02B	2.557(9)	Ce3-018	2.697(9)
Ce1-05A	2.732(8)	Ce3-01C	2.731(5)
Ce1-06B	2.610(5)	Ce3-03A	2.612(8)
Ce1-07A	2.489(8)	Ce3-011B	2.466(9)
Ce1-08A	2.573(9)	Ce3-015A	2.565(8)
Ce1-09A	2.711(8)	Ce3-016B	2.567(8)
Ce1-021C	2.447(8)	Ce3-017A	2.518(8)
Ce1-025A	2.554(9)	Ce3-022A	2.686(7)
Ce1-029A	2.559(7)	Ce3-023D	2.557(9)
Ce1-030A	2.688(9)	Ce3-024A	2.569(8)
Ce2-022	2.581(10)	Ce4-025	2.683(8)
Ce2-04B	2.609(8)	Ce4-01D	2.687(5)
Ce2-05A	2.683(8)	Ce4-02C	2.599(7)
Ce2-010A	2.482(6)	Ce4-09A	2.524(10)
Ce2-013A	2.556(8)	Ce4-020B	2.463(10)
Ce2-014A	2.483(9)	Ce4-026B	2.476(8)
Ce2-015A	2.674(8)	Ce4-027D	2.553(9)
Ce2-018A	2.532(6)	Ce4-028A	2.718(9)
Ce2-023A	2.558(10)	Ce4-029B	2.564(6)
Ce2-024A	2.704(10)	Ce4-030A	2.591(8)
C1-01	1.285(14)	C6-016	1.302(15)
C1-02	1.281(11)	C6-017	1.227(14)
C1-03C	1.306(9)	C6-018B	1.315(13)
C2-04	1.294(11)	C7-019D	1.266(14)
C2-05	1.296(10)	C7-020A	1.312(11)
C2-06	1.269(15)	C7-021B	1.294(10)
C3-07	1.262(13)	C8-022B	1.292(20)
C3-08A	1.284(12)	C8-023B	1.279(13)
C3-09A	1.312(14)	C8-024B	1.243(15)
C4-010D	1.279(13)	C9-025A	1.313(15)
C4-011C	1.271(15)	C9-026B	1.269(13)
C4-012C	1.277(13)	C9-027C	1.254(14)
C5-013D	1.253(11)	C10-029	1.284(19)
C5-014B	1.289(13)	C10-028B	1.277(14)
C5-015C	1.299(10)	C10-030B	1.244(12)

structure, and Table 5 lists the interatomic distances. The final stages of the least-squares refinement involved a conversion to anisotropic displacement parameters for the four Ce (rare-earth element) sites and the eight Na sites, and the addition of a weighting scheme involving an extinction correction. A refinement of the enantiomorph was tried but without significant improvement in the final R values. The observed and calculated structure-factors, as well as the anisotropic displacement factors, have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Description and Discussion of the Structure

The crystal structure of petersenite-(Ce) has many similarities to that of burbankite, which was solved by Voronkov *et al.* (1967) and later refined by Effenberger *et al.* (1985). The crystal structure of burbankite (Fig. 2a), in the noncentrosymmetric space-group $P6_3mc$, has two large cationic sites. The A site, with [8] coordination, is occupied by Na and Ca atoms, whereas the B site, with [10] coordination, is occupied by Sr and lesser amounts of Ba, Ca and rare-earth elements.

The crystal structure of remondite-(Ce) (Fig. 2a) (Ginderow 1989), has the same unit-cell volume as burbankite, but the symmetry is lowered to that of the noncentrosymmetric space-group $P2_1$ owing to ordering involving the large cations. The A site of burbankite becomes three sites occupied entirely by Na atoms having [8] coordination in the remondite-(Ce) structure, whereas the B site of burbankite degenerates into three M sites, each with [10] coordination in remondite-(Ce). The order in remondite-(Ce) seems to primarily involve the M sites, as evidenced by their different refined occupancy-factors (Ginderow 1989). This subtle degree of order is sufficient to give biaxial optical properties and some doubling of lines in the XRPD pattern (Table 2).

In the petersenite-(Ce) structure, the order of cations is more pronounced than in remondite-(Ce). Although the distribution of the carbonate groups and the large cations in petersenite-(Ce) (Fig. 2b) is similar to that of burbankite and remondite-(Ce) (Fig. 2a), there is a change in the ratio of cations in [8] coordination (*i.e.*, Na sites) to cations in [10] coordination (*i.e.*, Ce sites). In burbankite and remondite-(Ce), this coordination ratio of [8] to [10] is 1:1, whereas in petersenite-(Ce) it is 2:1. This shift in the structure is sufficient to give the pronounced supercell, which is readily seen in both the XRPD pattern (Table 2) and the single-crystal X-ray-diffraction films. Refining the occupancy factor of each of the Na sites reveals that the Na1 and Na2 sites contain some atoms of higher atomic number (*i.e.*, Ca or *REE*). In Figure 2a, it is evident that these two sites are [10]-coordination sites in remondite-(Ce) and subsequently in burbankite. Thus we may conclude that an increase in the proportion of Ca or *REE* (Table 1) causes a change from

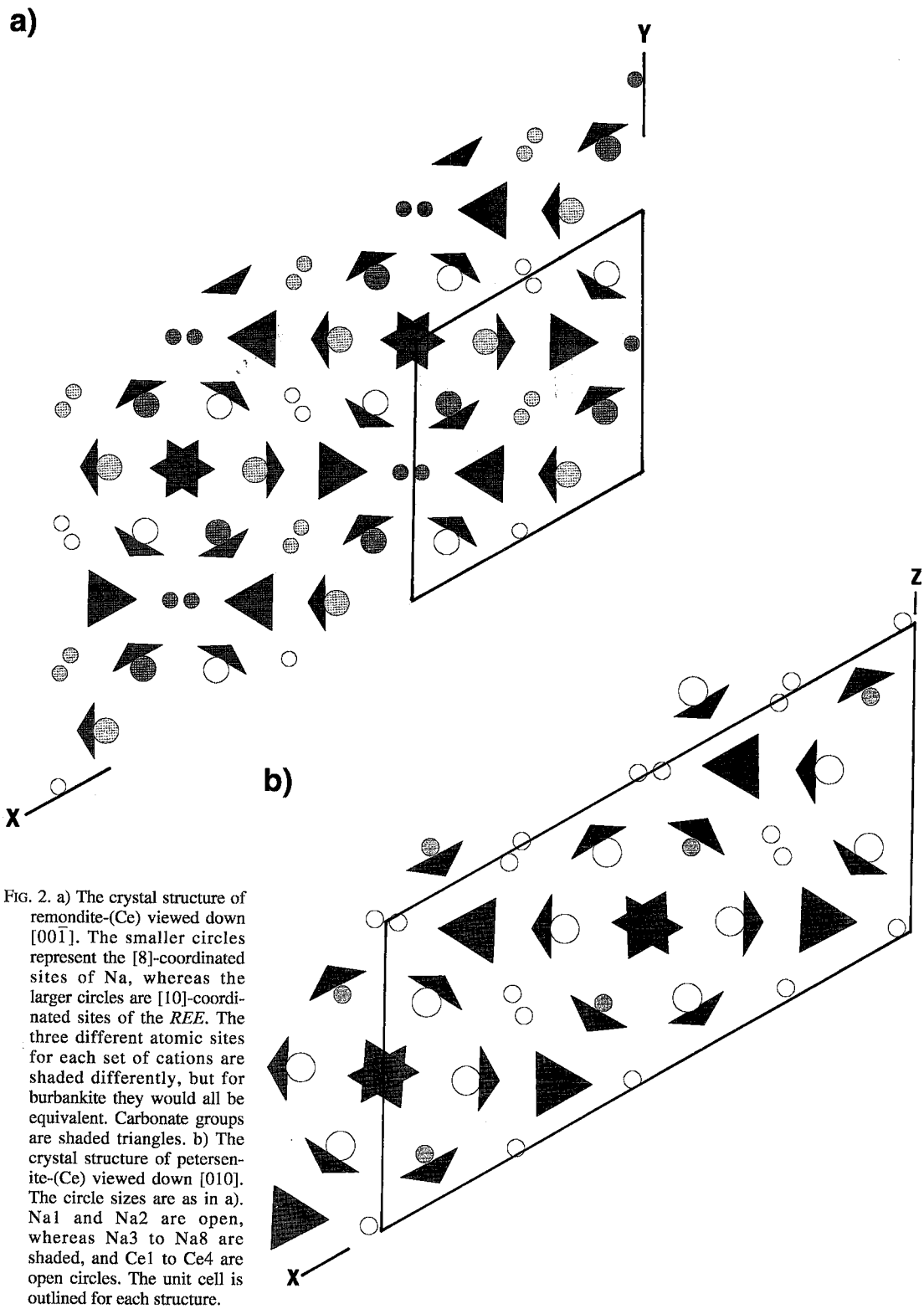

FIG. 2. a) The crystal structure of remondite-(Ce) viewed down [00$\bar{1}$]. The smaller circles represent the [8]-coordinated sites of Na, whereas the larger circles are [10]-coordinated sites of the *REE*. The three different atomic sites for each set of cations are shaded differently, but for burbankite they would all be equivalent. Carbonate groups are shaded triangles. b) The crystal structure of petersenite-(Ce) viewed down [010]. The circle sizes are as in a). Na1 and Na2 are open, whereas Na3 to Na8 are shaded, and Ce1 to Ce4 are open circles. The unit cell is outlined for each structure.

the petersenite-(Ce) structure to the remondite-(Ce) structure while maintaining the same space-group but losing the supercell.

As (CO_3) groups do not polymerize owing to simple bond-valence considerations (Grice & Ercit 1986), the crystal structures of carbonate minerals tend to be layered, with (CO_3) slabs being interleaved with layers of large cations, predominantly alkaline, alkaline-earth and rare-earth cations. This rather simple arrangement gives rise to very few structure-types but a large number of mineral species. The great diversity of species results from: 1) the numerous possible substitutions in the layer of cations, 2) variability of cation:(CO_3) ratio, 3) the variation in thickness and content of large cations of the carbonate layer, 4) addition of an (H_2O) layer, and 5) the addition of other anionic groups such as $(SiO_4)^{4-}$, $(PO_4)^{2-}$ and $(BO_3)^{3-}$ or $(BO_4)^{5-}$. The following brief discussion concerns itself with *REE* carbonate minerals only and their structural relationship to petersenite-(Ce). It will show how subtle changes in the crystal structure gives rise to so many species.

The thickness of the carbonate layer is determined by the orientation of the triangular polyhedron, which in its two extremes may be either "flat-lying" or "standing-on-edge". The "flat-lying" carbonate layers are of two types: a uniformly flat layer, as in the calcite and dolomite structures, for which no *REE* carbonates have been reported, and a "corrugated" layer, as in the aragonite structure, to which ancylite-(La) may be compared (Dal Negro *et al.* 1975). Figure 3 shows the "corrugated" layer of carbonate groups interleaved with the (*REE*,Ca) atoms in [10] coordination. *REE* minerals having "standing-on-edge" carbonate layers are much more common. The fluorcarbonate minerals, which are members of the bastnäsite – parisite – röntgenite – synchysite group, owe their syntactic intergrowths to various stacking combinations of (CeF), (CO_3) and [Ca(CO_3)] layers (Ni *et al.* 1993). From the crystal-structure analysis of cebaite-(Ce) (Li & Hashimoto 1984), it is evident that the barium fluorcarbonates cebaite-(Ce), huanghoite-(Ce) and zhonghuacerite-(Ce) have syntactic intergrowths similar to those of the bastnäsite group. Figure 4 shows the bastnäsite-(Ce) structure (Ni *et al.* 1993) as an example of this type of carbonate "standing-on-edge" layering.

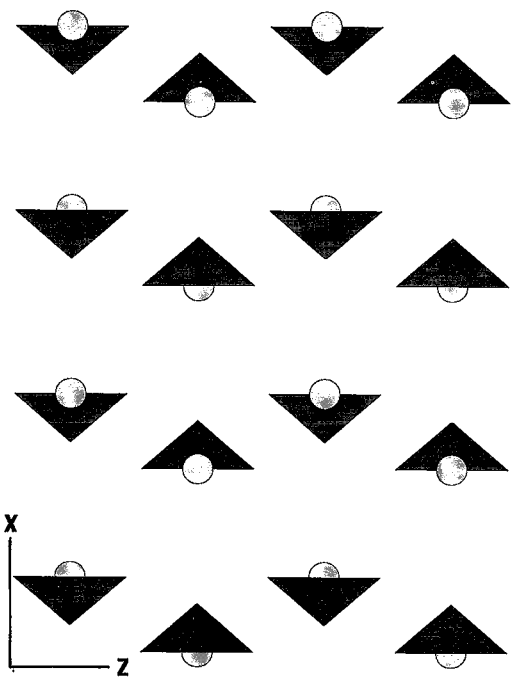

FIG. 3. The crystal structure of ancylite-(La) viewed down [010], showing "corrugated, flat-lying" carbonate layers and large *REE* atoms.

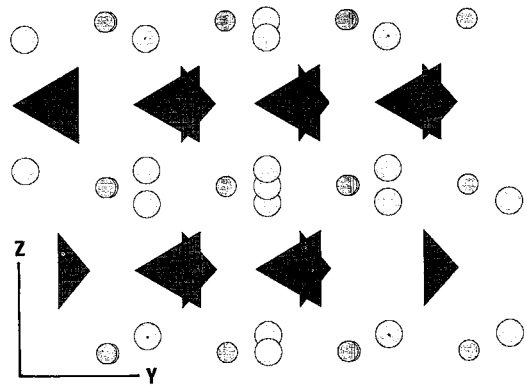

FIG. 4. The crystal structure of bastnäsite-(Ce) viewed down [100], showing "standing-on-edge" carbonate layers and the CeF layer, with Ce a small circle, and F, a large circle.

In addition to the "flat" and "standing-on-edge" carbonate structures described above, a whole series of modifications exist with mixtures of the two types of layer. These crystal structures are invariably complex and found only in rare minerals. Figure 5 shows an integral carbonate layer in sahamalite-(Ce) (after Pertlik & Preisinger 1983) along (110), which is composed of "flat", "standing-on-edge" and "standing-on-base" slabs of carbonate. These are sandwiched by Mg and *REE* polyhedra. In the lanthanite structure (Dal Negro *et al.* 1977), there is a distinct "standing-on-edge" layer of carbonate on (100) between La polyhedra, with another (CO_3) polyhedron, "standing-on-base" sharing the water layer on (010) (Fig. 6).

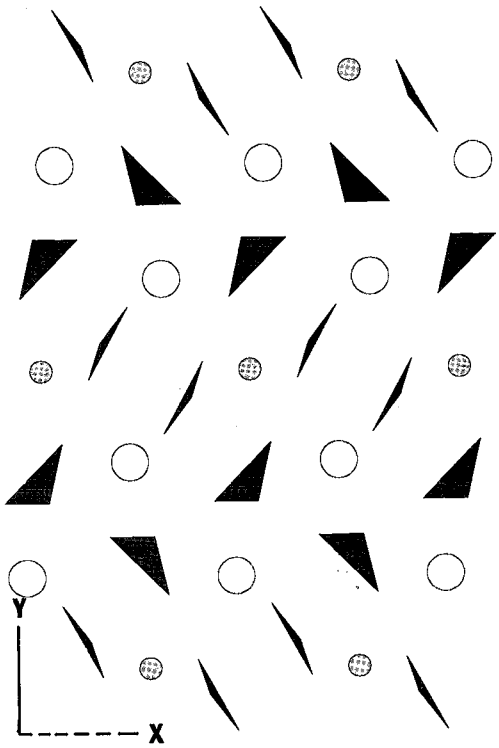

FIG. 5. The crystal structure of sahamalite-(Ce) viewed down [001], with the carbonate groups layered, but with varying orientations. The Mg is a small circle, and Ce, a large circle.

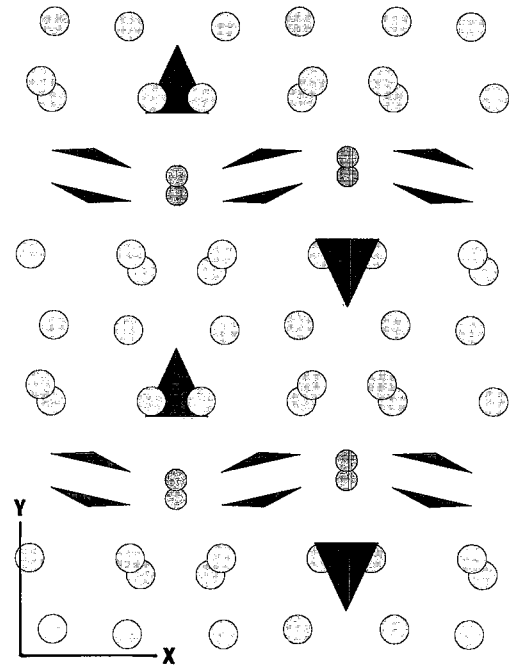

FIG. 6. The crystal structure of lanthanite-(La) viewed down [011], showing the two types carbonate layers, "standing-on-edge", and "standing-on-base", plus water interleaved with layer of La polyhedra.

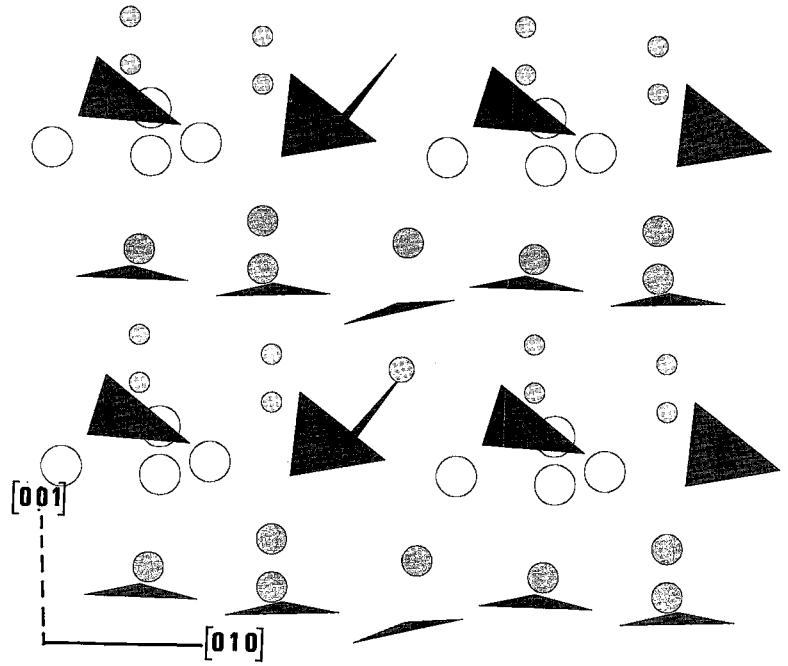

FIG. 7. The crystal structure of weloganite viewed down [100] (rotated 7° about [010]), showing the two types of carbonate layers, "flat-lying" and "standing-on-base", plus water (large, open circles) interlayered with layers of large cations. Na atoms are shown as small, lightly shaded circles, Zr, as circles of medium size and shading, and Sr atoms, as large, darker shaded circles.

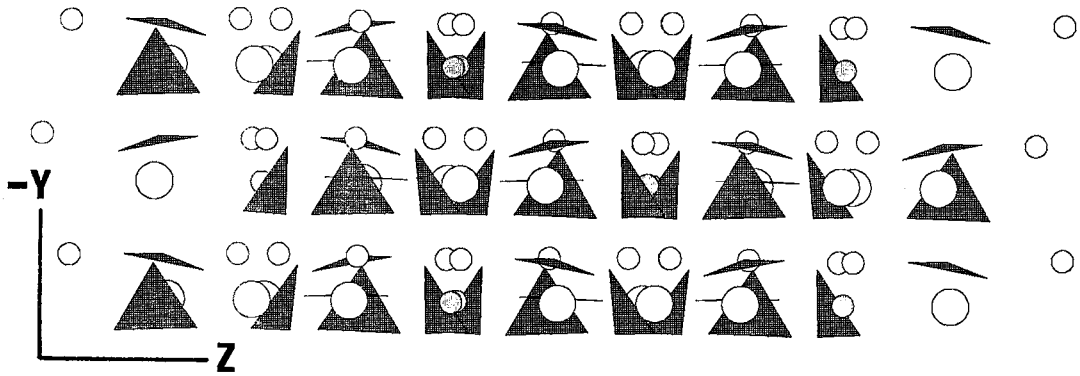

FIG. 8. The crystal structure of petersenite-(Ce) viewed down [100], showing the "flat-lying" [$Na_3(CO_3)$] layers and inclined [$REE_2Na(CO_3)_4$] layers. Atom designation is the same as in Figure 2, with smaller circles representing Na atoms, and larger circles, the *REE* atoms.

Donnayite-(Y) and mckelveyite-(Y) have the weloganite structure (Fig. 7) (Grice & Perrault 1975). In this structure, the layering is parallel to (001), with a carbonate – water layer of the type described for the lanthanite structure, as well as a "flat-lying" carbonate layer, but no longer consisting entirely of carbonate groups in the sense that it also contains Na atoms. It is this complexity of mixed layering that we have in petersenite-(Ce) and other members of the burbankite group. The layering on (010) (Fig. 8) is composed of four slabs; 2 × [$REE_2Na(CO_3)_4$] and 2 × [$Na_3(CO_3)$]. In the first type of slab, the (CO_3) polyhedra are both "flat-lying" and inclined "standing-on-base", whereas in the second type of slab, the (CO_3) polyhedra are approximately "flat-lying". These mixed layered structures, although reducing the possibility of syntactic intergrowth, increase the structural variability and order within the *REE* carbonates.

ACKNOWLEDGEMENTS

The authors thank Dr. F.C. Hawthorne, University of Manitoba, for allowing them to use the fully automated four-circle diffractometer. J.D.G. and R.A.G. acknowledge with gratitude a Research Advisory Committee Grant, Canadian Museum of Nature. The authors appreciate the improvements to this manuscript brought about by the helpful suggestions of two anonymous referees, Associate Editor Roger Mason and Editor R.F. Martin.

REFERENCES

CESBRON, F., GILLES, C., PELISSON, P. & SAUGUES, J.-C. (1988): La remondite-(Ce), un nouveau carbonate de terres rares de la famille de la burbankite. *C.R. Acad. Sci. Paris, Ser.* **II, 307**, 915-920.

CHEN, T.T. & CHAO, G.Y. (1974): Burbankite from Mont St. Hilaire, Quebec. *Can. Mineral.* **12**, 342-345.

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.

DAL NEGRO, A., ROSSI, G. & TAZZOLI, V. (1975): The crystal structure of ancylite, $(RE)_x(Ca,Sr)_{2-x}(CO_3)_2(OH)_x(2–x)H_2O$. *Am. Mineral.* **60**, 280-284.

_____, _____ & _____ (1977): The crystal structure of lanthanite. *Am. Mineral.* **62**, 142-146.

EFFENBERGER, H., KLUGER, F., PAULUS, H. & WÖLFEL, E.R. (1985): Crystal structure refinement of burbankite. *Neues Jahrb. Mineral., Monatsh.*, 161-170.

GINDEROW, D. (1989): Structure de $Na_3M_3(CO_3)_5$ (M = Terre Rare, Ca, Na, Sr), rattaché à la burbankite. *Acta Crystallogr.* **C45**, 185-187.

GRICE, J.D. & ERCIT, T.S. (1986): The crystal structure of moydite. *Can. Mineral.* **24**, 675-678.

_____ & PERRAULT, G. (1975): The crystal structure of triclinic weloganite. *Can. Mineral.* **13**, 209-216.

HORVATH, L. & GAULT, R.A. (1990): The mineralogy of Mont Saint-Hilaire, Quebec. *Mineral. Rec.* **21**, 284-360.

LI, F.H. & HASHIMOTO, H. (1984): Use of dynamical scattering in the structure determination of a minute fluorocarbonate mineral cebaite $Ba_3Ce_2(CO_3)_5F_2$ by high-resolution electron microscopy. *Acta Crystallogr.* **B40**, 454-461.

NI, Y., HUGHES, J.M. & MARIANO, A.N. (1993): The atomic arrangement of bastnäsite-(Ce), $Ce(CO_3)F$, and structural elements of synchysite-(Ce), röntgenite-(Ce), and parisite-(Ce). *Am. Mineral.* **78**, 415-518.

PERTLIK, F. & PREISINGER, A. (1983): Crystal structure of sahamalite $(Mg,Fe)RE_2(CO_3)_4$. *Tschermaks Mineral. Petrogr. Mitt.* **31**, 39-46.

SHELDRICK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.

VORONKOV, A.A., SHUMYATSKAYA, N.G. & PYATENKO, YU. A. (1967): Crystal structure of burbankite. *Sov. Phys. Crystallogr.* **12**, 107.

Received May 20, 1993, revised manuscript accepted September 13, 1993.