

Developing Ni as a geological tracer: A new method for Ni separation

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Before nickel (Ni) can be utilised as a geological tracer, it is critical to have the ability to fully isolate Ni from geologic materials. The separation procedure is necessary to remove/reduce the potential for interference during mass spectrometry, removing elemental interferences (eg. Cu, Fe, Zn) and organic components.

Our approach involves techniques designed to ensure complete sample dissolution and to achieve optimal recovery and purity of Ni. The procedure includes:

1. Complete sample digestion via carius tube/P-T Asher (in a reverse aqua regia solution), followed by HF:HNO₃ based dissolution [1].
2. Isolation of Ni using a two-stage column procedure. Stage 1 (anion resin) removes Cu and Fe, the latter being the major potential interference during analysis. Stage 2 (cation resin) purifies and elutes the Ni and also removes organics.
3. Determination of the Ni isotope composition by Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS; Neptune) using a in-house Cu reference material to correct for Ni mass bias.

Preliminary measurements of ⁵⁸Ni/⁶²Ni on NIST 986 deviate by ~0.06 ‰ from the certified NIST 986 value [2], and show excellent reproducibility (±118 ppm, 2SD; n=20). Our preliminary data are more accurate than that reported by Tanimizu and Hirata ([3]; 2.5 ‰ offset from accepted value). The good reproducibility of our data on NIST 986 suggests that we should be able to resolve and quantify Ni isotope variations in samples in the low per mil range (≥ 0.5 ‰), which is essential for the development of Ni a geological tracer.

[1] Ottley, C. J., Pearson, D. G. and Irvine, G. J. (2003) *Plasma Source Mass Spectrometry: Applications and Emerging Technologies*, Royal Society of Chemistry, 221-230. [2] Gramlich, J. W., Machlan, L. A., Barnes, I. L. and Paulsen, P.J. (1989) *J. Res. Natl. Bur. Stand.*, **94**, 347-356. [3] Tanimizu, M. and Hirata, T., (2006) *Jour. Anal. Atom. Spec.* **21**, 1423-1426.

Pyroxenite melts involved in magma genesis in Kamchatka

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Several models have been proposed to explain systematic geochemical changes along the Central Kamchatka Depression (CKD) correlating with the slab dip and the distance from volcanoes to the subducting slab [1-3]: (1) mixing of primitive basaltic and silicic crustal magmas, (2) mixing of peridotite and eclogite melts, (3) temperature control of peridotite-melt equilibria, and (4) mixing of pyroxenite and peridotite melts. To test these hypotheses we have carried out a high precision analysis [4] of major and trace elements (Ca, Ni, Mn, Cr, Co, Al) in olivine phenocrysts from 6 volcanoes along the CKD, from Southern (SG: Kliuchevskoi and Tolbachik volcanoes) and Northern (NG: Shishinsky Complex Shiveluch, Zarechny and Kharchinsky volcanoes) volcanic groups. Our results reveal a systematic difference between the composition of the most magnesian olivines (Fo89-92.5) along CKD. SG olivines have systematically higher Ca/FeO (112-140), Mn/FeO (124-130) and lower Ni/MgO (35-60) (all in ppm/wt%) compared to NG olivines (61-111, 107-117, 51-91).

The best explanation for the systematic differences between SG and NG olivines and rock compositions is mixing of pyroxenite and peridotite-derived melts [2]. By using the approach of ref. [4], we estimate that SG parental melts contain no more than 20% pyroxenite-derived component, whereas its amount increases to 35-60% in NG parental melts. The SG primitive rocks have lower Si, Na, Sr/Y and higher Fe, Mg, Ca, Ti, Y than NG rocks, also consistent with a primarily peridotite source [5]. Systematically lower amount of peridotite-derived component in NG parental melts can be related to concurring effects of lower temperatures, shorter melting columns and, possibly, larger amount of pyroxenite in the mantle wedge, resulting from reaction of peridotite with abundant slab melts generated at the edge of the subducting Pacific plate.

[1] Yogodzinski *et al.* (2000) *Nature* **409**, 500-504. [2] Portnyagin *et al.* (2007) *AGU Geophys. Monograph* **172**, 203-244. [3] Portnyagin & Manea (2008) *Geology*, **38**, 519-522. [4] Sobolev *et al.* (2008) *Science* **321**, 536. [5] Herzberg & Azimov (2008) *Geochem. Geophys. Geosyst.* **9**, Q09001.