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Studying the Local Distribution of Thorium in Eudialyte Deposits Associated with Peralkaline Igneous Rocks (Greenland) by Electron Microscopy & Spectroscopic Techniques

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Rare Earth Elements (REEs) are considered to be strategic metals, having a wide range of technological applications (e.g., Hatch, 2012). Due to high demand in industry and technology, the European Union (EU) has identified the study of REE resources as a top priority (e.g., Binnemans *et al.*, 2018). As we are exploring for alternative REE deposits (e.g. Gamaletsos *et al.*, 2019 and references therein), it is important to consider the environmental challenges associated with their exploitation, such as studying the spatial distribution of elements like thorium / Th (e.g. Gamaletsos *et al.*, 2011). Eudialyte deposits, associated with peralkaline igneous rocks, are the dominant EU alternatives to currently exploited Chinese REE deposits from ion adsorption clays and carbonatites (e.g., Smith *et al.*, 2016). Due to relatively low Th contents in peralkaline igneous rocks, typically sub-continental crust (<100 ppm Th), eudialyte exploitation could avoid potential issues of radioactive contamination in tailings that bedevil, e.g. monazite and xenotime extraction. However, the partitioning of Th and REEs at the micro-/nano-scale in eudialyte deposits is poorly studied. Here we utilize the technical advance of combining synchrotron radiation (SR) μ-XRF/-XAFS and electron microscopic (SEM-EDS/-WDS, EPMA, SEM-FIB, TEM/HRTEM) techniques (Fig. 1), along with LA-ICP-MS to study the local distribution of Th in one of the largest European eudialyte deposits, i.e. the Ilímaussaq Complex in South Greenland (Larsen and Sørensen, 1987).

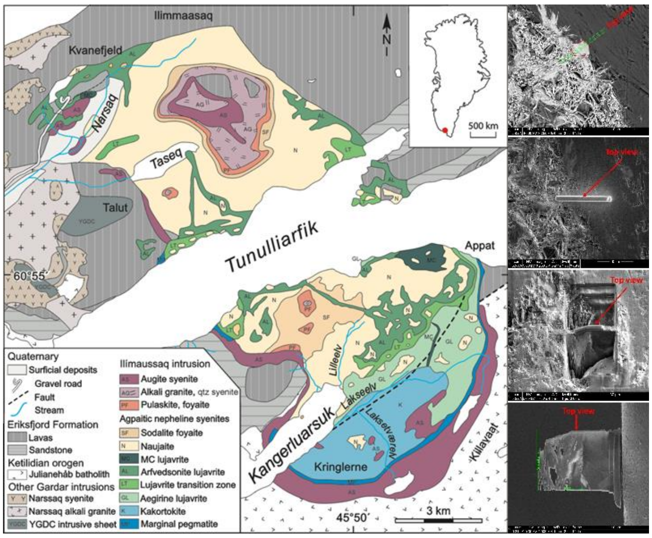

Figure 1. Geological map of the Ilímaussaq complex (modified after Borst et al., 2019 and references therein) and SEM-FIB preparation of a representative sample undergone TEM/HRTEM study.

The Ilímaussaq complex is an oval-shaped peralkaline composite intrusion, part of the Mesoproterozoic Gardar province in South Greenland (**Fig. 1**). During at least four intrusive pulses, augite syenites, alkali-to-peralkaline granites, quartz syenites and volumetrically layered eudialyte-bearing nepheline syenites ("kakortokite") crystallized (e.g., Larsen & Sørensen, 1987; Borst *et al.*, 2019). The kakortokites comprise alkali feldspar, nepheline, sodalite, aegirine, arfvedsonite and eudialyte, with aenigmatite, rinkite-group minerals, fluorite, apatite and analcime as common accessory phases (e.g., Borst *et al.*, 2018). Of particular economic interest are the eudialyte-group minerals (EGM), i.e. a group of complex Na-Ca-zirconosilicates which occur as major phases and contain wt.% significant concentrations of rare earth elements (ca. 2.5 wt.% REE_2O_3). A proportion of the primary EGM have been partially-to-fully replaced by fine intergrowths of variety of EGM alteration products (i.e. catapleiite, aegirine, nacareniobsite-(Ce) and other REE-rich secondary phases), resulting from late-magmatic hydrothermal alteration (e.g. Karup-Møller & Rose-Hansen., 2013; Borst *et al.*, 2016).

Preliminary SR (Fig. 2) and e-microscopic observations at altered EGM domains reveal the presence of Th-bearing phases at the micro-/submicro-/nano-scale. Similar micro-scale heterogeneity is observed for the REEs in eudialyte replacement products. We also collected Th L_{III}-edge μ-XAFS spectral data of Th-enriched micro-areas, previously identified by SR μ-XRF mapping that confirmed the heterogeneous distribution of the actinide, which provide information on the local structural environment of Th within altered EGM domains. Several Th-bearing phases were detected along altered margins of eudialyte, in secondary phases, and interstitial to primary phases such as feldspar, amphibole and eudialyte. In fresh magmatic EGM, Th is undetectable by SR μ-XRF; however, actinides are detected in fresh EGM crystals by means of LA-ICP-MS indicating very low concentrations typically below 40 ppm. Furthermore, LAICPMS detected all the REE, including Y and Sc in fresh EGM crystals. Significant variation of Ta and Nb and less of LREE in fresh EGM is recorded by LA-ICP-MS. HREE variations are within analytical uncertainty. Similar variation in Ce concentration was additionally recorded by SR μ-XRF mapping. The above variations might be associated with the sector zoning in fresh EGM as it is demonstrated by Borst *et al.* (2018).

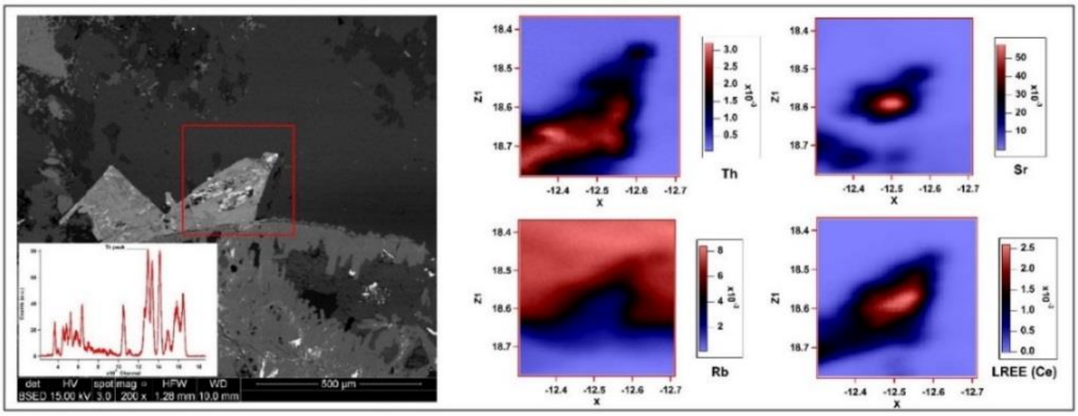

Figure 2. SR μ-XRF data of a representative sample from the eudialyte deposit of the Ilímaussaq Complex, demonstrating relative heterogeneity of Th, Sr, Rb and Ce concentrations in altered rinkite and eudialyte.

Regardless of low bulk contents of Th in peralkaline igneous rocks, we find localized relative enrichments of Th at the micro-/nano-scale associated with hydrothermal alteration products after rinkite and EGM, probably. Either thorium, which is enriched in the melt until the final stages of magmatic crystallization, partitions into the late-magmatic fluids at the hydrothermal stage as part of further cooling or it is redistributed from the eudialyte during alteration. Further research of how elements like Th, which are at low concentrations in bulk and are localized at the micro-/nano-scale, are transported and distributed within the ore and gangue minerals of peralkaline deposits will be important to inform and enhance the development of sustainable metallurgical processing routines for these ore types. Since traces of Th may be transferred into the metallurgical residues, the monitoring of its paths from the ore feed towards to the residues is needed.

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