

ALTERATION OF EUDIALYTE AND IMPLICATIONS FOR THE REE, ZR, AND NB RESOURCES OF THE LAYERED KAKORTOKITES IN THE ILÍMAUSSAQ INTRUSION, SOUTH WEST GREENLAND

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Abstract

The layered kakortokites in the southern part of the Ilímaussaq Intrusion are of great economic interest due to their high concentrations of REE, Zr, Nb and Ta. The prospective metals are largely contained in eudialyte, a complex sodium-zirconosilicate and one of the major cumulus phases. Eudialyte-group minerals are easily extracted from the host rock through magnetic separation, and contain 12 wt% ZrO₂, 2 % TRE₂O₃ and 1% Nb₂O₅ on average. Petrographic investigations show that a large fraction of eudialyte at Ilímaussaq is replaced by complex aggregates of secondary minerals as a result of interaction with late-stage magmatic, presumably Na- and F- rich aqueous fluids. The alteration effectively fractionates the major components into the secondary minerals, producing separate Zr-, Nb and REE- phases, leading to an increased complexity of the mineralisation and potential ore recovery.

Introduction

The Ilímaussaq Complex in Southern Greenland hosts some of the most evolved alkaline rock types in the world and is the type-locality of agpaitic nepheline syenites. The term agpaitic exclusively refers to peralkaline rocks with a molar (Na+K)/Al ratio greater than 1.2, containing complex zircono- and titanosilicates, such as eudialyte- and rinkite-group minerals, instead of common high field strength element-bearing (HFSE) phases like zircon, titanite and ilmenite^{1,2}. Eudialyte represents a prime REE, Nb and Zr resource provided by these rock types. The mineral can be readily separated from other minerals (alkali feldspar, arfvedsonite and feldspathoids) by simple magnetic separation and is highly soluble in acids, providing a potential low-cost ore material. Other occurrences of agpaitic rocks are the Khibina and Lovozero complexes in the Kola Peninsula, Mont Saint-Hilaire in Canada, the Tamazeght Complex in Morocco and Norra Kärr in Sweden. All are characterized by extreme enrichment in alkali metals, halogens (F, Cl, Br) and HFSE (e.g. Zr, Ti, Y, Nb, Ta and REE), and many host exploitable resources of these elements³.

The Ilímaussaq Complex has the potential for two types of world-class multi-element magmatic ore deposits; 1) the Kringlerne deposit, studied here, which occurs in cumulates forming the lower part of the intrusion⁴, and 2) the Kvanefjeld deposit in the most evolved lujavrites exposed in the Northern part of the intrusion⁵. The Kringlerne deposit comprises a ~500 m thick series of rhythmically layered amphibole-, eudialyte- and feldspar- rich nepheline syenites (black, red and white kakortokites, respectively), which is currently being explored as a potential REE, Zr, Nb and Ta economic deposit. The resource estimates are 4.3 Bt with an average grade of 1.8 % ZrO₂, 0.2 % Nb₂O₅ and 0.5 % TREO. The enormous tonnages and relatively high proportion of heavy relative to light rare earth elements (HREE/LREE) in eudialyte (approximately 1:3) compared to currently exploited REE deposits, make the deposit especially attractive^{3,6}. Proposed on-site processing involve coarse crushing followed by magnetic separation, producing concentrates of 1) eudialyte, 2) arfvedsonite-aegirine and 3) a mixture of felsic minerals.

Field observations combined with petrographic and electron-microprobe (EPMA) analyses show that a significant amount of eudialyte in the kakortokites has been altered forming a suite of secondary minerals including catapleiite (Na-Zr silicate), aegirine, pectolite, analcime, alkali-feldspar, nacareniobsite-(Ce) (REE-Nb silicate), britholite (REE-phosphosilicate), monazite (REE-phosphate) and pyrochlore (formulas provided in Table 1), previously described in detail by Karup-Møller et al.^{7,8}. The bulk composition of pseudomorphosed eudialyte appears to be preserved, but with major components, notably Zr, REE and Nb, redistributed among the newly formed minerals. The goals of this study are to improve the general knowledge of the relative timing and processes of crystallisation and alteration, the de facto distribution of elements of economic interest and possible implications for beneficiation of the ore.

Table 1: Selection of relevant minerals mentioned in text

Mineral name	Formula
aegirine	NaFe(Si ₂ O ₆)
arfvedsonite	Na ₃ (Fe,Mg) ₄ FeSi ₈ O ₂₂ (OH) ₂
analcime	NaAlSi ₂ O ₆ H ₂ O
pectolite	NaCa ₂ Si ₃ O ₈ (OH)
eudialyte	Na ₁₅ Ca ₆ (Fe,Mn,Na) ₃ (Zr,Ti) ₃ (Si,Nb) ₂ Si ₂₄ O ₇₂ (O,OH,H ₂ O) ₃ (Cl,OH) ₂
catapleiite	(Na,Ca) ₂ ZrSi ₃ O ₉ ·2H ₂ O
zircon	(Zr,REE)SiO ₄
apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)
britholite-(Ce)	(Ca,Ce) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)
Ca-rich A1	HCa ₃ REE ₆ (SiO ₄) ₆ (F□)
Ca-poor A1	(Fe,Mn,Ca) _{1.5} REE ₆ Si ₆ FO ₂₂
monazite	(Ce,La,Nd,Th)PO ₄
mosandrite – rinkite group	(Na,Ca) ₃ (Ca,Ce) ₄ (Ti,Nb,Zr) (Si ₂ O ₇) ₂ (O,F) ₄
nacareniobsite-(Ce)	Na ₃ Ca ₃ (Ce,La)Nb(Si ₂ O ₇) ₂ O F ₃
pyrochlore	(Na,Ca) ₂ Nb ₂ O ₆ (OH,F)

fergusonite-(Ce)	(Ce,La,Y)NbO ₄
fermite	(Ca,Ce,Na)(Nb,Ta,Ti) ₂ (O,OH,F) ₆

Eudialyte Group Minerals

Eudialyte group minerals (EGM), the most prominent index minerals for agpaitic rocks, encompass a large compositional range and are inferred to crystallise at various stages in the magmatic history⁹. Eudialyte group minerals have a complex structure, with a general structural formula of $N_{15-16}M(1)_6M(2)_3Z_3M(3)M(4)[Si_{24}O_{72}]OH_{2-6}X_2$, where N, M and Z refer to different crystallographic sites incorporating variable amounts of Na, Ca, Fe, Mn, Sr, REE, Nb, Si, Zr and Ti as well as volatile components (H₂O, Cl, F, OH)^{10,11}. In the kakortokites EGM are generally Fe-rich, approaching eudialyte *sensu stricto* compositions, with a general formula of $Na_{15}Ca_6(Fe,Mn)_3Zr_3Si(Si_{25}O_{72})(O,OH,H_2O)_3(Cl,OH)_2$, with the major part of the REE and Nb situated in the M1 and M3 site, respectively¹². Owing to their great compositional variability and sensitivity to hydrothermal re-equilibration, EGM typically record late-stage magmatic and hydrothermal processes in agpaitic systems¹³⁻¹⁵. These processes could result in partial or complete decomposition of the eudialyte into complex aggregates of secondary minerals^{8,14,15}.

Analytical Methods

Eudialyte and its decomposition assemblages were analysed in approximately 30 samples, including black, red and white kakortokites from layers -11 to +16⁴, using optical microscopy, back-scatter electron imagery (BSE) and wavelength dispersive electron microprobe analyses using a JEOL JXA-8200 at University of Copenhagen. All analyses were run at an acceleration voltage of 15 kV, beam current 15 nA and a beam diameter of 5 or 20 μm, using a set-up similar to that described by Karup-Møller et al. (2010, 2013). Counting times range from 10-60 seconds, depending on the abundance and volatility (Na) of the respective elements. Background counting times were half of the peak counting times.

Petrographic observations

Primary eudialyte description

The eudialyte-group minerals form well-developed idiomorphic crystals with an average grain size of 0.5 - 1 mm. In all three varieties of kakortokite (black, red and white) EGM are part of the early crystallising assemblage^{4,12}. In black kakortokites EGM occur between, or are fully enclosed by arfvedsonite crystals. In white kakortokite eudialyte crystals are generally interlocked between gravitationally aligned laths of feldspar and grains of nepheline. Intact EGM exhibit complex sector-zoning, fine oscillatory zoning (sub-μm) as well as concentric core to rim zonation (Fig. 1a). Hour-glass sector zoning is present in most crystals and represents a crystallographically controlled feature, presumably caused by preferential incorporation of certain elements on a specific set of growth surfaces¹⁶. Sector-zoning is associated with minor differences in Nb and Ce (LREE) contents (< 0.2 wt%) between light and dark sectors.

Rims showing uniformly high or low backscatter-index typically occur along specific faces of primary sector-zoned eudialyte crystals (Fig. 1a). These rims are distinctly enriched or depleted in REE and presumably reflect changes in the REE-budget of the evolving (interstitial) melt in the final stages of crystallisation.

Alteration paragenesis

A significant proportion of the cumulus eudialyte was subjected to late-stage replacement reactions. First-stage alteration occurs as irregular replacement or symplectite formation along margins and cracks and is associated with crystallisation of fine-grained anhedral crystals of the Na-zirconosilicate catapleiite (mineral formulas provided in Table 1), as well as μm -sized Ce- and Nb-rich phases. Upon further alteration an increasing volume of eudialyte is consumed until the grain is completely replaced by secondary phases (Fig. 1b,c,d). Relics of eudialyte in some pseudomorphs retained their original composition, although they are locally associated with minor loss of Na and Cl. In pseudomorphs representing fully decomposed eudialyte, several assemblages of secondary minerals are distinguished. Most assemblages are dominated by catapleiite as the main replacing Zr-phase (35 wt% ZrO_2). Catapleiite compositions range from a nearly pure Na-end-member to being Ca-rich (up to 0.6 apfu Ca). Aegirine is the main Fe-bearing phase in nearly all pseudomorphs. Nacareniobsite-(Ce) is found in most assemblages and hosts most of the Nb and REE contents originally present in the eudialyte (Fig. 1b). Both aegirine and nacareniobsite-(Ce) have near-ideal end-member compositions. This is in contrast to their magmatic counterparts, which show significant solid-solution trends in the aegirine-augite¹⁷ and rinkite-mosandrite-nacareniobsite-(Ce) series¹⁸.

Analcime, albite and/or potassium feldspar are found in most assemblages, filling the interstitial space between catapleiite and other phases (Fig. 1b,c,d). Pectolite is also common and is often found intergrown with aegirine. Rare earth elements are concentrated into a wide range of minerals, many uncommon, and generally present as μm -sized crystals⁸. The most commonly observed mineral is a Ca-rich or Ca-poor REE-silicate containing up to 65% TREO. These REE-minerals were first described by Karup-Møller et al. (2010), as new REE-phases with a presumed apatite structure (possibly P-poor members of the britholite-group) and were referred to as Ca-rich and Ca-poor A1, respectively. The REE-minerals occur as clusters of acicular crystals randomly distributed in the pseudomorphs (Fig. 1b). More P-rich varieties, approaching compositions of britholite-(Ce) (following a $\text{REE}^{3+} + \text{Si}^{4+} \Leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ coupled substitution scheme), are also present in several decomposition assemblages. A Ba-REE silicate (8 wt% BaO, 2% Nb_2O_5 , 55% REO (La+Ce+Nd) and 22 % SiO_2) is found in six samples. The mineral is texturally indistinguishable from the more common REE-silicates described above and forms similar aggregates of acicular crystals (Fig. 1d). Several REE-phases typically occur together in a single pseudomorph. At higher P contents, pseudomorphs contain monazite as the main REE-bearing phase, associated with secondary apatite and fluorite. Monazite-bearing assemblages have only been observed in two samples of the present study, both in white kakortokites (Fig. 1c). Because magmatic eudialyte contains virtually no P and only ppm-level F and Ba, these components are presumably introduced by the alteration-mediating fluids. The

absence of Cl-bearing phases in the pseudomorphic assemblage suggests a significant net loss in Cl from these domains, which is consistent with the findings of Karup-Møller et al. (2010). Niobium mainly partitions into nacareniobsite-(Ce), although some pseudomorphs contain additional Nb-phases, i.e. pyrochlore, fersmite or fergusonite as small (<5µm) dispersed grains^{7,8,14}. The alteration of eudialyte is associated with zeolitisation (primarily analcime) of feldspars and feldspathoids and replacement of magmatic arfvedsonite by secondary aegirine along the margins of the pseudomorphosed eudialyte grains (Fig. 1b).

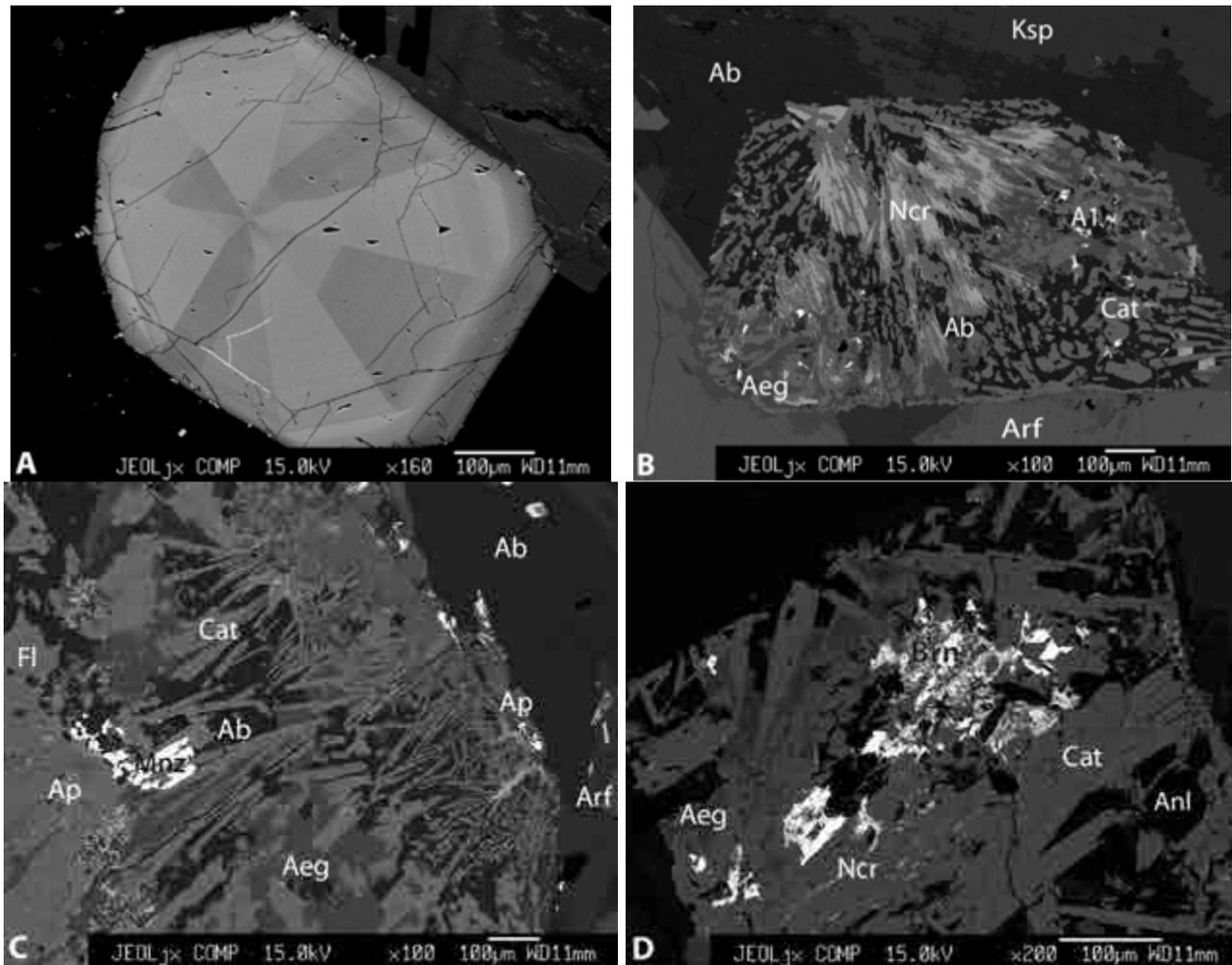


Figure 1: Back-scatter electron (BSE) images of eudialyte and pseudomorphs after eudialyte; (A) Euhedral eudialyte crystal (Layer 4 Black) with 8-fold sector zoning, µm-scale oscillatory zoning and multiple concentric rims; (B) Common eudialyte pseudomorph assemblage (Layer 1 red), with catapleiite (Cat), interstitial albite (Ab), prismatic nacareniobsite-(Ce) (Ncr), acicular Ca-poor A1-silicate (A1, see text) and aegirine (Aeg). Pseudomorph surrounded by arfvedsonite (Arf) and exsolved feldspar (Ab and Ksp); (C) Part of pseudomorph (Layer 3 white) with monazite (Mnz), apatite (Ap), fluorite (Fl), catapleiite, aegirine and albite; (D) Part of pseudomorph (Layer 2 white) with unknown Ba-REE-Nb-phase (Brn), catapleiite, interstitial aegirine, analcime (Anl) and nacareniobsite-(Ce) between the catapleiite plates.

Extent of alteration

The alteration of eudialyte ranges from partial replacement along the margin and cracks of EGM crystal to complete pseudomorphic replacement. In hand specimen, altered EGM are easily recognised by their pale orange-grey colour, which is distinctly different from the glassy pink original eudialyte. Eudialyte pseudomorphs cluster in zones of intense alteration, but completely decomposed grains may equally be in direct contact with fully preserved crystals. No petrographic link is observed between the distribution of the pseudomorphically replaced eudialyte and the proximity to cracks or veins that could have provided a pathway for percolating fluids. It is therefore suggested that the alteration occurred as a result of reactions with late-stage magmatic fluids present at crystal boundaries and in interstitial spaces at the final stages of solidification. The varying assemblages (monazite vs REE-silicate A1) could reflect variations in the composition of the evolving interstitial magmatic fluids, which may be linked to the local mineralogy e.g. the presence of magmatic apatite, fluorite or sodalite. The extent of eudialyte alteration is independent of lithology and is extremely variable throughout the kakortokites, complicating precise evaluation of the degree and mode of alteration and net loss or gain of elements. Current observations suggest that up to 20% of the primary eudialyte is altered, i.e., 20% or more of the REE, Nb and Zr potential is contained in minerals not currently targeted for processing.

Discussion

Extensive auto-metasomatism and pseudomorphic replacement of primary magmatic minerals due to a continuous transition from melt to hydrothermal fluid in the final stages of solidification is a common feature of agpaitic complexes¹⁹. Late magmatic fluids are dominated by H₂O-CO₂ or CH₄ and generally enriched in Na, Cl and F, allowing them to complexate and remobilise HFSE and REE^{19,20}. Remobilisation of incompatible elements by such fluids can both up and down-grade the resource potential, and is hence an important aspect in the paragenesis of alkaline rocks.

This study clearly demonstrates the wide-spread decomposition of eudialyte into complex aggregates of secondary minerals. These aggregates are invariably dominated by catapleiite-group minerals, suggesting alteration by Na-rich, hydrous fluids. Zircon-bearing assemblages have not been described from the current sample set and are apparently only related to severely altered kakortokites and pegmatitic rock types within the complex^{7,8}.

Late-stage alteration of eudialyte has also been described from North Qoroq, Greenland¹⁵; Pilanesberg, South Africa¹⁴ and Sushina, India²¹, indicating a large variety in possible eudialyte replacement products depending on both the primary composition of the eudialyte and the physico-chemical parameters of the metasomatising fluids. An overview of reported eudialyte decomposition assemblages is provided by Mitchell and Chakrabarty (2012). In all cases, the bulk compositions of the replacing phases reflect the initial composition of the primary eudialyte, and distinct fractionation of the HFSE and REE into the secondary phases is observed. In

the case for Kringlerne, we infer that the auto-metasomatic alteration of eudialyte is not associated with large-scale remobilisation of the elements of interest and does not affect the overall ore grade of the deposit. Irrespectively, the increased complexity of the secondary REE-, Nb, and Zr- paragenesis and major reduction in grain size (< 10 µm) will have a significant impact on the recovery of the ore metals.

An important step in optimizing ore recovery is to include the secondary REE, Nb and Zr assemblages in the magnetic separation process. It is currently unknown how the alteration products of eudialyte are distributed during magnetic separation and whether they are concentrated in the eudialyte separate (i.e. the REE-Nb-Zr ore) or the other separates. Two aspects are thus worth considering in future processing tests of eudialyte concentrates: 1) the magnetic susceptibility of the secondary ore minerals and 2) the dissolution kinetics of the secondary phases in relation to the acid treatment procedures used for eudialyte. An example provided by Zakharov et al. (2011) indicated that low Zr recovery from Lovozero eudialyte concentrates was related to the presence of acid resistant Na-Zr-phases, which formed as a consequence of late-stage magmatic alteration of eudialyte. Similar complications may be expected for Zr, REE and Nb recovery from Ilímaussaq eudialyte concentrates with secondary phases that are insoluble during eudialyte dissolution procedures. Subsequently, acid treatment should be optimised for digestion of secondary ore bearing phases in addition to eudialyte.

Conclusions

The kakortokites at the Ilímaussaq Intrusion provide a world-class REE, Zr and Nb deposit which is unique in its size, exposure and mineralogy. Partial decomposition of the primary ore mineral eudialyte through interaction with late-stage magmatic fluids formed complex secondary REE-, Nb- and Zr- phases, such as catapleiite, nacareniobsite-(Ce), britholite-(Ce), monazite and fergusonite-(Ce). The alteration led to increased dissemination and fractionation of the prospective metals in the host rock, while leaving the overall ore grade intact. Further studies on the mineralogical properties and extraction techniques of the secondary REE-, Nb- and Zr- minerals will be of great value for optimal beneficiation of the kakortokites, with potential applications to other agpaitic ore deposits.

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