

# Biogeochemical expressions of buried REE mineralization at Norra Kärr, southern Sweden



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## Summary

Biogeochemical samples were collected from the Norra Kärr Alkaline Complex, a rare earth element (REE) and zirconium enriched mineral deposit in Southern Sweden, to determine which sample type is the most appropriate grassroots exploration medium for delineating concealed REE mineralization. We found that the fern species *Dryopteris filix-mas* and *Athyrium filix-femina*, which are widespread in the region, are particularly efficient at concentrating high levels of REE in their leafy tissue.

Three fern species displayed distinct elemental fractionation. Each species showed enrichment in the light rare earth elements (LREE), especially *Athyrium filix-femina*. *Dryopteris filix-mas*, showed the most enrichment in heavy rare earth elements (HREE) and *Pteridium aquilinum* had lower levels of REE than the other two species.

The best contrast was observed in *Dryopteris filix-mas* samples collected over mineralization compared to samples taken over barren Våxjö granites, suggesting that *Dryopteris filix-mas* is the preferred biogeochemical sample medium for REE exploration in this region.

## 1. Introduction

Biogeochemical exploration is an effective but underused method for delineating covered mineralization. Plants are capable of accumulating REE in their tissue, and ferns (pteridophytes) are especially adept because they are a primitive land plant. Complex plants, like trees, have developed barrier mechanisms to protect their cells from build-up of elements such as heavy metals or REE, which may be harmful to the plant at high concentrations (Kovalevskii, 1979). In contrast, less evolved plants lack these barrier mechanisms and accumulate all elements equally, therefore can absorb higher proportions of heavy elements in their tissue. Based on findings from several authors (Dunn, 1998; Wyttenbach et al., 1998; Fu et al., 1998; et. al., Zhang, 2002; Dunn, 2007) it appears that ferns are suitable sample media for REE exploration.

There is a paucity of information regarding the capacity of biogeochemical methods to explore for buried HREE (those REE with a higher mean atomic mass than ca 153) mineralization. The Norra Kärr Alkaline Complex (NKAC; Fig. 1) is well suited to evaluate the efficacy of biogeochemical sampling because the REE mineralization there is challenging to detect by conventional exploration techniques. The nepheline syenite hosting the REE has very similar density to the surrounding Våxjö granites, so is indistinguishable by gravity surveys. The deposit lacks sulphide minerals, so cannot be identified by induced polarity (IP) surveys. Also, Norra Kärr has unusually low amounts of uranium and thorium for a deposit of its type, and therefore the deposit is not easily recognizable in the country-wide Swedish Geological Survey (SGU) radiometric surveys. Extensive glaciation of the study area presents an additional challenge 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) (Fig. 2), all accumulate REE in their leafy tissue and are ubiquitous in the study area, making them an ideal biogeochemical exploration media.

Recently, it has been shown that low levels of REE can benefit plant growth (Volokh et al., 1990; Welch, 1995; Guo et al., 1996) and REE 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 REE in soil-plant systems to better understand the distribution and accumulation of REE 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) undertook a comprehensive study on the distribution patterns of REE in the fern *Matteuccia* to

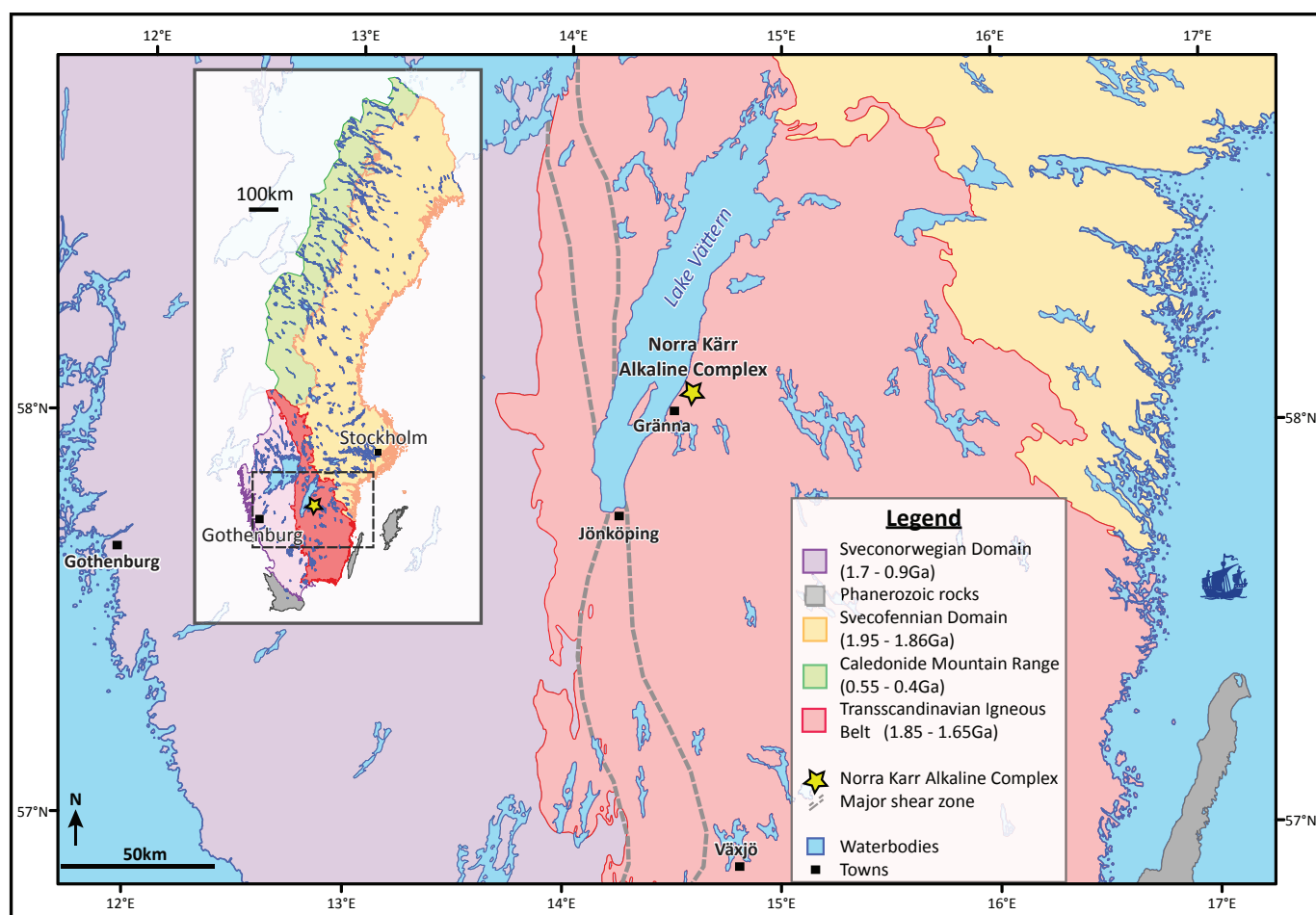


Fig. 1. Geological map of southern Sweden; Norra Kärr Alkaline Complex is indicated by the star.



Fig. 2. Fern species in the study area. a) *Athyrium filix-femina*, b) *Dryopteris filix-mas*, c) *Pteridium aquilinum*. Note the distinct differences in spore morphology.

investigate the implication for intake of fresh silicate particles by plants. They demonstrated that the content of REE in ferns decreased from root to leaf to stem, and hypothesized that the source of REE 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.

## 2. Geology, physiographic setting, and land use

### 2.1. Geology

The Norra Kärr REE and Zr Alkaline complex is 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”, occupies a shallow topographic low; the centre of the intrusive complex is slightly elevated. The western contact of the syenite is covered by a low-lying swampy area and, at the eastern edge of the intrusion, a small creek drains into a lake that 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 elongate north-south.

Mineralization is hosted within the peralkaline nepheline syenite complex and is associated with a zone of ductile deformation along a large north-south trending dip-slip fault. The deposit dips roughly 45° to the west, and is wholly

surrounded by barren Våxjö granites.

The four main rock units at Norra Kärr, described in detail by Saxon et al., (2015) are locally referred to as: 1) grennaite (generally a fine-grained, grey-green rock composed of alkali feldspar, nepheline, aegerine, eudialyte, and catapleiite); 2) kaxtorp (a coarse-grained, dark alkaline rock with microcline augen and an aegerine, alkali amphibole and nepheline groundmass); 3) lakarp (an “often medium grained, albite–arfvedsonite–nepheline dominated rock with some microcline–rosenbuschite and minor titanite–apatite–fluorite” (Reed, 2011)); and 4) pulaskite (a rock composed of albite, microcline, aegerine, alkali amphibole, minor biotite and nepheline). The two main alkali zirconosilicates hosting the REE mineralization are eudialyte  $[\text{Na}_4(\text{Ca}, \text{REE})_2(\text{Fe}, \text{Mn})\text{ZrSi}_8\text{O}_{22}(\text{OH}, \text{Cl})_2]$  and catapleiite  $[(\text{Na}, \text{Ca})_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}]$  (Reed, 2011). Both of these minerals are relatively easily weathered, making the REE at Norra Kärr more bioavailable. The strongest REE response in the biogeochemical samples corresponds with the pegmatitic grennaite, which is the most richly endowed unit of the complex.

## 2.2. Quaternary geology and land use

The Quaternary cover over the NKAC was mapped by the Swedish Geological Survey as “thin or discontinuous soil cover on bedrock” (Swedish Geological Survey 2011). The bedrock has also been mapped, but is not well constrained due to the extensive cover. Regional ice-flow direction was generally north-south or slightly south-easterly. Based on field assessments it appears that the surficial material over the NKAC is glaciofluvial outwash because it lacks the clay content and highly compact nature of typical glacial tills.

The land use around Norra Kärr is variable, changing abruptly from grassy agricultural grazing land to typical boreal Swedish forest to thickly vegetated silviculture plantations. Soil profiles above the NKAC indicate that the ground is very disturbed by agricultural practice, which has been ongoing in the region for hundreds of years, and consequently developed soil horizons are rare.

## 3. Results

### 3.1. Analytical methods

The analytical package we used was Acme Laboratories’ Group IVE-MS ultratrace package including all the REE. This involved pre-treating the sample with  $\text{HNO}_3$  to oxidize the organic material under cool conditions before digesting in aqua regia, followed by determinations for 65 elements by ICP-MS, and ICP-ES for some of the major elements.

### 3.2. Background contrast and detection limits

The best contrast between anomaly and background was observed in the *Dryopteris filix-mas* samples (Fig. 3). LREE are more abundant than HREE in the Earth’s crust, so they naturally accumulate in higher absolute values in the plants, and because *Athyrium filix-femina* can contain significant amounts of REE in its leaf tissue, it would seem to be a logical sample type. However, *Dryopteris filix-mas* shows a better response ratio over the NKAC, so it is a better choice of sample medium.

With the exception of Eu, the concentration of LREE in all samples exceeds the 0.02 ppm detection limit. In his comprehensive review of REE in soils and plants, Tyler (2004) included Eu with the LREE, a convention that we follow here. Of the 25 samples that reported Eu values below detection limit, only 3 were collected above the deposit. One of these was from directly over the kaxtorp unit, which has the lowest levels of REE (less than 0.21% TREO) of any rock type in the complex; the other two samples were from parts of the complex that contain porphyritic catapleiite (0.26% TREO).

Each of the HREE reported some values below the detectable limit, but some elements, particularly Tb, Ho, Tm, and Lu, reported a larger proportion below detection limit than the other HREE. Eleven out of 88 samples showed Tm values less than 0.02 ppm, and only 5 of the 88 samples had reportable Lu. Approximately 40% of the samples had less than detection levels of Tm and Ho. The HREE Gd, Dy, and Er had the most reportable results, but still between 13% and 25% of the samples returned values below the detection limit. Only two of the below detection limit samples for Gd and Dy were located over the deposit, and these are the same samples that ran below

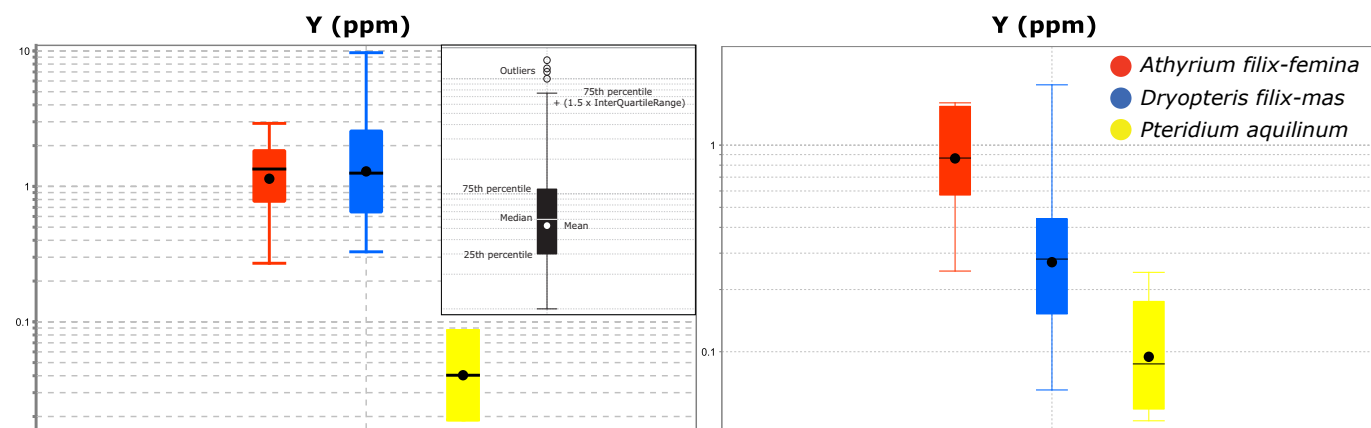


Fig. 3. Yttrium content in ferns collected over the Norra Kärr deposit (left) and in the background (right), coloured by species type.



detection limit for Eu.

The higher levels of Gd, Dy, and Er relative to the other HREE are due to the fact that lanthanides with even atomic numbers (64, 66, and 68 respectively) have greater relative crustal abundances than elements with odd atomic numbers. This pattern, inherent in the rock samples, is being preserved and displayed in the vegetation samples.

### 3.3. REE concentrations

The three species of ferns had significantly different trace element compositions. *Pteridium aquilinum* had the lowest levels of all REE analysed; *Athyrium filix-femina* had the highest REE values, and *Dryopteris filix-mas* had intermediate values between the other two species.

The similar behaviour and mobility within the HREE compared to the LREE is well documented (Tyler et al. 2004). There are strong correlations in this dataset, with confidence greater than the 90<sup>th</sup> percentile, among the LREE and HREE such that any one of these elements can be selected as a proxy and used to represent each group. Consequently, only Nd and Dy data are presented and graphed hereafter.

The amount of Dy ranges from below the detection limit to 0.34 ppm over the deposit, and from below the detection limit to 0.24 ppm off the deposit. The ranges of Nd are from 0.49 ppm to 20.2 ppm over the deposit, and 0.25 ppm to 15.4 ppm off the deposit.

### 3.4. Levelling

Different species of ferns can naturally accumulate different amounts of REE in their plant structure (Fig. 3, 4a, 4b), so to make a coherent biogeochemical response map over the deposit and surrounding area, REE values must be levelled to account for variation in sample species. The levelling method undertaken here was Z-Score,  $\log_{10}$ , with a power transformation ( $y = ((x^{\lambda-1})/\lambda)$ ). Employing a  $\log_{10}$  transformation recasts the trace element data into a more normal distribution, and a Z-Score transformation was used instead of a median calculation because levelling by the median does not account for the spread of the data, so any variables with a wide distribution will be predominant. The other advantage to using a Z-Score transformation is that the outliers, ranging from 1.5 to 3 standard deviations, are preserved for each variable. Outliers are classified as 1.5 x (Q3-Q1) and are represented as open circles; far outliers are classified as 3 x (Q3-Q1) and are represented as open triangles (Fig. 4).

## 4. Discussion

The biogeochemical samples collected above mineralization are elevated in both the heavy and light REE, particularly the LREE, compared to samples collected above the surrounding country rock (Fig. 6). Of the three fern species sampled, *Athyrium filix-femina* had the highest levels of LREE, and the highest average value for the HREE. However, *Dryopteris filix-mas* was most enriched in Gd, Tb, Dy, Ho, Er, Yb, and Y. These differences can be displayed using Tukey outlier “box

and whisker” plots (Figs. 3, 4). These plots divide the data into four parts by calculating the median, 75<sup>th</sup>, and 25<sup>th</sup> percentiles, which are represented as the black line in the centre, and the upper and lower limits of the coloured box, respectively. Any values that fall outside of this range are considered outliers and will be displayed as points either above or below the vertical coloured line, which is referred to as the ‘whisker’. The black circle near the centre of the coloured box is the mean of the population. Figure 3 shows the distribution of Y content above the deposit and in the background.

Figure 5 shows the fern data, coloured by species, in a chondrite-normalized plot (Boynton, 1984). No *Pteridium aquilinum* samples are plotted here because at least one HREE for each *Pteridium aquilinum* sample was below the reportable detection limit and creates a sawtooth effect, which is also visible for *Athyrium filix-femina* and *Dryopteris filix-mas* for Tm and Lu (Fig. 5). There is enrichment of LREE in *Athyrium filix-femina* (red lines). All species, with the exception of three *Dryopteris filix-mas* samples, are depleted in HREE, particularly Dy in *Pteridium aquilinum*. The three HREE-enriched *Dryopteris filix-mas* were all sampled near the most prospective rock types at Norra Kärr, the pegmatitic grennaite, strongly suggesting that this is the source of their elevated levels of Gd, Tb, Dy, Ho, Er, Tm, and Yb.

There is a slight negative Eu anomaly displayed in the *Athyrium filix-femina* and *Dryopteris filix-mas* samples (Fig. 5).

The plan maps in Figure 6 show the REE content, levelled for species type, across the deposit. Only profiles for Nd and Dy are displayed because they had the most reproducible analytical results and are good representatives for the LREE and HREE, respectively.

As shown in Figure 6a, there is a positive HREE (Dy) response directly over the grennaite in the two central lines. Also of note are the two slight elevations in the southernmost line where samples were collected over the catapleiite phyrlic units (displayed as purple dots in Fig. 6), as well as a positive response directly over a catapleiite phyrlic zone in the northeast corner of the deposit. Along the southernmost line, there is a depletion over the kaxtorpita unit because this rock type has the lowest amounts of REE in the deposit (0.2% TREO).

Very similar patterns are displayed in the LREE (Nd) profiles (Fig. 6b) but the central line, which shows a strong and uniform HREE response, has a slightly erratic LREE pattern over the same interval.

## 5. Conclusions

This biogeochemical orientation survey shows that

- all ferns, particularly *Athyrium filix-femina* and *Dryopteris filix-mas*, are able to uptake appreciable amounts of REE into their leafy tissue ferns collected over areas of known mineralization, particularly the pegmatitic grennaite units and zones with phenocrysts of catapleiite display positive responses
- *Athyrium filix-femina* fractionates the LREE more

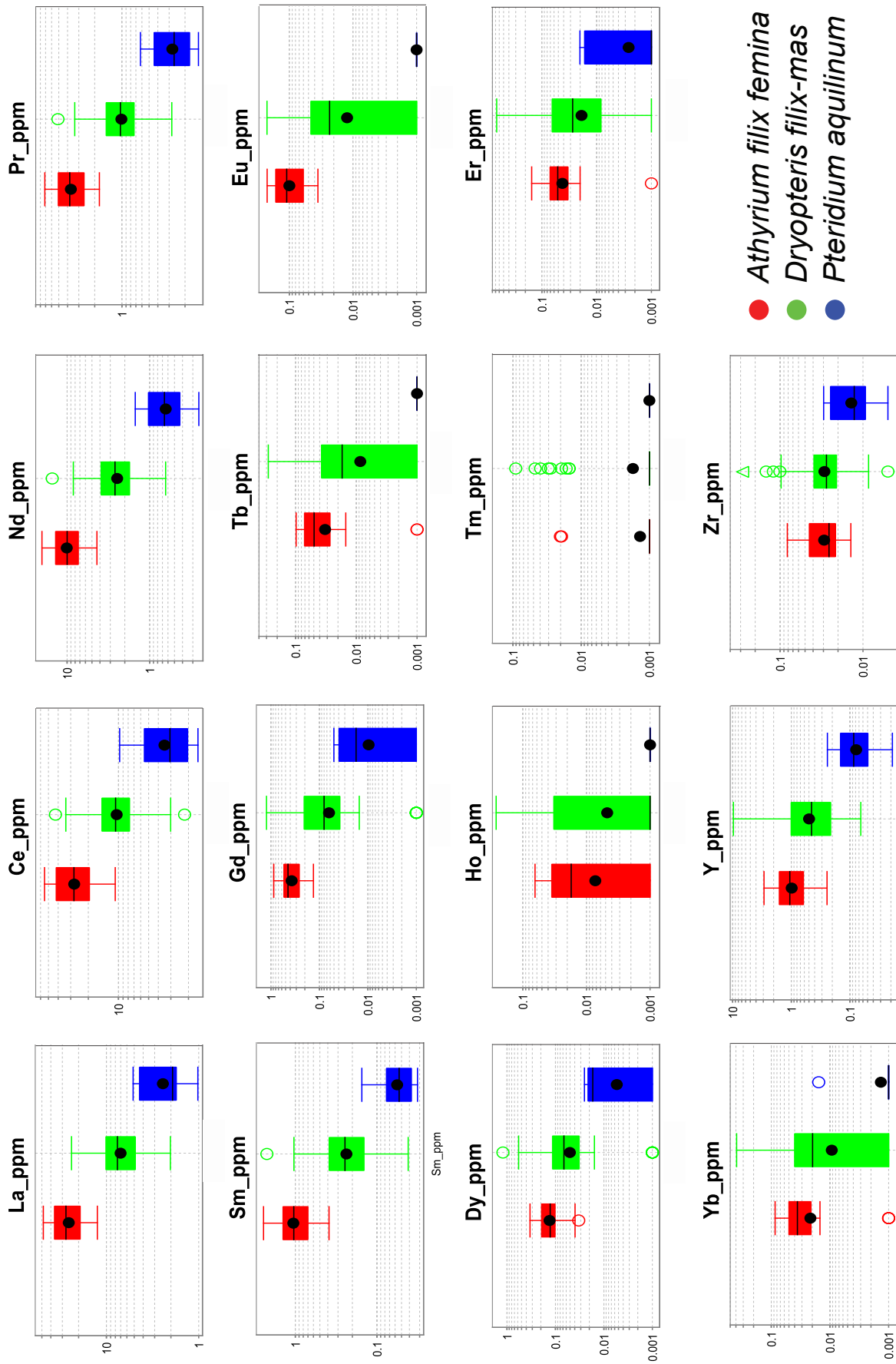


Fig. 4a. Unlevelled Tukey plots of all REE.

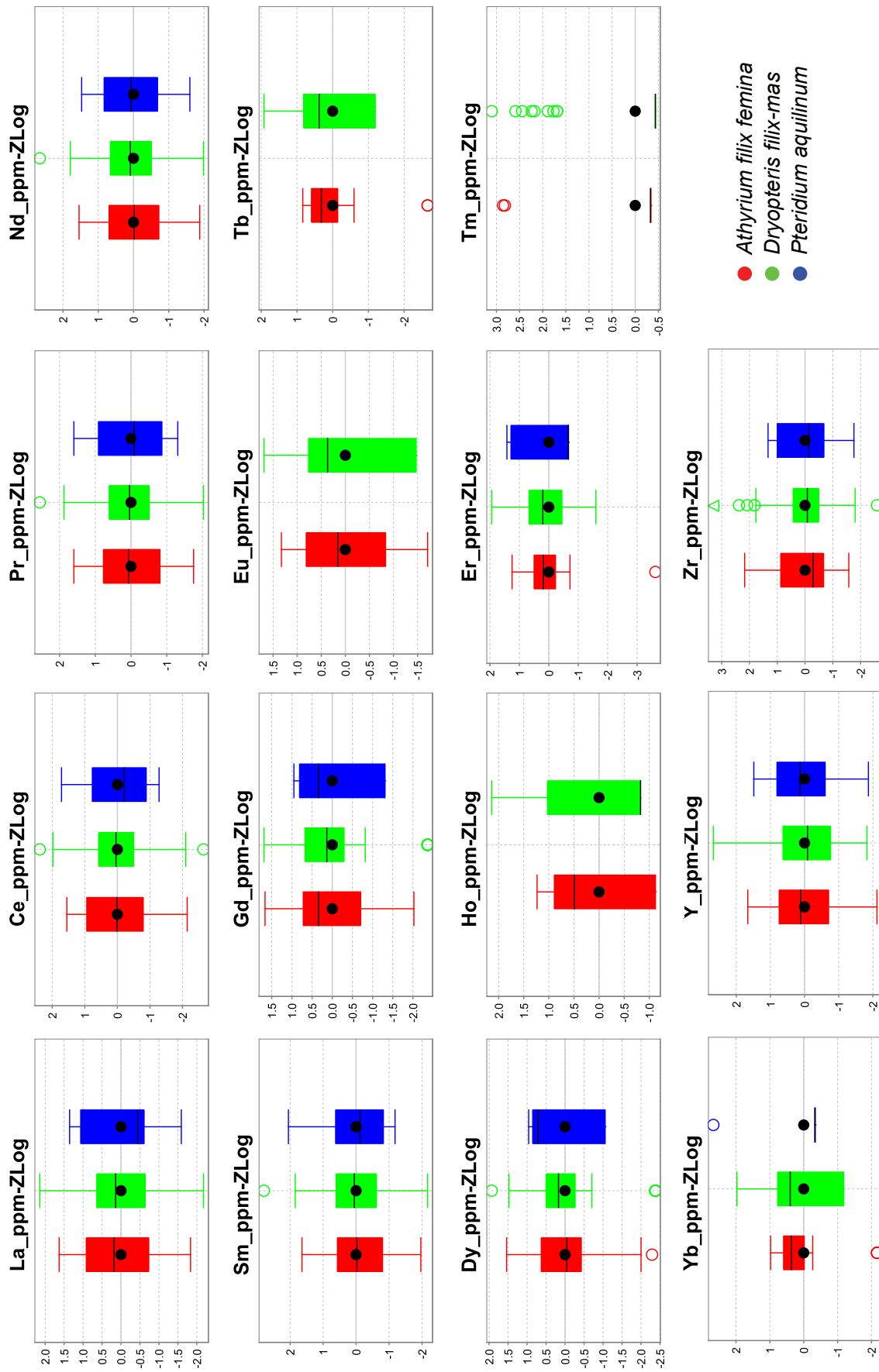


Fig. 4b. Levelled Tukey plots of all REE.

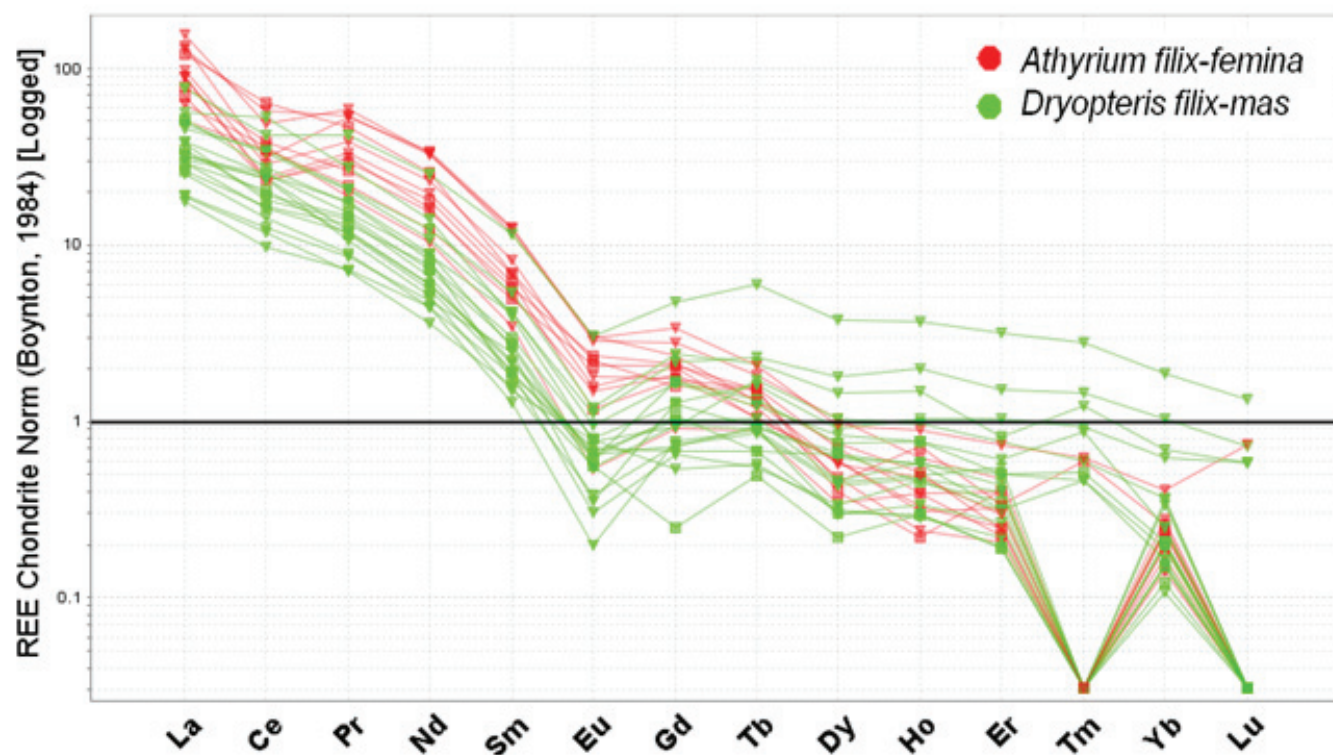


Fig. 5. Chondrite-normalized REE concentrations for *Athyrium filix-femina* and *Dryopteris filix-mas* (data above detection limit only).

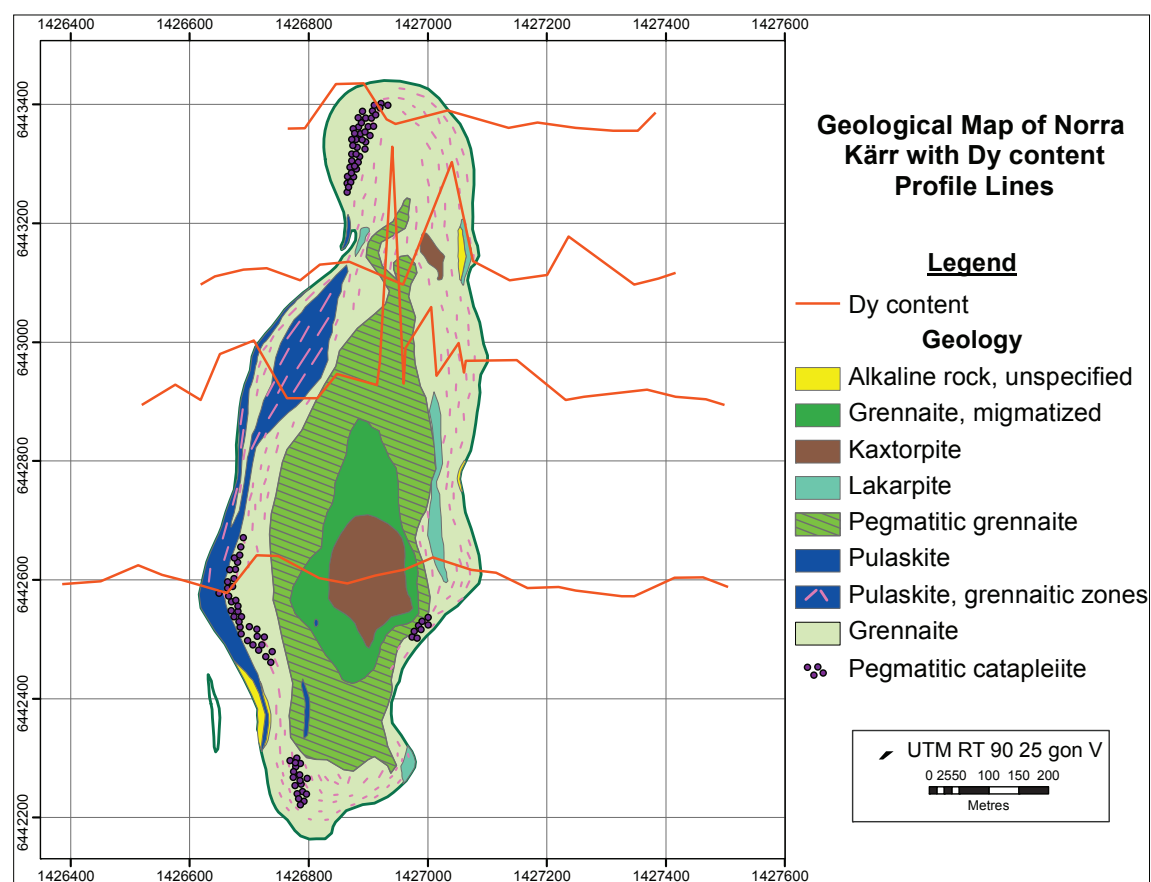
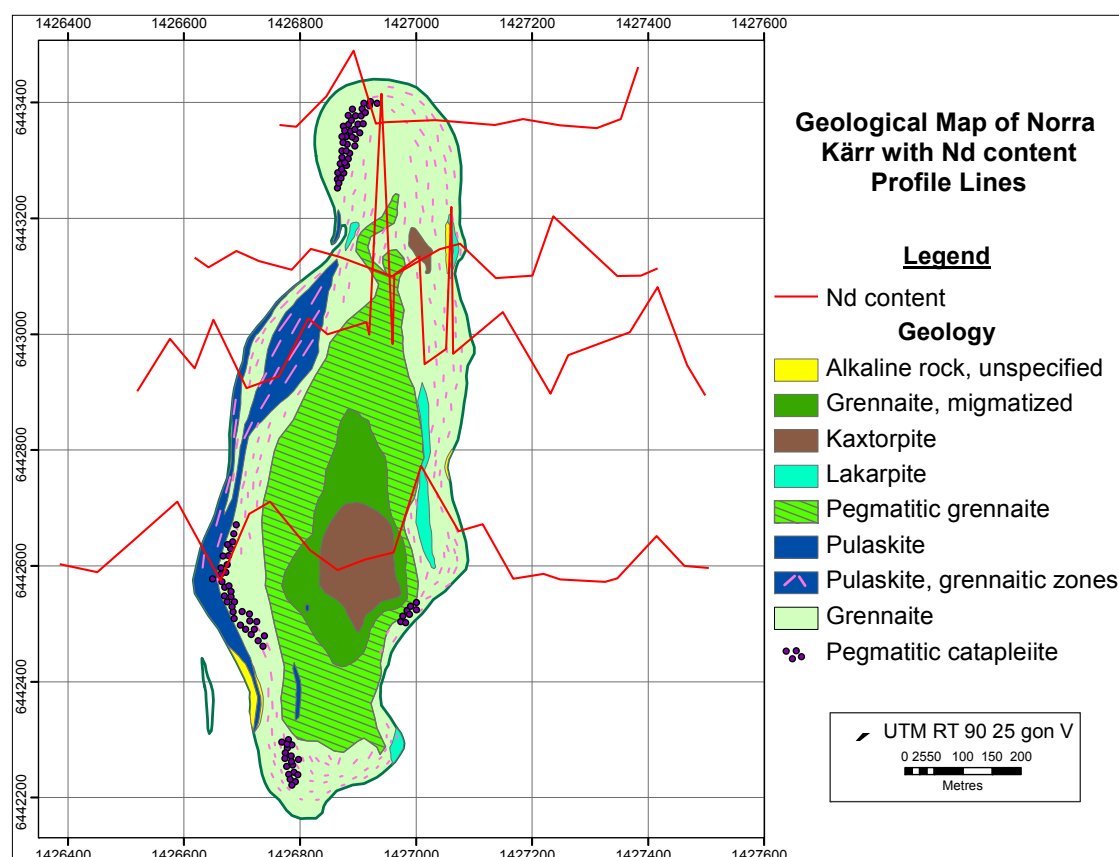


Fig. 6a. Section maps of Dy content levelled for species type, representative of HREE, over Norra Kärr.



**Fig. 6b.** Section maps of Nd content levelled for species type, representative of LREE, over Norra Kärr.

strongly than *Dryopteris filix-mas* or *Pteridium aquilinum*

- *Athyrium filix-femina* has higher absolute contents of LREE and HREE in its leaves; however, the contrast between background and anomalous areas is more clear with *Dryopteris filix-mas*, making it the preferable biogeochemical sampling medium

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## References cited

- Boynton, W.V., 1984. Cosmochemistry of the rare earth element: meteorite studies. Elsevier, Amsterdam, 63-114.
- Ding, S., Liang, T., Zhang, C., Huang, Z., Xie, Y., and Chen, T., 2006. Fractionation mechanisms of Rare Earth Elements (REEs) in hydroponic wheat: An application for metal accumulation by plants. Environmental Science and Technology, 40, 2686-2691.
- Ding, S., Liang, T., Yan, J., Zhang, Z., Huang, Z., and Xie, Y., 2007. Fractionations of rare earth elements in plants and their conceptive model. Science in China Press, 50, 47-55.
- Dunn, C.E., 1998. Regional and detailed biogeochemical surveys in the Nechako NATMAP area and in the Babine Porphyry Belt In: Struik, L.C., D.G.M. (Eds.), New Geological Constraints on Mesozoic to Tertiary Metallogenesis and on Mineral Exploration in Central British Columbia: Nechako NATMAP Project. Short Course Extended Abstracts, Cordilleran Section of the Geological Association of Canada, p. 17.
- Dunn, C.E., 2007. Biogeochemistry in Mineral Exploration. Elsevier, Amsterdam, 231-341.
- Fu, F., Akagi, T., and Shinotsuka, K., 1998. Distribution Pattern of Rare Earth Elements in Fern - Implications for intake of fresh silicate particles by plants. Biological Trace Element Research, 64, 13-26.
- Guo, F., Wang, Y., Sun, J., and Chen, H., 1996. REE Bound Proteins in Natural Plant Fern *Dicranopteris dichitoma* by MAA. Journal of Radioactivity and Nuclear Chemistry, 209, 91-99.
- Kovalevskii, A.L., 1979. Biogeochemical Exploration for Mineral Deposits. Amerind Publishing, New Delhi, India, 136p (English translation of 1974 publication in Russian).
- Li, F., Shan, X., Zhang, T., and Zhang, S., 1998. Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Environmental Pollution, 102, 269-277.
- Reed, G.C., 2011. NI 43-101 Technical Report, Norra Kärr REE — Zirconium Deposit. Pincock, Allen & Holt, Gränna, Sweden.
- Saxon, M., Leijd, M., Forrester, K., and Berg, J., 2015. Geology, Mineralogy, and Metallurgical Processing of the Norra Kärr Heavy REE Deposit, Sweden. In: Simandl, G.J. and Neetz, M., (Eds.), Symposium on Strategic and Critical Materials Proceedings, November 13-14, 2015, Victoria, British Columbia, British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Paper 2015-3, pp. 97-107.
- Tyler, G., 2004. Rare earth elements in soil and plant systems - A review. Plant and Soil, 267, 15.
- Volokh, A.A., Gorbunov, A.V., Gundorina, S.F., and Revich, B.A., 1990. Phosphorus fertilizer production as a source of rare-earth



- elements pollution of the environment. *Science of the Total Environment*, 95, 141.
- Welch, R.M., 1995. Micronutrient nutrition of plants. *Critical Review of Plant Science*, 14, 49-82.
- Wyttenbach, A., Furrer, V., Schleppi, P., and Tobler, L., 1998. Rare earth elements in soil and soil-grown plants. *Plant and Soil*, 199, 267-273.
- Zhang, Z., Wang, Y., Li, F., Xiao, H., and Chai, Z., 2002. Distribution characteristics of rare earth elements in plants from a rare earth ore area. *Journal of Radioactivity and Nuclear Chemistry* 252, 461-465.

