# QAQARSSUKITE-(Ce), A NEW BARIUM–CERIUM FLUORCARBONATE MINERAL SPECIES FROM QAQARSSUK, GREENLAND

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## Abstract

Qaqarssukite-(Ce), ideally $BaCe(CO_3)_2F$, is a newly identified mineral species from the Qaqarssuk carbonatite complex, southern West Greenland. It occurs as yellow-brown to brown individual crystals or aggregates. These crystals are up to 50 μm, and aggregates attain 2 mm across. The mineral comprises a significant amount of the potential ore at this locality. Associated minerals include calcite, dolomite, strontianite, phlogopite and pyrite. The mineral has a subadamantine to greasy luster and a white streak. It is soft (Mohs hardness 3–4) and brittle, with an uneven fracture. Qaqarssukite-(Ce) is uniaxial positive, ω 1.672(3), ε 1.751(5), and is nonpleochroic. It is trigonal, space group $P\bar{3}c1$, with unit-cell parameters refined from powder-diffraction data: $a$ 7.2036(9), $c$ 18.172(3) Å, $V$ 816.6(2) Å$^3$ and $Z = 6$. The strongest eight X-ray powder-diffraction lines [$d$ in Å($I$)($hkl$)] are: 5.14(28)(102), 4.55(43)(004), 3.671(32)(104), 3.534(41)(111), 3.348(100)(112), 3.093(40)(113), 2.569(35)(204) and 2.078(60)(300). Electron-microprobe and crystal-structure analyses yield CaO 2.82, SrO 3.92, BaO 27.41, La$_2$O$_3$ 8.82, Ce$_2$O$_3$ 20.26, Pr$_2$O$_3$ 1.85, Nd$_2$O$_3$ 6.64, Sm$_2$O$_3$ 0.37, Eu$_2$O$_3$ 0.18, TiO$_2$ 1.41, P$_2$O$_5$ 0.05, F 5.04, CO$_2$ (23.00), O = F –2.12, total 99.65 wt.%. The empirical formula, based on seven anions and two [CO$_3$] groups, is (Ba$_{0.68}$Ca$_{0.19}$Sr$_{0.14}$)$_{\Sigma1.01}$ (Ce$_{0.47}$La$_{0.21}$Nd$_{0.15}$Pr$_{0.04}$Sm$_{0.01}$Ti$_{0.07}$)$_{\Sigma0.95}$ (CO$_3$)$_2$ F$_{1.01}$. The density calculated from the empirical formula is 4.64 g/cm$^3$. The structure has been refined to $R = 0.111$. The structure has three chemically distinct layers parallel to (001): (1) carbonate groups oriented perpendicular to the layering, (2) a layer of Ce–O–F polyhedra, and (3) a layer of Ba–O–F polyhedra. Qaqarssukite-(Ce) has a polymorphic relationship with huanghoite-(Ce), but the crystal structure resembles that of synchysite-(Ce). The mineral is named after the locality.

*Keywords*: qaqarssukite-(Ce), new mineral species, crystal structure, rare-earth elements, carbonatite complex, Qaqarssuk, Greenland.

## Sommaire

La qaqarssukite-(Ce), de formule idéale BaCe(CO$_3$)$_2$F, est une espèce minérale récemment découverte dans le complexe carbonatitique de Qaqarssuk, dans le secteur sud du Groënland occidental. Elle se présente en cristaux isolés jaunâtres ou bruns ou en amas. Les cristaux atteignent 50 μm, et les aggrégats, 2 mm de diamètre. Ce minéral serait une composante importante du minerai potentiel à cet endroit. Lui sont associés calcite, dolomite, strontianite, phlogopite et pyrite. Le minéral possède un éclat subadamantin à gras, et une rayure blanche. Il est relativement mou (dureté de Mohs de 3 à 4) et cassant, avec une fracture inégale. La qaqarssukite-(Ce) est uniaxe positive, ω 1.672(3), ε 1.751(5), et non pléochroïque. Elle est trigonale, groupe spatial $P\bar{3}c1$, avec les paramètres réticulaires suivants, affinés à partir de données en diffraction X, méthode des poudres: $a$ 7.2036(9), $c$ 18.172(3) Å, $V$ 816.6(2) Å$^3$ et $Z = 6$. Les huit raies les plus intenses du spectre de diffraction [$d$ en Å($I$)($hkl$)] sont: 5.14(28)(102), 4.55(43)(004), 3.671(32)(104), 3.534(41)(111), 3.348(100)(112), 3.093(40)(113), 2.569(35)(204) et 2.078(60)(300). Les analyses obtenues avec une microsonde électronique et une ébauche de la structure cristalline ont donné: CaO 2.82, SrO 3.92, BaO 27.41, La$_2$O$_3$ 8.82, Ce$_2$O$_3$ 20.26, Pr$_2$O$_3$ 1.85, Nd$_2$O$_3$ 6.64, Sm$_2$O$_3$ 0.37, Eu$_2$O$_3$ 0.18, TiO$_2$ 1.41, P$_2$O$_5$ 0.05, F 5.04, CO$_2$ (23.00), O = F –2.12, pour un total de 99.65% (poids). La formule empirique, fondée sur sept anions et deux groupes [CO$_3$], est (Ba$_{0.68}$Ca$_{0.19}$Sr$_{0.14}$)$_{\Sigma1.01}$ (Ce$_{0.47}$La$_{0.21}$Nd$_{0.15}$Pr$_{0.04}$Sm$_{0.01}$Ti$_{0.07}$)$_{\Sigma0.95}$ (CO$_3$)$_2$ F$_{1.01}$. La densité calculée à partir de la formule empirique est 4.64 g/cm$^3$. La structure a été affinée jusqu'à un résidu $R$ de 0.111. Elle contient trois couches chimiquement distinctes parallèles à (001): (1) des groupes de carbonate orientés perpendiculairement aux couches, (2) un niveau de polyèdres à Ce–O–F, et (3) un niveau de polyèdres à Ba–O–F . La qaqarssukite-(Ce) possède une relation polymorphique avec la huanghoïte-(Ce), mais sa structure cristalline ressemble à celle de la synchysite-(Ce). Le nom rappelle la localité-type.

(Traduit par la Rédaction)

*Mots-clés*: qaqarssukite-(Ce), nouvelle espèce minérale, structure cristalline, terres rares, complexe carbonatitique, Qaqarssuk, Groënland.

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## INTRODUCTION

In 2002, a joint project of the Canadian Museum of Nature and the Geological Museum, University of Copenhagen, was initiated to investigate the crystal chemical and the paragenetic relationships of the rapidly expanding family of rare-earth-element (REE) carbonate minerals. The most important sources of REE carbonates are from alkaline rocks and carbonatites. Reports of an unusual suite of REE carbonates from a little-known carbonatite complex 60 km east of the town of Maniitsoq (Sukkertoppen), southern West Greenland (65° 23' N, 51° 40' W), sparked the authors' interest. A field investigation of the Qaqarssuk complex (Fig. 1) was completed in the summer of 2003.

One of the REE carbonates that had been reported from this locality is huanghoite-(Ce), on the basis of results of chemical analyses alone (Knudsen 1991). As a result of our investigation, we have shown that this mineral in fact has a polymorphic relation with huang-hoite-(Ce), and is structurally similar to synchysite-(Ce). In this paper, we present the data describing this new species, which we have named qaqarssukite-(Ce) after the locality. The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (#2004–019). Cotype material is housed in the collection of the Canadian Museum of Nature under catalogue numbers CMNMC 84398 and CMNMC 84399.

## OCCURRENCE

The Qaqarssuk carbonatite complex was discovered by Kryolitselskabet Øresund A/S (The Cryolite Mining Company) in 1962. Over a period of more than 20 years, it was investigated as a possible source for Nb, REE and P. The 173-Ma-old complex was emplaced into the West Greenland Archean gneiss complex in at least two stages, with concomitant metasomatic alteration of the wallrock (Fig. 2). The main-stage carbonatites consist of olivine sövite, sövite and dolomite carbonatite ring-dykes, whereas the late-stage carbonatites consist of fine-grained dolomite carbonatite, ferrocarbonatite, late-stage sövite and REE carbonatite. A detailed description of the field relations, petrography, mineral chemistry and geochemistry of carbonatites and related fenitized rock was presented by Knudsen (1991).

Qaqarssukite-(Ce) is found in the core of the intrusion, in the REE carbonatite. At this site, the REE carbonatite is a vein approximately 1 m in width. The REE carbonatite containing qaqarssukite-(Ce) is sugary, fine to medium grained, and mottled in shades of yellow-brown, brown and white. The new species accounts for much of the potential ore in this complex. Associated minerals include calcite, dolomite, strontianite, phlogopite and pyrite.

## PHYSICAL AND OPTICAL PROPERTIES

Qaqarssukite-(Ce) occurs as individual, idiomorphic crystals to 50 μm (Fig. 3) and as complex aggregates up to 2 mm across, embedded in a sugary, fine- to medium-grained yellow-brown rock composed mainly of calcite and dolomite. The mineral is yellow-brown (honey) to dark brown in color, with a white streak. It is translucent with a subadamantine to greasy luster. It does not fluoresce in long- or short-wave ultraviolet light. It is relatively soft (Mohs hardness 3–4). No cleavage is evident; the brittle mineral breaks with an uneven fracture.

The density was not measured by the sink–float method, as qaqarssukite-(Ce) has a density higher than that of methylene iodide. The density could not be measured by Berman balance owing to the small grain-size and the presence of inclusions. The calculated density is 4.64 g/cm$^3$.

Qaqarssukite-(Ce) is uniaxial positive, ω 1.672 ± 0.003, and ε 1.751 ± 0.005 (for λ = 590 nm). It is nonpleochroic. A Gladstone–Dale calculation gives a compatibility index of 0.023, which is regarded as excellent (Mandarino 1981).

## CHEMICAL COMPOSITION

Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (pers. commun., C. Davidson, CSIRO). To minimize burn-up of the sample, a 40 μm beam diameter was



FIG. 1. The Qaqarssuk carbonatite complex. The hills are largely composed of erosion-resistant mafic rocks. The white cook tent of the present authors' 2003 field party is in the center of the field of view, whereas the orange huts to the right housed the Cryolite Mining Company in 1962. The type locality for qaqarssukite-(Ce) is just at the back of the highest hill on the horizon, on the right side of the photograph.
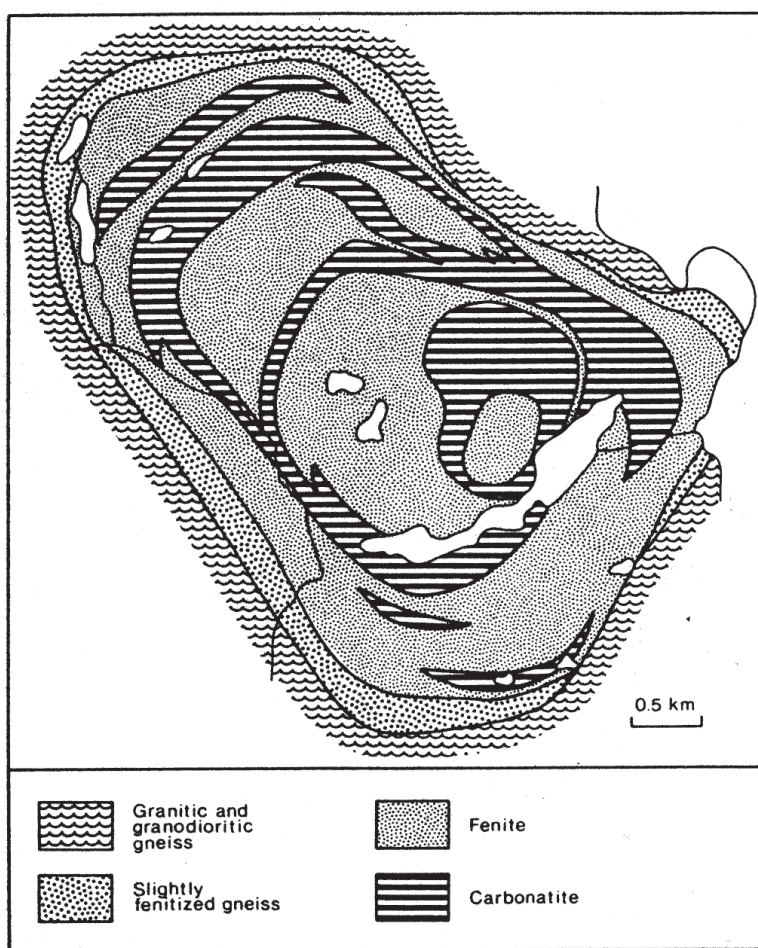
FIG. 2.    Simplified geological map of the Qaqarssuk Carbonatite Complex (after Knudsen 1985).

employed. The operating voltage of the electron probe was 15 kV, and the beam current was 20 nA. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100 s energy-dispersion scan indicated no elements with Z greater than 8 other than those reported here. Two analyses were performed on each of two crystals. The presence of $CO_2$ was confirmed by infrared-absorption spectroscopy and crystal-structure analysis. The following standards were used in the electron-microprobe analyses: calcite ($CaK\alpha$), celestine ($SrL\alpha$), synthetic sanbornite ($BaL\alpha$), a set of synthetic REE phosphates ($LaL\alpha$, $CeL\alpha$, $PrL\alpha$, $NdL\alpha$, $SmL\alpha$, $EuL\alpha$, $PK\alpha$), rutile ($TiK\alpha$) and synthetic $La(CO_3)F$. The following elements were sought but not detected: Na, K, Y, the lanthanides Gd and Lu, Th, U and S. The data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The raw data for the REE were corrected for overlaps. The chemical composition (with ranges) is CaO 2.82 (2.50–3.15), SrO 3.92 (3.6–5.19), BaO 27.41 (26.94–27.88), $La_2O_3$ 8.82 (8.64–9.00), $Ce_2O_3$ 20.26 (20.21–20.31), $Pr_2O_3$ 1.85 (1.67–2.03), $Nd_2O_3$ 6.64 (6.43–6.86), $Sm_2O_3$ 0.37 (0.32–0.42), $Eu_2O_3$ 0.18 (0.03–0.33), $TiO_2$ 1.41 (1.35–1.47), $P_2O_5$ 0.05 (0.00–0.10), F 5.04 (4.81–5.27), $CO_2$ 23.00, O = F –2.12, total 99.65. The empirical formula, based on seven anion atoms and two [$CO_3$] groups, as determined in the crystal-structure analysis, is $(Ba_{0.68}Ca_{0.19}Sr_{0.14})_{\Sigma1.01}$ $(Ce_{0.47}La_{0.21}Nd_{0.15}Pr_{0.04}Sm_{0.01}Ti_{0.07})_{\Sigma0.95}$ $(CO_3)_2$ $F_{1.01}$. This simplifies to the ideal formula $BaCe(CO_3)_2F$. Qaqarssukite-(Ce) readily dissolves with effervescence in concentrated HCl.

## INFRARED SPECTROSCOPY

Two samples, one heated, the other unheated, were analyzed by Fourier transform infrared spectroscopy (FTIR). For FTIR, a portion of the sample was positioned on a diamond anvil microsample cell and was analyzed using a Spectra–Tech IR–Plan microscope interfaced to a Bomem Michelson MB–120 spectrometer. The spectra thus obtained (digital versions deposited; see below) were found to be virtually identical (Fig. 4). The spectra are dominated by [$CO_3$] vibration modes (cm$^{-1}$): $\nu_2 + \nu_6$: asymmetric stretch additive combination, 1797 and 1762 (sharp, weak); $\nu_3$: asymmetric stretch, 1489 and 1420 (very strong); $\nu_1$: symmetric stretch, 1070 (sharp, weak); $\nu_2$: out-of-plane bending, 854 (sharp, moderate); $\nu_4$ in-plane bending, 723 and 689 (sharp, moderate). Also, the 3478 peak (weak, broad) is a result of [OH] stretch. The doubling of peaks indicates two [$CO_3$] groups. The IR spectrum of qaqarssukite-(Ce) resembles that of synchysite, including the [OH] stretching-vibration peak. The corresponding peaks in the synchysite-(Y) spectrum are (cm$^{-1}$): 3440, 1816, 1744, 1464, 1482, 1079, 871, 741 and 602 (Jones & Jackson 1993). The most notable difference with the bastnäsite-(Ce) spectrum (Jones & Jackson 1993) is the single $\nu_3$ peak at 1443 cm$^{-1}$, whereas qaqarssukite-(Ce) has two at 1489 and 1420 cm$^{-1}$. The splitting of the single peak is due to a single [$CO_3$] group with site symmetry lower than an isolated [$CO_3$] group and with C–O bond distances that are quite different from each other in qaqarssukite-(Ce). Bastnäsite-(Ce) also has a single [$CO_3$] group, but with a higher site-symmetry and C–O bond distances that are almost equal (Ni *et al.* 1993).
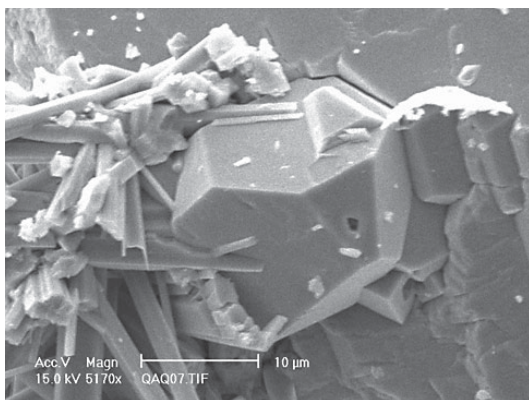


FIG. 3. Scanning electron microscope photograph of specimen number CMNMC 84398 showing a blocky, stepped group of qaqarssukite-(Ce) crystals with several broken needles of strontianite.

## X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession single-crystal photographs showed qaqarssukite-(Ce) to be trigonal with apparent diffraction-symmetry $\bar{3}m$. The crystals invariably show weak, diffuse spots with streaks. This is indicative of a large mosaic spread within the crystal-structure domains. Subsequent more precise work on single crystals using a four-circle diffractometer indicated the space group $P\bar{3}c1$. X-ray powder-diffraction data, obtained with a Bruker microdiffractometer with 2-D grid detector, a crystal-to-detector distance of 6 cm, using Cu$K\alpha$ radiation, are given in Table 1. The instrument had been calibrated with synthetic corundum. Indexing the powder data was aided with powder-pattern intensities

TABLE 1. X-RAY POWDER-DIFFRACTION DATA: QAQARSSUKITE-(Ce), HUANGHOITE-(Ce) AND SYNCHYSITE-(Ce)

| Qaqarssukite-(Ce) This study | | | | | Huanghoite-(Ce) JCPDS 15–286 | | Synchysite-(Ce) JCPDS 18–254 | |
|---|---|---|---|---|---|---|---|---|
| *I* meas. | *I* calc.* | *d* meas. | *d* calc.** | *hkl* | *I* | *d* | *I* | *d* |
| 28 | 20 | 5.135 | 5.143 | 102 | | | 60 | 9.1 |
| 43 | 28 | 4.548 | 4.543 | 004 | | | 50 | 4.53 |
| 32 | 28 | 3.671 | 3.672 | 104 | 70 | 3.91 | | |
| 41 | 39 | 3.534 | 3.533 | 111 | | | 100 | 3.55 |
| 100 | 100 | 3.348 | 3.348 | 112 | 100 | 3.21 | 40 | 3.32 |
| 40 | 43 | 3.093 | 3.096 | 113 | | | 30 | 3.07 |
| 28 | 25 | 2.949 | 2.950 | 202 | | | | |
| 22 | 22 | 2.728 | 2.725 | 106 | | | 100 | 2.80 |
| 35 | 39 | 2.569 | 2.571 | 204 | 70 | 2.50 | | |
| 7 | 6 | 2.319 | 2.318 | 116 | | | 20 | 2.30 |
| 10 | 13 | 2.281 | 2.282 | 212 | | | 20 | 2.28 |
| 13 | 11 | 2.172 | 2.173 | 206 | | | | |
| 22 | 14 | 2.133 | 2.134 | 108 | | | | |
| 39 | 26 | 2.107 | 2.106 | 117 | | | | |
| 60 | 49 | 2.078 | 2.080 | 300 | 90 | 2.01 | 50 | 2.06 |
| 6 | 9 | 1.9203 | 1.9213 | 118 | 100 | 1.937 | 20 | 2.01 |
| 19 | 27 | 1.8893 | 1.8908 | 304 | | | | |
| 13 | 17 | 1.8616 | 1.8605 | 216 | | | 40 | 1.873 |
| | | | | | | | 5 | 1.821 |
| 16 | 16 | 1.7635 | 1.7612 | 222 | 40 | 1.759 | 10 | 1.777 |
| | 8 | | 1.7665 | 119 | | | 10 | 1.749 |
| | 7 | | 1.7262 | 223 | | | | |
| 10 | 8 | 1.7198 | 1.7143 | 306 | | | 10 | 1.704 |
| 5 | 8 | 1.6354 | 1.6359 | 218 | | | 30 | 1.661 |
| 6 | 7 | 1.6171 | 1.6169 | 314 | 70 | 1.616 | | |
| 5 | 7 | 1.5014 | 1.5016 | 11 10 | 70 | 1.557 | 30 | 1.528 |
| 4 | 4 | 1.4755 | 1.4751 | 404 | | | 30 | 1.401 |
| | 4 | | 1.4716 | 10 20 | | | | |
| 12 | 8 | 1.3624 | 1.3623 | 20 20 | | | | |
| 7 | 12 | 1.3460 | 1.3463 | 412 | 70 | 1.335 | 10 | 1.345 |
| | | | | | 60 | 1.325 | 10 | 1.329 |
| 3 | 4 | 1.2743 | 1.2742 | 12 20 | 50 | 1.252 | 30 | 1.290 |
| | | | | | | | 10 | 1.230 |
| 4 | 4 | 1.2008 | 1.2006 | 330 | 30 | 1.201 | 10 | 1.189 |
| | | | | | 50 | 1.176 | | |
| 2 | 4 | 1.1612 | 1.1608 | 334 | 30 | 1.157 | 30 | 1.160 |
| | | | | | 60 | 1.083 | 10 | 1.152 |
| | | | | | | | <10 | 1.122 |
| | | | | | | | 10 | 1.101 |
| | | | | | | | 10 | 1.050 |

\* calculated from crystal-structure determination.
\*\* calculated from XRPD cell refinement with $a$ = 7.2036(9), $c$ = 18.172(3) Å.
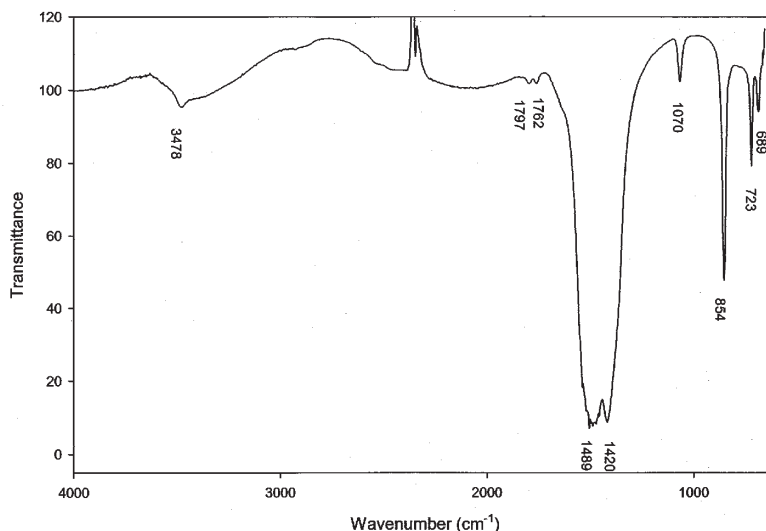
FIG. 4.   Infrared-absorption spectra for qaqarssukite-(Ce).

TABLE 2.  COMPARISON OF QAQARSSUKITE-(Ce), HUANGHOITE-Ce) AND SYNCHYSITE-(Ce)

|  | qaqarssukite-(Ce) | huanghoite-(Ce) | synchysite-(Ce) |
|---|---|---|---|
| Simplified formula | $BaCe(CO_3)_2F$ | $BaCe(CO_3)_2F$ | $CaCe(CO_3)_2F$ |
| Crystal system | trigonal | trigonal | monoclinic |
| Space group | $P\bar{3}c1$ | $R\bar{3}m$ | $C2/c$ |
| Cell parameters | $a$ 7.210 Å | $a$ 5.072 Å | $a$ 12.33 Å |
|  | $c$ 18.19 Å | $c$ 38.46 Å | $b$ 7.110 Å |
|  |  |  | $c$ 18.74 Å |
|  |  |  | $\beta$ 102.7° |
| X-ray powder data ($d$, Å) | present study | JCPDS 15-286 | JCPDS 18-254 |
|  |  |  | 9.1(60) |
|  | 5.14(20) |  |  |
|  | 4.55(43) | 3.91(70) | 4.53(50) |
|  | 3.671(32) |  |  |
|  | 3.534(41) |  | 3.47(70) |
|  | 3.348(100) | 3.21(100) | 3.32(40) |
|  | 3.093(40) |  | 3.07(40) |
|  | 2.949(28) |  | 2.80(100) |
|  | 2.728(22) |  |  |
|  | 2.569(35) | 2.50(70) |  |
|  | 2.319(7) |  | 2.30(20) |
|  | 2.281(10) |  | 2.28(20) |
|  | 2.172(13) |  |  |
|  | 2.133(22) |  |  |
|  | 2.107(39) |  | 2.06(50) |
|  | 2.078(60) | 2.01(90) | 2.01(20) |
|  | 1.889(19) | 1.937(100) | 1.934(50) |
|  | 1.764(16) | 1.759(40) | 1.873(40) |
|  | 1.719(10) | 1.616(70) | 1.661(30) |
|  | 1.501(5) | 1.557(70) | 1.528(30) |
|  | 1.346(7) | 1.335(70) | 1.401(30) |
| Optical data | uniaxial +ve | uniaxial –ve | uniaxial +ve |
|  | $\omega$ 1.672 | $\omega$ 1.765 | $\omega$ 1.648 |
|  | $\varepsilon$ 1.751 | $\varepsilon$ 1.603 | $\varepsilon$ 1.745 |

TABLE 3.  QAQARSSUKITE-(Ce): DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

| | | | |
|---|---|---|---|
| Simplified formula: | $BaCe(CO_3)_2F$ | Reflections collected: | 7294 |
| Space group: | $P\bar{3}c1$ | Unique reflections: | 816 |
| Radiation: | Mo$K\alpha$ | Observed reflections | |
| Graphite | | (> $4\sigma$ $F_o$): | 1325 |
| monochromator | | R(int): | 0.070 |
| $a$ | 7.242(1) Å | Goof (all data) | 1.319 |
| $c$ | 18.192(3) Å | $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ | |
| $V$ | 826.2(4) Å³ | $= 0.111$ (for $F_o$) | |
| $Z$ | 6 | $= 0.124$ (for all $F$) | |
| $\mu$ | 5.06 mm⁻¹ | $wR^2 = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2] =$ | |
| | | 0.246 for $w = 1/\{\sigma^2 F_o^2 +$ | |
| | | $[0.1(Max(F_o^2,0) + 2 F_c^2)/3]^2\}$ | |

calculated from the crystal-structure analysis. The crystallography and chemical composition of qaqarssukite-(Ce), huanghoite-(Ce) and synchysite-(Ce) have many similarities (Table 2).

In the final of three data collections, an equant fragment of 120 μm was mounted on a CCD-equipped Bruker P4 fully automated four-circle diffractometer operated at 50 kV and 40 mA. With the CCD detector, a full sphere of intensity data was collected out to $2\theta$ = 60° using a 30 s frame time and a crystal-to-detector distance of 4 cm. With these operating conditions, no decrepitation was evident in the final analysis of the intensity standards. Information relevant to the data collection and structure determination is given in Table 3. The three-dimensional data were corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical plate-absorption correction was done on the basis of 7948 reflections

and reduced the merging $R$ of this dataset from 0.089 before the absorption correction to 0.061 after the absorption correction. It is important to note that in each of the three full datasets collected there were "apparent reflections" that violated $c$-glide systematic absences; yet when the datasets were compared, these "apparent reflections" were neither the same in number nor in Miller indices, and in all cases, the $I/\delta(I)$ was small. We concluded that these "apparent reflections" are spurious reflections due to the presence of an additional, attached fragment of a crystal. For all 11 crystals studied with single-crystal X-ray-diffraction techniques, additional reflections were noted, and we had to resign ourselves to the fact that for this locality, qaqarssukite-(Ce) crystals are imperfect. Improved data will have to await another find of this mineral.

Phasing of a set of normalized structure-factors gave a mean value for $|E^2 - 1|$ of 0.925. A calculated sharpened Patterson function for space group $P\bar{3}c1$ located three heavy-element sites, and five lighter-element sites. This model refined to $R = 0.29$. The atoms Ba and Ce have similar scattering factors, but appreciably different ionic radii. As the ionic radius of Ce is approximately 30% less than that of Ba, Ce was placed at the site with the shorter bond-lengths. A C-atom site was added following a series of $\Delta F$ synthesis maps, which, in turn, reduced the $R$ index to 0.172. The occupancy factors refined for the three heavy-atom sites (Ce, Ba1 and Ba2) gave values 0.36(1), 0.157(6) and 0.30(1), where ideally for these sites the occupancy is 0.500, 0.167 and 0.333. This gives 42 $e^-$ at the Ce site and 51 $e^-$ total at the Ba sites. These site-refinement results indicate a
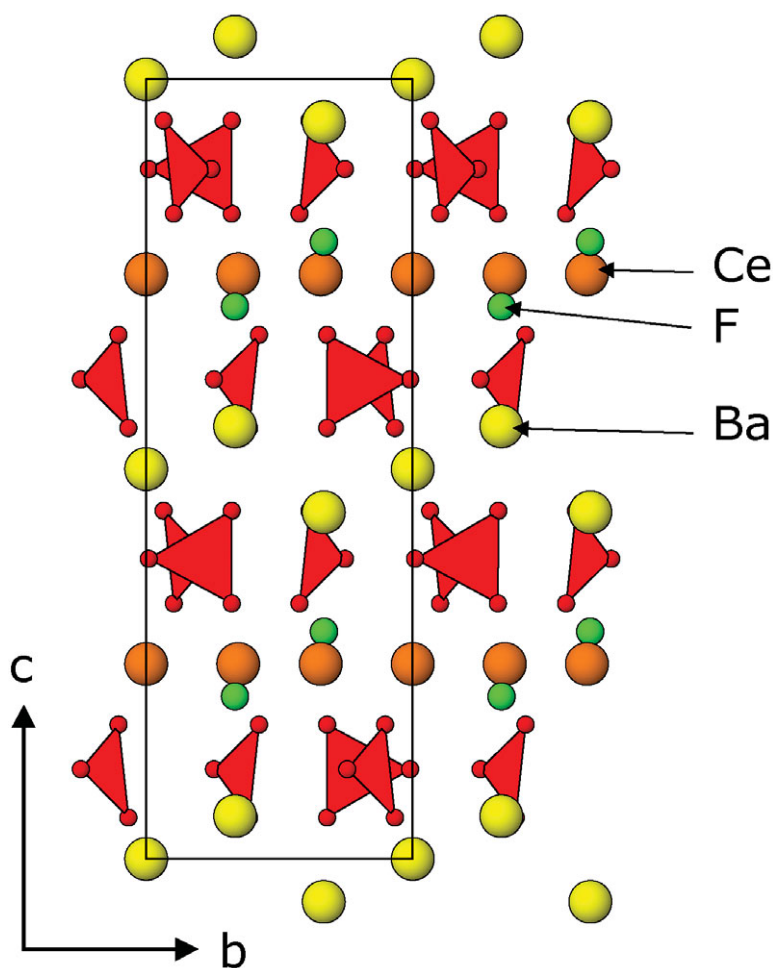


FIG. 5.    The structure of qaqarssukite-(Ce) projected along [100]. Red triangles represent (CO$_3$) polyhedra, the F atoms are shown in green, the Ba atoms are yellow, and the Ce atoms are shown in orange.

slight mixing of REE at the Ba sites and alkaline earths at the Ce site. In the final least-squares refinement, all atom positions were refined with anisotropic-displacement factors to a residual $R$ of 0.112. The addition of an isotropic-extinction factor did not improve the results. The $|E^2 - 1|$ statistic is a bit low for centrosymmetric structures, and lowering the symmetry to $P3$ did improve the $R$ index to 0.076, but this model yields very distorted [CO_3] polyhedra and unrealistic refinements of the displacement factors. Every attempt was made to constrain the refinement, as there were a large number of highly correlated parameters in the non-centrosymmetric model, but these attempts did not resolve the problems with the model. The non-centrosymmetric model could not be unequivocally rationalized with this dataset, and at present, it is best to assume that qaqarssukite-(Ce) is centrosymmetric.

Table 4 contains the final positional and anisotropic-displacement factors, and Table 5 contains selected interatomic distances and angles. 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.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of qaqarssukite-(Ce) has three large-cation sites, each with distinct polyhedra. The Ce site, with 9-fold coordination, occupies a [CeO_6F_3] polyhedron that may be described as a distorted, tricapped trigonal prism. This polygon has 14 triangular faces, which may be assigned the face symbol $[3^{14}]$. The polygon has nine vertices, three surrounded by four faces and six surrounded by five faces and denoted by vertex symbol $(4^3 5^6)$. In contrast to the Ce sites, the Ba sites have more regular polyhedra. The [BaO_12] polyhedron is an icosahedron with face symbol $[3^{20}]$ and vertex symbol $(5^{12})$. The [BaO_9F] polyhedron is a truncated trigonal scalenohedron with face symbol $[3^{16}]$ and vertex symbol $(4^3 5^6 6^1)$.

The crystal structure of qaqarssukite-(Ce) is layered on (001) (Fig. 5). The layering of REE-bearing carbonates was described in detail by Grice *et al.* (1994). In qaqarssukite-(Ce), there are two types of layer: (1) thick slabs composed of a unit of Ce and F atoms and "standing-on-end" [CO_3] polyhedra (Grice *et al*. 1994), and (2) Ba atoms and "standing-on-end" [CO_3] polyhedra. These slabs are well bonded together by the



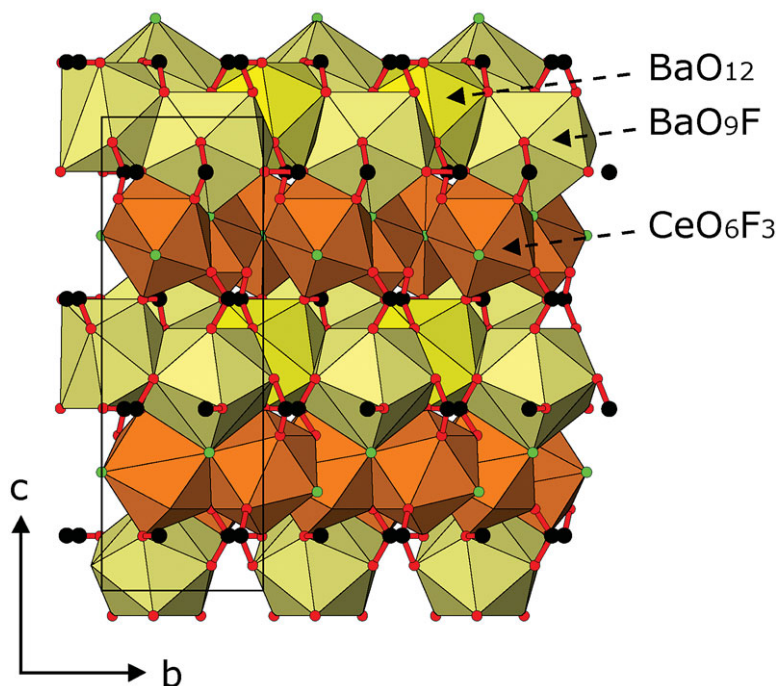FIG. 6. The structure of qaqarssukite-(Ce) projected along [100]. The [BaO_9F] polyhedra are pale yellow, the [BaO_12] polyhedra are darker yellow, and the [CeO_6F_3] polyhedra are orange. Fluorine atoms are shown in green, and the O atoms are shown in red. The black C atoms are at the center of (CO_3) polyhedra.

TABLE 4.  QAQARSSUKITE-(Ce): ATOM COORDINATES AND DISPLACEMENT FACTORS

| Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ | $U_{eq}$ |
|------|-----|-----|-----|----------|----------|----------|----------|----------|----------|----------|
| Ce | 0.3483(4) | 0 | ¼ | 0.014(1) | 0.014(1) | 0.017(1) | -0.002(1) | -0.0012(5) | 0.0070(7) | 0.0150(8) |
| Ba1 | 0 | 0 | 0 | 0.010(1) | 0.010(1) | 0.019(1) | 0 | 0 | 0.0053(6) | 0.013(1) |
| Ba2 | ⅔ | ⅓ | 0.0561(2) | 0.015(1) | 0.015(1) | 0.016(1) | 0 | 0 | 0.0074(5) | 0.0152(8) |
| C | 0.135(4) | -0.218(4) | 0.113(1) | 0.01(1) | 0.01(1) | 0.03(1) | 0.004(9) | 0.001(9) | 0.004(9) | 0.014(9) |
| O1 | 0.242(3) | -0.005(3) | 0.116(1) | 0.03(1) | 0.011(9) | 0.021(9) | 0.003(7) | 0.008(8) | 0.008(8) | 0.021(5) |
| O2 | 0.071(3) | -0.310(3) | 0.049(1) | 0.02(1) | 0.02(1) | 0.04(1) | -0.002(9) | -0.004(8) | 0.019(9) | 0.024(4) |
| O3 | 0.590(3) | -0.094(3) | 0.175(1) | 0.02(1) | 0.02(1) | 0.04(1) | 0.011(9) | 0.009(8) | 0.016(8) | 0.023(5) |
| F1 | ⅔ | ⅓ | 0.704(1) | 0.018(8) | 0.018(8) | 0.02(1) | 0 | 0 | 0.009(4) | 0.020(6) |
| F2 | 0 | 0 | ¼ | 0.04(2) | 0.04(2) | 0.09(5) | 0 | 0 | 0.02(1) | 0.06(2) |

carbonate groups and the shared edges of [CeO$_6$F$_3$] and [BaO$_9$F] polyhedra (Fig. 6).

The chemical formula of qaqarssukite-(Ce), BaCe(CO$_3$)$_2$F, and its crystal structure resemble those of synchysite-(Ce), CaCe(CO$_3$)$_2$F. Within the polysomatic series from bastnäsite-(Ce), Ce(CO$_3$)$_2$F (Ni *et al.* 1993), to synchysite-(Ce), CaCe(CO$_3$)$_2$F (Wang *et al.* 1994), to parisite-(Ce), CaCe$_2$(CO$_3$)$_2$F$_2$ (Ni *et al.* 2000), the crystal structures are well known. They consist of layers of [CeFCO$_3$] and [CaCO$_3$] in varying proportions. Donnay & Donnay (1953) were the first to study and resolve the crystallography of this series, but crystal structures were not solved until later (references given above). The monoclinic structure of synchysite-(Ce) is pseudohexagonal, with *a* 7.11 and *c* 18.74 Å. These cell parameters closely resemble those of qaqarssukite-(Ce), *a* 7.20 and *c* 18.26 Å. The (001) structure layers in synchysite-(Ce) have compositions (1) CaCO$_3$ with Ca in 7-fold and 8-fold coordination with O atoms and (2) CeF(CO$_3$) with Ce in 9-fold coordination with F and O atoms (Fig. 7). The large coordination-number of the Ca sites accommodates some Ce in each site, 29% in the 8-fold coordination site, and 25% in the 7-fold coordination site (Wang *et al.* 1994). In the qaqarssukite-(Ce) structure, the large Ba atom necessitates a large sphere of coordination, just as in the "Ca" sites of synchysite. The gross similarities in the chemical formula and structural layering are very evident in these two minerals.

Qaqarssukite-(Ce) has a polymorphic relation with huanghoite-(Ce), hence the earlier misidentification of the mineral at Qaqarssuk based on results of chemical analyses only (Knudsen 1991). The crystal structure of huanghoite-(Ce) (Yang & Pertlik 1993) resembles that of lukechangite-(Ce) (Grice & Chao 1997), but it is very different from that of qaqarssukite-(Ce). Huanghoite-(Ce) has layers of "flat-lying" (Grice *et al.* 1994) carbonate groups separated by layers of large polyhedra centered by Ba or Ce atoms (Fig. 8). The distinct change in the attitude of the carbonate groups, from "standing-on-edge" in qaqarssukite-(Ce) to "flat-lying" in huanghoite-(Ce), is a result of the changes in the large-cation polyhedra. In qaqarssukite-(Ce),

TABLE 5.  QAQARSSUKITE-(Ce): SELECTED BOND-LENGTHS (Å) AND BOND-ANGLES (°)

**[CeO$_6$F$_3$] polyhedron**

| Ce | – O3 | ×2 | 2.50(2) |
|----|------|----|---------|
| Ce | – F1 | ×2 | 2.505(9) |
| Ce | – F2 |    | 2.522(3) |
| Ce | – O1 | ×2 | 2.55(2) |
| Ce | – O3 | ×2 | 2.57(2) |
| <Ce | – φ> |   | <2.530> |

**[BaO$_{12}$] polyhedron**

| Ba1 | – O2 | ×6 | 2.70(2) |
|-----|------|----|---------|
| Ba1 | – O1 | ×6 | 2.75(2) |
| <Ba1 | – O> |   | <2.725> |

**[BaO$_9$F] polyhedron**

| Ba2 | – F1 |     | 2.69(3) |
|-----|------|-----|---------|
| Ba2 | – O2 | ×6 | 2.76(2) |
| Ba2 | – O1 | ×3 | 3.02(2) |
| <Ba2 | – φ> |   | <2.837> |

**Carbonate polyhedron**

| C | – O3 | 1.28(3) | O2 | – O3 | 125(2) |
|---|------|---------|----|------|--------|
| C | – O2 | 1.31(3) | O1 | – O3 | 117(23) |
| C | – O1 | 1.34(3) | O1 | – O2 | 118(2) |
| <C | – O> | <1.310> | <O | – O> | <120.0> |

Ce has nine-fold coordination [CeO$_6$F$_3$], whereas in huanghoite-(Ce), the coordination number increases to ten, [CeO$_9$F]. For both minerals, the coordination of one Ba site remains the same, twelve-fold [BaO$_{12}$], whereas the other Ba site increases its coordination number from nine in qaqarssukite-(Ce) [BaO$_9$F] to twelve in huanghoite-(Ce) [BaO$_6$F$_6$]. This increase in coordination number of the large cations effectively increases the cell volume from 819 Å$^3$ for qaqarssukite-(Ce) to 857 Å$^3$ for huanghoite-(Ce). The values cited are for six formula units, and represent a 5% increase in volume.

GENESIS OF QAQARSSUKITE-(CE)

On the basis of the fractionation of carbon isotopes between calcite and dolomite, the estimated temperature of emplacement for the Qaqarssuk carbonatite complex lies between 300 and 600°C (Knudsen 1991). Qaqarssukite-(Ce) crystallized very late in the second episode of carbonatite emplacement, at the lower end of this
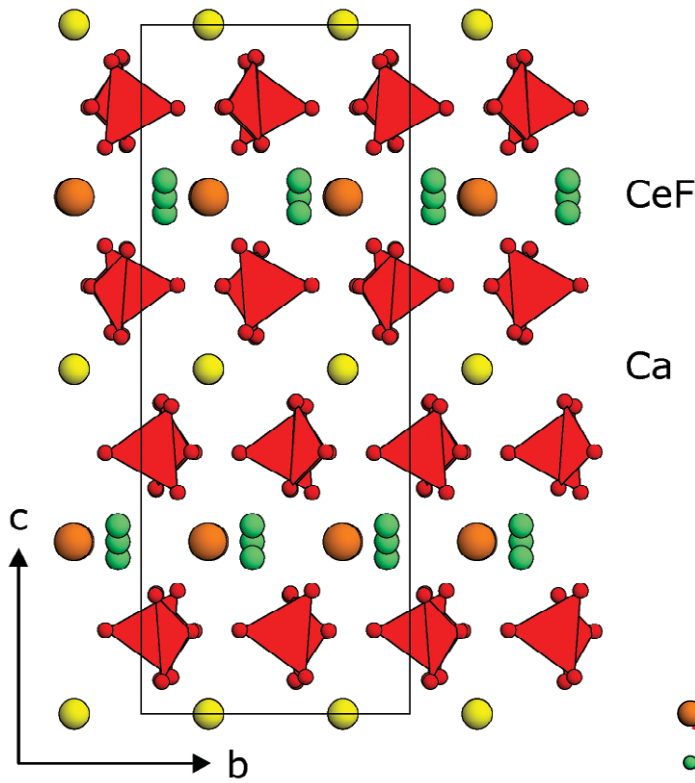
CeF

Ca

FIG. 7. The structure of synchysite-(Ce) projected on [100]. Red triangles represent $(CO_3)$ polyhedra, the F atoms are shown in green, the Ca atoms are shown in yellow, and the Ce atoms are shown in orange



$BaO_6F_6$

$BaO_{12}$

$CeO_9F$

FIG. 8. The structure of huanghoite-(Ce) projected on [100]. The same color scheme is used as with qaqarssukite-(Ce); the $[CO_3]$ groups parallel to (001) are shown as red lines.
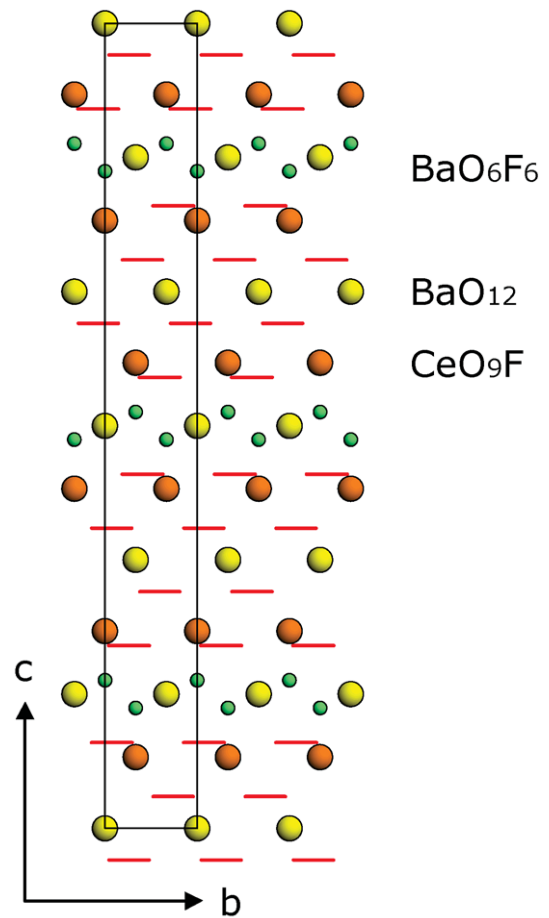
temperature range. No estimate of the pressure is given, but it is known that huanghoite-(Ce) has been synthesized at 730°C (maximum) and 200 MPa (maximum) (Mercier & LeBlanc 1993). The pressure of formation for qaqarssukite-(Ce) should be greater than this, on the basis of a decrease in molar volume. We conclude then that the mechanism of polymorphic change from huanghoite-(Ce) to qaqarssukite-(Ce) reflects the greater efficiency of packing of atoms at higher pressures and lower temperatures.

## ACKNOWLEDGEMENTS

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