Optimising the REE-Zr-Nb potential of eudialyte and its alteration products from the Ilímaussaq complex, South Greenland

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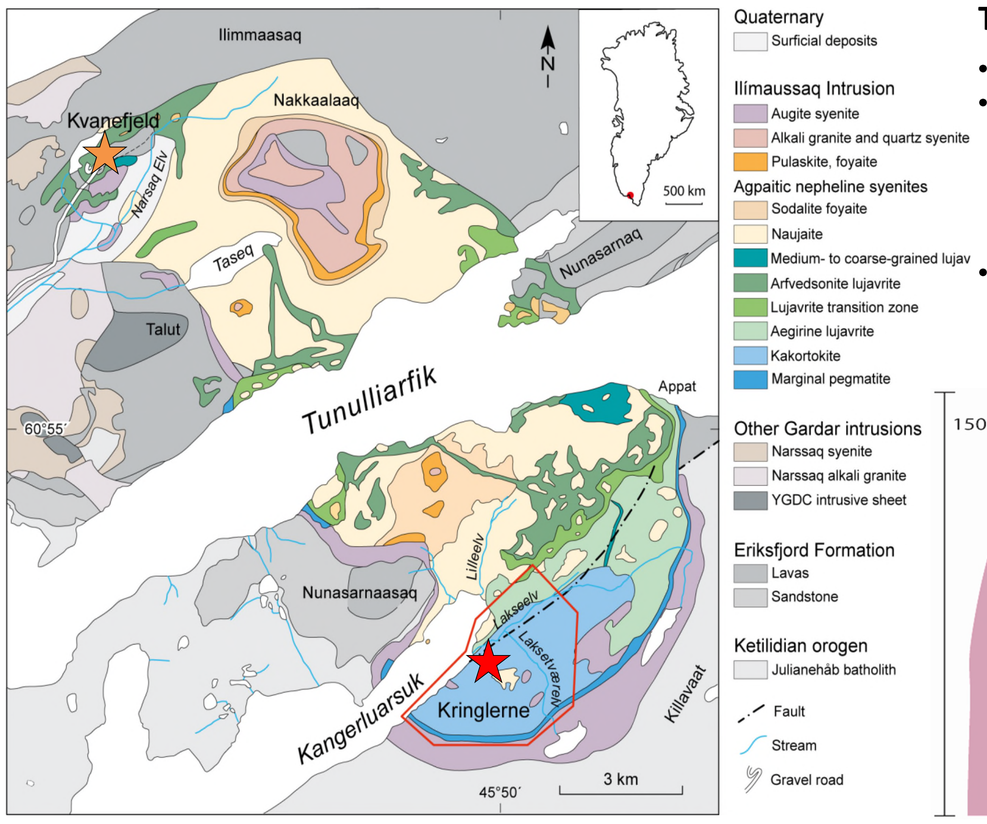
Introduction

Eudialyte-group minerals are complex alkali-zirconosilicates that crystallise in peralkaline igneous rocks known as **agpaitic nepheline syenites**[1]. They provide important unexploited resources for rare earth elements (REE) and other critical metals such as Zr, Nb and Ta[1, 2,3,4]. Europe hosts significant eudialyte deposits in rift-related alkaline intrusions, e.g. Ilímaussaq (Greenland), Lovozero and Khibiny (Russia) and Norra Kärr (Sweden)[5]. With relatively high contents of the more critical heavy REE, and low U and Th contents compared to conventionally exploited REE phases, eudialyte is particularly attractive as a more sustainable source of REE.

Eudialyte crystallises in highly persodic and volatile-rich (Cl, F, OH) conditions, and is commonly replaced by fine-intergrowths of hydrous secondary REE, Zr, Nb phases during late-magmatic fluid activity[6,7]. As this may influence metal recovery, we studied eudialyte alteration assemblages in the world's largest eudialyte deposit, hosted in layered floor cumulates of the Ilímaussaq complex[1,8]. Based on detailed petrographic observations, we performed semi-quantitative mass balance calculations and chemographic modelling to constrain fluid evolution and HFSE and REE mobility. Future work will employ µ-XRF, µ-XRD, XAFS and TEM to study REE distribution and coordination in fresh and altered eudialyte from various EU localities.



The Ilímaussaq complex

- Part of the Mesoproterozoic Gardar province
- Dominant rock type **agpaitic nepheline syenites**
  - Peralkaline, molar (Na+K)/Al > 1.2
  - Contain complex Na-Zr-Ti phases, e.g. eudialyte, steenstrupine and rinkite, instead of zircon, titanite or ilmenite
- Hosts two world-class crititical metal deposits:
  - ★ Kvanefjeld (U, Th, REE, Zn)
  - ★ Kringlerne (Zr, REE, Nb, Ta)

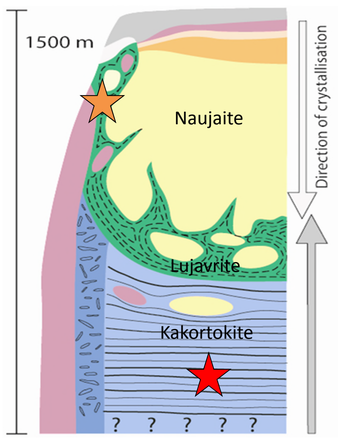
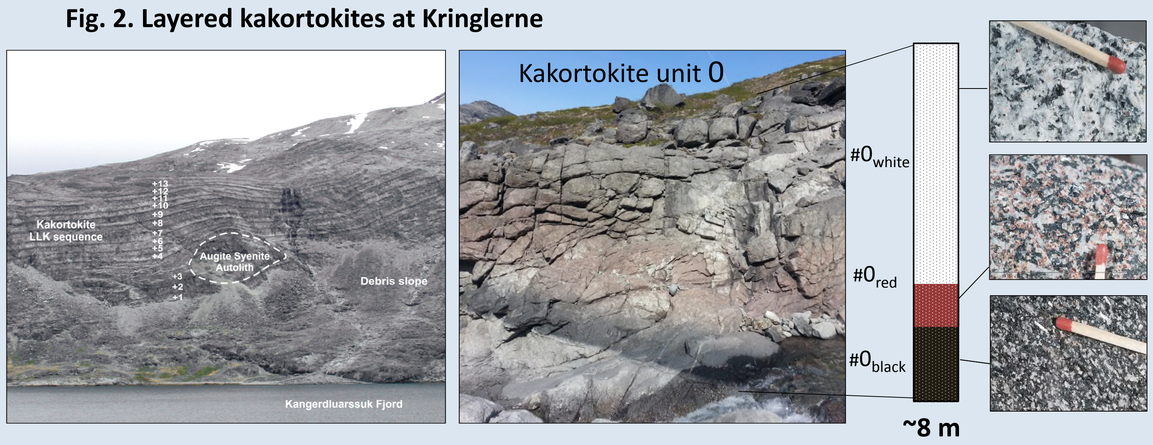


Fig. 1. Geological map[9] and cross section of Ilimaussaq

Fig. 3. Eudialyte crystal in nepheline, c. 1 mm

Fig. 2. Layered kakortokites at Kringlerne



Kringlerne eudialyte deposit

- Covers rhythmically layered floor cumulates, e.g. kakortokites, and related rocks in southern half of the complex (Fig. 1)
- Kakortokites are alternating layers of black, red and white nepheline syenites, respectively enriched in arfvedsonite, eudialyte, nepheline plus alkali feldspar (Figs. 2, 3)
- Over 29 three-layered units are exposed, numbered from -11 to +17
- The lower boundary of the deposit is below current exposure[8]

Licence holder: TANBREEZ Mining Greenland A/S
Inferred resources: 4.3 billion tons @ 1.8 % ZrO_2, 0.2% Nb_2O_5, 0.5 % TREO (of which 27% HREE and 73% LREE, Fig. 4)[8]
Primary ore mineral: eudialyte
Accessory ore minerals: nacareniobsite-(Ce), rinkite, catapleiite

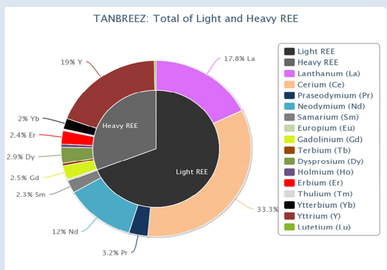


Fig. 4. Eudialyte REE distribution source: TANBREEZ

Eudialyte alteration studies

Petrographic studies reveal that up to 30% of the primary magmatic eudialyte experienced minor to complete pseudomorphic replacement by complex intergrowths of secondary Zr, REE, Fe and Nb phases (Fig. 5). Three alteration assemblages are identified, typically dominated by the Zr-phase catapleiite, and occasionally zircon or gittinsite (Fig. 5). Rare earths and Nb are hosted in nacareniobsite-(Ce), fersmite and finely disseminated allanite-(Ce), britholite-(Ce), monazite-(Ce), and an unknown group of Ca-Ba-REE-phospho-sillicates (e.g. A1[6], Fig. 6). The latter are most abundant, but too small (>10 µm) for quantitative analyses using common micro-analytical techniques (EMP, XRD, LA-ICPMS).

Fluid evolution and HFSE-REE mobility

- Mass balance calculations for the catapleiite-type alteration indicate that Zr, Fe, Nb and REE are retained in the pseudomorph assemblage
- H_2O, F, Al and P are added to the assemblage, while Cl, Na and Si are released to the fluid
- HFSE and REE immobility is linked to high pH of the late-magmatic fluids
- Gittinsite alteration is inferred to relate to interaction with externally derived Ca-Sr-F rich fluids. A relative abundance of HREE phases in the gittinsite paragenesis, e.g. fergusonite-(Y) and unknown Ca-Y-silicates, suggest remobilisation of LREE by lower pH fluids

Extraction and processing

- Eudialyte is magnetically concentrated on site and shipped for further processing [8]
- Hydrometallurgical processing studies of eudialyte concentrates are currently solving issues with Si-gel and formation of acid resistant phases that partially hinder metal recovery[10,11]
- This, in addition to relatively low total REE contents, requires high purity concentrates to ensure sufficient recovery [10,11,12]
- Above studies underline the importance of further mineralogical characterisation

Fig. 5a. Magmatic eudialyte
Preserved euhedral, sector-zoned eudialyte crystals

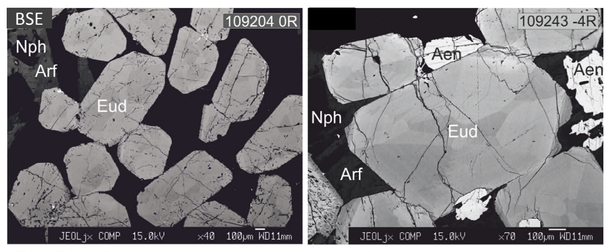


Fig 5b. Alteration assemblage I
Pseudomorphs after eudialyte dominated by catapleiite

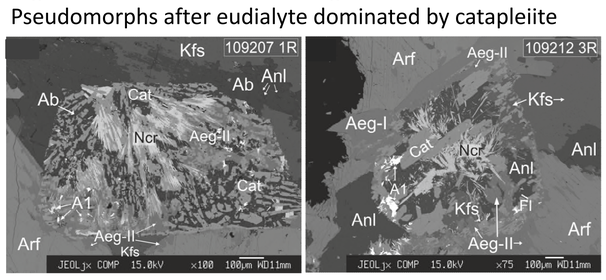


Fig. 5c. Alteration assemblage II
Pseudomorph after eudialyte dominated by gittinsite

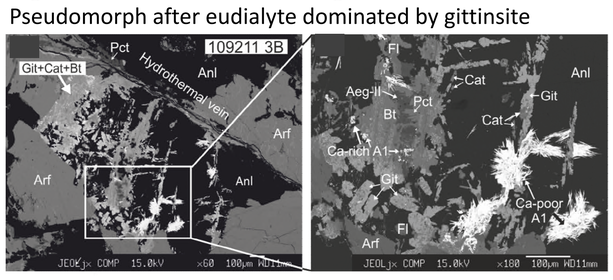
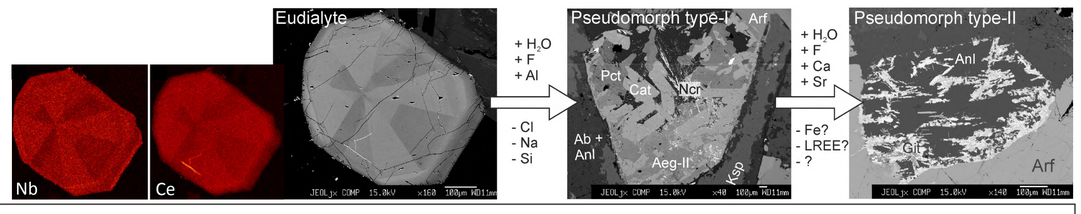


Fig. 6. Paragenetic diagram of eudialyte alteration, indicating fluid evolution and element fluxes



Mineral	Formula	Paragenesis	Magmatic stage: Eudialyte	Late- and postmagmatic: I Catapleiite	II Gittinsite	III Zircon
Alkali feldspar	$(Na,K)AlSi_3O_8$					
Nepheline	$(Na,K)AlSiO_4$					
Sodalite	$Na_8(Al_6Si_6O_{24})Cl_2$	*Agpaitic*				
Analcime	$NaAlSi_2O_6 \cdot H_2O$	*High alkalinity*				
Eudialyte group	$Na_{15}Ca_6(Fe,Mn)_3Zr_3(Si,Nb)Si_{25}O_{72}(O,OH,H_2O)_3(Cl,OH)_2$	*Moderate αH2O*			Sr-Eud	
Arfvedsonite	$Na_3(Fe,Mg)_4FeSi_8O_{22}(OH)_2$					
Aegirine	$NaFeSi_2O_6$	Aeg-I		Aeg-II	Aeg-II	Aeg-II
Aenigmatite	$Na_2Fe_5TiSi_6O_{20}$					
Apatite	$Ca_{4.5}REE_{0.5}(PO_4)_3(OH,F)$					
Fluorite	CaF_2					
Rinkite - Mosandrite group	$Na_2(Ca,REE)_4(Ti,Nb)(Si_2O_7)_2(OH,O,F)_4$					
Catapleiite group	$(Na,Ca,[])_2ZrSi_3O_9 \cdot 2H_2O$				Ca-rich	
Nacareniobsite-(Ce)	$Na_3Ca_3REE\,Nb(Si_2O_7)_2O\,F_3$	*Agpaitic*				
Britholite-(Ce) group (A1)	$(Ca,REE)_5(SiO_4,PO_4)_3(OH,F)$	*High αH2O*				
Monazite	$(REE,Th)PO_4$	*High to moderate alkalinity*				
Pectolite group	$NaCa_2Si_3O_8(OH)$					
Gittinsite	$CaZrSi_2O_7$	*Transitional-Miaskitic*				
Annite	$KFe_3(AlSi_3O_{10})(OH)_2$	*Increased αCaO at high αH2O*				
Allanite-(Ce)	$(Ca,REE)(Al_2Fe)Si_2O_7(SiO_4)OOH$	*Reduced alkalinity*				
Zircon	$(Zr,REE)SiO_4$	***Miaskitic**, reduced alkalinity and αH2O*				

Conclusions

Subsolidus replacement of eudialyte is a common feature in peralkaline intrusions. In Ilímaussaq, alteration is dominated by catapleiite formation and affects up to 30% of the eudialyte. Alteration does not modify the overall grade of the deposit, but merely the minerals in which the metals reside. The fluids responsible are predominantly late-magmatic Na, Cl, F-rich aqueous fluids of high pH, which exsolved at the final stages of crystallisation.

Future work

Understanding eudialyte replacement at Ilímaussaq and other localities could help to improve yield and increase the economic value of eudialyte deposits worldwide. Future work will therefore focus on studying REE distribution and coordination in eudialyte and secondary REE phases from various EU localities using synchrotron radiation and nano-techniques (µ-XRF, µ-XRD, XANES, XAFS, TEM). Element mapping will provide insight into how REE, Zr and Nb are redistributed and mobilised on the micro- and nanoscale.

This work is part of the SoS RARE consortium, which brings together geologists and metallurgists to understand REE mobility in natural systems and develop sustainable ways to exploit REE resources, for example using luminescence of REE minerals to develop 'smart' sorting tools (see Horsburgh et al., this conference).

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