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Biogeochemical expression of rare earth element and zirconium mineralization at Norra Kärr, Southern Sweden

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ABSTRACT

Biogeochemical samples were collected from the Norra Kärr Alkaline Complex, a rare earth element (REE) and zirconium enriched deposit in Southern Sweden, to determine which sample medium is the most effective grassroots exploration tool for delineating concealed REE mineralization. The fern species *Dryopteris filix-mas* and *Athyrium filix-femina* were found to be widespread in the study area and surrounding countryside, and particularly efficient at concentrating high levels of REEs in their leaf tissue.

There was distinct elemental fractionation in all three fern species. Each species showed enrichment in the LREEs (light rare earth elements), especially *A. filix-femina. D. filix-mas* showed the most enrichment in HREEs (heavy rare earth elements); *Pteridium aquilinum* had lower levels of REEs than the other two species. The best contrast was observed in *D. filix-mas* samples from areas over mineralization compared to samples

The best contrast was observed in *D. filix-mas* samples from areas over mineralization compared to samples taken over barren Växjö granites, which suggests that *D. filix-mas* is the preferred biogeochemical sample medium for REE exploration in this environment.

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1. Introduction

Biogeochemical exploration is an effective but underutilized method for delineating covered mineralization. Plants are capable of accumulating REEs in their tissue, and ferns (pteridophytes) are especially adept because they are one of the most primitive land plants. Less evolved plants can accumulate more elements in their tissue, particularly elements which are harmful at high concentrations, such as heavy metals or REEs, than more highly evolved land plants. This behavior stems from the adaptation of barrier mechanisms within the plant to protect its cells from potentially toxic levels of certain elements (Kovalevskii, 1979).

There is a paucity of information regarding the efficacy of biogeochemical methods to explore for buried HREE mineralization. The Norra Kärr Alkaline Complex is a suitable study area to confirm the effectiveness of biogeochemical sampling because the REE mineralization there is challenging to detect by conventional exploration techniques. The nepheline syenite hosting the REEs has very similar density to the surrounding Växjö granites, so it is indistinguishable by specific gravity surveys. The deposit lacks sulphide minerals, so it cannot be identified by induced polarity (IP) surveys. Also, Norra

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Kärr has unusually low amounts of uranium and thorium for a deposit of its type, and the deposit is not distinguishable in the country-wide Swedish Geological Survey (SGU) radiometric surveys. Extensive glaciation of the study area presents additional challenges because conventional soil surveys are not reliable exploration methods in areas of transported cover.

Biogeochemical surveys provide a viable approach to mineral exploration in most terrains because they are rapid, relatively inexpensive, and are effective in areas of disturbance or transported cover. The ferns sampled at Norra Kärr, *Athyrium filix-femina* (lady fern), *Dryopteris filix-mas* (wood fern), and *Pteridium aquilinum* (bracken), all accumulate REEs in their leafy tissue and are ubiquitous in the study area, making them ideal biogeochemical exploration media.

Recently it has been shown that low levels of REEs can be beneficial to plant growth (Guo et al., 1996; Volokh et al., 1990; Welch, 1995) and subsequently REEs have been added to agricultural fertilizers to increase crop yield. This practice has been most widely embraced in China, and as a result many researchers there have begun studying REEs in soil-plant systems to better understand the distribution and accumulation of REEs in the natural environment. Research has been carried out mainly on rice and corn (Li et al., 1998) as well as soybeans and wheat (Ding et al., 2006, 2007). Fu et al. (1998) did a comprehensive study on the distribution patterns of REEs in the fern *Matteuccia* to investigate the implication for intake of fresh silicate particles by plants. They demonstrated that the content of REEs in ferns decreased

from root to leaf to stem, and hypothesized that the source of REEs was from the silicate fraction of the soil.

This study evaluates the biogeochemistry of common ferns as appropriate indicators of REE enrichment and considers which species is the most effective in delineating HREE deposits.

1.1. Geology and physiographic setting

The Norra Kärr REE and Zr Alkaline Complex is located approximately 300 km southwest of Stockholm and 10 km northeast of Gränna in southern Sweden (Fig. 1). Norra Kärr, which is Swedish for "northern bog", is situated in a shallow topographic low and is slightly elevated at the center of the intrusive complex. There is a low-lying swampy area at the western contact of the syenite, and at the eastern edge of the intrusion there is a small creek draining into a lake which sits directly above the eastern contact with the surrounding granites. Nepheline syenite outcrops in several places, but for the most part is overlain by 1–4 m of Quaternary sediments. The complex is approximately 1300 m long, 480 m wide, and is elongated in the N–S direction.

Mineralization is hosted in a peralkaline nepheline syenite complex. Nepheline, a feldspathoid, frequently occurs in "silica undersaturated" alkaline intrusions. Mineralization is associated with a zone of ductile deformation caused by a large north–south trending dip-slip fault. The deposit dips roughly 45° to the west, and is wholly surrounded by barren Växjö granites.

The two main alkali zirconosilicates hosting the REE mineralization are eudialyte [Na₄(Ca,REE)₂(Fe,Mn)ZrSi₈O₂₂(OH,Cl)₂] and catapleiite [(Na,Ca)₂ZrSi₃O₉ \cdot 2H₂O]. Both of these minerals are relatively easily weathered, making the REEs bioavailable at Norra Kärr. There are

Stockholm

Southern Sweden
Lake Vattern Area
Norra Karr Complex

Fig. 1. Map of Sweden with inset of Lake Vättern area. Location of the Norra Kärr deposit is indicated by the star.

4 main rock types: grennaite, kaxtorpite, lakarpite, and pulaskite. All are type localities and named after nearby towns and local farms.

Grennaite is the dominant rock type; it is generally a fine grained, grey-green rock composed of alkali feldspar, nepheline, aegerine, eudialyte, and catapleiite. The concentration of Zr and REEs in the grennaite unit is much higher than any other rock type in the area, especially in areas where the grennaite is migmatized or pegmatitic. Kaxtorpite is effectively barren of REE mineralization, and is the most radioactive part of the deposit, though it only has approximately 10 ppm Th. Kaxtorpite is a coarse grained, dark alkaline rock with microcline augen and an aegerine, alkali amphibole and nepheline groundmass. Lakarpite is "an often medium grained, albitearfvedsonite-nepheline dominated rock with some microclinerosenbuschite and minor titanite-apatite-fluorite" (Reed, 2011). Pulaskite occurs along the western side of the deposit, and is composed of albite, microcline, aegerine, alkali amphibole, minor biotite and nepheline. Rosenbuschite, apatite, titanite, and fluorite occur as accessory minerals in the pulaskite units. Typically the pulaskite and grennaite are inter-layered, and in places the grennaite appears to be brecciating the pulaskite.

A summary of the various rock types found at Norra Kärr is shown in Table 1 and displayed in Fig. 2. The GTC ("grennaite") domain is the large, outermost pale green unit, the PGT domain ("pegmatitic grennaite") is the hatched green unit, the GTM domain ("migmatized grennaite") is the dark green inner unit, and the KAX domain ("kaxtorpite") is the central brown unit.

The total rare earth oxide (TREO) content is very low in the center of the deposit, and increases towards the edges. The richest unit is the pegmatitic grennaite, with up to 0.69% TREO. The inferred REE mineral resource at Norra Kärr is 60.5 million tonnes averaging 0.54% TREO with 53% HREO (Tasman Metals website, accessed Sept 21st 2012).

Blaxland (1977) determined that the complex was 1580 ± 62 Ma using a whole-rock Rb/Sr isochron. The current "official" age of the complex, 1545 ± 61 Ma, was recalculated using new radiometric constraints by Welin (1980). Current U/Pb isotope research using LA-ICP-MS on zircons from the complex suggests that the existing age is slightly younger, but still within the error limits (Sjöqvist, unpublished data).

Table 1Description of main rock types at Norra Kärr.

Domain	Rock code	Description
GTC	GT	Grennaite. Fine grained with little to no larger catapleiite grains. Less than 5% pegmatitic schlieren. Very fine grained to fine-grained groundmass.
	GTC	Grennaite with more than 3% large catapleiite laths/needles. Generally foliated. Very fine grained groundmass.
	GTCE	Grennaite with both catapleiite and eudialyte blasts/grains.
PGT	GT1	Grennaite with 5–10% "pegmatitic" schlieren and/or zones.
	GT2	Grennaite with 10-30% "pegmatitic" schlieren and/or zones.
	GT3	Grennaite with 30–50% "pegmatitic" schlieren and/or zones.
	GTP	Grennaite with 50–70% coarse pegmatitic zones and schlieren.
	PGT	70–90% pegmatitic grennaite with 10–30% fine-grained Grennaite zones/slabs.
	GTR	Medium grained "grennaite". Partly coarse pegmatite.
	NEP	>90% nepheline-syenite (grennaite) pegmatite.
GTM	GTM	Re-crystallized, intensely deformed grennaite.
	GTMi	Slightly, re-crystallized grennaite. In part showing crenulated folding.
KAX	KAX	Kaxtorpite. Microcline-eckermannite-aegirine+/-nepheline- pectolite-natrolite. Often intensely folded.
	KAG	Kaxtorpite with some interfolded grennaite bands. Often intensely folded.
	GTK	Grennaite with interfolded kaxtorpite bands

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