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# Isotopic (Nd, Hf, Sr) composition of super-large rare metal deposits from the Kola Peninsula using in-situ LA-MC-ICPMS

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# Introduction

The Khibina and Lovozero massifs represent two of the world's largest complexes of layered peralkaline intrusions. They are part of the Kola Alkaline Province, which comprises 25 magmatic centers within the Kola Peninsula and northern Karelia in Russia and Finland (Fig. 1). They are emplaced in Archean granite gneisses. They are located 20 km apart and represent two 360-380 Ma old lopolith-like complexes of similar size and shape. Eight intrusive pulses have been distinguished within the Khibina intrusion whereas three major pulses has been identified at Lovozero. A schematic profile of the 30 by 40km Lovozero intrusion is shown on figure 1. These two alkaline massifs are characterised by an extreme enrichment in volatiles (F, Cl, S), in elements like the REE and in alkalies. A previous investigation of whole rock Sr and Nd isotopic composition of the Khibina and Lovozero massifs demonstrated that the mantle source of these world's largest alkaline intrusions is significantly depleted (Kramm and Kogarko, 1994). The paradox is that the alkaline rocks of the Kola Peninsula are most enriched in rare elements, in alkalis and in LREE, but are generated by low degrees of partial melting of an extremely depleted mantle source. This can only be explained by extreme mantle metasomatism, which transports rare elements, alkalis and volatile components to the site of magma generation.

The intrusions are characterised by the exceptional occurrence of unique Nd, Hf and Sr rich minerals. Apatite, rare metal loparite and eudyalite deposits occur in these massifs together with more complex minerals such as mosandrite, pyrochlore and belovite. These minerals occur in various proportions throughout the layered intrusions and we have measured their Nd, Hf and Sr isotopic composition in-situ by laser ablation MC-ICP-MS.



Figure 1: Simplified schematic cross-section of the Lovozero intrusion, with vertical scale approximately twice the horizontal scale (modified from Kramm and Kogarko, 1994). The layering of the Differentiated Complex is illustrated in a simplified form. The base of the intrusion is not well known.

## **RESULTS AND DISCUSSION**

#### Analytical techniques

All isotopic analyses were performed on a ThermoFinnigan Neptune MC-ICP-MS, fitted with 9 Faraday collectors with  $10^{11} \Omega$  resistors and operated with low resolution slits. Solutions were introduced into the mass spectrometer in 2% HNO3 using a Cetac Aridus microconcentric desolvating nebuliser with ESI 50µl PFA nebuliser and a PFA spray chamber. All laser ablation was carried out using a Merchantek/ New Wave UP213. Helium was used as a carrier gas and mixed with Ar coming from the desolvating nebulizer. The liquid standard solution JMC475, JNdi and NBS981 have been used to calculate the mass bias respectively on Hf, Nd and Sr isotopes. In order to apply the accurate mass bias for isobaric interferences correction for the Nd, Hf and Sr isotope measurements, the 50-100ppb standard solutions were spiked with 1-5 ppb of Sm, Lu and Rb respectively. During the relevant analytical period repeated analysis of an in house plagioclase solid standard gave <sup>87</sup>Sr/<sup>86</sup>Sr values of  $0.70313 \pm 5$  while the TIMS analysis gave  $0.70306 \pm 5$ . Repeated analysis of the zircon standard 91500 gave  $^{176}\text{Hf}/^{177}\text{Hf}$  values of 0.28225  $\pm$  6 (25) while the



solution mode MC-ICP-MS result is 0.282308 ± 8 (Woodhead et al, 2004). No solid standard was available for the in-situ Nd isotope measurements. Solid samples for laser ablation were mounted in epoxy and polished to expose the sample. Hf isotope analyses were performed using a 0.2mJ energy beam at 10Hz frequency, while rastering the sample along a 60 by 200 micron line using a 3 micron/s speed. Each complete analysis took around 100 s (1 blocks of 60 integrations of 1.049 s each including a 30s baseline measurement). Nd and Sr isotopes analyses were performed using a 0.2mJ energy beam at 10Hz frequency while rastering the sample along a line of 40 by 250 microns using a 1 micron/s speed. Each complete analysis took around 190 s (4 blocks of 4 integrations of 8.2 s each including a 30s baseline measurement).

Figure 2 shows the comparison of the average initial Nd and Sr isotopic compositions of all minerals from Khibina and Lovozero by LA-MC-ICPMS during this study with the whole rock analysis by TIMS provided by Kramm and Kogarko (1994). The agreement of both analytical techniques is within analytical error.



*Figure 2:* Average ɛNd against the average Sr isotopic composition of the minerals (blue square). The isotopic compositions of the whole rocks (red square) are shown by comparison (Kramm and Kogarko, 1994). The five reservoir types are from White (1985) and the components are from Zindler and Hart (1986).

#### Samples

Table 1 shows the list of minerals analysed for their Hf, Nd and/or Sr isotopic compositions. Eudyalite is the most common mineral for our Hf analyses and Loparite

is the dominant source for the combined Sr



and Nd isotopic data. Occasionally apatite or belovite occurred together with loparite, while late pegmatite also contains pyrochlore together with belovite and some rare zircon.

Mineral	Formula	Isotope
Belovite	$Sr_3Na(Ce,La)(PO_4)_3(F,OH)$	Sr
Eudyalite	Na <sub>15</sub> Ca <sub>6</sub> (Fe,Mn)3Zr <sub>3</sub> (Si,Nb)	Hf
	(Si <sub>25</sub> O <sub>73</sub> )(O,OH,H <sub>2</sub> O) <sub>3</sub>	
	(Cl,OH) <sub>2</sub>	
Loparite	(Ce,Na,Ca)(Ti,Nb)O <sub>3</sub>	Sr, Nd
Mosendrite	$(Ca,Na,Ce)_{12}(Ti,Zr)_2Si_7O_{31}$	Nd
	$H_6F_4$	
Pyrochlore	$(Na,Ca)_2Nb_2O_6(OH,F)$	Sr
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH, F, Cl)	Sr, Nd
Zircon	ZrSiO <sub>4</sub>	Hf

Table 1: List of analysed minerals, their chemical formula and the isotopic systems studied.

#### Results

Figure 3 and 4 show the average initial Nd, Hf and Sr isotopic composition of the minerals, compared with the five mantle reservoir types of White (1985) and the three kimberlite groups defined by Smith (1983) and Skinner et al. (1994). The Khibina intrusion has a depleted isotopic signature with average  $\epsilon$ Nd and  $\epsilon$ Hf values at +4.2 +/- 0.3 (2  $\sigma$ ) and +8 +/- 2.2 (2  $\sigma$ ) respectively. For Lovozero, the average  $\epsilon$ Nd and  $\epsilon$ Hf value is slightly more radiogenic with +3.2 +/- 0.4 (2 $\sigma$ ) and +6.4 +/-2.3 (2  $\sigma$ ) respectively.

The Sr isotopic compositions of Khibina are on average  $0.70365 \pm 0.00004 (2 \sigma)$  while the Sr isotopic composition of Lovozero varies from 0.70334 to 0.714. The latter, most radiogenic Sr values are from belovite and pyrochlore from the late pegmatite stage of the Lovozero intrusion. The high initial isotopic value can be related either related to (1) extreme Rb/Sr fractionation within the intrusion or (2) to analytical interferences.

(1) The accumulation of radiogenic Sr could be related to the significant fractionation of the Rb/Sr ratio by early minerals (loparite, apatite) and enrichment of residual liquids in Rb. The late mineral puatovite (CsFeS2) in the pegmatites contains up to 1.3% Rb. A very fast increase in the Rb/Sr ratio in residual melts/fluids would result in a significant growth of radiogenic Sr in these late minerals.

(2) The unusually high Sr initials were only observed in belovite and pyrochlore, which are both Na-rich minerals. The possible interference of <sup>86</sup>ArNa<sub>2</sub> species on <sup>86</sup>Sr during the measurement could be responsible for an analytical bias.

Alkaline rocks and ores of the Lovozero and Khibina rare metal deposits have a depleted mantle Nd, Hf and Sr isotopic signature similar to OIB but different to the kimberlites.



*Figure 3:*  $\epsilon$ Nd versus  $\epsilon$ Hf average isotopic composition of the minerals (red square) compared with the OIB. The isotopic composition of the three groups of Kimberlites is also shown (data from Nowell et al, 2004).



**Figure 4:** EHf versus the Sr average isotopic composition of the minerals (red square) compared with the OIB and the kimberlites.

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