Towards a new proxy for Holocene climate change: Magnesium-isotope fractionation during low-Mg calcite precipitation in a limestone cave

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We here present a complete analytical dataset of magnesium isotopes (δ^{26}Mg) from a monitored cave in NW Germany (Bunker Cave). The data set includes δ^{26}Mg values of loess-derived soil above the cave (-1.0±0.5‰), soil water (-1.2±0.5‰), the carbonate hostrock (-3.8±0.5‰), dripwater in the cave (-1.8±0.2‰), speleothem low-Mg calcite (stalactites, stalagmites; -4.3±0.6‰), cave loam (-0.6±0.1‰) and runoff water (-1.8±0.1‰) in the cave, respectively. Apparent Mg isotope fractionation between dripwater and speleothem low-Mg calcite is about $1000\ln\alpha_{\text{Mg-cc-Mg (aq)}} = -2.4‰$. A similar Mg isotope fractionation ($1000\ln\alpha_{\text{Mg-cc-Mg (aq)}} \approx -2.1‰$) is obtained by abiogenic precipitation experiments carried out at aqueous Mg/Ca ratios and temperatures close to cave conditions.

Can cratonic mantle be formed in subduction-related settings?

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Cratonic lithosphere is believed to differ from off-craton mantle in modal and chemical composition. Some distinctive features of cratonic mantle, like enrichments in silica and opx, can be related to 'hydrous' partial melting at active plate margins [1]. Comparisons of residual peridotites from modern or recent subduction settings to cratonic peridotites are relevant to the subject but are hindered by (i) rarity of supra-subduction mantle samples and (ii) common overprinting of residual peridotites by metasomatism and alteration.

New data on harzburgite xenoliths from the andesitic Avacha volcano in Kamchatka [2] are remarkably consistent with those for peridotites dredged in the Izu-Bonin-Mariana forearc [3]. These supra-subduction zone harzburgites show a combination of variable but generally high modal opx (18-30%) with low modal cpx (1.5-3%) and have higher opx (and SiO_2) and lower cpx (as well as Al_2O_3 and CaO) at given olivine or MgO contents than normal refractory peridotite xenoliths in continental basalts. The high SiO_2 in some of the rocks may be due either to fluid fluxing during melting in the mantle wedge or selective metasomatic enrichments in SiO_2 to transform some olivine to opx. High SiO_2 ≥46% may be related to opx-rich veins in the harzburgites.

Many peridotite xenoliths from the Siberian craton from this and earlier [4] work fall into the supra-subduction mantle field defined in this study but the majority show broad data scatter and typically have higher Ca and Al at given SiO_2. The latter are most common in high-T, sheared peridotites and seem to be produced by refertilization of residual mantle by melt percolation. New data on fresh coarse-grained spinel and garnet-poor harzburgites from the Udachnaya kimberlite are used to better constrain modal and major oxide compositions of initial melting residues, as well as their possible relation to subduction settings, during the formation of the Siberian craton. Silica-rich harzburgites (SiO_2 ≥46%) may be less common in the Siberian craton than in the Kaapvaal craton.

[1] Pearson & Wittig (2008) *J. Geol. Soc. London* **165**, 895–914. [2] Ionov (2010) *J. Petrol.* **51**, 327–361. [3] Parkinson & Pearce (1998) *J. Petrol.* **39**, 1577–1618. [4] Boyd *et al.* (1997) CMP **128**, 228–246.