Minerals of the eudialyte group from the Sagåsen larvikite quarry, Porsgrunn, Norway

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Introduction

Eudialyte, a Na-rich zirconosilicate with varying amounts of Ca, Fe, Mn, REE, Nb, K, Y, Ti, Cl and F, was first described from the Ilimaussaq alkaline complex, South Greenland by Stromeyer (1819). Since then, the mineral has been described from many other alkaline deposits, and is a characteristic mineral in agpaitic nepheline syenites and their associated pegmatites. In recent years, eudialyte (*senso lato*) has been the subject of extensive studies. The broad compositional variations and new insight into the crystal chemistry of the mineral group resulted in the definition of several new species by the Eudialyte Nomenclature Subcommittee under the Commission on New Minerals and Mineral Names of the International Mineralogical Association (Johnsen et al. 2003b).

Brown eudialyte (*s. l.*) is a common constituent of the agpaitic pegmatites in the Langesundsfjord district in the western part of the Larvik plutonic complex (Brøgger 1890). Recent chemical analyses of the mineral have shown that some localities contain ferrokentbrooksite (Johnsen et al. 2003a). Other localities hold eudialyte (*senso stricto*). Ferrokentbrooksite is the ferrous-iron-dominant analogue of kentbrooksite with Fe as the predominant element replacing Mn. Kentbrooksite is the Mn-REE-Nb-F end member in a solid solution series between eudialyte (*s. s.*) and ferrokentbrooksite, with an extension to oneillite (Johnsen et al. 1998, Johnsen et al. 1999, Johnsen et al. 2003a), as well as to carbokentbrooksite and zirsilite-(Ce) (Khomyakov et al. 2003). Carbokentbrooksite has a significant content of carbonate and Na > REE for the N4 site, while zirsilite-(Ce) has REE > Na (with Ce predominant) for the N4 site.

In the autumn of 2003 a huge pegmatite dike was uncovered in the Sagåsen larvikite quarry at Mørje, Porsgrunn. Throughout the winter and spring of 2004, an abundance of yellow and orange, rarely brown, minerals of the eudialyte group was found. Because of the conspicuous variation in colour of these eudialyte group minerals, we felt it would prove interesting to confirm their correct identity. This paper reports the chemical composition and an interpretation of the results in view of the new species of the eudialyte group.

Occurrence

The Sagåsen larvikite quarry is situated at the southwestern part of the Sagåsen hill, at the bottom of the Mørjefjord in Porsgrunn community, Telemark county. The location is practically the same as the formerly famous Saga I quarry, but lower in the hill-side. The well-known larvikite quarries at Tvedalen are 1-3 km to the south-east, and in Vestfold county. The pegmatite dike is generally 2.5 m in thickness, with a gentle fall (approximately 10°) towards SW. The thickness narrows in the south-western part of the dike, and eventually pinches out. The dike stretches the whole width of the quarry, about 50 m in 2004, but has not yet been completely uncovered towards the south. The whole of its extent is therefore not known. The pegmatite is terminated towards a tectonic zone in the northern part of the quarry.

The pegmatite is mainly composed of from microcline, sodalite, nepheline, biotite, amphibole, aegirine and *spreustein* (natrolite pseudomorphs after nepheline and sodalite). The major mineral individuals are between 10-50 cm in size. The northern part of the dike comprises nepheline syenite pegmatite with sodalite practically absent, while the southern part is dominated by large individuals of dark greyish green sodalite. Leucophanite, astrophyllite and the eudialyte group minerals are mainly confined to the sodalite rich part of the pegmatite. In the northern wall of the quarry, the pegmatite was exposed showing a central core, approximately 50 cm thick and several metres long, of white saccharoidal albite with abundant dark green aegirine crystals. Most of the rare minerals are confined to nests located in the interstices between the main minerals of the pegmatite. Parts of the pegmatite have strongly suffered hydrothermal alteration, with formation of typical late stage minerals like fluorapophyllite, eudidymite, epididymite, behoite, berborite, ancylite-(Ce), parisite-(Ce) and bastnäsite-(Ce). Nearly 70 different mineral species are identified from the pegmatite (Table 1). In addition, a few unknown minerals remain to be identified.

The eudialyte group minerals

The eudialyte group minerals are among the youngest minerals crystallised during the magmatic stage of the pegmatite formation. In the Sagåsen pegmatite they occur as up to fist-size masses filling interstices between feldspar individuals. The masses of eudialyte group minerals generally have an outer rim, varying from a mm to a cm thick, composed of finely crystalline aegirine, zircon, pyrochlore and fluorite. These minerals also occur in veins crisscrossing the masses of eudialyte minerals. There has also been observed eudialyte masses, which are completely altered into a mixture of aegirine, zircon, astrophyllite, pyrochlore and fluorite. Rosenbuschite and tadzhikite have been observed embedded in the eudialyte minerals.

The colours of the eudialyte group minerals in the Sagåsen pegmatite are usually in different shades of orange and yellow, but transitions to brownish yellow and brown have been observed. Especially the larger masses may show considerable variation of colours within the same sample.

Chemical composition

Two samples of the eudialyte group minerals showing the most extreme colours (yellow and brown) were chosen for complete chemical analysis. The analyses on the main and minor elements, except Ti, Al, Fe and the rare earth elements, were done in wavelength-dispersive mode on a JEOL 733 electron microprobe using the same analytical conditions and calibration standards as reported in the description of ferrokentbrooksite (Johnsen et al. 2003a). Carefully handpicked material was decomposed by nitric and sulphuric acids, and the concentrations of Ti, Al and the REE were determined by PerkinElmer Elan DRC-II ICP-MS, while Fe was determined by AAS. The amount of CO_2 was determined by LECO CS-200 elemental analyser. The results are shown in Table 2.

Infrared spectra of the yellow and brown eudialyte group minerals were obtained on ground material pressed into a KBr pellet and recorded using a PerkinElmer S-2000 FT-IR spectrometer in the range 4000-450 cm^{-1}. The broad absorption bands at approximately 3480 and 1640 cm^{-1} are assigned to the [OH] stretching mode and the [H_2O] bending mode, respectively. The bands between 1100 and 450 cm^{-1} are due to the stretching and bending vibrations in the [SiO_4] group. The two bands at 1425 and 1506 cm^{-1} are attributed to the stretching mode of a [CO_3] group. The spectra are similar to each other, except that the bands due to [CO_3] are weaker in the brown sample compared to the yellow sample, reflecting the different concentrations of carbonate in the two samples. The infrared spectra are rather similar to that of *xanthopite* reported by Larsen et al. (2005), except that the latter mineral has stronger carbonate bands.

X-ray crystallography

X-ray powder diffraction data on the eudialyte group minerals were obtained using a Philips X'pert diffractometer (Cu$K\alpha_1$ radiation, λ = 1.54056 Å). Si (NBS 640a) was used as internal standard. Indexing and least squares refinement were done by the program CELREF, and the unit cell dimensions found on the yellow zirsilite-(Ce) are a = 14.2628(72) Å, c = 30.0631(2) Å, and V = 5296 Å^3.

Discussion

According to Johnsen et al. (2003b), the general formula of the eudialyte group minerals is $[N(1)N(2)N(3)N(4)N(5)]_3[M(1a)M(1b)]_3M(2)_3M(3)M(4)Z_3[Si_{24}O_{72}]O'_4X_2$, where X = Cl, F, OH or CO_3. This large number of separate structural sites gives theoretically a potential for thousands of different species. At present there are about twenty species within the eudialyte group. The complexity of the crystal structure makes it difficult to construct an accurate formula without structural information. However, a procedure for determining an empirical formula on the basis of chemical data has been given by Johnsen & Grice (1999). Following this procedure, the yellow eudialyte mineral from Sagåsen is zirsilite-(Ce), which is a new species in the list of minerals from the pegmatites within the Larvik plutonic complex. The brown mineral is ferrokentbrooksite. The empirical formulae are given at the bottom of Table 2. Despite the fact that the two minerals contain significant amounts of carbonate, the Eudialyte Nomenclature Subcommittee recommended that the X sites be ignored in the nomenclature (Johnsen et al. 2003b).

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Table 1. Minerals identified from the Sagåsen pegmatite (Spring 2005).

Mineral	**Abundance**
aegirine	xxxx
albite	xxxx
analcime	xxx
ancylite-(Ce)	xx
arsenopyrite	xx
astrophyllite	xxx
bastnäsite-(Ce)	x
behoite	x
berborite	x
biotite (annite)	xxxx
boehmite	xx
britholite-(Ce)	x
calcite	x
cancrinite	xxx
carbonat-fluorapatite	x
catapleiite	x
chiavennite	x
chlorite	xx
epididymite	x
eudidymite	x
ferrokentbrooksite	xxx
fluorapophyllite	x
fluorite	xxx
galena	xx
gibbsite	x
goethite	x
gonnardite	x
gonyerite	x
hambergite	x
helvite	x
hematite	x
heulandite-(Ca)	x
hydrocerussite	x
ilmenite	x

Mineral	**Abundance**
kentbrooksite	x
låvenite	x
leucophanite	xxx
löllingite	x
microcline	xxxx
molybdenite	xx
monazite-(Ce)	x
montmorillonite	x
mosandrite	x
natrolite	xxxx
neotocite	xx
nepheline	xxxx
nordstrandite	x
parisitt-(Ce)	x
pectolite	x
polylithionite	x
powellite	x
pyrite	x
pyrochlore	xxx
pyrophanite	x
pyrrhotite	x
rhodochrosite	x
rosenbuschite	x
sodalite	xxxx
sphalerite	xx
tadzhikite-(Ce)	x
thomsonite	x
thorite	xx
tritomite-(Ce)	xx
tvedalite	x
wöhlerite	xxx
zircon	xxx
zirsilitt-(Ce)	xxx

xxxx major mineral
xxx = subordinant mineral
xx = rare
x = very rare

Table 2. Chemical composition (in oxide weight- %) of zirsilite-(Ce) and ferrokentbrooksite from the Sagåsen quarry, and corresponding number of atoms per formula unit based on 29(Si+Al+Zr+Ti+Hf+Nb+Ta).

Zirsilite-(Ce) (yellow)			
SiO_2	43.89	Si	24.867
TiO_2	0.47	Ti	0.200
ZrO_2	10.43	Zr	2.881
HfO_2	0.48	Hf	0.078
Al_2O_3	0.17	Al	0.114
Y_2O_3	1.11	Y	0.335
La_2O_3	2.39	La	0.499
Ce_2O_3	3.96	Ce	0.821
Pr_2O_3	0.30	Pr	0.062
Nd_2O_3	0.76	Nd	0.154
Sm_2O_3	0.10	Sm	0.020
Eu_2O_3	0.01	Eu	0.000
Gd_2O_3	0.13	Gd	0.024
Tb_2O_3	0.03	Tb	0.006
Dy_2O_3	0.18	Dy	0.033
Ho_2O_3	0.05	Ho	0.009
Er_2O_3	0.17	Er	0.030
Tm_2O_3	0.03	Tm	0.005
Yb_2O_3	0.22	Yb	0.038
Lu_2O_3	0.03	Lu	0.005
Nb_2O_5	3.23	Nb	0.827
Ta_2O_5	0.21	Ta	0.032
FeO	2.73	Fe	1.294
MnO	6.36	Mn	3.052
MgO	0.00	Mg	0.000
CaO	7.84	Ca	4.759
SrO	0.11	Sr	0.036
Na_2O	10.83	Na	11.897
K_2O	0.21	K	0.152
F	0.00	F	0.000
Cl	0.80	Cl	0.768
H_2O*	0.86	H	3.232
CO_2	0.99	C	0.766
-O≡F	0.00		
-O≡Cl	0.13		
Total	98.94		

Ferrokentbrooksite (brown)			
SiO_2	46.03	Si	25.098
TiO_2	0.63	Ti	0.258
ZrO_2	11.25	Zr	2.991
HfO_2	0.36	Hf	0.056
Al_2O_3	0.12	Al	0.077
Y_2O_3	0.75	Y	0.218
La_2O_3	0.99	La	0.199
Ce_2O_3	1.32	Ce	0.263
Pr_2O_3	0.09	Pr	0.018
Nd_2O_3	0.24	Nd	0.047
Sm_2O_3	0.04	Sm	0.008
Eu_2O_3	0.01	Eu	0.000
Gd_2O_3	0.06	Gd	0.011
Tb_2O_3	0.01	Tb	0.002
Dy_2O_3	0.09	Dy	0.016
Ho_2O_3	0.02	Ho	0.003
Er_2O_3	0.09	Er	0.015
Tm_2O_3	0.01	Tm	0.002
Yb_2O_3	0.09	Yb	0.015
Lu_2O_3	0.01	Lu	0.002
Nb_2O_5	2.04	Nb	0.503
Ta_2O_5	0.11	Ta	0.016
FeO	4.90	Fe	2.234
MnO	3.41	Mn	1.575
MgO	0.00	Mg	0.000
CaO	9.49	Ca	5.544
SrO	0.17	Sr	0.054
Na_2O	12.12	Na	12.813
K_2O	0.41	K	0.285
F	0.00	F	0.000
Cl	1.16	Cl	1.072
H_2O*	0.81	H	2.928
CO_2	0.48	C	0.357
-O≡F	0.00		
-O≡Cl	0.26		
Total	97.04		

* Determined by stoichiometry, calculated assuming 2(OH+Cl).

Empirical formula for zirsilite-(Ce) (yellow):
$(Na_{11.90}K_{0.10})_{\Sigma 12.00}(Ce_{0.82}La_{0.50}Nd_{0.15}Pr_{0.06}Yb_{0.04}Dy_{0.03}Er_{0.03}Sm_{0.02}Gd_{0.02}Tb_{0.01}Ho_{0.01}Tm_{0.01}$
$Lu_{0.01}Y_{0.33}Ca_{0.10}K_{0.05}Sr_{0.04})_{\Sigma 2.23}(Ca_{4.66}Mn_{1.34})_{\Sigma 6.00}(Mn_{1.71}Fe_{1.29})_{\Sigma 3.00}(Zr_{2.88}Hf_{0.08}Ti_{0.06})_{\Sigma 3.02}$
$(Nb_{0.83}Ti_{0.14}Ta_{0.03})_{\Sigma 1.00}(Si_{24.87}Al_{0.11})_{\Sigma 24.98}O_{73}[O,OH,(CO_3)_{0.77}Cl_{0.77}]_{\Sigma 5.00}\cdot H_2O$

Empirical formula for ferrokentbrooksite (brown):
$(Na_{12.81}Ce_{0.26}La_{0.20}Nd_{0.05}Pr_{0.02}Dy_{0.02}Sm_{0.01}Gd_{0.01}Er_{0.01}Yb_{0.01}Ca_{0.34}K_{0.29}Y_{0.22}Sr_{0.05})_{\Sigma 14.30}$
$(Ca_{5.20}Mn_{0.80})_{\Sigma 6.00}(Fe_{2.23}Mn_{0.77})_{\Sigma 3.00}(Zr_{2.99}Hf_{0.06})_{\Sigma 3.05}(Nb_{0.50}Ti_{0.26}Si_{0.18}Ta_{0.02})_{\Sigma 0.96}$
$(Si_{24.92}Al_{0.08})_{\Sigma 25.00}O_{73}[O,OH,(CO_3)_{0.36}Cl_{1.07}]_{\Sigma 5.00}\cdot H_2O$