Sulfide Re-Os Dating in Modally Metasomatised Peridotites, Insights from Letlhakane (Botswana)

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Mantle xenoliths are a geochemist's window into the chemical and mineralogical make-up of the sub continental lithospheric mantle. However, metasomatism can obscure the primary composition and melt depletion history of the xenoliths. Therefore, whole-rock Re-Os age analysis of peridotite xenoliths may provide only a minimum estimate for the age of the lithospheric mantle, and likely reflects the presence of multiple generations of base metal sulfides (BMS) or platinum group minerals (PGM), which differ in age as well as mineralogy and habit. While metasomatic sulphides and/or PGM are likely to yield 'artificially young' Re-Os ages, refractory PGM such as Os-Ir-Ru alloys and refractory sulphides (e.g. laurite) should preserve older ages as a result of their high Os concentrations and resilience to overprinting and isotopic resetting. Together they provide the perfect target to investigate the Os isotopic heterogeneity in mantle samples.

Peridotite xenoliths found associated with the Letlhakane kimberlite (Magondi Belt, Botswana) provide us with a unique opportunity to study modal metasomatic effects on Re-Os and PGE systematics [1]. Whole rock analysis of xenolith samples from Letlhakane show co-variations of Re-Os T_{RD} ages and highly siderophile element fractionations (e.g. Pd/Ir: 0.1, T_{RD}: 2.7Ga – Pd/Ir 1.69, T_{RD} 1.6Ga), due to variable degrees of metasomatic overprint. Three samples that cover the entire metasomatic range were chosen to measure single grain sulfides for Re-Os via micro-distillation. Preliminary results show a wide range in sulfide T_{RD} ages, from future ages to over 3.0 Ga, even in the most metasomatised sample. The habit and structure of the sulfide seems to be the most important factor. Disseminated sulfides occuring in veinlets have the youngest age and most radiogenic ¹⁸⁷Os/¹⁸⁸Os. On the other hand, discrete interstitial sulfides exhibit unradiogenic ¹⁸⁷Os and Archean ages. Our preliminary findings stress the micro-scale heterogeneity of Os isotopic signatures, which likely reflects mulitple host mineral generations whose origins are linked to the complex multi-event petrogenetic history of mantle samples.

[1] Stiefenhofer et al. (1997) Contrib. Mineral Petrol. 127, 147-158.

The Role of Reactive Intermediates in Redox Transformations of Iron in Photolyzed Acidic Natural Organic Matter Solutions

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Recent studies of the dark oxidation of Fe(II) in previously photolysed acidic solutions of natural organic matter (NOM) (Garg *et al.* [1]) suggest the superoxide-mediated formation of semiquinone radicals which act as effective oxidants of Fe(II) (Schematic 1).



Schematic 1. Photolysis of NOM generates HO_2^* which, in turn, oxidize hydroquinone species (A^2) present in NOM to semiquinone radicals (A^{-}). These radicals are effective oxidants for low concentrations of Fe(II). After Garg *et al.* [1]

In comparison, on continuous photolysis, light-generated singlet oxygen appears to oxidise A^{\cdot} to the quinone form (A) with short-lived organoperoxy radicals (ROO*) capable of oxidizing Fe(II) (Garg *et al.* [2]).

[1] Garg, S., Ito, H., Rose, A.L. and Waite, T.D. (2013). *Environ. Sci. Technol.* **47**, 1861–1869. [2] Garg, S., Jiang, C., Rose, A.L. and Waite, T.D. Environ. Sci. Technol. (submitted March 2013).