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HORVÁTHITE-(Y), RARE-EARTH FLUOROCARBONATE, A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

JOEL D. GRICE[1]

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4

GEORGE Y. CHAO

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

ABSTRACT

Horváthite-(Y), ideally, $NaY(CO_3)F_2$, is a new mineral species from Mont Saint-Hilaire, Quebec. It occurs as tabular crystals up to 1 × 1 × 0.25 mm stacked in fan-shaped groups. It is colorless to pale beige, with a white streak and a vitreous luster. Associated minerals include microcline, aegirine, dawsonite, rhodochrosite, sodalite, natrolite, albite, sérandite, siderite, taeniolite, catapleiite, astrophyllite, genthelvite, and a franconite-group mineral. It is soft (Mohs hardness ~4), brittle, with an uneven fracture and with very good {100} cleavage. Horváthite-(Y) is biaxial negative, α 1.457(1), β 1.543(1), γ 1.622(1), $2V_{meas.}$ = 82(1)° and $2V_{calc.}$ = 83°. It is orthorhombic, space group *Pmcn*, *a* 6.964(3), *b* 9.173(6), *c* 6.302(2) Å, *V* 402.6(4) Å^3 and $Z = 4$. The strongest eight X-ray powder-diffraction lines [*d* in Å (*I*)(*hkl*)] are 5.19(90)(011), 3.477(100)(200), 2.800(50)(130), 2.087(50)(132,222), 2.057(50)(141,013), 1.966(50)(321), 1.849(50)(330) and 1.763(50)(213,051). An average electron-microprobe analysis gave Na_2O 12.62, CaO 1.86, Y_2O_3 45.07, Gd_2O_3 0.45, Dy_2O_3 2.49, Er_2O_3 3.02, Yb_2O_3 1.64, Ho_2O_3 0.81, Tb_2O_3 0.12, F 17.22 and CO_2 19.83, O = F –7.23, total 97.90 wt.%. The proportion of CO_2 was calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula based on three atoms of oxygen is: $(Na_{0.90}Ca_{0.07})_{\Sigma 0.97}$ $(Y_{0.89}Gd_{0.01}Dy_{0.03}Er_{0.04}Yb_{0.02}Ho_{0.01})_{\Sigma 1.00}(CO_3)F_{2.01}$ or, ideally, $NaY(CO_3)F_2$. $D_{calc.}$ is equal to 3.613 g/cm^3, and $D_{meas.}$ exceeds 3.3 g/cm^3. The structure has been refined to R = 1.6%. The structure is layered perpendicular to [100], with a Na – Y – carbonate group layer and a layer of F atoms. The structure of horváthite-(Y) seems unique among mineral structures, but resembles that of synthetic $BaCu(CO_3)F_2$.

Keywords: horváthite-(Y), new mineral species, carbonate, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La horváthite-(Y), de composition idéale $NaY(CO_3)F_2$, est une nouvelle espèce minérale découverte au mont Saint-Hilaire, Québec. Elle se présente en cristaux tabulaires atteignant 1 × 1 × 0.25 mm, en agencements radiés. Elle est incolore ou beige pâle, avec une rayure blanche et un éclat vitreux. Lui sont associés microcline, aegyrine, dawsonite, rhodochrosite, sodalite, natrolite, albite, sérandite, siderite, taeniolite, catapléiite, astrophyllite, genthelvite, et un minéral du groupe de la franconite. Sa dureté est d'environ 4 (échelle de Mohs); elle est cassante, avec une cassure inégale et un excellent clivage {100}. La horváthite-(Y) est biaxe négative, α 1.457(1), β 1.543(1), γ 1.622(1), $2V_{mes.}$ = 82(1)° et $2V_{calc.}$ = 83°. Elle est orthorhombique, groupe spatial *Pmcn*, *a* 6.964(3), *b* 9.173(6), *c* 6.302(2) Å, *V* 402.6(4) Å^3 et $Z = 4$. Les huit raies les plus intenses du spectre de diffraction X [méthode des poudres; *d* en Å (*I*)(*hkl*)] sont: 5.19 (90)(011), 3.477(100)(200), 2.800(50)(130), 2.087(50)(132,222), 2.057(50)(141,013), 1.966(50)(321), 1.849(50)(330) et 1.763(50)(213,051). Une analyse représentative à la microsonde électronique donne Na_2O 12.62, CaO 1.86, Y_2O_3 45.07, Gd_2O_3 0.45, Dy_2O_3 2.49, Er_2O_3 3.02, Yb_2O_3 1.64, Ho_2O_3 0.81, Tb_2O_3 0.12, F 17.22 et CO_2 19.83, O = F –7.23, pour un total de 97.90% (en poids). La proportion de CO_2 a été établie par stoechiométrie à partir des résultats d'un affinement de la structure cristalline. La formule empirique, fondée sur une base de trois atomes d'oxygène, est: $(Na_{0.90}Ca_{0.07})_{\Sigma 0.97}(Y_{0.89}Gd_{0.01}Dy_{0.03}Er_{0.04}Yb_{0.02}Ho_{0.01})_{\Sigma 1.00}(CO_3)F_{2.01}$ ou, de façon idéale, $NaY(CO_3)F_2$. La densité calculée est égale à 3.613, et la densité mesurée dépasse 3.3. La structure a été affinée jusqu'à un résidu R de 1.6%. La structure est faite de couches perpendiculaires à [100], avec des agencements à Na – Y – carbonate dans une couche et des atomes de F dans l'autre. La structure de la horváthite-(Y) semble unique dans le règne minéral, mais elle ressemble à celle du composé synthétique $BaCu(CO_3)F_2$.

Mots-clés: horváthite-(Y), nouvelle espèce minérale, carbonate, structure cristalline, mont Saint-Hilaire, Québec.

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[1] *E-mail address*: jgrice@mus-nature.ca

INTRODUCTION

There are 34 rare-earth element (*REE*) fluorocarbonate mineral species known, and these provide one of the major economic sources for *REE*. Many of the new *REE* carbonate minerals being described today are not of economic interest owing to their existence only in small quantities, but their value may be in their crystal-chemical properties. Recently, there has been a great deal of interest in fluorocarbonates for industrial applications. *REE* fluorocarbonates have useful optical properties, and the 3*d* transition-metal fluorocarbonates are being investigated for their magnetic properties. This interest has led to a great deal of effort to synthesize new compounds. Many of these have natural equivalents, whereas others have not yet been found in nature. These synthetic equivalents provide extremely valuable study material for mineralogists, as many of the minerals are not found in crystals suitable for crystal-structure analysis (Mercier & Leblanc 1993a, b). The new mineral horváthite-(Y) is yet another material with a composition and crystal structure that have not been reported until now in either natural or synthetic systems.

Mont Saint-Hilaire is known throughout the world for its diversity in mineral species. This diversity results from the complex geochemistry, and horváthite-(Y) is an expression of this complexity. At this locality, 41 carbonate minerals have been identified (Horváth & Gault 1990), as well as approximately 10 unknowns (Chao *et al.* 1990). Of the identified carbonates, 17 contain the rare earths as essential elements (Grice 1996), and of these, six contain fluorine as an essential anion: bastnäsite-(Ce), cordylite-(Ce), horváthite-(Y), parisite-(Ce), reederite-(Y) and synchysite-(Ce).

The new mineral, horváthite-(Y), found originally in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, is named in honor of Elsa (1947–) and László Horváth (1937–), a husband-and-wife team dedicated to the collection, study and documentation of Mont Saint-Hilaire minerals. They have published articles, provided valuable research material to many scientists, and distributed extensive suites of Mont Saint-Hilaire minerals to museums around the world. 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 catalogue no. CMNMI81536.

OCCURRENCE

Mont Saint-Hilaire is an alkaline intrusive complex and one of the ten Monteregian Hills, a series of plutons aligned along the St. Lawrence Valley for almost 150 km eastward from Oka to Megantic, Quebec.

The cotype specimen was collected in 1994 by Steve and Janet Cares and recognized as a new mineral by the second author. At present, horváthite-(Y) must be considered a very rare mineral, as there are only a few mg known to exist. The specimens were collected in the southeastern corner of the Poudrette quarry, from a large pegmatite dike, approximately 1.5 to 2.0 m wide, in the nepheline syenite intrusive unit. The portion of the pegmatite in which horváthite-(Y) was found is quite altered. Many of the minerals with horváthite-(Y) inclusions are etched and corroded. Horváthite-(Y) is associated with microcline, aegirine, dawsonite, rhodochrosite, sodalite, natrolite, albite, sérandite, siderite, taeniolite, catapleiite, astrophylite, genthelvite, and a franconite-group mineral. In another part of the same pegmatite dike, horváthite-(Y) is also associated with UK96, an alteration product of UK96, sphalerite, rhodochrosite, and microcline.

PHYSICAL AND OPTICAL PROPERTIES

Horváthite-(Y) has two distinct habits: 1) it occurs as stacks of (100) plates, measuring approximately 1 × 1 × 0.25 mm (Fig. 1a), and 2) as blocky aggregates of radiating crystals 1–5 mm across with individual, striated, prismatic crystals up to 1 mm long on [010]. The aggregates are commonly "wagon-wheel" or cylindrical in habit. Forms include {100} > {001} > {010} and minor

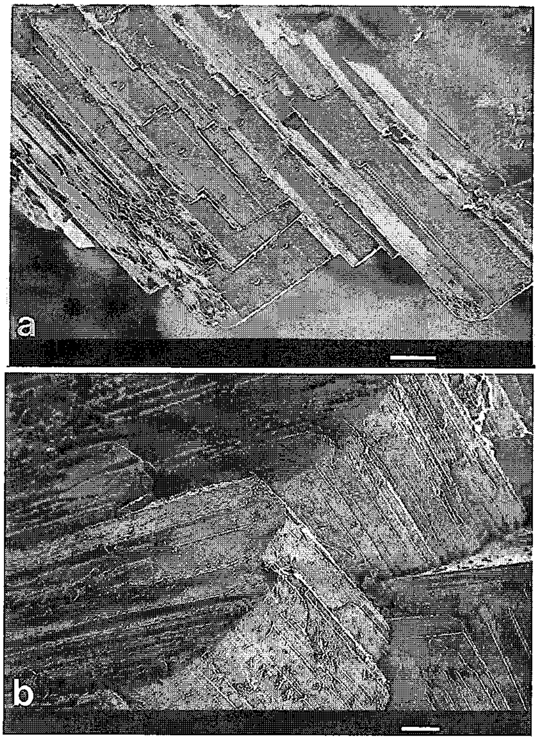

FIG. 1. Scanning electron microscope photomicrographs of horváthite-(Y): a) platy on (100) and b) blocky aggregates striated along [010]. The scale bar represent 10 μm.

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

I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
15	5.54	5.55	110	5	1.856	1.854	042
90	5.19	5.19	011	50	1.849	1.849	330
20	4.59	4.59	020	25	1.833	1.832	241
5	3.706	3.708	021			1.831	312
100	3.477	3.482	200	5	1.774	1.774	150
35	3.273	3.273	121	50	1.763	1.765	213
35	3.145	3.151	002			1.762	051
5	2.888	2.892	211	40	1.741	1.741	400
50	2.800	2.800	130	5	1.652	1.651	411
5	2.773	2.773	220	15	1.595	1.595	332
15	2.738	2.740	112	10	1.578	1.579	341
10	2.596	2.597	022	5	1.572	1.572	251
5	2.338	2.336	202	10	1.545	1.546	152
5	2.292	2.293	040	5	1.532	1.536	313
5	2.252	2.250	310			1.529	060
5	2.193	2.194	032	5	1.524	1.523	402
5	2.156	2.159	231	5	1.512	1.512	143
		2.155	041	5	1.475	1.475	323
50	2.087	2.093	132	5	1.445	1.446	422
		2.082	222	5	1.401	1.400	260
50	2.057	2.059	141	10	1.374	1.375	062
		2.048	013			1.373	134
50	1.966	1.968	321	10	1.327	1.326	413

- 114.6 mm Gandolfi camera, Cu*K*α radiation (Ni filtered), intensities estimated visually
- d_{calc} based on refined cell parameters: *a* 6.964(3), *b* 9.173(6), *c* 6.302(2) Å

TABLE 2. HORVÁTHITE-(Y): DATA COLLECTION INFORMATION

Space Group	*Pmcn*	Measured reflections	2272
a (Å)	6.959(2)	Merged reflections	629
b (Å)	9.170(2)	*R*merge(%) (refinement on *F*)	2.2
c (Å)	6.301(1)	Observed reflections [> 4σ(*F*)]	499
V (Å³)	402.1(2)	Minimum transmission	0.087
Radiation	Mo*K*α	Maximum transmission	0.137
Monochromator	Graphite	Refined parameters	48
μ (mm⁻¹)	14.5	R/R_w (%)	1.6/1.4
Unit-cell contents 4[$NaY(CO_3)F_2$]			

{110}, {011} and {101}. The mineral is colorless to pale beige, translucent to transparent, with a white streak and vitreous luster. It is brittle, with very good {100} and good {010} cleavages. The mineral is relatively soft (Mohs hardness 4) and does not fluoresce in ultraviolet light. The mineral sinks in methylene iodide (>3.3 g/cm^3) and has a calculated density of 3.61 g/cm^3.

Horváthite-(Y) is biaxial negative, with indices of refraction α 1.457(1) β 1.543(1) and γ 1.622(1); $2V_{meas.}$ is equal to 82(1)°, and $2V_{calc.}$, 83° (for $\lambda = 590$ nm). The optical orientation is $Y = a$, $X = b$ and $Z = c$. There is no dispersion; the mineral is weakly pleochroic with $Y \approx Z$ pale brown, and X colorless. A Gladstone–Dale calculation gives a compatibility index of 0.008, which is regarded as superior (Mandarino 1981).

CHEMICAL COMPOSITION

Chemical analyses were performed on a Cambridge Microscan MK5 electron microprobe. The wavelength-dispersion (WD) mode was used with an operating voltage of 15ngkV, and the beam current was 0.30 μA. Data reduction was done using a modified version of EMPADR VII (Rucklidge & Gasparrini 1969). Two analyses were performed on a single grain using a beam 50 μm in diameter. Data for all elements in the samples were collected for 5 s. The following standards were used: albite (Na*K*α), YIG (Y*L*α), LiF (F*K*α) and *REE*-bearing glasses (Ca*K*α, Gd*L*α, Dy*L*α, Er*L*α, Yb*L*α, Ho*L*α, Tb*L*α). An average result of two electron-microprobe analyses (with ranges, in weight %) gave Na_2O 12.62 (12.59–12.64), CaO 1.86 (1.47–2.24), Y_2O_3 45.07 (44.76–45.38), Gd_2O_3 0.45 (0.32–0.58), Dy_2O_3 2.49 (2.39–2.60), Er_2O_3 3.02 (2.43–3.60), Yb_2O_3 1.64 (1.44–1.84), Ho_2O_3 0.81 (0.75–0.86), Tb_2O_3 0.12 (0.10–0.14), F 17.22 (16.25–18.20), CO_2 19.83, O = F –7.23, total 97.90. The proportion of CO_2 was calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula, based on three atoms of oxygen, is $(Na_{0.90}Ca_{0.07})_{\Sigma 0.97}(Y_{0.89}Gd_{0.01}Dy_{0.03}Er_{0.04}Yb_{0.02}Ho_{0.01})_{\Sigma 1.00}(CO_3)F_{2.01}$ or, ideally, $NaY(CO_3)F_2$.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession-camera photographs show horváthite-(Y) to be orthorhombic, diffraction symmetry 2/*mmm*, with $P2_1cn$ (#33) or *Pmcn* (#62) as possible choices of space group, on the basis of systematic absences of reflections. X-ray powder-diffraction data, obtained with a Gandolfi camera having a diameter of 114.6 mm, and using Cu*K*α radiation, are given in Table 1.

For the intensity-data measurements, a crystal fragment (0.13 × 0.08 × 0.06 mm) of cotype horváthite-(Y) was used. Intensity data were collected on a fully automated Siemens *P*3 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated Mo*K*α radiation. A set of 25 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Four asymmetric units of intensity data were collected (*i.e.*, $\pm h \pm k + l$) up to $2\theta = 60°$ using a θ:2θ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Information relevant to the data collection and structure determination is given in Table 2. Reduction of the intensity data, structure determination and initial refinement of the structure were accomplished by means of the SHELXTL (Sheldrick 1990) package of computer programs. For the ellipsoidal absorption correction, eleven 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 5.45% before the absorption correction to 2.35% after the absorption correction.

The phasing of a set of normalized structure-factors gives a mean value $|E^2 - 1|$ of 0.957, indicative of a centrosymmetric space-group. The phase-normalized structure-factors, with a combined figure of merit

(CFOM) of 0.081, were used to give an *E*-map which located the Y, Na and four sites occupied by lighter elements (O or F). These refined by least squares to $R = 22\%$. The next stages in the structure determination of horváthite-(Y) involved establishing the (CO_3) group and the F site. In the final least-squares refinement, all atomic positions were refined with anisotropic displacement-factors to a residual of $R = 1.6\%$. An extinction correction did not improve the least-squares refinement. The final residual electron densities were +0.51 and –0.59 $e^-/Å^3$. Calculations of the bond-valence sum (Brese & O'Keeffe 1991) confirmed the F site.

Table 3 contains the final positional and equivalent isotropic displacement parameters and bond-valence sums; and Table 4, the selected interatomic distances and angles. Anisotropic displacement factors and observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, K1A 0S2, Canada.

TABLE 3. HORVÁTHITE-(Y): ATOMIC COORDINATES, ISOTROPIC DISPLACEMENT FACTORS ($Å^2$ X 10^3) AND BOND VALENCE SUMS (v.u.)

Atom	*x*	*y*	*z*	U_{eq}	BVS*
Na	1/4	0.2175(2)	0.1711(2)	23(1)	1.15
Y	3/4	0.42143(3)	-0.01305(5)	9.2(1)	3.07
C	3/4	0.0590(4)	0.0401(5)	14(1)	4.13
O1	1/4	-0.1856(3)	-0.1309(4)	19(1)	2.01
O2	3/4	0.4554(3)	0.3421(4)	26(1)	2.15
O3	1/4	0.0508(3)	-0.1625(4)	22(1)	1.99
F	0.5607(2)	0.6300(2)	0.0420(2)	18(1)	1.04

* constants from Brese and O'Keeffe (1991)

TABLE 4. HORVÁTHITE-(Y): INTERATOMIC DISTANCES (Å) and ANGLES (°)

Na polyhedron		Y polyhedron	
Na-O2	2.405(3)	Y-O1	2.345(3)
Na-O3	2.369(3)	Y-O1a	2.449(3)
Na-O3	2.599(3)	Y-O2	2.259(3)
Na-F	2.344(2) X 2	Y-O3	2.364(3)
Na-F	2.377(2) X 2	Y-F	2.220(1) X 2
⟨Na-ϕ⟩	2.402	Y-F	2.348(2) X 2
		⟨Y-ϕ⟩	2.319
		C triangle	
C-O1	1.294(4)	O1-O2	122.3(3)
C-O2	1.255(4)	O1-O3	116.3(3)
C-O3	1.268(4)	O2-O3	121.4(3)
⟨C-O⟩	1.272	⟨O-O⟩	120.0

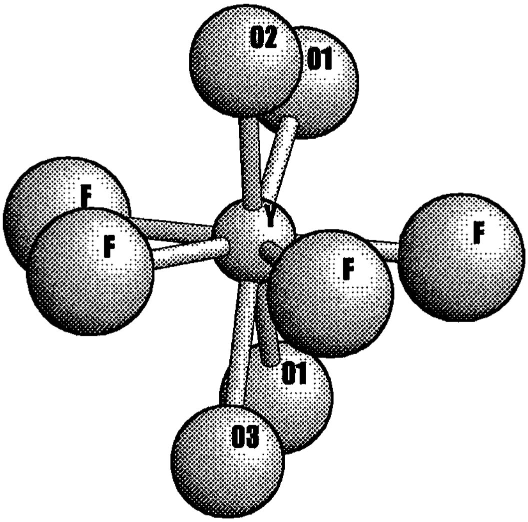

FIG. 2. The $[Y–\varphi_8]$ polyhedra in horváthite-(Y), viewed approximately along [010].

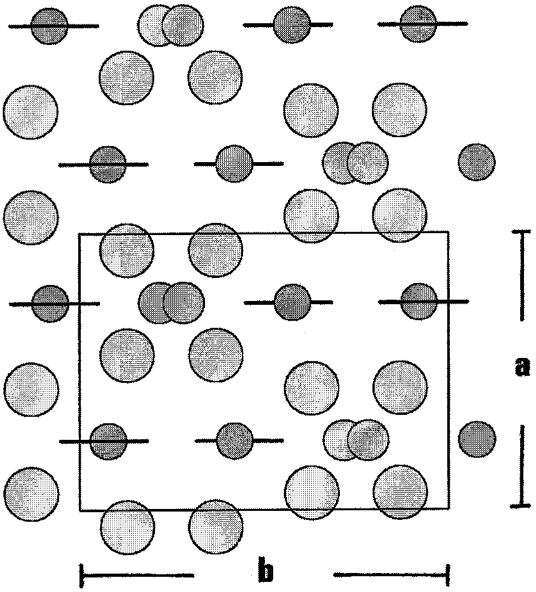

FIG. 3. The horváthite-(Y) structure projected along [001]. Dark lines represent $[CO_3]$ polyhedra, large light-shaded circles, F atoms, small light-shaded circles, Na atoms, and small dark-shaded circles, Y atoms.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The horváthite-(Y) structure has two large cation sites: the Na polyhedron has seven-fold coordination, whereas the Y polyhedron has eight-fold coordination. Each may be described as a bifurcated octahedron, with the four shorter bonds to the F atoms describing the equatorial plane, whereas the longer cation–oxygen bonds are the axes. In the (Na–φ_7) "octahedron", only one oxygen-vertex is bifurcated, whereas in the (Y–φ_8) "octahedron", both oxygen-vertices are bifurcated (Fig. 2).

The crystal structure of horváthite-(Y) is layered parallel to (100) (Fig. 3). The layering of *REE* carbonates is described and illustrated in detail by Grice *et al.* (1994). In horváthite-(Y), there are two layers of differing composition: 1) NaY(CO_3), and 2) F. The carbonate groups are of the "flat-lying" type (Grice *et al.* 1994).

Most *REE* fluorocarbonate minerals are layered with "standing on end" (CO_3) groups. Of these, there are two distinct types (Grice *et al.* 1996). The members of the bastnäsite – parisite – röntgenite – synchysite group are based on syntactic intergrowths of various combinations of stacking of rare-earth elements, fluorine, alkaline earths and carbonate groups. The bastnäsite-(Ce) structure (Ni *et al.* 1993) is an example of this group, with two types of layer, a CeF layer and a segregated "standing on end" (CO_3) layer. Similar syntactic stacking is evident in the barium fluorocarbonates cebaite-(Ce) and synthetic $Ba_2Ce(CO_3)_3F$ (Mercier & Leblanc 1993a, b), which is likely the newly described mineral 95–040 (Mandarino & Grice 1996) and a probable polymorph of zhonghuacerite-(Ce). The structure of cebaite-(Ce) (Yang 1995) is an example of mixed layers of "standing on end" (CO_3) sharing the slab with the larger Ba, Ce and F

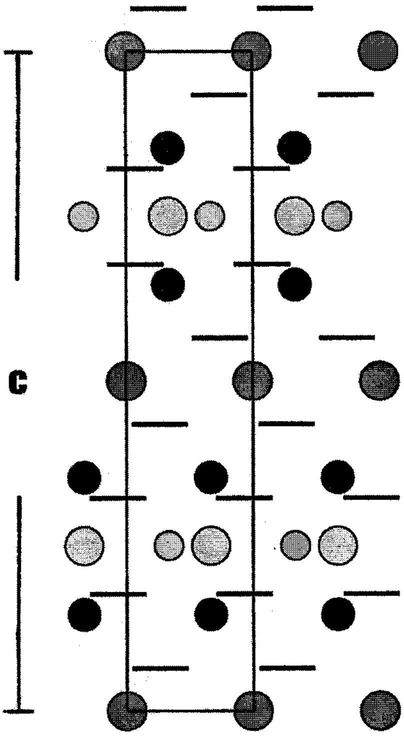

FIG. 4. The baiyuneboite-(Ce) structure projected along [100]. Dark lines represent [CO_3] polyhedra, large light-shaded circles, F atoms, small light-shaded circles, Na atoms, large dark-shaded circles, Ba atoms, and small dark-shaded circles, Ce atoms.

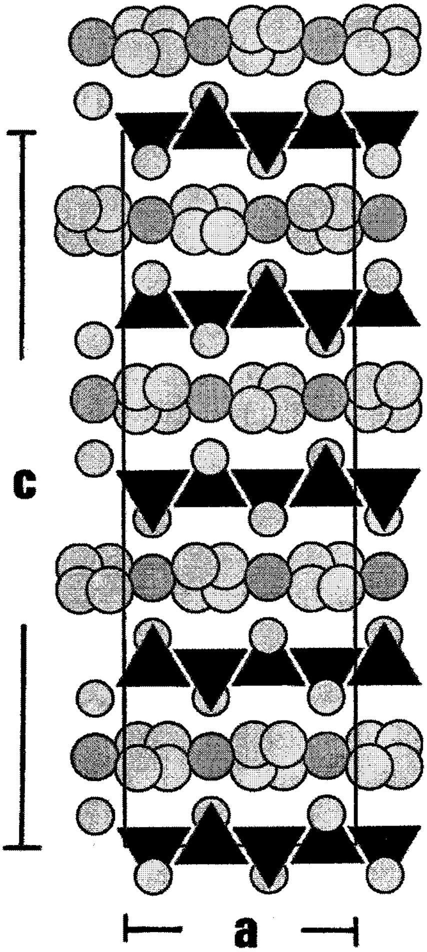

FIG. 5. The structure of synthetic $KGd(CO_3)F_2$ projected along [010]. Dark triangles represent [CO_3] polyhedra, large dark-shaded circles, Gd atoms, large light-shaded circles, F atoms, and smaller dark-shaded circles, K atoms.

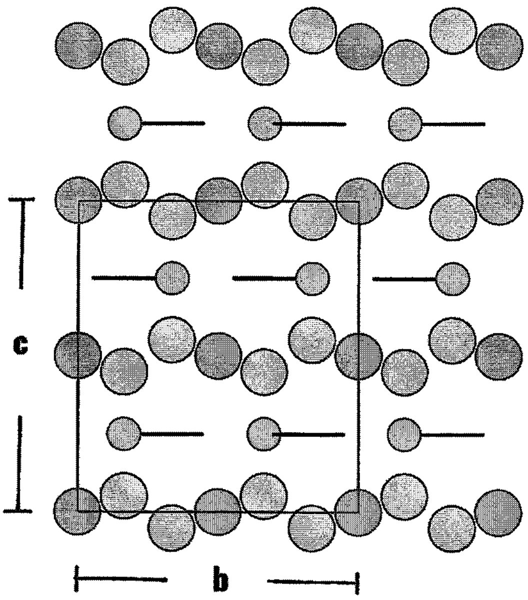

FIG. 6. The structure of synthetic $BaCu(CO_3)F_2$ projected along [100]. Dark lines represent $[CO_3]$ polyhedra, large dark-shaded circles, Ba atoms, large light-shaded circles, F atoms, and smaller dark-shaded circles, Cu atoms.

atoms. The structures of bastnäsite-(Ce) and cebaite-(Ce) are illustrated in Grice *et al.* (1996).

REE fluorocarbonates with crystal structures having flat-lying (CO_3) as seen in horváthite-(Y) are much less common. Examples of this type of structure are huanghoite-(Ce), $BaCe(CO_3)_2F$ (Yang & Pertlik 1993), baiyuneboite-(Ce), $NaBaCe_2(CO_3)_4F$ (Fu *et al.* 1987), and lukechangite-(Ce), $Na_3Ce_2(CO_3)_4F$ (Grice & Chao 1997). In contrast to horváthite-(Y), each of these has (CO_3) layers separate from the layers of F, *REE*, and alkali or alkaline earths (Fig. 4). Grice & Chao (1997) compared the layering in the closely related crystal structures of baiyuneboite-(Ce), isostructural phases lukechangeite-(Ce) and synthetic $Na_3La_2(CO_3)_4F$ (Mercier *et al.* 1993), and isostructural phases huanghoite-(Ce) and synthetic $BaSm(CO_3)_2F$ (Mercier & Leblanc 1993a). Mercier (1994) synthesized a number of phases with cation-to-anion ratios similar to horváthite-(Y), $NaY(CO_3)F_2$, *i.e.*, 1:1:1:2. The structure of $KGd(CO_3)F_2$ (Mercier 1994) is comprised of two layers, a layer of "standing on edge" (CO_3) plus K atoms and a GdF_2 layer (Fig. 5). Although this structure, and the closely related structure of brenkite, $Ca_2(CO_3)F_2$ (Leufer & Tillmanns 1980), do not resemble that of horváthite-(Y), the structure of $BaCu(CO_3)F_2$ has features that are more similar to it. The $BaCu(CO_3)F_2$ structure (Mercier & Leblanc 1993c) has two distinct layers: a $Cu(CO_3)$ layer with "flat lying" (CO_3) groups, and a BaF_2 layer (Fig. 6).

Genesis of horváthite-(Y)

Horváthite-(Y) occurs in a late-stage pegmatite portion of an alkaline, highly agpaitic rock. This stage of crystallization favors the presence of cations having weak acid strengths (*i.e.* cations with a low valence such as Na or a large coordination number such as the *REE*). During crystallization, weak Lewis acids are stabilized by weak Lewis bases such as F^- and $(CO_3)^{2-}$. Hence *REE* fluorocarbonates, such as horváthite-(Y), crystallize in this type of environment.

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