Determination of hexavalent Cr reduction using Cr stable isotopes: Isotopic fractionation factors for *in situ* redox manipulation zones

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Cr stable isotope measurements can provide estimates of the extent of Cr (VI) reduction, which immobilizes the Cr and renders it less toxic. Cr isotope fractionation occurs during Cr (VI) reduction, but the intensity of isotopic fractionation is known to vary with reaction mechanism, and thus the relationship between observed $^{53}Cr/^{52}Cr$ ratio shifts and the extent of reduction must be properly calibrated for use in each particular setting. The degree of variability is poorly understood at present.

The Cr isotope method should prove useful in studying the performance of *In Situ* Redox Manipulation (ISRM) zones. Here, we report site-specific fractionation factors for an ISRM zone created by injecting sodium dithionite at the 100D area of the U.S. DOE's Hanford site.

We determined Cr isotope fractionation factors for Cr (VI) reduction in batch experiments with sediments cored from the ISRM zone and pure mineral phases thought to occur within it. Sodium dithionite injection creates reduced Fe (II) phases (sorbed Fe (II), $FeCO_3$, FeS, and perhaps other phases such as green rust) in the sediment, among which sorbed Fe (II) is thought to be dominant. The fractionation factor was determined in two experiments with sediments collected at two different depths from a borehole down-gradient from a dithionite injection well in the 100D ISRM zone. Results indicate ε was 3.5‰ ($\varepsilon = \alpha$-1, where α is the fractionation factor; $\varepsilon \approx \delta_{reactant} - \delta_{product}$). This coincides with a preliminary ε value of 3.5‰ for Cr (VI) reduction by synthesized $FeCO_3$. The value of ε for Cr (VI) reduction by synthesized green rust is 2.7‰, significantly lower than the ISRM sediments, suggesting that green rust is probably not a dominant reducing phase. Further work will determine fractionation factors for reduction by FeS and Fe (II) sorbed onto/into hematite particles.

So far, it appears fractionation factors for Cr (VI) reduction by ISRM sediment and likely ISRM phases fall within a narrow range similar to that observed in the few previously published Cr isotope studies. This aids in interpretation of Cr isotope data from the ISRM zones, by providing a better calibration of the relationship between $\delta^{53}Cr$ and the extent of Cr (VI) reduction.

In situ geochemistry of garnet peridotites of Lashaine, Tanzania craton: Re-fertilization in sub-cratonic lithospheric mantle

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In situ major- and trace-element geochemical analyses and detail petrography for 25 garnet peridotite xenoliths, within tuff cone of ankaramitic scoria in Lashaine at the Tanzania craton margin, provide information regarding multiple mantle processes in the sub-cratonic lithosphere.

Based on the modal composition, investigated xenoliths are classified as garnet lherzolite (GL) and garnet harzburgite (GH). GL is characterized by an ubiquitous presence of discrete (Cr, Ca)-rich garnet (Grt; ~6wt% Cr_2O_3, 5-6wt% CaO), (Na, Cr)-rich clinopyroxene (Cpx; ~3.5wt% Na_2O, ~3.6wt% Cr_2O_3), and Grt exsolution lamellae in orthopyroxene (Opx). GH contains irregular-shaped garnetite clot (up to 1.5 cm in size) of fine-grained Cr-rich, Ca-poor Grt (~5wt% Cr_2O_3, 1-3 wt% CaO). GL and GH yield P-T conditions of <6.5 GPa at >1000°C and ~ 4.5 GPa at ~ 850°C, respectively. Most Grts in both GL and GH are partly replaced by Cr-spinel and Al-rich Opx-Cpx. In addition, (Na, Cr)-rich Cpx in GL is mantled by less-jadeitic rims with abundant melt inclusions. These textures indicate that both GL and GH experienced upwelling from the garnet to spinel stability field, associated with decompression melting.

Lamellae Grt within Opx in GL is characterized by a MREE-depleted sinuous REE pattern, which is commonly observed in diamond-bearing kimberlitic Grt. In GL, trace element compositions of remnant Grt, and (Na, Cr)-rich Cpx are homogeneous with LREE-enriched patterns. These results indicate interaction between deep lithospheric mantle and kimberlitic alkaline melts prior to upwelling of the GL body during the decompression event. On the other hand, remnant Grt in GH preserves less-enriched LREE pattern. Owing to either incipient metasomatic melt fluxing in primary depleted mantle or apparently shallower level of disposition of GH in the mantle than that of GL, GH might have been experienced feebler re-fertilization compared to GL. This different degree of re-fertilization in depleted lithospheric root at the craton margin has implications for the interpretation of global tectonic framework.