

## CARBOCERNAITE, A CANADIAN OCCURRENCE

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### ABSTRACT

The first Canadian occurrence of carbocernaite, a rare-earth carbonate is recorded. The mineral occurs as pink to reddish lath-shaped grains in carbonate veins in a grey syenite alkaline complex. The locality is on the east side of Sturgeon Narrows, a part of Sturgeon Lake which is situated southeast of Sioux Lookout in the district of Thunder Bay, Ontario.

Chemical analysis shows that the mineral contains 21.1 wt % RE oxides where cerium is the principal rare-earth (RE) element. Results of the analysis yielded a formula  $(Ca_{2.13}Sr_{1.24}RE_{0.74})(CO_3)_{4.0}F_{1.16}$  which differs from carbocernaite from the type locality in the Kola Peninsula in that the mineral contains a significant amount of fluorine, is a more strontium-rich variety, and contains no sodium or barium.

Results of the thermal analysis and study by x-ray powder diffraction are in close agreement with the data published for carbocernaite from the type locality.

### INTRODUCTION

Carbocernaite, a new rare-earth carbonate, was first discovered by Bulakh *et al.* (1961) in the Vuoriyarvi intrusion of alkalic and ultra-basic rocks on the Kola Peninsula. Its crystal system, unit cell parameters, and physicochemical properties were reported, and an analysis of 0.4g of sample gave a formula of  $4[Ca_{0.37}Na_{0.23}RE_{0.22}Sr_{0.16}Ba_{0.03}]CO_3$ ; cerium is the principal rare-earth (RE) element. The mineral occurs in dolomite-calcite carbonatite veins, 0.5-1.0m in width, in pyroxenites and ijolites, as accessory grains, and as crystals on walls of cavities, closely associated with chlorite and ankerite.

More recently, occurrences of carbocernaite have also been reported from eastern Siberia (Zdorik 1966) and from the central part of the Phan Si Pan Range, North Vietnam (Bulakh & Izokh 1966). Data published on the carbocernaite from eastern Siberia deal only with the compositional aspects of the mineral and contain no information about its properties or structure.

Bulakh's study of the material from North Vietnam confirmed his earlier observations on the properties of the mineral from the Kola peninsula, and a new chemical analysis showed its composition to be similar

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to the carbocernaite from the other localities. However, the material investigated appears to contain more BaO and less SrO.

Carbocernaite has now been identified from the east side of Sturgeon Narrows, a part of the Sturgeon Lake which is situated about 70 air miles southeast of Sioux Lookout and is in the district of Thunder Bay, Ontario. Geology of the area is outlined in an Ontario Department of Mines Report No. 24, Metionga Lake Area by David P. Rogers, 1964.

Results of differential thermal analysis, thermo-gravimetric analysis, and x-ray powder diffraction are in close agreement with the data published for carbocernaite from the type locality in the Kola Peninsula. However, a chemical analysis shows that the carbocernaite in this study contains significant amounts of fluorine, is a more strontium-rich variety and contains no sodium or barium.

#### PHYSICAL PROPERTIES

Carbocernaite occurs as distinct layers and clusters of variable width in an albite-biotite-calcite carbonatite. The mineral is closely associated with purple fluorite and calcite and together they give the rock a definite gneissic appearance. The layers of carbocernaite are even more distinct on the weathered surface because the mineral is more resistant to weathering than the surrounding calcite. Associated minerals are pyrite, quartz, barite, galena, chalcopyrite, and minor amounts of another rare-earth carbonate, ancylite.

In colour, carbocernaite varies from pale pink to brick red, depending on the amount of admixed iron oxide in the grains. Individual grains seldom exceed  $1 \times 0.5$  mm in size. The mineral has a greasy luster, is fairly brittle, and has a Mohs' hardness of about 3. Specific gravity, as determined by heavy-liquid separation, is from 3.33 and 3.45.

The optical properties of the mineral could not be determined because each grain consists of minute aggregates of slightly altered crystals.

#### CHEMICAL COMPOSITION

For the chemical analysis, a 0.95-g concentrate was obtained by means of heavy-liquid and magnetic separations. The concentrate contains an estimated 3 to 5 percent impurities such as fluorite, pyrite, and calcite.

The analysis was made by the staff of the Chemical Analysis Section, Extraction Metallurgy Division, Mines Branch. Analyses for the principal constituents calcium, strontium, rare-earths, and iron were determined in the filtrate obtained from the material soluble in 20 percent hydrochloric

acid. Calcium and strontium values were obtained by atomic absorption spectrometry, iron by spectrophotometry, and the rare-earth by x-ray emission on a purified rare-earth concentrate. Carbonate, fluorine, and chlorine were determined on separate portions of the whole sample.

A semi-quantitative emission spectrographic analysis did not reveal the presence of major constituents other than those determined by chemical analysis.

Results of the chemical analysis are given in Table 1. Recalculation of the analysis to 100 percent, after corrections for impurities of insolubles and iron (due to admixed iron oxide), yielded a formula  $(Ca_{2.18}Sr_{1.24}RE_{0.74})(CO_3)_{4.0}F_{1.16}$ .

Thin-section and electron-probe studies of the carbocernaite from Sturgeon Narrows revealed minute inclusions of fluorite and calcite which undoubtedly will also be present in the sample concentrated for the chemical analysis. There is no way to determine the amount of calcite in the sample as both minerals are readily soluble in 20% HCl. The

TABLE 1. CHEMICAL ANALYSIS

	Weight Percent	Recalculated after Subtraction of Impurities	Molecular Ratios	Atomic Ratios	Atoms Per Cell	
CaO	19.59	21.03	.375	.375	2.13	} 4.11
SrO	21.05	22.60	.218	.218	1.24	
Fe <sub>2</sub> O <sub>3</sub>	2.47	—	—	—	—	
RE <sub>2</sub> O <sub>3</sub>	20.00	21.47	.065	.130	0.74	
CO <sub>3</sub>	28.82	30.94	.703	.703	4.00	
F	3.60	3.86	.203	.203	1.16	
Cl	0.08	0.09	—	—	—	
Insolubles	2.87	—	—	—	—	
	<u>98.48</u>	<u>99.99</u>				

Chemical Formula  $(Ca_{1.13}Sr_{1.24}RE_{0.74})(CO_3)_{4.00}F_{1.16}$

*Rare-Earths*

La <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	Pr <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Tb <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>
27.87	52.60	4.81	13.66	.46	.30	.10	.10	.10

Ho., Er, Tm, Yb, Lu, Y < 0.03 Sum 100.03%

Note: Because of the method of analysis, the normal correction for the oxygen equivalent of fluorine is not required.

rather high fluorine content leads one to suspect that this element is due to inclusions of fluorite. However, fluorite is not soluble in 20% HCl and, because the insoluble fraction is too small to account for the 3.6% fluorine being present as fluorite, one must assume that fluorine is part of carbo-cernaite.

In the original description of carbo-cernaite, Bulakh *et al.* (1961) proposed the formula  $4(ACO_3)$  where A represents Ca, Sr, RE, Na, K, and Ba. Fluorine was not reported in the analysis of carbo-cernaite from the Kola Peninsula, though small amounts were detected in the material from North Vietnam. Bulakh suggested that the presence of F could indicate the entry into carbo-cernaite of  $(OH)^-$  isomorphously replaced by fluorine, the presence of which he could not confirm. The analysis of carbo-cernaite in this study seems to support this assumption. It is possible that the Canadian mineral contains some OH, though it was not analyzed for; consequently, the  $(F,OH)$  group might equal 2 in the formula.

The rather different proportions of rare-earth metals should be noted. Bulakh *et al.* (1961) reported equal proportions of  $CeO_2$  and  $La_2O_3$  for carbo-cernaite from the Kola Peninsula, whereas the Canadian mineral has twice the amount of  $CeO_2$  to  $La_2O_3$ ; no values were reported for the North Vietnamese carbo-cernaite.

The presence of iron in the formula is uncertain. Electron-probe and optical studies reveal admixed iron oxide, finely disseminated in the material, that probably accounts for the iron reported in the analysis.

#### THERMAL ANALYSIS

A sample weighing 410.1 mg was submitted to R. Lake of the Mineral Sciences Division, Mines Branch for differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The sample was estimated to contain from 5 to 10 percent impurities such as pyrite, biotite, calcite, and fluorite. Results of the analysis are presented in Figures 1 and 2.

The DTA curve shows that a strong exothermal reaction occurs at  $444^\circ$  with a small weight loss of 1.0%; three distinct endothermal peaks at  $565^\circ$ ,  $625^\circ$  and  $860^\circ$ , with corresponding weight losses of 4.1%, 2.7% and 17.6%, respectively. Smaller, less distinct endothermal reactions occur at approximately  $700^\circ$ ,  $800^\circ$  and  $900^\circ C$ . A total weight loss of 25.9% was recorded when the sample was heated at  $1250^\circ C$ .

The strong exothermal peak at  $444^\circ$  is difficult to account for by a change in the mineral itself. It is believed that this reaction is due to

small amounts of liquid from the heavy liquid separations remaining in the grains. The distinct endothermic peak at  $860^{\circ}$  represents evolution of the gaseous phase and decomposition of the mineral.

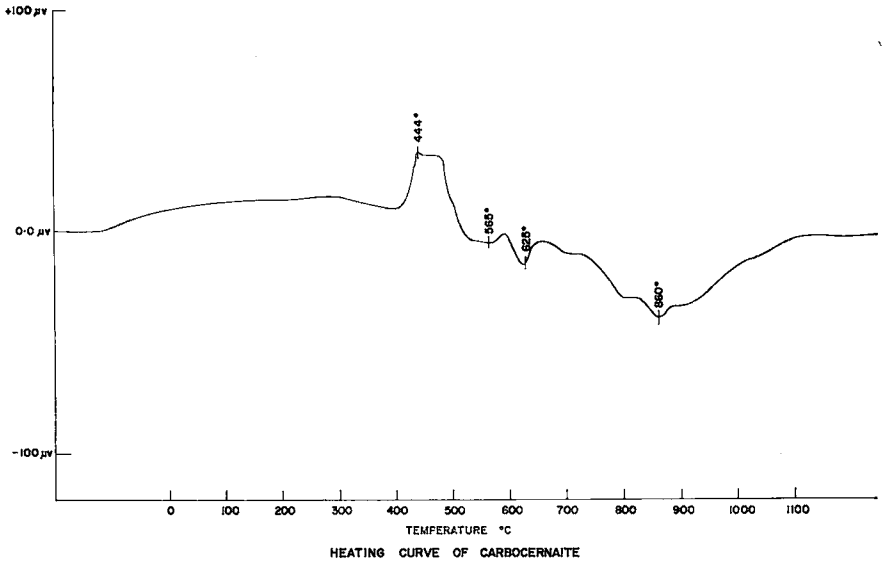


FIG. 1. Heating curve (DTA) of carbocearnite, Sturgeon Lake, Ontario.

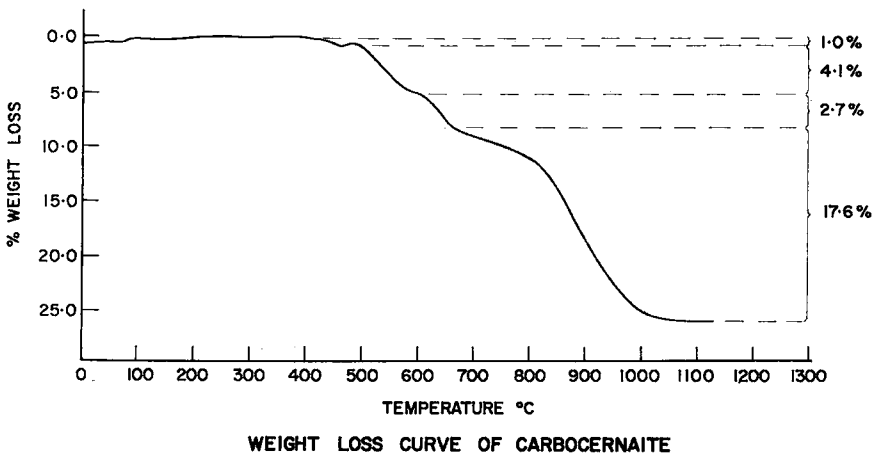


FIG. 2. Thermogravimetric curve (TGA) of carbocearnite, Sturgeon Lake, Ontario.

TABLE 2. X-RAY DIFFRACTION DATA FOR CARBOCERNAITE  
(114.6 mm. camera with Fe-filtered Co radiation)

Orthorhombic  $a = 6.410$   $b = 7.279$   $c = 5.198\text{\AA}$

$hkl$	$d(\text{calc.})\text{\AA}$	Sturgeon Narrows, Canada (this study)		Kola Peninsula, U.S.S.R. (Bulakh <i>et al.</i> 1961)	
		$I(\text{est.})$	$d(\text{meas.})\text{\AA}$	$I(\text{est.})$	$d(\text{meas.})\text{\AA}$
100	6.410	30	6.387	10B	6.70
001	5.198	40	5.187	40	5.30
110	4.810	50	4.813	40	4.93
101	4.037	50	4.053	30	4.11
020	3.639	10	3.644	50	3.67
111	3.531	40	3.534	40	3.59
200	3.205	20B	3.185	30	3.21
021	2.981	100	2.989	100	3.01
210	2.933	30	2.926	—	—
201	2.728	} 10B	2.713	10	2.72
121	2.703				
002	2.599	20	2.604	70B	2.61
211	2.555	30	2.559	—	—
030	2.426	10	2.419	10	2.43
112	2.287	20	2.282	70B	2.29
130	2.269	20	2.277	—	—
221	2.183	10	2.185	—	—
300	2.137	10	2.138	—	—
131	2.080	20	2.082	50	2.086
310	2.050	10	2.049	—	—
202	2.019	50	2.013	90	2.019
212	1.945	30	1.948	50B	1.952
311	1.908	10	1.908	—	—
040	1.820	20	1.819	80	1.817
321	1.737	10	1.741	30	1.745
041	1.717	10	1.716	50	1.712
013	1.686	10	1.682	10	1.674
141	1.659	10	1.665	40	1.658

## X-RAY DIFFRACTION DATA

The carbocernaite grains were not suitable for single-crystal studies because each grain consisted of an aggregate of randomly oriented crystals; the unit-cell dimensions were therefore calculated from the *x*-ray powder data by a least-squares method. The unit-cell dimensions, based on Bulakh's (1961) data of an orthorhombic cell, are  $a = 6.410\text{\AA}$ ,  $b = 7.279\text{\AA}$ , and  $c = 5.198\text{\AA}$ . The *x*-ray powder data for carbocernaite in this study and those reported by Bulakh for material from the Kola Peninsula are given in Table 2. The main differences between the two sets of data are that more lines were recorded in this study and that there is better agreement between measured and calculated values for the larger *d*-spacings.

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## REFERENCES

- BULAKH, A.G., KONDRAT'YEVA, V.V. & BARONOVA, Ye. N. (1961): Carbocernaite, a new rare-earth carbonate; *Zapiski Vses. Mineralog. Obshch.* **90**, 42-49 (in Russian).  
BULAKH, A.G. & IZOKH, E.P. (1966): New data on carbocernaite: *Doklady Akad. Nauk. SSSR* **175**, 118-120 (in English).  
ZDORIK, T.V. (1966): Geol. Mestorozhd. Redkikh Elem. (*The geology of deposits of rare elements*) Fasc. 30, p. 121.

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