

New insights into San Carlos mantle xenoliths using iron isotopes

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Iron isotopic compositions of mantle minerals can provide powerful tracers for geochemical processes in the mantle, such as partial melting, metasomatism, and oxidation. Predictions of equilibrium fractionation from theory and Mössbauer data conflict, making the meaning of Fe isotope fractionation in the mantle uncertain. To address this, we studied inter-mineral iron isotopic fractionation of minerals from five distinct mantle-xenolith lithologies from San Carlos, Arizona. The samples represent a broad range of mineral modes and include a clinopyroxenite, a websterite, a lherzolite, a harzburgite, and a dunite. All samples except for the websterite are Group I inclusions, which are typically rich in Mg and Cr, and consist of mainly olivine-rich rocks. Group II inclusions, represented here by the websterite, are enriched in Al and Ti, and commonly contain more clinopyroxene than orthopyroxene [1]. Each xenolith exhibits Fe-isotopic variation between minerals in a single sample, and between samples. In all cases where spinel and olivine coexist in a sample, the ⁵⁷Fe/⁵⁴Fe of spinel is greater than that of the corresponding olivine, agreeing with predictions of equilibrium fractionation from theory. ⁵⁷Fe/⁵⁴Fe values of clinopyroxenes and orthopyroxenes from the xenoliths show no clear systematic differences. Plots of δ⁵⁷Fe of the pyroxenes versus δ⁵⁷Fe of the other minerals show that the pyroxenes underwent some open-system processes and are not in equilibrium with the coexisting olivine and spinel. We interpret this as a result of varying degrees of disequilibrium in the samples due to late stage open-system processes, such as metasomatism or partial melting, affecting the pyroxenes only. A strongly linear reverse correlation between olivine content and bulk rock ⁵⁷Fe/⁵⁴Fe was found for all samples except the websterite (the only type II xenolith measured). The strong linear relationship among Group I samples, and deviation from the trend in websterite, suggests Fe isotope systematics can be added to the list of differences used to distinguish between Group I and Group II xenoliths.

[1] Frey & Prinz 1978 *EPSL* **38**, 129–176.

Soluble Mn(III), Mn(II) and total Mn in sediment porewaters: Soluble Mn(III) is ubiquitous

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Recent research shows that soluble manganese(III) or [Mn(III)]_{aq}, that material which passes through a 0.2 μm filter, exists in natural waters such as the Black Sea, the Baltic Sea and Chesapeake Bay and can constitute a large fraction of the dissolved Mn pool at the oxic/anoxic interface. Recently Madison *et al.* [1] have reported a direct and accurate spectrophotometric method to measure [Mn(III)]_{aq} in sediment porewaters. The method is capable of rapid and simultaneous determination of [Mn(III)]_{aq}, [Mn(II)]_{aq}, and total soluble Mn. This method was successfully applied to the determination of all soluble Mn species in sediment porewaters of the Lower St. Lawrence Estuary collected during cruises in 2009 and 2010 and in Delaware salt marsh sediments. In all samples, [Mn(III)]_{aq} accounts for up to 80% of the total dissolved Mn pool in the upper oxic and suboxic sediments with concentrations ranging from the detection limit of 50 nM to 80 μM. Data will be presented that highlight the role [Mn(III)]_{aq} plays in Mn cycling and how it can impact several important geochemical cycles.

[1] A.S. Madison, B. M. Tebo, G. W. Luther, III. (2011) *Talanta* **84**, 374–381.