

## Cordylite-(Ce): A crystal chemical investigation of material from four localities, including type material

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### ABSTRACT

Six cordylites from the four known localities [Narssarsuk (Greenland), Mont St. Hilaire (Canada), Bayan Obo (China), and Kola Peninsula (Russia)] were investigated by electron microprobe and X-ray single-crystal structure determination, and a seventh sample was investigated by X-ray methods only. The material studied included type cordylite. The idealized formula for cordylite is redefined as  $(\text{Na}_{1-x}\text{Ca}_x)\text{BaCe}_2(\text{CO}_3)_4\text{F}$ ;  $0 < x < 1$ , with Ce for the sum of REE; the SrO content may reach about 5.7%. All of our structure refinements ( $P6_3/mmc$ ;  $a \cong 5.10$ ,  $c \cong 23.10$  Å) agree very well among themselves and with the published structures of “baiyuneboite-(Ce)” and unnamed  $(\text{Ca}_{0.5}\square_{0.5})\text{BaCe}_2(\text{CO}_3)_4\text{F}$ . Cordylite has a sheet structure formed of (001) layers of [Ba] [CO<sub>3</sub>] [Ce,CO<sub>3</sub>] [Na,F] [Ce,CO<sub>3</sub>] [CO<sub>3</sub>] [Ba] stacked along [001]. The interatomic distances are as expected, with the exception of unshielded Na-F distances of 2.94 Å; unlike the carbonate groups in basnäsite and synchysite, the carbonate groups in cordylite-(Ce) are parallel (001). Investigation of type cordylite showed that the formula proposed by Flink, i.e.,  $\text{BaCe}_2(\text{CO}_3)_3\text{F}_2$ , is to be modified to that given above, with  $x \cong 0$  for Flink’s material. Baiyuneboite-(Ce), a mineral previously approved by the IMA CNMMN but later withdrawn because of potential similarities with cordylite, is confirmed here as being essentially identical to type cordylite.

### INTRODUCTION

Cordylite-(RE) is a member of the rare earth (RE) fluorocarbonate minerals, a group of minerals that supplies the vast majority of the world’s supply of RE elements. The name cordylite was introduced by Flink (1899) for a rare mineral in an alkali pegmatite from Narssarsuk, Greenland. From wax-yellow crystals up to 3 mm in size, Flink determined hexagonal symmetry on the basis of morphology. Chemical analysis led to the formula  $\text{Ce}_2\text{F}_2\text{BaC}_3\text{O}_9$ , with the remark that the data did not exactly match the formula. Flink emphasized the close similarity in chemical composition between cordylite and parisite, with Ba in cordylite corresponding to Ca in parisite. Böggild (1906) added to the morphological knowledge and determined refractive indices.

Oftedal (1931) used oscillation photographs to derive a hexagonal cell with  $a = 4.35$ ,  $c = 22.8$  Å, and a space group with highest possible symmetry  $P6_3/mmc$ . He postulated cell contents of  $\text{Ba}_2\text{Ce}_4\text{F}_4(\text{CO}_3)_6$  and determined the coordinates of the Ba and Ce atoms. Oftedal (1931) mistakenly published  $d_{100}$  for  $a$ . His value for  $a$  should have been 5.02 Å, in good agreement with modern val-

ues. This change gives reasonable agreement of  $d_{\text{calc}}$  with  $d_{\text{meas}}$  and is consistent with subsequent measurements by Donnay and Donnay (1955). Donnay and Donnay (1955) considered the space group to be  $P6_2c$  or  $P6_3/mmc$ . On the basis of strong negative birefringence they postulated that the planes of the carbonate groups were oriented perpendicular to the  $c$  axis.

Chen and Chao’s (1975) measurements of two tiny crystals from pegmatite dikes of the nepheline syenite of Mont St. Hilaire, Quebec, Canada, confirmed the X-ray results of Donnay and Donnay (1955). On the basis of an electron microprobe analysis, the formula is  $(\text{Ba}_{0.92}\text{Ca}_{0.07}\text{Sr}_{0.04})(\text{Ce}_{1.37}\text{La}_{0.59}\text{Th}_{0.01})(\text{CO}_3)_3\text{F}_{1.58}$ . The deficiency of F was attributed to the omission of H<sub>2</sub>O during the analysis. No Na was reported. However, this element was found in re-examination of the data (letters of G.Y. Chao to J. Zemann).

Discovery of similar material in the enormous REE deposit at Bayan Obo, Inner Mongolia, China, complicated matters. Zhang and Tao (1985) considered the material as cordylite, but drew attention to a Na<sub>2</sub>O content of 1.79 wt%. Fu and Su (1987) named a mineral from the same locality “baiyuneboite-(Ce).” Its X-ray crystallographic and optical constants were very close to those published previously for cordylite (Donnay and Donnay

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1955; Chen and Chao 1975). On the basis of 10 microprobe analyses [with  $\text{Na}_2\text{O} = 4.7(4)$  wt% and  $\text{F} = 2.5(2)$  wt%] and in agreement with a careful X-ray structure determination in space group  $P6_3/mmc$ , Fu et al. (1987) derived the idealized formula  $\text{NaBaCe}_2(\text{CO}_3)_4\text{F}$ . The name was approved by CNMMN of the IMA, but approval was later withdrawn by the Chairman of the Commission because baiyuneboite and cordylite could be identical (Jambor and Grew 1990).

Shen and Mi (1991) published the determination of an unnamed mineral from Bayan Obo with the ideal formula  $(\text{Ca}_{0.5}\square_{0.5})\text{BaCe}_2(\text{CO}_3)_4\text{F}$ . The lattice constants were very close to those published for cordylite (Donnay and Donnay 1955; Chen and Chao 1975) and for bayuneboite (Fu et al. 1987), but in the structure determination they used space group  $P\bar{6}2c$ , a subgroup of  $P6_3/mmc$ . Their atomic arrangement is very close to that published by Fu et al. (1987) for bayuneboite, but with 0.5 Ca instead of 1.0 Na. Shen and Mi (1992) later concluded that the previous formula of cordylite (Flink 1899), as well as the deduced structure (Ofteidal 1931), had to be incorrect and that the real formula of cordylite should be  $(\text{Na}_{1-x}\text{Ca}_{x/2})\text{BaCe}_2(\text{CO}_3)_4\text{F}$ . Zaitsev et al. (1990) analyzed cordylite from the carbonatites of the Kola Peninsula, Russia, and found relatively high contents of SrO and FeO but retained the formula  $\text{BaCe}_2(\text{CO}_3)_3\text{F}_2$  for the mineral.

For general information on the mineralogy, the reader is referred to Böggild (1953) for Narssarssuk, to Horvath and Gault (1990) for Mont St. Hilaire, and to Zhang and Tao (1986) and Zhang et al. (1995) for Bayan Obo.

The aim of this work is to clarify the relationships among the various phases reported as cordylite (or kordylite) [including cordylite-(Ce), "baiyuneboite-(Ce)," and unnamed  $(\text{Ca}_{0.5}\square_{0.5})\text{BaCe}_2(\text{CO}_3)_4\text{F}$ ], compare the phase from the different localities, and to clarify the nomenclature problems of this mineral. Two groups were working on the problem simultaneously, and we have combined our several crystal structure and chemical analyses. Thus portions of the work listed below are attributed to the "Miami group" or the "Vienna group." Although affiliations are listed above, the Vienna Group also includes Yang Zhuming, Beijing, who did crystal structure work in Vienna on material from Bayan Obo and from the Kola peninsula, and J.J. Rønsbo, Copenhagen, who did microprobe work on type cordylite from Greenland and on cordylite from Mont St. Hilaire, both structurally investigated in Vienna. We demonstrate that the earlier proposed mineral "baiyuneboite" or "baiyuneboite-(Ce)" is actually cordylite-(Ce), validating the withdrawal of mineral status by the IMA CNMMN. In this work, Ce always stands for the sum of rare earth elements.

## EXPERIMENTAL METHODS

The Miami group refined the atomic arrangement of two cordylite-(Ce) samples. One is from an alkaline pegmatite, Narssarssuk, Greenland (Harvard Mineralogical Museum no. 84438), where the type sample of cordylite-(Ce) was found by Flink (1899). It is transparent, sub-

hedral, and slightly yellowish, coexisting with synchysite-(Ce) and other alkaline minerals. The other is from Mont St. Hilaire, Quebec, Canada. It is an euhedral, optical-quality hexagonal plate, slightly yellowish in color. Good (001) cleavage can be found in both the samples.

The Vienna group investigated cordylite-(Ce) from all four known localities. The cordylite from Narssarssuk was type material from the mineral collection of the Geologisk Museum, Copenhagen. From the same collection an original crystal of Flink (1899), M.M. no. 392, was investigated by single-crystal X-ray diffractometry. A standard microprobe analysis of this crystal (designated "Narssarssuk 1\*" in Tables 1–5) could not be obtained because the beam seriously damaged the crystal. A qualitative EDX test showed, however, appreciable amounts of Na, contrary to the analysis published by Flink (1899).

In both groups the crystals were carefully checked by photographic X-ray methods before intensity collection. At Miami, the Narssarssuk crystal was cut into a parallelepiped of  $0.14 \times 0.13 \times 0.12$  mm, the crystal from Mont St. Hilaire into a cube of edge lengths 0.14 mm.

The structure investigations were made in Vienna on a STOE AED2 diffractometer using program system SHELXL-93 (Sheldrick 1993), with absorption correction by  $\Psi$  scans. The Miami investigations were undertaken on an Enraf-Nonius CAD-4 diffractometer using the SDP package of programs (Frenz 1985), with absorption corrections by  $\Psi$  scans and subsequently by the absorption surface method as implemented in program DIFABS (Walker and Stuart 1983). Both groups used graphite monochromated Mo-radiation. In Vienna, unit-cell parameters constrained to hexagonal symmetry were obtained for the five cordylites by least-squares methods from carefully measured setting angles of 24 to 48 reflections; at Miami, unconstrained unit-cell parameters were obtained in both cases by the same procedure from 25 setting angles. Further details of data collection and crystal data are contained in Table 1; for complete details of the Miami experimental procedures, the reader is referred to Ni et al. (1993).

The solution of the structures was not difficult, either by Patterson and subsequent Fourier methods or by direct methods (Multan-80; Main et al. 1980). The ideal formula obtained for all crystals is  $(\text{Na}_{1-x}\text{Ca}_{x/2})\text{BaCe}_2(\text{CO}_3)_4\text{F}$ ,  $0 \leq x \leq 1$ ; the value of  $x$  could not be determined by X-ray methods because the scattering power of Ca is close to twice that of Na. All crystals contain some Sr (Table 5) but the content never exceeds a few weight percent. The final least-squares refinements were made in space group  $P6_3/mmc$ . Refinements were also attempted in the subgroup  $P\bar{6}2c$  but no conclusive indications to prefer this space group were found.

The atomic coordinates obtained are compiled in Table 2, the anisotropic displacement parameters in Table 3<sup>1</sup>.

<sup>1</sup> For a copy of Table 3, Document AM-98-005, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (see inside back cover of a current for web address).

**TABLE 1.** Crystal data and technical details on structure refinement for cordylite from various localities

Locality	Narssarsssuk			Mont St. Hilaire		Kola Pen.	Bayan Obo
	1*	1	2	1	2	1	1
<i>a</i> (Å)	5.0905(8)	5.1011(4)	5.0913(7)	5.097(1)	5.0942(9)	5.108(1)	5.109(1)
<i>b</i>	5.0905(8)	5.1011(4)	5.0918(9)	5.097(1)	5.0925(6)	5.108(1)	5.109(1)
<i>c</i>	23.102(10)	23.096(4)	23.070(5)	23.075(10)	23.049(3)	23.129(10)	23.289(9)
$\alpha$ (°)	90	90	89.99(2)	90	90.00(1)	90	90
$\beta$	90	90	90.00(2)	90	89.98(1)	90	90
$\gamma$	120	120	120.00(2)	120	120.01(1)	120	120
<i>V</i> (Å <sup>3</sup> )	518.4(5)	520.5(2)	517.9(3)	519.2(2)	517.8(2)	522.6(2)	526.4(5)
2 $\theta$ max (°)	80	80	60	70	60	60	60
No. data pts.	1342	7115	3076	1315	3074	3802	3315
No. unique	682	691	398	504	397	350	350
No. >4 $\sigma$ <sub>I</sub> †	653	597	260	305	268	289	264
<i>R</i> <sub>merge</sub>	0.081	0.064	0.018	0.14	0.018	0.060	0.067
<i>R</i> <sub>I</sub> ‡	0.051	0.034	0.023	0.073	0.023	0.025	0.038
<i>R</i> <sub>wI</sub> ‡	0.136	0.083	0.031	0.130	0.035	0.056	0.107
<i>a</i>	0.0382	0.0446	—	0.040	—	0.026	0.04
<i>b</i>	6.44	1.25	0	0	0	1.45	7.7
$\Delta\rho_{\text{max}}$ (eÅ <sup>-3</sup> )	3.8	2.3	1.39	3.3	1.41	2.0	2.8
$\Delta\rho_{\text{min}}$ (eÅ <sup>-3</sup> )	2.8	2.6	1.99	3.5	1.58	0.60	1.01

Notes: Numbers in parentheses denote one standard deviation. 1 = Results from Vienna group. *R*<sub>merge</sub> values of Vienna group are based on *F*<sup>2</sup>. 2 = Results from Miami group. *R*<sub>merge</sub> values of the Miami group are based on *F*.

\* Type sample from Narssarsssuk, Greenland.

† No. >3 $\sigma$ <sub>I</sub> data by Miami group.

‡ For refinements of Vienna group:

$$R \text{ [for } Fo > 4\sigma(Fo)]: R = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}$$

$$R_w \text{ [for all } Fo^2]: R_w = \frac{[\sum w(Fo^2 - Fc^2)^2 / \sum wFo^4]^{1/2}}{}$$

$$w = 1/[\sigma^2(Fo^2) + (a \times P)^2 + b \times P]; \quad P = \{[\max(0 \text{ or } Fo^2)] + 2Fc^2\}/3.$$

**TABLE 2.** Atomic coordinates and equivalent isotropic *U*(Å<sup>2</sup>) for atoms in cordylite from various localities

Locality	Narssarsssuk			Mont St. Hilaire		Kola Pen.	Bayan Obo
	1*	1	2	1	2	1	1
<i>x</i>	0	0	0	0	0	0	0
Ba <i>y</i>	0	0	0	0	0	0	0
2a <i>z</i>	0	0	0	0	0	0	0
<i>U</i> (Å <sup>2</sup> )	0.013(0)	0.016(0)	0.0124(5)	0.013(1)	0.0114(4)	0.019(0)	0.031(1)
<i>x</i>	1/3	1/3	1/3	1/3	1/3	1/3	1/3
Ce <i>y</i>	2/3	2/3	2/3	2/3	2/3	2/3	2/3
4f <i>z</i>	0.35352(2)	0.35385(1)	0.35351(4)	0.35339(7)	0.35331(3)	0.35452(3)	0.35451(6)
<i>U</i> (Å <sup>2</sup> )	0.009(0)	0.012(0)	0.0093(3)	0.010(0)	0.0082(2)	0.014(0)	0.021(0)
<i>x</i>	1/3	1/3	1/3	1/3	1/3	1/3	1/3
Na <i>y</i>	2/3	2/3	2/3	2/3	2/3	2/3	2/3
2d <i>z</i>	3/4	3/4	3/4	3/4	3/4	3/4	3/4
<i>U</i> (Å <sup>2</sup> )	0.007(1)	0.016(1)	0.020(2)	0.011(3)	0.016(2)	0.022(1)	0.029(2)
<i>x</i>	1/3	1/3	1/3	1/3	1/3	1/3	1/3
F <i>y</i>	2/3	2/3	2/3	2/3	2/3	2/3	2/3
2c <i>z</i>	1/4	1/4	1/4	1/4	1/4	1/4	1/4
<i>U</i> (Å <sup>2</sup> )	0.031(4)	0.038(2)	0.027(5)	0.034(7)	0.024(4)	0.047(3)	0.066(7)
<i>x</i>	0	0	0	0	0	0	0
C1 <i>y</i>	0	0	0	0	0	0	0
4e <i>z</i>	0.6775(4)	0.6780(2)	0.6802(5)	0.6783(9)	0.6779(5)	0.6790(4)	0.6778(8)
<i>U</i> (Å <sup>2</sup> )	0.009(1)	0.012(1)	0.012(3)	0.007(4)	0.012(3)	0.016(2)	0.025(4)
<i>x</i>	0.1448(6)	0.1448(3)	0.1448(7)	0.1452(12)	0.1445(5)	0.1442(4)	0.1441(8)
O1 <i>y</i>	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$
12k <i>z</i>	0.6764(2)	0.6763(1)	0.6761(2)	0.6758(4)	0.6760(2)	0.6770(2)	0.6762(3)
<i>U</i> (Å <sup>2</sup> )	0.013(1)	0.018(1)	0.014(2)	0.012(2)	0.016(2)	0.020(1)	0.032(2)
<i>x</i>	2/3	2/3	2/3	2/3	2/3	2/3	2/3
C2 <i>y</i>	1/3	1/3	1/3	1/3	1/3	1/3	1/3
4f <i>z</i>	0.4333(4)	0.4333(3)	0.4326(5)	0.4337(10)	0.4340(5)	0.4335(4)	0.4342(9)
<i>U</i> (Å <sup>2</sup> )	0.008(1)	0.014(1)	0.011(3)	0.017(6)	0.009(3)	0.020(2)	0.030(4)
<i>x</i>	0.5205(6)	0.5218(4)	0.5210(8)	0.5197(12)	0.5217(6)	0.5214(5)	0.5212(11)
O2 <i>y</i>	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$	2 $\times$
12k <i>z</i>	0.4348(2)	0.4347(2)	0.4350(2)	0.4346(5)	0.4352(2)	0.4351(2)	0.4350(4)
<i>U</i> (Å <sup>2</sup> )	0.017(1)	0.022(1)	0.019(2)	0.016(2)	0.012(2)	0.024(1)	0.043(2)

Note: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group. Numbers in parentheses denote one standard deviation.

\* Type sample of cordylite from Narssarsssuk, Greenland.

**TABLE 4.** Interatomic distances (Å) in cordylite from various localities

Locality	Narssarsuk			Mont St. Hilaire		Kola Pen.	B. Obo
	1*	1	2	1	2	1	1
Ba-O2 × 12	2.963(3)	2.969(3)	2.961(5)	2.967(6)	2.958(3)	2.968(4)	2.976(5)
O2-O2 × 6 (h†)	2.232(3)	2.216(2)	2.225(3)	2.247(7)	2.215(4)	2.227(5)	2.229(12)
O2-O2 × 6 (h‡)	2.858(3)	2.884(2)	2.868(3)	2.850(7)	2.879(4)	2.881(5)	2.880(12)
O2-O2 × 6 (§)	3.034(7)	3.072(1)	3.019(3)	3.038(16)	3.012(4)	3.026(6)	3.053(13)
Ce-O1 × 6	2.644(3)	2.651(1)	2.643(4)	2.643(5)	2.642(3)	2.663(3)	2.660(6)
Ce-O2 × 3	2.500(4)	2.502(4)	2.504(4)	2.494(9)	2.516(4)	2.498(4)	2.505(8)
Ce-F × 1	2.3915(5)	2.3985(2)	2.3876(8)	2.386(2)	2.3812(6)	2.417(1)	2.434(1)
O1-O1 × 3 (h  )	2.211(3)	2.216(2)	2.211(3)	2.220(7)	2.209(2)	2.209(4)	2.209(9)
O1-O1 × 3 (h#)	2.879(3)	2.885(2)	2.882(3)	2.877(7)	2.885(2)	2.899(4)	2.900(9)
O1-O2 × 6	2.980(6)	2.975(5)	2.973(7)	2.963(13)	2.977(5)	3.004(5)	3.000(11)
O2-O2 × 3 (h§)	2.858(3)	2.884(2)	2.868(3)	2.850(7)	2.879(4)	2.881(5)	2.880(12)
F-O1 × 6	3.067(3)	3.072(1)	3.071(4)	3.076(6)	3.071(3)	3.068(4)	3.086(6)
Na-O1 × 6	2.378(4)	2.382(2)	2.383(4)	2.385(7)	2.383(3)	2.377(3)	2.400(6)
Na-F × 3	2.939	2.945	2.940	2.943	2.941	2.949	2.950
O1-O2 × 6 (h#)	2.879(3)	2.885(3)	2.882(3)	2.877(7)	2.885(2)	2.899(4)	2.900(9)
O1-O1 × 3 h	3.401(7)	3.404(3)	3.410(9)	3.424(13)	3.411(9)	3.377(6)	3.439(12)
C1-O1 × 3	1.277(2)	1.280(1)	1.2796(9)	1.283(4)	1.2759(4)	1.276(2)	1.276(4)
O1-O1 × 3 (h  )	2.211(3)	2.216(2)	2.211(3)	2.220(7)	2.209(2)	2.209(4)	2.209(9)
Δ	0.03(1)	0.04(1)	0.09(1)	0.06(2)	0.04(1)	0.05(1)	0.04(2)
C2-O2 × 3	1.289(2)	1.280(1)	1.2855(5)	1.298(4)	1.2790(3)	1.286(4)	1.287(6)
O2-O2 × 3 (h†)	2.232(3)	2.217(2)	2.225(3)	2.247(7)	2.215(4)	2.227(5)	2.229(12)
Δ	0.04(1)	0.03(1)	0.06(1)	0.02(3)	0.03(1)	0.04(1)	0.02(2)

Notes: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group. h = Interatomic distance on (001). Δ = offset of carbon from the oxygen plane in carbonate group. Numbers in parentheses denote one standard deviation.

\* Type sample of cordylite from Narssarsuk, Greenland.

† Common edge between BaO<sub>12</sub> and CO<sub>3</sub>.

‡ Common edge between BaO<sub>12</sub> and CeO<sub>9</sub>F.

§ Common edge between two BaO<sub>12</sub>.

|| Common edge between CeO<sub>9</sub>F and CO<sub>3</sub>.

# Common edge between CeO<sub>9</sub>F and NaO<sub>6</sub>.

**TABLE 5.** Chemical analyses and calculated chemical formulas for cordylite-(Ce) from various localities

Locality	Narssarsuk		Mont St. Hilaire		Kola Pen.	B. Obo	NaBaCe <sub>2</sub>	Ca <sub>0.5</sub> BaCe <sub>2</sub>
	1	2	1	2	1	1	(CO <sub>3</sub> ) <sub>4</sub> F	(CO <sub>3</sub> ) <sub>4</sub> F
<b>Chemical composition (wt%)</b>								
Na <sub>2</sub> O	4.73(40)	4.1(1)	4.96(15)	4.298(2)*	1.28	1.92	4.43	—
CaO	1.09(78)	0.79(5)	0.80(8)	0.71(13)	3.78	2.54	—	4.02
BaO	22.22(8)	19.80(81)	22.48(29)	19.26(106)	22.97	23.20	21.92	22.01
SrO	1.44(18)	0.96(23)	0.61(11)	0.96(22)	5.67	1.12	—	—
Ce <sub>2</sub> O <sub>3</sub>	22.10(58)	28.06(19)	24.10(41)	28.64(69)	19.67	23.68	46.92	47.12
La <sub>2</sub> O <sub>3</sub>	14.61(25)	15.06(73)	13.88(73)	12.42(48)	8.41	10.63	—	—
Nd <sub>2</sub> O <sub>3</sub>	4.58(23)	4.20(55)	5.43(34)	5.13(48)	7.75	6.26	—	—
Pr <sub>2</sub> O <sub>3</sub>	1.78(18)	2.80(52)	2.24(40)	3.20(98)	2.24	2.20	—	—
F	3.60(15)	2.45(7)	3.62(21)	3.02(47)	2.72	2.73	—	—
CO <sub>2</sub>	25.36	21.97	23.40	22.85	—	—	25.16	25.27
Other	—	0.82	—	0.74	0.24	0.26	—	—
<b>Atoms in unit cell (Formula basis: Sr + Ba + ΣREE = 6.00)</b>								
Na	2.17	1.79	2.23	1.91	0.57	0.88	2.00	—
Ca	0.28	0.19	0.20	0.17	0.93	0.64	—	1.00
Ba	2.06	1.75	2.04	1.73	2.06	2.15	2.00	2.00
Sr	0.20	0.13	0.08	0.13	0.75	0.15	—	—
Ce	1.92	2.31	2.05	2.40	1.65	2.05	4.00	4.00
La	1.28	1.25	1.19	1.05	0.71	0.93	—	—
Nd	0.39	0.34	0.45	0.42	0.63	0.53	—	—
Pr	0.15	0.22	0.19	0.27	0.19	0.19	—	—
F	2.70	1.74	2.66	2.19	—	—	2.00	2.00
C	8.21	6.75	7.41	7.15	—	—	8.00	8.00

Notes: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group. CO<sub>2</sub> content by difference. Flink's (1899) type crystal from Narssarsuk was not analyzed.

\* By Direct Current Argon Plasma Spectrometer (DCP).

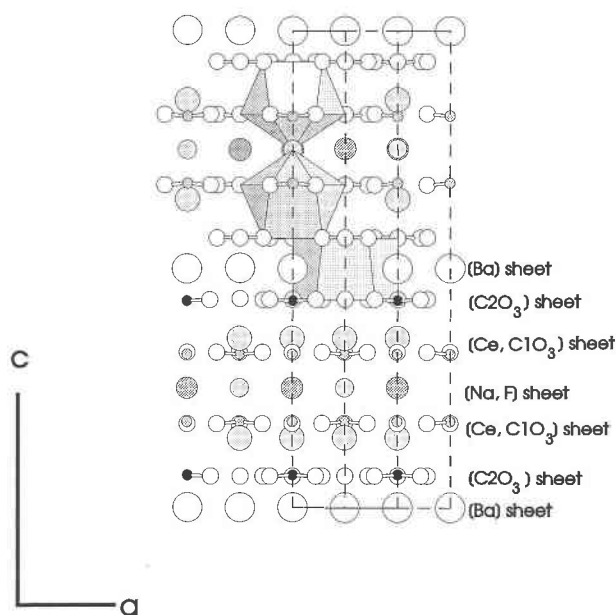


FIGURE 1. Cordylite-(Ce) crystal structure projected on (010). The upper two polyhedra depict Ce polyhedra, and the lower polyhedron is a Ba polyhedron. C-O is linked by bond. The largest open circle represents Ba; the second largest lightly stippled circle Ce; the third largest dark shaded circle Na; the smaller stippled circle F; the smallest shaded circle C1; the smallest black dot C2; and open small circle O1 or O2 linked to C1 or C2, respectively.

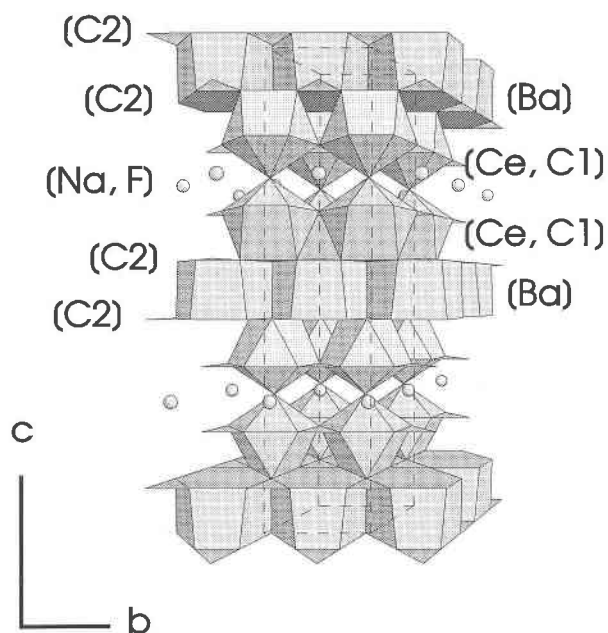


FIGURE 2. Perspective view of cordylite-(Ce) polyhedral crystal structure, illustrating the (001) layers. The hexagonal prisms represent  $BaO_{12}$  polyhedra, which are connected with  $CeO_9F$  polyhedra by sharing edges on both sides. The  $CeO_9F$  polyhedra connect to each other by sharing an F on the apex, which is on the mirror along with Na represented by the spheres. The (001) triangles are carbonate groups. The unit cell is outlined by a dashed line.

Results for the seven cordylites agree very well, often to minor details. For the least-squares refinement of cordylite from the Kola Peninsula based on the formula  $(Na_{1-x}Ca_x)Ba(Ce_{2-x}Sr_x)(CO_3)_4F$  because of its SrO content of 5.67 wt% (Table 5): restricting the formula to electronic neutrality resulted in  $x = 0.40(1)$ , giving Ce:Sr  $\sim 4.0$ , in good agreement with  $\Sigma REE: Sr \sim 4.3$ , as observed in the chemical analysis.

### DESCRIPTION OF THE STRUCTURE

The structure can be symbolized as a stacking of sheets in (001) as: [Ba]-[C2O<sub>3</sub>]-[Ce,C1O<sub>3</sub>]-[Na,F]-[Ce,C1O<sub>3</sub>]-[C2O<sub>3</sub>]-[Ba] (depicted in Figs. 1 and 2). The Na and F atoms occupy the same sheet, and this also holds for the C1 and O1 atoms, and the C2 and O2 atoms, respectively. By allowing differences up to 0.69 Å, the Ce atoms belong to the same sheet as the C1 and O1 atoms.

The Ba atoms (point symmetry  $3m$ ) are coordinated to twelve O atoms in the form of a distorted hexagonal prism, the Ce atoms (point symmetry  $3m$ ) to nine O atoms and one F atom, and the Na atoms (point symmetry  $\bar{6}m2$ ) to six O atoms in the form of a trigonal prism and further to three F atoms at 2.94 Å. Both types of CO<sub>3</sub> groups (point symmetry  $3m$ ) are slightly aplanar, and their O planes are parallel (001).

The BaO<sub>12</sub> polyhedra share six edges among themselves, six edges with CeO<sub>9</sub>F polyhedra, and six edges with CO<sub>3</sub> groups. The CeO<sub>9</sub>F polyhedra share three edges

with BaO<sub>12</sub> polyhedra, three edges with NaO<sub>6</sub> trigonal prisms, and three edges with CO<sub>3</sub> groups, but only corners among themselves. The NaO<sub>6</sub> trigonal prisms share six edges with the CeO<sub>9</sub>F polyhedra; if three F neighbors are included into the coordination, the thus formed NaO<sub>6</sub>F<sub>3</sub> polyhedra share six O<sub>2</sub>F faces with the CeO<sub>9</sub>F polyhedra.

The complete atomic arrangement can be visualized as being built from  $Ce(CO_3)_2F$  layers parallel to (001). Two such layers share the F atoms so that  $Ce_2(CO_3)_4F$  double layers are formed that house the Na atoms in cavities. Those double layers are situated at heights  $c/4$  and  $3c/4$ , and they are intercalated by the Ba atoms.

### STEREOCHEMICAL DISCUSSION AND COMPARISON WITH RELATED STRUCTURES

The interatomic distances (Table 4) agree well with expected values. A notable exception is the unusually large Na-F distance, 2.94 Å, which occurs three times around the Na atoms. The bond distance yields a bond valence of 0.03 v.u., suggesting that the F atoms might not be considered in the first coordination sphere; however, the Na-F vector is not shielded by any O atoms, thus the Na trigonal prism is perhaps better described as a tri-capped trigonal prism. In this context it should be noted that in all seven refinements yielded displacement parameters of  $U_{11}$  for F significantly larger than  $U_{33}$ .

In the carbonate groups the deviations of the C atoms

from the plane of its coordinating O atoms is of the usual order of magnitude (cf. Zemann 1981; Effenberger et al. 1983; Chevrier et al. 1992). The orientations of the aplarity relative to the surroundings follow the rules given by Zemann (1981).

Bond valence sums (Brown 1981) calculated for all atoms in the refined crystal structure of Greenland cordylite-(Ce) by Miami authors yielded Ba = 2.03 v.u., Ce = 3.06 v.u., F = 0.95 v.u., C1 = 4.05 v.u., C2 = 3.97 v.u., O1 = 2.05 v.u., and O2 = 2.04 v.u., all in excellent agreement with the formal valence of the ions. The (Na,Ca)O<sub>6</sub>F<sub>3</sub> site yielded 1.32 v.u. for Na and 2.01 v.u. for Ca, assuming full occupancy by the respective ions.

The results of our seven structure refinements agree very well with those published by Fu et al. (1987) for "baiyuneboite-(Ce)." Our atomic arrangement is also very close to that given by Shen and Mi (1991) for the unnamed mineral (Ca<sub>0.5</sub>□<sub>0.5</sub>)BaCe<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F, although the space group *P6̄2c* is proffered by those authors. In the structure given by Shen and Mi (1991) the positions of all atoms but one correspond within the limits of accuracy to space group *P6<sub>3</sub>/mmc*. The exception is their atom O1 for which they give the coordinates 0.455(4), 0.498(4), 0.0656(4). A shift of this atom by 0.19(2) Å could cause that the *x* and *y* coordinates to become equal and yield space group *P6<sub>3</sub>/mmc* for their structure.

Mercier et al. (1993) recognized that the synthetic phase Na<sub>3</sub>La<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F contains double sheets that are practically identical with those in "baiyuneboite" but intercalated by two Na atoms instead of one Ba. They further noted that huanghoite, BaCe(CO<sub>3</sub>)<sub>2</sub>F (Qian et al. 1982; Mercier and Leblanc 1993a; Yang and Pertlik 1993), contains very similar Ce(CO<sub>3</sub>)<sub>2</sub>F layers. However, the layers in huanghoite are not condensed into double sheets but are intercalated by two kinds of Ba atoms. We can also note that in these two structures the carbonate groups are slightly aplanar and that also Na-F = 2.94 Å, which is similar to cordylite. For the more remote relationships to zhonghuacerite, Ba<sub>2</sub>Ce(CO<sub>3</sub>)<sub>3</sub>F, and cebaite, Ba<sub>3</sub>Ce<sub>2</sub>(CO<sub>3</sub>)<sub>5</sub>F<sub>2</sub>, in both of which the planes of the CO<sub>3</sub> groups are essentially parallel to each other, the reader is referred to Mercier and Leblanc (1993b) and Yang et al. (1996).

The most common members of the important group of REE- and Ca-REE-fluorocarbonates, bastnäsite and synchysite (both free of Ba), are also hexagonal or pseudo-hexagonal. From a geometrical point of view they can be described to be built from sheets: e.g., bastnäsite, Ce<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub>, by a [001] sequence of [CeF]-[CO<sub>3</sub>]-[CeF] (Ni et al. 1993), and synchysite, CaCe(CO<sub>3</sub>)<sub>2</sub>F, by a [001] sequence of [Ca]-[CO<sub>3</sub>]-[CeF]-[CO<sub>3</sub>]-[Ca] (Wang et al. 1994). However the planes of the CO<sub>3</sub> groups in bastnäsite or synchysite are perpendicular to (001) and not parallel to each other, and the coordination of the Ce and Ca atoms are different from those of the Ce and Ba atoms in cordylite. Thus the stereochemical relationships of bastnäsite and synchysite to cordylite are remote.

## PROBLEMS OF CHEMICAL COMPOSITION AND NOMENCLATURE

Table 4 and the literature on cordylite (e.g., Yang et al. 1994) show a remarkable variation in the Na/Ca ratio. In material from Narssarsuk, Mont St. Hilaire, and Bayan Obo by (Fu and Su 1987), Na predominates over Ca as "baiyuneboite." Much of the Bayan Obo material as well as cordylite from Kola peninsula were found to be relatively rich in Ca. The situation is complicated by a SrO content reaching approximately 5.7 wt% in cordylite from the Kola Peninsula with Sr replacing at least in part the Ce atoms. No reliable analyses for H<sub>2</sub>O in cordylite are available to our knowledge. From the ligation of the F atom (point symmetry  $\bar{6}m2$ ) by two Ce and three Na atoms, extensive replacement of F by OH is improbable if the Na position is fully occupied.

As the replacement of Na<sub>1.0</sub> by Ca<sub>0.5</sub>□<sub>0.5</sub> has very little influence on the properties of the crystal, including lattice parameters and X-ray intensities, the determination of the occupancy of the position depends on microprobe analysis. Splitting into two species with end-members NaBaCe<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F and (Ca<sub>0.5</sub>□<sub>0.5</sub>)BaCe<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F would in practice cause considerable difficulties and is deemed undesirable.

We agree with Shen and Mi (1992) that the old analyses of cordylite as well as the structure proposed by Oftedal (1931) need modification. Our investigation of type material redefined the formula as NaBaCe<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F and yielded a structure practically identical to that given by Fu et al. (1987) for "baiyuneboite-(Ce)." Cordylites from Narssarsuk, Mont St. Hilaire, Bayan Obo, and Kola peninsula are isostructural, but the Na/Ca ratio and, to a minor extent, the Sr content vary.

As type material of cordylite (Flink 1899; Böggild 1906) is deposited in the mineral collection of the Geological Institute, Copenhagen, and as the original description clearly allows definition of the mineral, it seems to us advisable to retain the name cordylite, in any case for members of this mineral with a composition near to the end-member NaBaCe<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>F and to abandon the name "baiyuneboite-(Ce)."

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