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Kentbrooksite from the Kangerdlugssuaq intrusion, East Greenland, a new Mn-REE-Nb-F end-member in a series within the eudialyte group: Description and crystal structure

OLE JOHNSEN*, JOEL D. GRICE** and ROBERT A. GAULT**

* Geological Museum, University of Copenhagen,
Øster Voldgade 5–7, DK-1350 Copenhagen, Denmark
e-mail: oj@savik.geomus.ku.dk
** Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4, Canada

Abstract: Kentbrooksite, ideally $(Na,REE)_{15}(Ca,REE)_6Mn_3Zr_3NbSi_{25}O_{74}F_2 \cdot 2H_2O$, is a new mineral from the Kangerdlugssuaq intrusion, East Greenland. The mineral occurs in alkaline pegmatitic bodies cutting pulaskite rocks and is found as anhedral to subhedral aggregates up to 2 cm. It is transparent, yellow-brown with white streak and vitreous luster. Hardness 5–6, brittle, uneven fracture and no cleavage. It is pyroelectric. The mineral is uniaxial negative, $\omega = 1.628(2)$ and $\varepsilon = 1.623(2)$, nonpleochroic. $D_{meas} = 3.10(4)$ g/cm^3, $D_{calc} = 3.08$ g/cm^3.

The mineral is trigonal, space group $R3m$, $a = 14.1686(2)$, $c = 30.0847(4)$ Å, $Z = 3$. The strongest reflections in the X-ray powder pattern are [d (Å), Int, (hkl)]: 2.839, 100, (404); 2.961, 91, (315); 11.385, 43, (101); 7.088, 41, (110); 3.380, 37, (131); 4.295, 34, (205); and 5.682, 30, (202). The empirical formula, based on 3.77 (Zr + Hf + Nb + Ti) pfu, is
$(Na_{14.93}REE_{0.44}Y_{0.42}K_{0.30}Sr_{0.15})_{\Sigma 16.24}(Ca_{3.27}Mn_{1.78}REE_{0.62}Na_{0.33})_{\Sigma 6.00}(Mn_{1.90}Fe_{0.72}Al_{0.13}Mg_{0.05})_{\Sigma 2.80}$
$(Nb_{0.55}Zr_{0.12}Ti_{0.10})_{\Sigma 0.77}Si_{0.60}(Zr_{2.81}Hf_{0.06}Ti_{0.13})_{\Sigma 3}[(Si_3O_9)_2(Si_9O_{27})_2O_2](F_{1.51}Cl_{0.27}OH_{0.22})_{\Sigma 2} \cdot 2.3H_2O$.
IR spectrum is given.

The structure has been refined from single-crystal X-ray diffraction data to $R1 = 4.1\%$. Kentbrooksite belongs to the eudialyte group and has the framework characteristic for this group, consisting of three-membered and nine-membered rings of SiO_4 tetrahedra cross-linked by Zr and M1 in octahedral coordination. Most important structural differences from *e.g.* eudialyte from the type locality (Ilimaussaq) are: $^{[5]}Mn$ substitution for $^{[4]}Fe$ in M2, $^{[6]}Nb$ (M3) substitution for $^{[4]}Si$ (M4), a high content of REE and F substitution for Cl. Kentbrooksite represents the ΣNb,REE,Mn,F end-member of a series within the eudialyte group.

Key-words: kentbrooksite, eudialyte, new mineral species, end-member, crystal structure, Kangerdlugssuaq, East Greenland.

Introduction

During a study of the chemical variation in eudialyte, a Na-rich zirconosilicate generally with significant amounts of Ca and Fe, Johnsen & Gault (1997) discovered that among some 60 analyses a few were characterized by very high contents of Mn and rare-earth elements (REE), largely at the expense of Fe and Ca. The highest content of Mn (~8 wt% MnO) was found in a sample from Amdrup Fjord, Kangerdlugssuaq intrusion in East Greenland, while the highest content of REE hitherto reported in an eudialyte (9.78 wt% REE_2O_3, Y_2O_3 not included) was found in a sample from Mt. St-Hilaire, Quebec, Canada. In both samples the sum of Mn and REE pfu were distinctly higher than the sum of Ca and Fe pfu. With the purpose of exploring the crystal-chem-

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ical details of these eudialyte samples, single-crystal data have been collected, and the present paper deals with the results from the Amdrup Fjord sample that on these grounds has gained status as a new mineral species named kentbrooksite.

The mineral is named after C. Kent Brooks in acknowledgement of his leadership of 14 geological expeditions to the Kangerdlugssuaq area of East Greenland and of his own significant contributions to the understanding of the area as a rifted continental margin. Both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material is deposited at the Geological Museum, University of Copenhagen and at the Canadian Museum of Nature, Ottawa.

Occurrence

Tertiary rifting in the North Atlantic area led to extensive plateau basalts, dike swarms and major plutons in East Greenland between the latitudes of 66 and 75 °N. This activity was most intense in the Kangerdlugssuaq area at around 68 °N whose geology has been described by Brooks & Nielsen (1982). The Kangerdlugssuaq intrusion is the largest of the syenitic plutons, occupying an area of about 800 km^2, making it among the world's largest syenite bodies (Wager, 1965; Kempe *et al.*, 1970).

All rocks of the intrusion are cut by pegmatites, which are of two types: a simple type consisting of minerals similar to those in the host rock and a complex type with variable grain-size and containing sodium-zirconium-titanium silicates such as kupletskite, låvenite, catapleiite, hjortdahlite and eudialyte. The former type are merely a coarser-grained version of the host rocks, whereas the latter are late-stage melts injected into the already consolidated rocks (Kempe & Deer, 1970).

Kentbrooksite comes from the latter type pegmatitic veins, dykes and sheets up to 2 m in thickness, which cut the pulaskites near the head of Amdrup Fjord. Coarse-grained, grey pulaskites, almost devoid of jointing and sheeting and only cut by a few basic dykes here form steep-sided pinnacles and towers. Anastomosing, relatively flat-lying sheets occur in swarms, largely high up in these mountains such that only a few can be examined *in situ*. However, on the gravel slopes below, which have been formed by crumbling of the coarse-grained pulaskite, many large blocks of this material can be readily found. Typical complex pegmatites are very inhomogeneous, zoned parallel to the walls with both extremely coarse-grained parts rich in alkali feldspar and nepheline, and relatively fine-grained parts, composed of aegirine needles and sugary albite. The Zr- or Ti-rich minerals tend to occur concentrated in pockets often in the more coarse-grained parts of the pegmatites.

Physical and optical properties

Kentbrooksite occurs as anhedral to subhedral aggregates up to 2 cm. It is transparent yellow-brown with a vitreous luster and a white streak. It is brittle with an uneven fracture and no distinct cleavage. The mineral has a hardness of 5–6 (Mohs' scale) and shows no fluorescence. The density, measured by suspension in heavy liquids, is 3.10(4) g/cm^3 which is in good agreement with the calculated density of 3.08 g/cm^3. The mineral is strongly pyroelectric. When cooled in liquid nitrogen, kentbrooksite attracts ashes of a cigar to a degree comparable with tourmaline.

Kentbrooksite is uniaxial negative, $\omega = 1.628(2)$ and $\varepsilon = 1.623(2)$ ($\lambda = 590$ nm); some grains are weakly biaxial. The mineral shows no pleochroism. A Gladstone-Dale calculation gives a compatibility index of –0.005, which is rated as superior (Mandarino, 1981).

Chemical composition

Chemical analyses were performed on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. The experimental setup and conditions for the microprobe analyses are described in detail by Johnsen & Gault (1997). An average of three analyses obtained from three different grains from specimen no. 1971.461 (crystal for crystal-structure refinement not included), with ranges and standards employed are presented in Table 1.

A CHN analysis gave 1.28 H_2O and no CO_2 or N, while optical-emission spectroscopy showed no Li or Be and only ~80 ppm B. All Fe and Mn are calculated as divalent. The divalent state of all Mn has been confirmed by optical-absorption spectroscopy.

The empirical formula, based on 3.77 (Zr + Hf + Nb + Ti) pfu derived by combining the atomic

Table 1. Kentbrooksite: Microprobe analysis and formula content.

Constituent	Wt%	Range	Probe standard	pfu*	
SiO_2	45.34	45.16-45.60	vlasovite	Si	24.60
ZrO_2	11.08	10.90-11.31	vlasovite	Zr	2.93
Na_2O	14.51	14.00-15.32	vlasovite	Na	15.26
CaO	5.62	5.48- 5.81	diopside	Ca	3.27
FeO	1.58	1.47- 1.67	almandine	Fe^{2+}	0.72
MnO	8.01	7.75- 8.28	tephroite	Mn^{2+}	3.68
K_2O	0.43	0.40- 0.48	sanidine	K	0.30
La_2O_3	2.23	2.08- 2.33	LaPO4 (synthetic)	La	0.45
Ce_2O_3	2.44	2.39- 2.52	CePO4 (synthetic)	Ce	0.49
Nd_2O_3	0.69	0.62- 0.76	NdPO4 (synthetic)	Nd	0.13
Y_2O_3	1.46	1.31- 1.57	YIG (Y-Fe-garnet, synth.)	Y	0.42
Nb_2O_5	2.26	2.19- 2.31	manganocolumbite	Nb	0.55
Al_2O_3	0.21	0.14- 0.31	almandine	Al	0.13
SrO	0.49	0.45- 0.53	celestine	Sr	0.15
TiO_2	0.56	0.44- 0.66	rutile	Ti	0.23
HfO_2	0.36	0.19- 0.43	vlasovite	Hf	0.06
MgO	0.06	0.05- 0.07	diopside	Mg	0.05
Cl	0.29	0.24- 0.35	scapolite	Cl	0.27
F	0.88	0.71- 1.19	phlogopite	F	1.51
H_2O#	1.28			H	4.63
O=Cl	-0.07				
O=F	-0.37				
TOTAL	99.34				

Average of 3 analyses obtained from three different grains. * pfu (per formula units) calculated on the basis of 3.77 (Zr + Hf + Nb + Ti) corresponding to the scattering power of the two sites hosting these atoms (see text). # Determined by CHN analysis

proportions of the four elements with the scattering power (epfu) of the two sites hosting these elements (Table 6), is

$$(Na_{14.93}REE_{0.44}Y_{0.42}K_{0.30}Sr_{0.15})_{\Sigma 16.24}(Ca_{3.27}Mn_{1.78}REE_{0.62}Na_{0.33})_{\Sigma 6.00}(Mn_{1.90}Fe_{0.72}Al_{0.13}Mg_{0.05})_{\Sigma 2.80}(Nb_{0.55}Zr_{0.12}Ti_{0.10})_{\Sigma 0.77}Si_{0.60}(Zr_{2.81}Hf_{0.06}Ti_{0.13})_{\Sigma 3}[(Si_3O_9)_2(Si_9O_{27})_2O_2](F_{1.51}Cl_{0.27}OH_{0.22})_{\Sigma 2}\cdot 2.3H_2O.$$

This calculation results in 78.30 anions which is in better agreement with crystal-structure refinement (Table 6) than exactly 78 as is also indicated by the calculated density. The general problems with formula calculation in the eudialyte group is described by Johnsen & Gault (1997). The simplified formula is

$$(Na,REE)_{15}(Ca,REE)_6Mn_3Zr_3NbSi_{25}O_{74}F_2\cdot 2H_2O.$$

Johnsen & Gault (1997) plot microprobe analyses of kentbrooksite and other members of the eudialyte group, and conclude that kentbrooksite represents the ΣNb,REE,Mn,F end-member of a series where the other end-member is the ΣSi,Ca,Fe,Cl component exemplified by eudialyte from the type locality Kangerdluarsuk, Ilimaussaq, SW-Greenland.

Infrared analysis

The infrared spectrum of kentbrooksite was obtained using a Bomem Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling device. The sample analysed was part of the type material. The spectrum (Fig. 1) has sharp peaks in the low-frequency range with considerable splitting of the vibration modes of the $[SiO_4]$ groups, attributable to a structure with more than one crystallographically distinct $[SiO_4]$ group (this was confirmed by the crystal-structure refinement). The absorption bands (cm^{-1}) in kentbrooksite are assigned to the following vibrational modes: 3273 plus shoulder: O-H stretching; broad 1504: H_2O bending; 1016 and 982: symmetric stretching of $[SiO_4]$; 746 and 677: bending of $[SiO_4]$; 485 and 452: could not be unequivocally assigned but there would be contributions from the larger

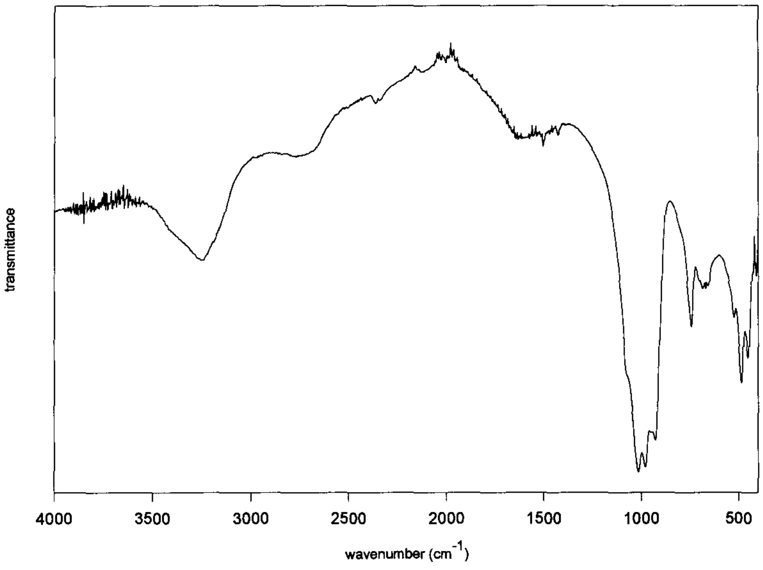

Fig. 1. Infrared spectrum of kentbrooksite.

polyhedra with cation-anion bond distances greater than 2 Å.

X-ray powder diffraction

X-ray powder-diffraction data collected on a Stoe transmission-type diffractometer are shown in Table 2. Cu*K*α_1 radiation was selected by a curved Ge monochromator and data were collected in transmission scan mode on a flat sample. Intensities were measured with a linear position-sensitive detector with an aperture covering a range of 6° in 2θ: step scan of 0.02°; 2θ range 5–90°; total time of data collection was 20 h. Least-squares refinements were performed using the Rietveld programme RIETAN-94 (Izumi, 1993; Kim & Izumi, 1994) based on structural parameters from single-crystal data. The refined unit-cell parameters are shown in Table 3.

Johnsen & Gault (1997) investigate the influence of the chemical composition on the X-ray powder data for ten members of the eudialyte group including kentbrooksite. It is shown that the intensity of some reflections, especially (003), is positively correlated to the ΣNb,REE,Mn,F pfu component. The *a* parameter is negatively correlated to this component while the *c* parameter does not show any simple correlation to any element or combination thereof.

Data collection and crystal-structure refinement

The single crystal of kentbrooksite used for the collection of X-ray diffraction intensity data is a ground sphere of cotype material. Intensity data were collected on a fully automated Nicolet *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. Slightly more than one asymmetric unit of intensity data was collected up to 2θ = 60° using a θ:2θ scan mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Data pertinent to the intensity data collection are given in Table 3.

Reduction of the intensity data and structure determination were done with the SHELXTL (Sheldrick, 1990) package of programs. Structure refinement was done by the SHELXL-93 program (Sheldrick, 1993). Data reduction included a correction for background, scaling, Lorentz, polarization and linear absorption. For the ellipsoidal-absorption correction, 11 intense diffraction maxima in the range 6 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 1.23% before absorption correction to 1.13% after absorption correction. This small improvement in the absorption

Table 2. Kentbrooksite: X-ray powder-diffraction data.

h	k	l	d_{calc}	d_{obs}	I_{obs}
1	0	1	11.362	11.385	43
0	0	3	10.028	10.061	10
0	1	2	9.508	9.528	23
1	1	0	7.084	7.088	41
1	0	4	6.412	6.417	15
0	2	1	6.011	6.014	22
2	0	2	5.681	5.682	30
2	0	5	4.296	4.295	34
1	1	6	4.093	4.091	15
2	1	4	3.948	3.947	22
3	0	3	3.787	3.786	19
1	2	5	3.673	3.672	5
0	1	8	3.596	3.595	5
2	2	0	3.542	3.540	17
0	2	7	3.520	3.522	19
1	3	1	3.382	3.380	37
2	2	3	3.340	3.339	5
3	1	2	3.319	3.320	8
2	0	8	3.206	3.205	22
3	0	6	3.169	3.167	11
2	1	7	3.152	3.152	25
1	1	9	3.023	3.021	16
0	4	2	3.006	3.005	11
3	1	5	2.962	2.961	91
1	2	8	2.921	2.921	7
2	2	6	2.893	2.892	14
4	0	4	2.840	2.839	100
2	3	2	2.767	2.766	5
0	4	5	2.733	2.732	4
0	2	10	2.701	2.700	8
4	1	0	2.678	2.677	6
1	3	7	2.668	2.667	11
3	2	4	2.636	2.635	14
0	3	9	2.588	2.587	22
2	1	10	2.524	2.523	4
0	5	1	2.446	2.445	7
0	4	8	2.377	2.376	6
3	3	0	2.361	2.361	4
2	4	1	2.312	2.311	12
2	3	8	2.254	2.253	4
1	5	2	2.181	2.180	9
4	2	5	2.164	2.163	6
4	0	10	2.148	2.147	15
3	1	11	2.132	2.131	8
0	1	14	2.117	2.116	6
5	1	4	2.114	2.114	8
1	4	9	2.090	2.090	4
3	2	10	2.056	2.055	5
2	4	7	2.041	2.040	4
4	3	1	2.013	2.012	4
0	6	3	2.004	2.003	4
4	2	8	1.974	1.973	16
3	3	9	1.929	1.928	6
6	0	6	1.894	1.893	7
2	4	10	1.837	1.836	4
2	5	6	1.829	1.828	6
4	3	7	1.826	1.825	4
5	1	10	1.778	1.777	5
4	4	0	1.771	1.770	27
4	2	11	1.769	1.768	5
0	4	14	1.760	1.760	8
2	3	14	1.708	1.707	4
6	2	1	1.699	1.699	4
2	6	2	1.691	1.690	5
0	7	5	1.683	1.682	4
4	4	6	1.670	1.699	13
2	4	13	1.638	1.638	4
2	6	5	1.637	1.637	6
4	0	16	1.603	1.603	9
1	6	10	1.589	1.589	4
6	2	7	1.582	1.582	4
3	2	16	1.564	1.564	5

Stoe diffractometer data, transmission scan mode on flat sample.
Cu$K\alpha_I$ radiation. Range: 5-60 2θ. Reflections with $I_{obs} < 4$ not included.
Data produced with RIETAN-94 programme (Izumi, 1993).
Refined parameters: a = 14.1686(2) Å, c = 30.0847(4) Å, V = 5230.3(2) Å^3.

correction is indicative of the degree of spherical perfection for the crystal. The minimum and maximum transmission factor for the linear-absorption correction is 0.789 and 0.908 respectively. Assigning phases to a set of normalized structure factors gave a mean value $|E^2-1|$ of 0.847, indicating a noncentrosymmetry. The structure was solved and refined in the space group $R3m$. The structure refined to $R1$ = 6.5% and $wR2$ = 13.8% with isotropic displacement factors and to $R1$ = 4.1% and $wR2$ = 8.8% with anisotropic displacement factors. The M2a, M3a and F sites, though, were kept isotropic during the final refinement. Refinement with isotropic displacement factors increased to $R1$ = 6.9% and $wR2$ = 14.6% when the structure was inverted, and the Flack

Table 3. Kentbrooksite: Crystal data and structure refinement.

Identification code	Kentbrooksite
Empirical formula	
$(Na_{14.93}REE_{0.44}Y_{0.42}K_{0.30}Sr_{0.15})_{\Sigma 16.24}(Ca_{3.27}Mn_{1.78}REE_{0.62}Na_{0.33})_{\Sigma 6.00}(Mn_{1.90}Fe_{0.72}Al_{0.13}Mg_{0.05})_{\Sigma 2.80}$ $(Nb_{0.55}Zr_{0.12}Ti_{0.10})_{\Sigma 0.77}Si_{0.60}(Zr_{2.81}Hf_{0.06}Ti_{0.13})_{\Sigma 3}[(Si_3O_9)_2(Si_9O_{27})_2O_2](F_{1.51}Cl_{0.27}OH_{0.22})_{\Sigma 2}\cdot 2.3H_2O$	
Formula weight	3238.6
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	*R*3*m*
Unit-cell dimensions	a = 14.199(2) Å
(4 circle data)	c = 30.139(4) Å
Volume	5260(1) $Å^3$
Z	3
Density (calculated)	3.08 g/cm^3
Density (measured)	3.10(4) g/cm^3
Absorption coefficient	3.597 mm^{-1}
F(000)	4745
Crystal size	sphere diameter 0.15 mm
θ range for data collection	1.79 to 30.12 deg.
Index ranges	-17<=h<=10, -10<=k<=17, -42<=l<=42
Reflections collected	2649
Independent reflections	2026 [*R*(int) = 0.0535]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2024 / 0 / 283
Goodness-of-fit on F^2	1.176
Final *R* indices [I>2σ(I)]	$R1 = 0.041$, $wR2 = 0.082$
R indices (all data)	$R1 = 0.047$, $wR2 = 0.088$
Absolute structure parameter	-0.04(4)
Largest diff. peak and hole	0.906 and -1.300 $e.A^{-3}$

parameter went from –0.07(7) to 0.94(8). Both a correction for (secondary isotropic) extinction and including the refinement of a twin fraction according to merohedral twinning resulted in insignificant changes in the refinements and were therefore omitted in the final refinement.

Table 4 reports the final atomic coordinates and isotropic displacement parameters for the kentbrooksite structure and Table 5 lists selected bond lengths. In Table 6 site-scattering values and site populations for selected sites are given. A list of observed and calculated structure factors as well as the anisotropic displacement factors can be obtained from the authors upon request (or through the E.J.M. Editorial Office – Paris).

Description of the structure

Kentbrooksite is a member of the eudialyte group and has the same basic structure characterized by the presence of both three-membered rings, $[Si_3O_9]^{6-}$, and nine-membered rings, $[Si_9O_{27}]^{18-}$ (Golyshev *et al.*, 1971; Giuseppetti *et al.*, 1971). Fig. 2 and 3 show that the structure can be perceived as a sequence of layers parallel to (001). A layer of discrete rings of six M1 octahedra linked together by M2 polyhedra is sandwiched between two basically identical layers of $[Si_3O_9]^{6-}$ and $[Si_9O_{27}]^{18-}$ rings. These 2:1 layers are linked together by a layer of Zr octahedra. The unit cell contains three 2:1 layers related to one another by a triad screw axis. This open structure is filled with Na plus variable amounts of other cations such as K, Ca, REE, Y and Sr, in polyhedra with 6 to 11 coordination.

Along the triad axes reaching from the constriction made by a $[Si_3O_9]^{6-}$ ring up through the sequence of layers to the next similar constriction, oblong cages (~25 Å long) exist in which additional cations, anions and possibly also non-

Table 4. Kentbrooksite: atomic coordinates $(\cdot\ 10^4)$, isotropic displacement parameters $(A^2 \cdot 10^3)$ and bond-valence sum (v.u.).

	x	*y*	*z*	*U*(eq)*	BVS**
M1	5940(1)	9257(1)	1674(1)	16(1)	2.16
M2	8179(2)	-8179(2)	1693(1)	14(1)	1.56
M2a	8437(15)	-8437(21)	1643(11)	30	0.13
M3	0	0	-1281(1)	14(1)	4.35
M4	0	0	0779(2)	11(2)	3.51
M4a	0	0	1167(11)	30	1.22
Na1a#	2223(7)	-2223(7)	0155(6)	33(3)	0.54
Na1b#	2499(33)	-2499(33)	-0006(17)	66(22)	0.61
Na2	4443(3)	-4443(3)	-6787(3)	22(2)	0.65
Na3a#	0890(20)	-0890(20)	2047(12)	70(8)	0.76
Na3b#	1150(23)	-1150(23)	2156(11)	35(10)	0.32
Na4	5670(1)	-5670(1)	1204(1)	16(1)	1.75
Na5	7387(4)	-7387(4)	3139(3)	63(3)	0.91
Zr	4980(1)	-4980(1)	0	9(1)	4.15
Si1	2628(1)	-2628(1)	2489(1)	14(1)	4.10
Si2	4036(2)	-4036(2)	0875(1)	17(1)	4.17
Si3	5394(2)	-5394(2)	2445(1)	11(1)	4.12
Si4	1247(2)	-1247(2)	0920(1)	10(1)	4.11
Si5	9460(2)	6764(2)	2632(1)	9(1)	4.00
Si6	7230(2)	0626(2)	0698(1)	10(1)	4.13
O1	3952(4)	-3952(4)	2451(4)	23(2)	2.01
O2	2217(5)	-2217(5)	2077(4)	32(3)	2.01
O3	2349(5)	-2349(5)	2966(4)	33(3)	1.96
O4	2713(4)	-2713(4)	0923(4)	29(2)	2.01
O5	4472(5)	-4472(5)	1252(4)	35(3)	2.05
O6	0942(5)	-0942(5)	3713(3)	30(3)	2.01
O7	6098(5)	0380(6)	2742(2)	15(1)	2.02
O8	5160(4)	-5160(4)	1959(3)	15(2)	1.87
O9	6044(4)	-6044(4)	2484(3)	23(2)	1.84
O10	7160(7)	9453(6)	0598(2)	25(2)	2.00
O11	1551(4)	-1551(4)	1385(3)	17(2)	1.92
O12	0596(4)	-0596(4)	1004(4)	36(3)	2.21
O13	3020(6)	8979(6)	-6268(2)	22(2)	1.98
O14	7037(6)	0743(6)	1211(2)	15(1)	2.02
O15	8435(4)	-8435(4)	0529(3)	15(2)	2.05
O16	7498(6)	7755(6)	2943(3)	21(2)	1.96
O17	9607(6)	7037(6)	2107(2)	18(1)	1.89
O18	8203(4)	-8203(4)	2780(3)	13(2)	2.21
O19	7299(4)	-7299(4)	1706(3)	21(3)	1.41
O20	0	0	0247(6)	21(5)	1.87
F1a#	0	0	-2626(26)	60	0.26
F1b#	0476(24)	0953(47)	-2592(17)	60	0.42
F2a#	0	0	2397(34)	60	0.41
F2b#	0	0	2097(22)	60	0.73
F2c#	0214(22)	0428(44)	2938(18)	60	0.28
F2d#	0	0	2635(40)	60	0.18
F2e#	0	0	1736(23)	60	0.64

**U*(eq) is defined as one third of the trace of the orthogonalized *U*ij tensor. # split positions.
** Parameters from Brese & O'Keeffe (1991), BVS calculated from apfu values in Table 6.

bonded H_2O may be located (Fig. 4). In the centres, or nearby the centres, of the nine-membered rings and bonded to the three innermost oxygens, M3 and M4 are located. The (Cl, OH, F) anions are accomodated on the triad axis in the silicate layers but outside the rings.

Table 5. Kentbrooksite: selected bond lengths [Å].

M1-O2	2.237(6)	Na1a-Na1b	0.83(8)
M1-O5	2.283(7)	Na1a-O16	2.552(14) x2
M1-O17	2.312(7)	Na1a-O4	2.61(2)
M1-O11	2.338(6)	Na1a-O6	2.633(11) x2
M1-O14	2.349(7)	Na1a-O10	2.68(2) x2
M1-O8	2.426(6)	Na1a-O18	2.72(2)
M2-O14	2.141(7) x2	Na1b-F2c	2.18(10) x2
M2-O17	2.150(7) x2	Na1b-O16	2.378(14) x2
M2-O19	2.162(10)	Na1b-O6	2.48(2) x2
		Na1b-F2c	2.83(11)
M3-O19	1.868(10) x3	Na1b-O4	2.84(4)
M3-O9	2.004(10) x3	Na1b-O18	2.88(4)
		Na1b-F2d	2.92(12)
M4-O20	1.60(2)		
M4-O12	1.610(11) x3	Na2-O15	2.538(12)
		Na2-O1	2.589(13)
Zr-O3	2.049(12)	Na2-O13	2.606(9) x2
Zr-O13	2.070(7) x2	Na2-O7	2.651(10) x2
Zr-O6	2.072(11)	Na2-O3	2.687(7) x2
Zr-O16	2.075(8) x2		
		Na3a-Na3b	0.72(2)
Si1-O3	1.588(12)	Na3a-F2b	2.19(5)
Si1-O2	1.598(11)	Na3a-F2e	2.38(6)
Si1-O1	1.639(5) x2	Na3a-F2a	2.42(6)
		Na3a-O11	2.57(2)
Si2-O5	1.560(11)	Na3a-O17	2.57(2) x2
Si2-O6	1.601(11)	Na3a-F2d	2.81(8)
Si2-O4	1.639(5) x2		
		Na3b-O17	2.405(10) x2
Si3-O8	1.570(9)	Na3b-O11	2.52(3)
Si3-O9	1.600(11)	Na3b-O2	2.63(6)
Si3-O7	1.643(7) x2	Na3b-O16	2.77(3) x2
		Na3b-F2b	2.83(6)
Si4-O11	1.585(9)	Na3b-F2a	2.91(6)
Si4-O12	1.619(11)		
Si4-O10	1.627(8) x2	Na4-O14	2.471(7) x2
		Na4-F1b	2.54(3) x2
Si5-O16	1.594(7)	Na4-O8	2.594(10)
Si5-O17	1.613(7)	Na4-O19	2.622(7) x2
Si5-O7	1.641(7)	Na4-F1a	2.87(4)
Si5-O18	1.651(4)	Na4-O13	2.913(8) x2
		Na4-O5	2.943(13)
Si6-O13	1.583(8)		
Si6-O14	1.592(7)	Na5-O20	2.212(13)
Si6-O15	1.634(4)	Na5-O18	2.273(12)
Si6-O10	1.642(7)	Na5-O9	2.577(11) x2
		Na5-O7	2.998(8) x2

The framework of the eudialyte structure, defined by the silicate rings combined with Zr and M1 octahedra, is essentially centrosymmetric. The centre of symmetry, however, is to a variable extent violated by the remaining part of the structure and in kentbrooksite, the polarity is distinct as demonstrated by the marked pyroelectric property, the *E*-statistics and Flack parameter.

The silicate rings

In kentbrooksite minor differences are seen in the two silicate layers clothing the M1/M2 layer. The tetrahedra in the two distinct three-membered rings tilt towards the *c* axis, the Si1 tetrahedra towards the positive end and the Si2 tetrahedra towards the negative end. A measure of the tilting is the (O2-O2)/(O3-O3) distance-ratio of 1.13 for Si1 tetrahedra and the (O5-O5)/(O6-O6) distance-ratio of 1.21 for Si2 tetrahedra.

The nine-membered rings are composed of three Si atoms (Si3 or Si4) on mirror planes and six Si atoms (Si5 or Si6) on general positions. The shape of the nine-membered ring and thus the distance between the three inner oxygens can be varied by rotation of the Si5/Si6 tetrahedra about the *c* axis and/or a rotation of the Si3/Si4 tetrahedra about a direction perpendicular to the mirror plane. In the nine-membered ring of the upper (or positive) layer, the distance between two of the three innermost oxygens (O9) is 2.65 Å thus matching the edge of a NbO_6 octahedron (M3). In the nine-membered ring of the lower (or negative) layer the distance between the innermost oxygens (O12) is 2.53 Å. The O12 triangle is the base of the M4 tetrahedra occupied by Si (Table 6). Thus the nine-membered ring of the lower layer is strictly speaking not a ring but a $[Si_{10}O_{28}]^{16-}$ platform. In other eudialyte structures, however, it might be possible that M4 accomodate other elements than Si, and it is therefore recommended to keep the term nine-membered ring.

The mean bond lengths (Å) of the Si tetrahedra are (from 1 to 6): ⟨1.616⟩, ⟨1.610⟩, ⟨1.614⟩, ⟨1.615⟩, ⟨1.625⟩ and ⟨1.613⟩, all reasonable values for Al-free tetrahedra. The bond-valence sums (BVS) vary from 4.00 to 4.17 v.u. (Table 4).

Zr and M1 sites

Zr, point symmetry *m*, is accomodated in a nearly regular octahedron combining one three-membered and two nine-membered rings in one layer with a corresponding set of rings in the next layer. The mean bond length within the octahedron is ⟨2.069⟩ Å. During the last refinement cycles the site-occupancy factor was allowed to refine and gave a site-scattering value corresponding to $(Zr_{2.81}Hf_{0.06}Ti_{0.13})_{\Sigma 3}$; BVS = 4.15 v.u.

The M1 site is in a general position and centre of a distorted octahedron with a mean bond length of ⟨2.324⟩ Å. M1 octahedra form edge-sharing six-membered rings cross-linked by M2 poly-

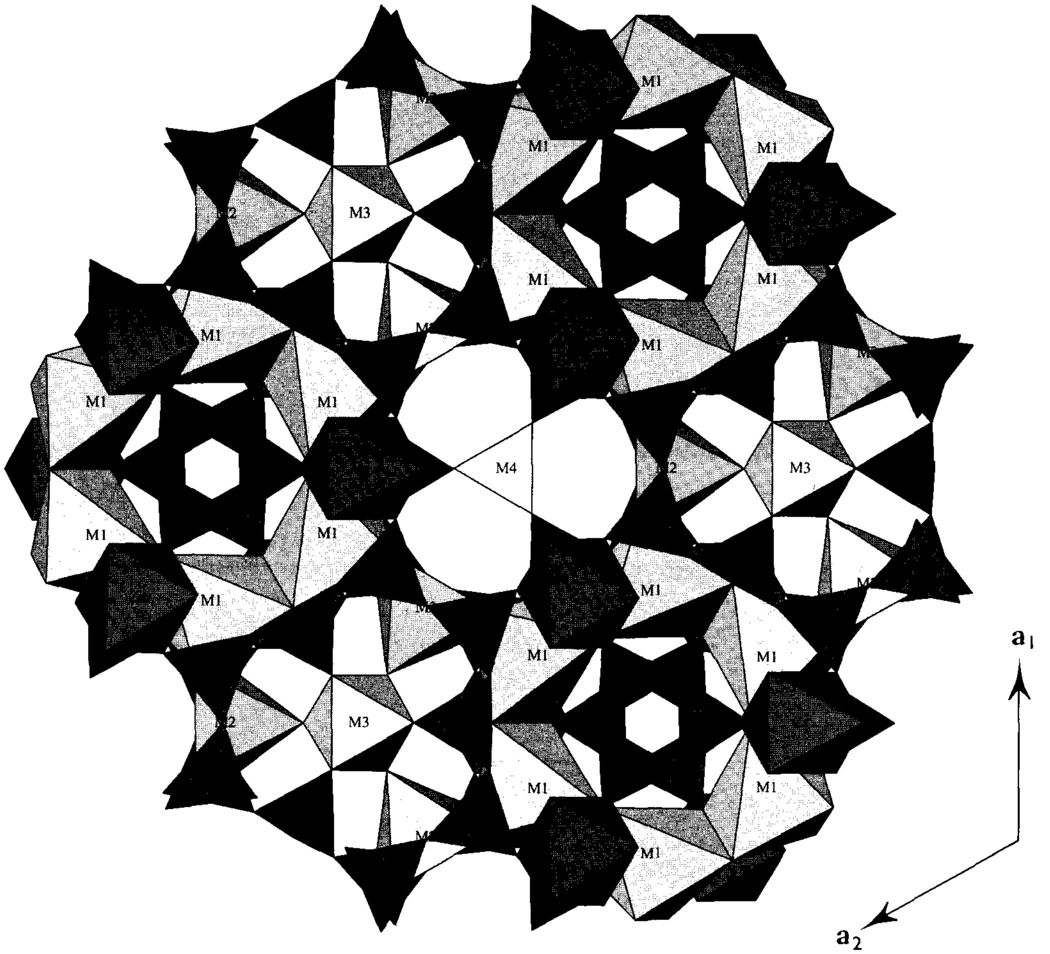

Fig. 2. Polyhedral model of kentbrooksite seen along [001]. Na polyhedra are not shown. ATOMS drawing (Dowty, 1995).

hedra. Ca is generally assigned to this site (Golyshev *et al.*, 1971; Giuseppetti *et al.*, 1971; Rastsvetaeva *et al.*, 1988). In kentbrooksite, however, the microprobe analyses (Table 1) show that there is far from enough Ca to fill this site. The scattering value of this site is relatively high and accordingly Ca must be accompanied by elements with higher scattering power. A site population of $(Ca_{3.27}, Mn^{2+}_{1.78}, REE_{0.62}, Na_{0.33})_{\Sigma 6}$ fits the scattering value and gives a reasonable BVS of 2.16 v.u.

M2 site

M2, point symmetry *m*, is a key site in kentbrooksite. In classical eudialytes, *i.e.* Ca- and Fe-rich eudialytes, M2 is dominated by Fe and coordinated only by four oxygens in an almost planar arrangement (Golyshev *et al.*, 1971; Giuseppetti *et al.*, 1971; Rastsvetaeva *et al.*, 1988; Pol'shin *et al.*, 1991). Rastsvetaeva *et al.* (1990) also mention Fe in five-fold and six-fold coordination. M2 in kentbrooksite is five-fold coordinated in a distorted square pyramid with a mean bond length of ⟨2.149⟩ Å. Four of the oxygens, O14 (x2) and O17 (x2), are shared with the M1 octahedra while the fifth oxygen, O19, is shared with the M3 octahedron (Fig. 5).

It is evident from the microprobe analysis in Table 1 that there is not sufficient Fe to dominate this site in kentbrooksite, while it is highly likely

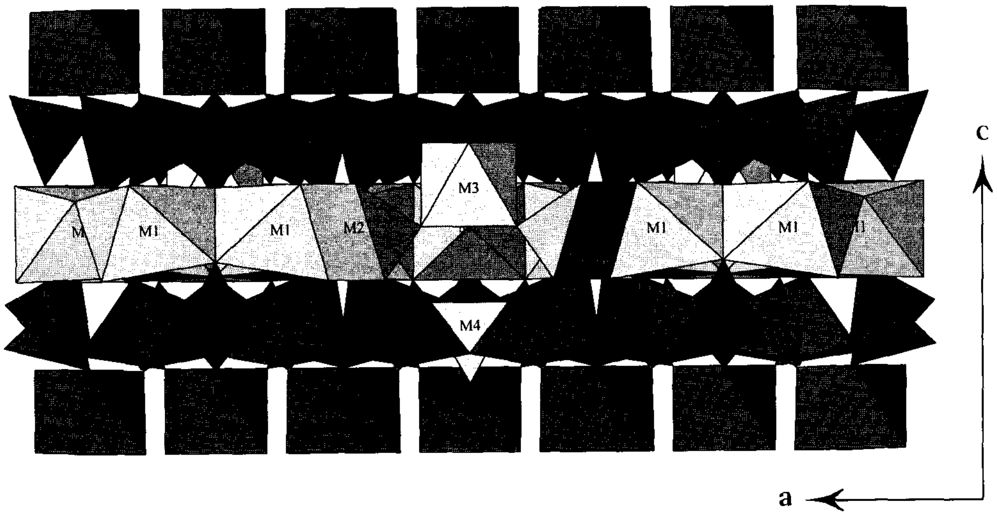

Fig. 3. Polyhedral model of kentbrooksite seen along [210]. Na polyhedra are not shown.

Table 6. Kentbrooksite: site-scattering values (epfu) and site populations (apfu) for selected sites.

Site	MAN*	N**	epfu	apfu
M1	24.91	6	149.46	3.27 Ca + 1.78 Mn^{2+} + 0.62 REE + 0.33 Na
M2	21.13	3	63.40	1.90 Mn^{2+} + 0.52 Fe^{2+} + 0.13 Al + 0.05 Mg + 0.40 □
M2a	2.35	3	7.05	0.27 Fe^{2+} + 2.73 □
M3	29.73	1	29.73	0.55 Nb + 0.10 Ti + 0.12 Zr + 0.23 □
M4	11.78	1	11.78	0.84 Si + 0.16 □
M4a	3.60	1	3.60	0.26 Si + 0.74 □
Zr	39.85	3	119.56	2.81 Zr + 0.06 Hf + 0.13 Ti
Na1#	12.54	3	37.61	12.46 Na
Na2	8.50	3	25.51	
Na3#	13.84	3	41.53	
Na5	10.81	3	32.43	
Na4	23.89	3	71.67	0.44 REE + 0.42 Y + 0.30 K + 0.15 Sr + 1.69 Na
O19	7.08	3	21.25	2.66 O + 0.34 □
O20	7.42	1	7.42	0.93 O
F1#	3.09	1	3.09	1.51 F + 0.27 Cl + 1.17 OH
	2.06	3	6.19	
F2#	13.83	1	13.83	
	1.88	3	5.63	

*MAN = mean atomic number, **N = number of equivalent sites in the structural formula.
Site-occupancy factors for Si1-Si6 and O1-O18 were fixed to unity.
split positions.

that Mn is the dominating element. Johnsen & Gault (1997) show that in 36 eudialyte analyses the content of Mn is negatively correlated to that of Fe as well as that of Ca, strongly indicating that Mn can enter both M1 and M2. The site scattering value for M2 is shown in Table 6 and so is the site population with Mn as the dominating atom giving a BVS of 1.56. The calculation is based on divalent Mn and Fe. The suggested assignment results in a vacancy that is in good agreement with

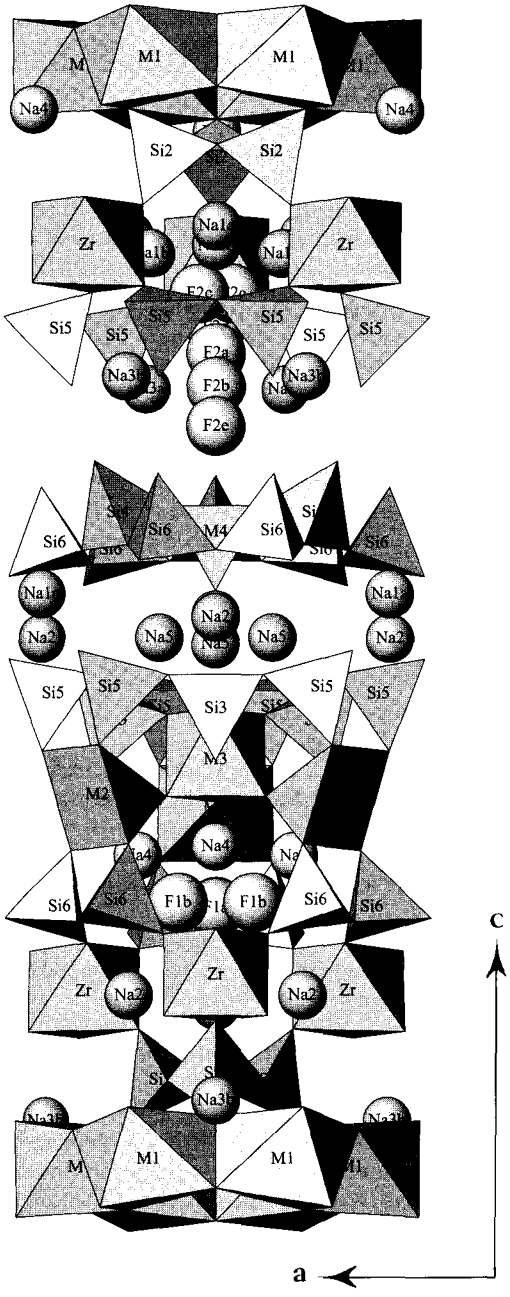

Fig. 4. Oblique view of a cage along the triad axis, from a three-membered ring (Si1) to the next ring (Si2) about 25 Å up.

the refined site occupancy factor of O19 which again is supported by the site population of M3.

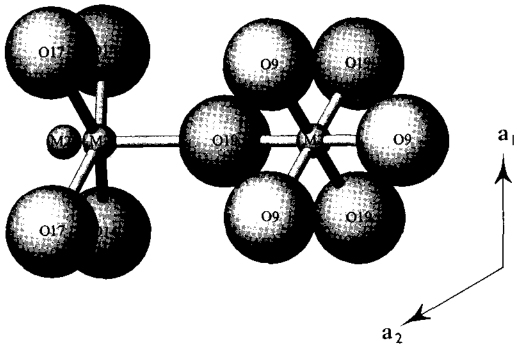

Fig. 5. Stick and ball model of the coordination of the M2, M2a and M3 sites.

A small maximum, 0.65 Å away from M2 and almost in the centre of the quadrangle made by the O14 and O17 oxygens, is not accounted for by the anisotropic displacement factors of M2. This maximum, labelled M2a (Fig. 5), corresponds closely to the four-fold coordinated Fe site found in some eudialyte structures. As seen in Table 6 it is suggested that the M2a site is hosting a small amount of Fe.

M3 and M4 sites

The M3 site has point symmetry $3m$ and is coordinated by six oxygens, the three inner oxygens (O9) from the nine-membered ring of the upper layer and three O19 shared with the M2 polyhedra. Mean bond length: ⟨1.936⟩ Å. This site corresponds to the Zr(2) site in the paper of Giuseppetti *et al.* (1971). In kentbrooksite, M3 is dominated by Nb with a vacancy of 0.23 pfu, a vacancy comparable to that of the O19 and M2 sites (Table 6).

The M4 site with point symmetry $3m$ is located in the centre of the nine-membered ring of the lower layer and coordinated by the three inner oxygens (O12) and one oxygen (O20) also on the triad axis. The mean bond length is ⟨1.61⟩ Å. Si and 16% vacancy is assigned to this site giving a BVS of 3.51. Minor disorder is seen at this site. A small maximum, labelled M4a, is located on the triad axis 1.17 Å away from M4 towards the positive end of the axis. This corresponds to M4a as the centre of a tetrahedron pointing in the opposite direction than the M4 tetrahedron. The apical ligand of M4a tetrahedron is F2e with a distance of 1.71 Å.

Na sites

In kentbrooksite there are five Na sites, all with point symmetry *m*. Two of them, Na1 and Na3, are best modelled as split positions. The location of the Na sites are shown in Fig. 4 and their coordination numbers and distances can be read from Table 5.

The Na4 site has a distinctly higher site-scattering value than the other Na sites. This is a clear indication that the small amounts of larger, heavy cations found by microprobe analysis (K,Y, Sr and partly REE) are concentrated at this site (Table 6). The site-scattering values for the other four Na sites vary from 25.51 to 41.53 epfu., *i.e.* from a little too low for full occupancy of Na to a little too high for full occupancy of Na alone. If these minor anomalies are neglected, these four sites accomodate 12.46 Na apfu which together with 1.69 Na apfu from Na4 and 0.33 Na apfu from M1 adds to a total of 14.48 Na apfu. When compared with the number found from microprobe analysis it is seen that there is an excess of 0.78 Na apfu (8.58 epfu). 8.58 is ~0.5% of the total number of epfu in the structure. Inspection of the site populations in Table 6 shows that all sites are satisfactorily accounted for regarding site populations with the possible exception of F2. This site is extremely disordered, and adding the scattering values for all F2 sites, F2a to F2e, give a total that cannot be accounted for by one (F,Cl,OH) only. The surplus is assigned to additional OH in Table 6, but it cannot be excluded that Na is present in these disordered sites as well.

F sites

The two F sites have ideally point symmetry 3*m*. However, both sites are disordered along the triad axes and along the mirror planes. F2 is extremely disordered as ligands to the Na1 and Na3 split positions. During refinement, F2 was best described as five split positions with fixed isotropic displacement factors and refinable atomic coordinates. The result is shown in Fig. 4 as the sequence from below and up: F2e, F2b, F2a, F2d (hidden) and F2c with point symmetry *m*. The F2e-F2c distance is 3.63 Å. The site population of the F sites are seen in Table 6 and includes additional OH or Na as suggested in the paragraph on the Na sites.

Conclusion

The major differences between kentbrooksite and other members of the eudialyte group are best exposed when kentbrooksite is compared with eudialyte from the type locality Ilímaussaq, South Greenland (Giuseppetti *et al.*, 1971), as these two members represent end-members in a solid solution series embracing nearly all members of the group (Johnsen & Gault, 1997):

(i) In kentbrooksite M2 is dominated by $^{[5]}$Mn and in eudialyte by $^{[4]}$Fe.

(ii) One of the two sites in the centres of the nine-membered rings (M3) is occupied by $^{[6]}$Nb in kentbrooksite while it is believed to be $^{[4]}$Si in both these sites (M4) in eudialyte.

(iii) Kentbrooksite contains a relatively large amount of REE, partly substituting for Ca in M1 partly for Na in Na4 when compared with eudialyte.

(iv) O19 is a key site in this group as the fifth ligand in $^{[5]}$M2, the ligand completing the M3 octahedron and as part of the coordination for the Na4 site. O19 is almost fully occupied in kentbrooksite, while the role of O19 is not well known in eudialyte.

(v) The anion site(s) on the triad axes outside the silicate rings are dominated by F in kentbrooksite and by Cl in eudialyte.

(vi) The non-centrosymmetry is distinct in kentbrooksite and is presumed primarily to be a result of the coupled (Nb$\rightleftarrows$Si)-(Mn$\rightleftarrows$Fe) substitution. The degree of non-centrosymmetry in other members of the eudialyte group is not well known yet.

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