

Kochite, a new member of the rosenbuschite group from the Werner Bjerger alkaline complex, East Greenland

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Abstract: Kochite, ideally $\text{Na}_2(\text{Na,Ca})_4\text{Ca}_4(\text{Mn,Ca})_2\text{Zr}_2\text{Ti}_2(\text{Si}_2\text{O}_7)_4(\text{O,F})_4\text{F}_4$, is a new member of the rosenbuschite group from the alkaline complex of Werner Bjerger, East Greenland. It occurs in nepheline syenite as lath-shaped to acicular crystals in aggregates up to 0.3×1.0 mm. Associated minerals are nepheline, alkali feldspar and lavenite. It is transparent with a brownish colour and has a vitreous lustre. It is brittle with a perfect {100} cleavage and an uneven fracture. The mineral is biaxial positive with α $1.684 \pm .002$, β $1.695 \pm .004$, γ $1.718 \pm .002$ and $2V_{\text{meas.}} = 73^\circ(2)$. The optical orientation is $X = c$ and $Z \wedge [100] \sim 20^\circ$. The pleochroism is weak with $X =$ colourless and $Z =$ pale yellow. The mineral is triclinic with $a = 10.032(2)$, $b = 11.333(2)$, $c = 7.202(1)$ Å, $\alpha = 90.192(4)$, $\beta = 100.334(5)$, $\gamma = 111.551(4)^\circ$, $Z = 1$. The 5 strongest X-ray lines are [d in Å (Int.)] 2.908(10), 2.600(8), 3.028(6), 1.868(6) and 1.670(5). An average of four electron microprobe analyses of kochite gave SiO_2 31.55, Al_2O_3 0.05, V_2O_5 0.03, TiO_2 8.44, ZrO_2 12.12, HfO_2 0.09, Nb_2O_5 1.86, Ta_2O_5 0.02, MgO 0.01, MnO 4.92, FeO 1.08, CaO 21.39, SrO 0.12, Na_2O 10.33, Y_2O_3 0.39, La_2O_3 0.25, Ce_2O_3 0.57, F 6.83, $\text{O} \equiv \text{F}$ 2.88, total 97.71 wt.%. The empirical formula, based on 8 Si atoms in accordance with the structure refinement ($R(F) = 4.0\%$), is $(\text{Na}_{1.70}\text{Sr}_{0.02})_{\Sigma 1.72}(\text{Na}_{2.77}\text{Ca}_{1.23})_{\Sigma 4.00}(\text{Ca}_{3.40}\text{Na}_{0.60})_{\Sigma 4.00}(\text{Mn}_{1.06}\text{Ca}_{0.82}\text{Y}_{0.05}\text{Ce}_{0.05}\text{La}_{0.02})_{\Sigma 2.00}(\text{Zr}_{1.40}\text{Fe}_{0.23}\text{Ca}_{0.36}\text{Hf}_{0.01})_{\Sigma 2.00}(\text{Ti}_{1.61}\text{Nb}_{0.21}\text{Zr}_{0.10}\text{Al}_{0.05}\text{V}_{0.03})_{\Sigma 2.00}(\text{Si}_2\text{O}_7)_4\text{F}_4(\text{O}_{2.39}\text{F}_{1.48})_{\Sigma 3.87}$. $D_{\text{meas.}} = 3.32$, $D_{\text{calc.}} = 3.31$ g/cm³. Kochite is an Mn-, Ti-analogue of rosenbuschite.

Key-words: kochite, rosenbuschite group, new mineral, crystal structure.

Introduction

The rosenbuschite group minerals are Na-, Ca-rich titanosilicates, normally occurring in alkaline rocks. The group shows a wide compositional variability hosting a large number of elements. Besides Si the group contains the cations Na, Ca, Y, Mn, Fe, Ti, Mg, Zr, Nb, and REE, which occur in various concentrations thus complicating the substitution schemes for the group. Christiansen *et al.* (2003) carried out a systematic study on a series of rosenbuschite group minerals in order to describe its crystal chemistry. During this study one specimen proved to be an unique, new mineral species.

Kochite is named in honour of Lauge Koch (1892-1964), a Danish geologist, who made significant contributions to the knowledge of the geology of Greenland, through a number of scientific expeditions. Lauge Koch also took the initiative to map the geology of Werner Bjerger, East Greenland (Bearth, 1959), which is the type locality of this new mineral.

The new mineral species and its name have been approved by the Commission on New Minerals and

Mineral Names, IMA. Type material of kochite is housed in the collection of the Geological Museum, University of Copenhagen under catalogue number GM 2002.94.

Occurrence

The mountain range of Werner Bjerger (72° N, 24° W) is one of a number of alkaline complexes along the eastern Coast of Greenland. The geology and mineralogy of the complex were described by Bearth (1959) and Brooks *et al.* (1982). Within this complex, kochite was found on the northern side of Hvide Ryg, which is a mountain composed of nepheline syenite. The mineral was found in a loose block located between the Sirius Glacier and Hvide Ryg.

Kochite occurs as an accessory phase in a nepheline syenite rock associated with nepheline, alkali-feldspar and accessory lavenite. Other minerals observed in nepheline syenites from this area are: albite (perthite), analcime, biotite, calcite, cancrinite, eudialyte, götzenite, hematite, rinkite, sodalite, titanite, wöhlerite and ægirine-augite.

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Table 1. Kochite: X-ray powder diffraction data.

$I_{\text{obs.}}$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	h	k	l
1	7.081	6.986	0	0	1
<1	5.539	5.478	1	-2	0
<1	4.281	4.302	2	-2	0
		4.234	1	-2	1
3	3.951	3.919	1	2	0
		3.881	2	-2	1
6	3.028	3.019	2	1	1
10	2.908	2.898	1	-2	2
		2.891	2	-2	-2
1	2.818	2.791	1	-4	0
<1	2.755	2.741	2	-4	0
8	2.600	2.600	0	4	0
2	2.462	2.482	3	-4	0
		2.451	2	2	-2
		2.444	1	2	2
		2.437	4	-2	0
1	2.281	2.284	1	4	0
		2.265	4	0	0
1	2.214	2.205	1	-4	2
		2.198	2	-4	-2
1	2.176	2.167	0	4	-2
		2.160	1	-4	-2
		2.153	4	-4	0
1	1.963	1.962	2	4	0
1	1.943	1.947	3	-4	2
		1.943	4	-4	-2
6	1.868	1.855	4	-2	2
		1.855	5	-2	-2
		1.841	4	2	0
1	1.791	1.784	1	0	-4
5	1.670	1.686	3	4	0
1	1.656	1.654	1	-6	2
		1.652	2	-6	2
		1.650	2	-6	-2
		1.647	3	-6	-2
2	1.554	1.545	5	-4	2
		1.544	6	-4	-2
1	1.536	1.538	4	0	-4
		1.536	2	0	4

Gandolfi camera data, 114.6 mm, CuK α radiation.

Chemical composition

Chemical analyses were done in wavelength-dispersive (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a $\phi\rho Z$ routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The operating voltage was 15 kV and the beam current was 20 nA. Due to the small size of the kochite crystals, the beam diameter was limited to 10 μm and this limitation is likely responsible for some Na migration resulting in low Na cation values and low totals. Data for all elements in the samples were collected for 25 s or 0.50 % precision, whichever was attained first. Standards used in the probe analyses were: synthetic pyroxene NaInSi₂O₆ (SiK α , NaK α), gehlenite (CaK α), chrysoberyl (AlK α), synthetic VP₂O₇ (VK α), rutile (TiK α), zircon (ZrL α), hafnon (HfL α), synthetic MnNb₂O₆ (NbL α), synthetic NiTa₂O₆ (TaL α), diopside (MgK α), tephroite (MnK α), almandine (FeK α), celestine (SrL α), synthetic yttrium iron garnet (YIG) (YL α), synthetic LaPO₄ (LaL α), synthetic CePO₄ (CeL α) and phlogopite (FK α). A 100 s energy-dispersive scan indicated no elements with $Z > 8$ other than those reported here. Also sought but not detected were: the rare earth elements (*REE*) from Pr to Lu, Th, U, Zn, P, K, Ba, W and Sn. A Ti overlap on V and the *REE* overlaps were corrected. Four analyses were performed on the same grain and the average (with ranges) is reported here: SiO₂ 31.55 (31.33-31.77), Al₂O₃ 0.05 (0.00-0.20), V₂O₃ 0.03 (0.03-0.03), TiO₂ 8.44 (8.21-8.80), ZrO₂ 12.12 (11.82-12.29), HfO₂ 0.09 (0.08-0.09), Nb₂O₅ 1.86 (1.60-2.18), Ta₂O₅ 0.02 (0.01-0.04), MgO 0.01 (0.00-0.03), MnO 4.92 (4.25-5.88), FeO 1.08 (0.68-1.47), CaO 21.39 (20.54-22.73), SrO 0.12 (0.09-0.14), Na₂O 10.33 (10.18-10.49), Y₂O₃ 0.39 (0.27-0.51), La₂O₃ 0.25 (0.20-0.27), Ce₂O₃ 0.57 (0.47-0.63), F 6.83 (6.20-7.46), O \equiv F 2.88, total 97.71 wt. %. Crystal structure analysis and infrared spectroscopic analysis (IR) indicate that neither OH nor H₂O is present in kochite. The empirical formula, based on 8 Si atoms from the crystal structure analysis is: (Na_{1.70}Sr_{0.02}) Σ 1.72(Na_{2.77}Ca_{1.23}) Σ 4.00(Ca_{3.40}Na_{0.60}) Σ 4.00(Mn_{1.06}Ca_{0.82}Y_{0.05}Ce_{0.05}La_{0.02}) Σ 2.00(Zr_{1.40}Fe_{0.23}Ca_{0.36}Hf_{0.01}) Σ 2.00(Ti_{1.61}Nb_{0.21}Zr_{0.10}Al_{0.05}V_{0.03}) Σ 2.00(Si₂O₇)₄F₄(O_{2.39}F_{1.48}) Σ 3.87 or ideally Na₂(Na,Ca)₄Ca₄(Mn,Ca)₂Zr₂Ti₂(Si₂O₇)₄(O,F)₄F₄.

The infrared-absorption spectrum of kochite was obtained using a Bomem Michelson MB-120 Fourier-transform infrared spectrometer equipped with a diamond-anvil cell as a microsampling device. Only a broad absorption band with peaks at 1045, 968, 926 and 871 cm⁻¹ were observed, which was interpreted to represent stretching and bending vibrations of [SiO₄] groups.

X-ray crystallography and crystal structure determination

X-ray powder diffraction data (Table 1) were obtained using CuK α -radiation and a Gandolfi camera with a diameter of 114.6 mm.

Physical and optical properties

Kochite occurs as lath-shaped to acicular grains in parallel to subparallel aggregates up to 0.3 \times 1.0 mm in size. The crystals are elongated along [010]. It is transparent with a weak colour of brown and has a vitreous lustre. The mineral is brittle with a perfect {100} cleavage and uneven fracture. The hardness is estimated to be 5 (Mohs' scale) corresponding to that of rosenbuschite.

The density, measured by suspension in a solution of methylene iodide and acetone, is 3.32 \pm .01, which compares well with the calculated density of 3.31.

Kochite is biaxial positive, α 1.684 \pm .002, β 1.695 \pm .004, γ 1.718 \pm .002; $2V_{\text{meas.}} = 73^\circ(2)$, $2V_{\text{calc.}} = 70^\circ$, (for $\lambda = 590$ nm). The optical orientation is $X = c$, $Z \wedge [100] \sim 20^\circ$. The mineral is weakly pleochroic with X being colourless and Z pale yellow. A Gladstone-Dale calculation gives a compatibility index of -0.003, which is regarded as superior (Mandarino, 1981).

Table 2. Kochite: Crystal data and structure refinement.

Space group	$P\bar{1}$
a	10.032(2) Å
b	11.333(2) Å
c	7.202(1) Å
α	90.192(4)°
β	100.334(5)°
γ	111.551(4)°
Unit cell volume	747.1(2) Å ³
Crystal size	0.108 x 0.072 x 0.036 mm ³
# of reflections observed.	9277
θ range for data collection	4.59° to 34.51°
Index ranges	-15 < h < 14, -17 < k < 18, -11 < l < 11
R_{int}	0.036
Data/params.	5529/287
$ E^2 - 1 $	1.272
$R(F)/wR(F^2)^*$	4.0/7.8
Goodness of fit.	1.027
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$	0.93/-1.11 e/Å ³

* $R(F)$ for $F_o > 4\sigma F_o$, $wR(F^2)$ for all data.

A crystal measuring $0.108 \times 0.072 \times 0.036$ mm was chosen for X-ray single-crystal data collection after optical inspection to avoid grains containing multiple crystallites. The crystal was mounted on a Bruker AXS four-circle diffractometer equipped with a CCD 1000 K area detector and a flat graphite monochromator using MoK α radiation from a fine focus sealed X-ray tube. Unit cell determination and data collection were done in the SMART system of programmes. The distance between the crystal and detector was 42 mm. Using ω - and ϕ -scans with a step size of 0.25°, intensities were measured for reflections within the θ -range of 4.59° to 34.51°. Integrated intensities were calculated using the programme SAINT. The programme X-PREP was used for space group determination and absorption correction of intensities corrected for absorption. During the semi-empirical absorption correction the crystal was modelled as an ellipsoid. Information relevant to the data collection is listed in Table 2.

Full matrix least square refinements on F^2 were carried out with the SHELXL-97 program (Sheldrick, 1997). The refinement procedure and determination of cation occupancies are described in Christiansen *et al.* (2003). Refined atomic coordinates and isotropic displacement parameters are given in Table 3.

Discussion

Kochite is a member of the disilicate (Liebau, 1985) rosenbuschite group. The structures (Fig. 1) of this group are composed of edge- and corner-sharing CN=6-8 polyhedra in combination with rows of Si₂O₇-groups. The edge-shared CN=6-8 polyhedra combine into [001]-ribbons and into (100)-layers, which are interconnected into a framework by sharing polyhedral apices. The rows of the disilicate groups are situated in interstitial tunnels of this polyhedral framework.

The CN=6-8 polyhedra host a wide variety of elements, *i.e.* Na, Mg, Ca, Ti, Mn, Fe, Y, Zr, Nb and REE. In

Table 3. Kochite: Atomic coordinates, site occupancies and equivalent isotropic displacement parameters (Å²).

Site	Site occupancy	x	y	z	U_{eq}
M1a	Zr _{0.64} Ca _{0.20} Fe _{0.12}	0.35449(5)	0.28056(4)	0.08802(5)	0.0080
M1b	Mn _{0.55} Ca _{0.39} Ce _{0.04} Y _{0.02}	0.36178(7)	0.78504(6)	0.09042(8)	0.0120
M2a	Na _{0.75} Ca _{0.25}	0.0067(1)	0.25331(9)	0.7552(1)	0.0130
M2b	Na _{0.56} Ca _{0.44}	0.9957(1)	0.25052(8)	0.2440(1)	0.0158
M3a	Ca _{0.74} Na _{0.26}	0.3590(1)	0.28910(8)	0.5885(1)	0.0170
M3b	Ca _{0.96} Na _{0.04}	0.36713(8)	0.79231(7)	0.5890(1)	0.0143
M4a	Na _{0.43} Ca _{0.07}	0.0000	0.0000	0.5000	0.0148
M4b	Na _{0.46} Ca _{0.04}	0.0000	0.5000	0.5000	0.0171
M5a	Ti _{0.41} Nb _{0.06} Zr _{0.03}	0.0000	0.0000	0.0000	0.0110
M5b	Ti _{0.46} Nb _{0.04}	0.0000	0.5000	0.0000	0.0210
Si1a	Si	0.2863(1)	0.01265(8)	0.3452(1)	0.0089
Si2a	Si	0.2824(1)	0.01179(8)	0.7918(1)	0.0092
Si1b	Si	0.2886(1)	0.51144(8)	0.3446(1)	0.0080
Si2b	Si	0.2880(1)	0.50965(8)	0.7939(1)	0.0083
O1a	O	0.2629(3)	0.0214(3)	0.5638(3)	0.0319
O1b	O	0.2650(3)	0.4949(3)	0.5643(3)	0.0260
O2a	O	0.3807(3)	0.1589(2)	0.3108(4)	0.0164
O2b	O	0.3886(3)	0.6576(2)	0.3306(4)	0.0167
O3a	O	0.3829(3)	0.1546(2)	0.8803(4)	0.0208
O3b	O	0.3996(3)	0.6531(2)	0.8637(3)	0.0179
O4a	O	0.3646(3)	0.9149(2)	0.3262(4)	0.0217
O4b	O	0.3589(3)	0.4088(2)	0.3026(4)	0.0192
O5a	O	0.3451(3)	0.9041(3)	0.8485(4)	0.0280
O5b	O	0.3438(3)	0.3987(2)	0.8688(3)	0.0209
O6a	O	0.1215(3)	0.9629(2)	0.2215(3)	0.0157
O6b	O	0.1241(3)	0.4688(2)	0.2234(3)	0.0140
O7a	O	0.1166(3)	0.9684(2)	0.8268(3)	0.0165
O7b	O	0.1252(3)	0.4781(2)	0.8333(3)	0.0158
X8a	O _{0.7} F _{0.3}	0.1277(3)	0.1840(2)	0.0361(3)	0.0111
X8b	F _{0.5} O _{0.5}	0.1159(3)	0.6853(2)	0.0336(3)	0.0237
F9a	F	0.1144(2)	0.2086(1)	0.5235(3)	0.0208
F9b	F	0.1220(2)	0.7063(1)	0.5279(3)	0.0226

U_{eq} is defined as one third of the orthogonalized vector.

gözenite Ca₂(Ca,Na)₂Ca₂NaTi(Si₂O₇)₂F₂F₂ and hainite (Ca,Zr,Y)₂(Na,Ca)₂Ca₂NaTi(Si₂O₇)₂F₂F₂ these elements are distributed over five crystallographically distinct posi-

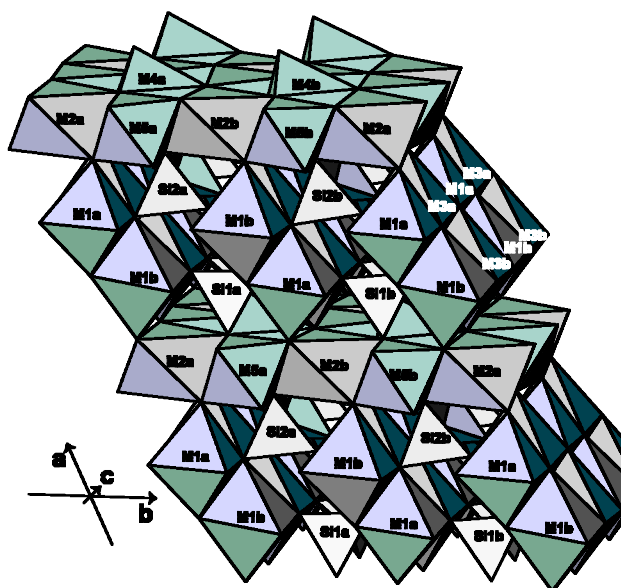


Fig. 1. Oblique view of the crystal structure of kochite. The cation positions are indicated.

tions whereas in kochite $Zr_2(Mn,Zr)_2(Na,Ca)_4Ca_4Na_2Ti_2(Si_2O_7)_4F_4O_4$ and rosenbuschite $Zr_2Ca_2(Na,Ca)_4Ca_4Na_2ZrTi(Si_2O_7)_4F_4O_4$ they are distributed over ten positions (Fig. 1). The doubling of the number of cation positions in kochite and rosenbuschite compared to that of götzenite and hainite is a consequence of the ordering of Ca and Zr in the M1 positions resulting in a doubling of the *b*-axis.

The structural investigations undertaken by Christiansen *et al.* (2003) showed, that kochite may be regarded as the Ti-, Mn-analogue of rosenbuschite. In rosenbuschite M1b is dominated by Ca, whereas in kochite it is dominated by Mn. In kochite M5a is dominated by Ti whereas in rosenbuschite it is dominated by Zr. As discussed by Christiansen *et al.* (2003) kochite may be regarded as the end-member of two compositional series: the first series has götzenite as the other end-member, and in the second series rosenbuschite is the other end-member.

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