

## Potential Target Minerals for Rare Earth Elements in Kringlerne District, Gardar Province, Greenland

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### ABSTRACT

Many important rare earth element (REE) deposits are associated with alkaline-peralkaline igneous rocks, and the peralkaline intrusion in Gardar Province, Greenland has formed the largest REE deposits in Greenland. Two REE deposits in Gardar Province, named Kvanefjeld and Kringlerne, are hosted by the Ilímaussaq alkaline complex. The Ilímaussaq alkaline complex includes rare types of peralkaline igneous rocks, classified as agpaitic nepheline syenites with several diagnostic minerals including eudialyte. Eudialyte-rich peralkaline rocks in the Ilímaussaq complex have been noted as significant REE resources. We collected rock samples from the Ilímaussaq complex in the Kringlerne district along the shore of Kangerluarsuk, and analyzed REE contents. The collected rock samples include agpaitic nepheline syenites (naujaite, kakortokite and lujavrite), and late-magmatic dykes intruding naujaite. The chemical analysis of rock samples showed that the REE contents were highest in dyke rock samples with up to 3.4% REO (rare earth oxides) (1.7% REO on average) and were generally higher in lujavrite (0.51 % REO on average) than in other agpaitic rocks (0.43% REO in naujaite and 0.46% REO in kakortokite on average). Even with the elevated total REE contents in the late-magmatic dykes, the heavy REE (HREE) contents were still lower than those in naujaite, kakortokite, and lujavrite. For exploitation of the Kringlerne deposits as REE resources, identification of rare earth minerals in REE-enriched rocks is essential. In this study, we also examined the REE distribution in primary and secondary mineral phases in selected REE-enriched rock samples.

### INTRODUCTION

The Ilímaussaq alkaline complex occurring in Gardar Province, South Greenland is one of the largest reported alkaline complexes. The Ilímaussaq alkaline complex is composed of rare peralkaline igneous rocks, classified as agpaitic nepheline syenites, often referred to as agpaites, which are mainly composed of kakortokite, lujavrite and naujaite, from bottom to top of the intrusion (Figure 1). Agpaitic rocks are characterized by (1) enrichment of rare earth elements (REEs), Zr, Nb, Ta, Fe(III), Li, Be, F and Cl, (2) depletion of Ca, Mg, and CO<sub>2</sub> relative to Si, and (3) occurrence of diagnostic minerals, mainly complex Zr/Ti silicates, such as eudialyte (Na-rich zirconosilicate) and rinkite (REE titanosilicate) (Edgar, 1974; Le Maitre, 1989; Sørensen, 2001). Some of those diagnostic minerals have been target minerals for critical materials, e.g. REEs, Zr, etc.

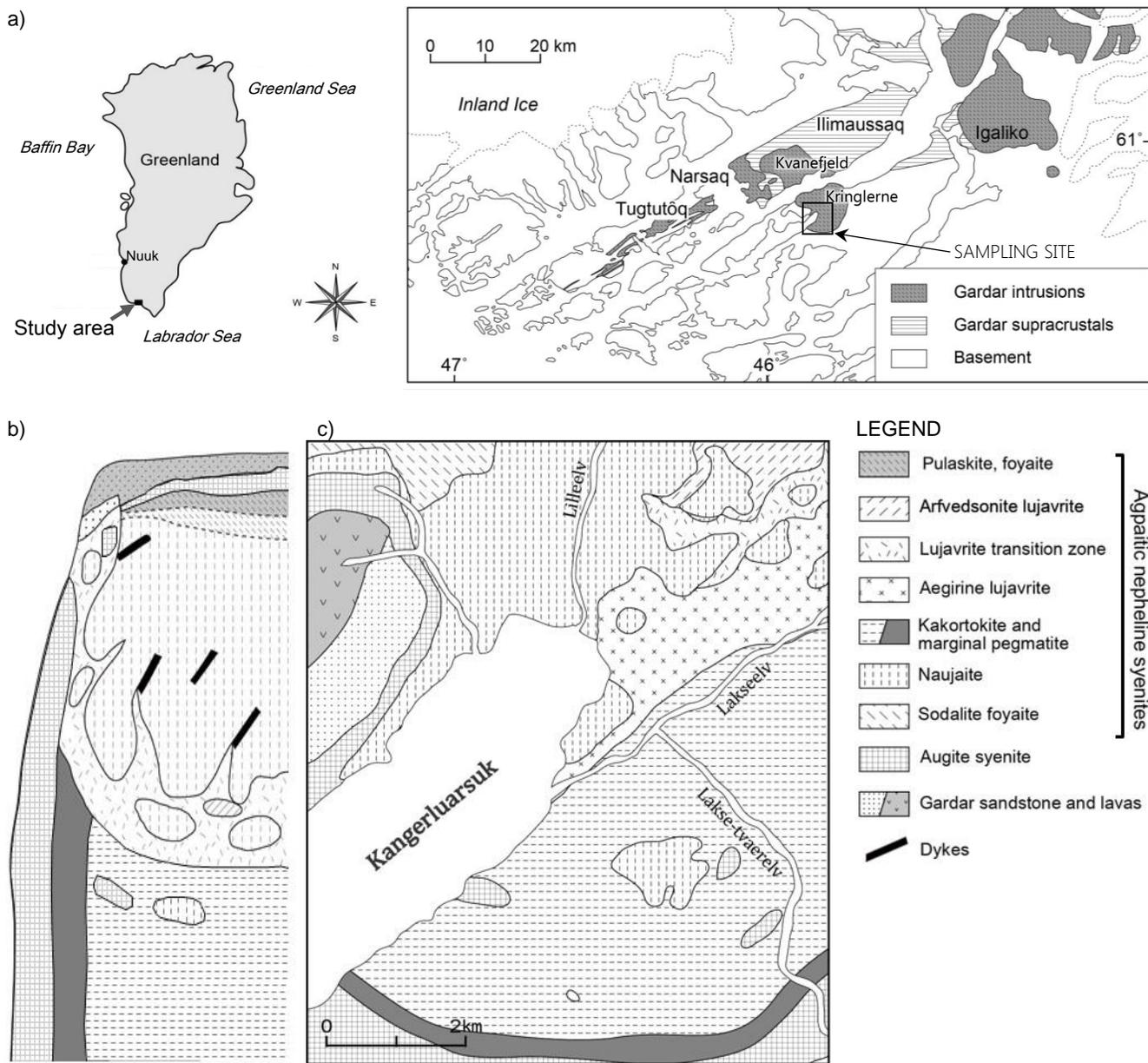
Eudialyte group minerals have been considered as the main REE minerals with their high REE contents and their high-volume occurrences (Sørensen, 1992; Sørensen, 2001). Eudialytes in the Ilímaussaq intrusion, in many cases, have been altered to form secondary minerals (Goodenough et al., 2016), which are often more concentrated with economic elements (Graser and Markl, 2008; Karup-Møller et al., 2010). Several alteration types have been identified based on their mineral assemblages and chemical compositions, e.g., catapleite type, zircon type, zirfesite type and gittinsite type (Ussing, 1912; Karup-Møller et al., 2010; Borst et al., 2016). Each type of secondary mineral assemblage is unique to the location (Borst et al., 2016), and the identification of those minerals is still in progress.

In this study, we investigated REE distribution in rock samples from the Kringlerne district in the southern part of the Ilímaussaq intrusion (Figure 1), where REEs are mainly retained in kakortokite (Figure 2). In selected kakortokite samples enriched with REEs, we also examined the REE minerals, including eudialytes and secondary minerals.

### GEOLOGY

Southern Greenland is composed of older basement rocks, mainly Archean gneiss (>2.8 Ga), and younger formations, mainly Paleoproterozoic Ketilidian rocks (~1.8 Ga) and Mesoproterozoic Gardar formation (1.3–1.1 Ga). Continental rifting in southern Greenland during Gardar period has stretched the crust formed of Archean and Paleoproterozoic basement rocks, and the accompanying magmatism formed alkaline Gardar intrusive complexes (Upton et al., 2003; Upton, 2013). Ilímaussaq complex (1162–1130 Ma) (Sørensen, 2001) is one of the latest-stage intrusive rock bodies in Gardar Province with extreme composition, being mainly composed of agpaitic nepheline syenites (Upton, 2013).

Petrogenesis of Ilímaussaq complex is still controversial, but the agpaitic magma is believed to have originated from the lithospheric mantle (Larsen and Sørensen, 1987; Marks et al., 2007; Graser et al., 2008; Upton, 2013). Earlier crystallization seems to form the roof-series rocks: pulaskite, foyalite, sodalite foyalite and naujaite, from uppermost to lowermost (Figure 1b).



**Figure 1:** Geological maps and section of the Ilímaussaq intrusion: (a) location of study area and regional geological map, (b) a schematic cross section of the Ilímaussaq intrusion, and (c) geological map of the sampling site, from or modified from Sørensen (2001).

Later crystallization has formed lujavrite and kakortokite, composing the intermediate and floor sequences of Ilímaussaq complex, respectively (Figure 1b). Layered kakortokite is composed of cyclic layers of black, red and white kakortokites, the dominant minerals being arfvedsonite, eudialyte and, nepheline/feldspar, respectively (Sørensen, 2001; Thrane et al., 2014). Then the latest hyperagpaite magma forms highly evolved lujavrite, pegmatites and hydrothermal veins, and alteration zones, such as fenitized volcanic rocks (Sørensen and Larsen, 2001; Andersen and Friis, 2015).

The Ilímaussaq intrusive rocks remain undisturbed and fairly well-preserved since the Gardar Province has barely encountered further tectonic deformation (Upton, 2013). Mesoproterozoic Gardar plutons are exposed at the surface as a result of extensive erosion accompanied by rifting processes, allowing the deep plutonic bodies to be observed at the surface (Upton, 2013).

## MATERIALS AND METHODS

### Sample Collection

Rock samples were collected in Kringlerne district mainly along the shore of Kangerluarsuk in June, 2013. Collected rock samples include augite syenite, kakortokite, naujaite and late-magmatic dykes in naujaite. Kakortokite samples were collected from each layer, red, white, or black, although, in some locations, the color of each layer unit was difficult to be identified in the field.

### Chemical Analysis

Elemental composition of the rock samples was analyzed in the Activation Laboratories Ltd. (Actlabs), Canada, using an inductive coupled plasma-mass spectrometer (ICP-MS). Elemental compositions of minerals were analyzed using an electron probe micro-analyzer (EPMA, Shimadzu EPMA-1610) at Jeonbuk Techno-Park. We used the accelerating voltage of 15 kV, the beam current of 20 mA, ZAF3 program for data correction and reference standards for X-ray microanalysis by Micro-Analysis Consultants, Ltd. (MAC) in Mineral, Rare Earth, and Universal Block. We report REE contents to include yttrium contents, which is often abbreviated as REY.

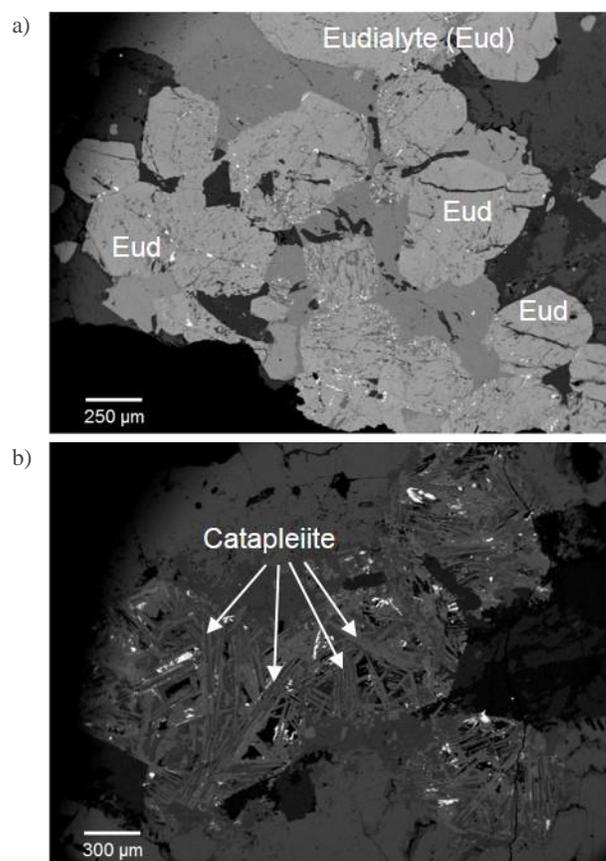
## RARE EARTH ELEMENT DISTRIBUTION

### Agpaites vs. Late-Magmatic Dykes

In the agpaitic nepheline syenites, the average total REE contents were 0.43–0.51% TREO (total rare earth oxide) depending on the rock type, and the maximum contents reached up to 1.70% TREO. Late-magmatic dykes intruding naujaite had significantly higher REE contents than agpaites, showing 1.7% TREO on average with the maximum of 3.4% TREO. The heavy REE oxide (HREO) contents in those dykes, however, was lower (Ave. 0.10% and Max. 0.18% HREO) than those in agpaitic rocks (Ave. 0.12–0.13% and Max. 0.23–0.54% HREO depending on the rock type). Among three types of agpaitic rocks, lujavrite had the highest average REE contents (0.51% TREO), while eudialyte-rich red layers of kakortokite showed an even higher average REE content of 0.86% TREO.

### Red vs. White REE-rich Kakortokites

We selected the most REE-enriched kakortokite samples, one rich in eudialytes (red) and another rich in nepheline and feldspar (white), and EPMA-analyzed for REE-rich minerals. In the red kakortokite sample, the most REE-concentrated minerals were secondary minerals mainly related to eudialytes, filling in the open space within the eudialyte crystals (Figure 2a). In the white kakortokite sample, the most REE-concentrated minerals were secondary minerals as well, but filling in the open space between prismatic crystals of catapleiite-group minerals (Figure 2b). Those catapleiite-group minerals seemed to have completely replaced subhedral hexagonal grains of a primary mineral, possibly eudialyte. Elemental distribution compared with REE distribution indicated diverse secondary REE minerals in those two kakortokite samples.



**Figure 2:** Back-scattered electron (BSE) images of eudialyte-rich (a) and nepheline/feldspar-rich (b) kakortokite samples with the highest REE contents.

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