

## Reevaluation of highly siderophile element concentrations and Re-Os isotopes in geological reference materials

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Highly siderophile elements (HSEs: Re, Au, Ir, Os, Ru, Rh, Pt and Pd) and the Pt-Re-Os isotope systems embedded within these elements are recognized as important tracers for understanding the origin and evolution of the Earth, complementary to the more commonly used lithophile elements and isotopes. Current database on HSE concentrations and Os isotopes in meteorological/geological samples are dominated by data from isotope dilution-mass spectrometry (ID-MS), which is expected to yield high quality data (excepting monoisotopic Rh and Au) regardless of chemical recovery. In most cases, ID-MS is coupled with sample digestion using inverse aqua regia in closed glass vessels under high pressure (~130 bars) and temperature (220-320°C) such as a Carius tube (CT) and high-pressure asher system (HPA). These acid digestion techniques are now apparently preferred over traditional flux fusion techniques such as NiS fire assay (NiS-FA) because of (1) much lower procedural blank levels; (2) less chance of incomplete spike/sample equilibration; and (3) capability of Re-Os determinations on the same sample aliquot. By contrast, two major issues have been associated with the limitation of acid digestion procedure. First, typical CT and HPA techniques, which can only process 1-2 g portions of samples, are vulnerable to the so-called nugget effect because most HSEs in rocks are generally concentrated in minor accessory phases such as base metal sulfides and platinum-group minerals. The second issue concerns the incomplete digestion if aqua regia cannot leach out any of the HSEs hosted in silicates and other acid-resistant phases such as spinel and HSE alloys. In order to overcome these potential drawbacks, considerable efforts have been devoted to obtaining better accuracy and precision by modifying CA and HPA digestion techniques.

We describe in this presentation a renewed analytical protocol that is suitable for small amount of samples (<2 g), with the aim of obtaining accurate <sup>187</sup>Os/<sup>188</sup>Os ratios and HSE concentrations (except for mono-isotopic Rh and Au) from a single aliquot of geological samples by using ID-ICP-MS and ID-N-TIMS. The optimum digestion method adopted after intensive tests with varying methodologies (i.e. Carius tube or microwave), conditions (i.e. temperature and duration) and protocol (i.e. HF desilicification before or after aqua regia attack) includes the regular inverse aqua regia attack in Carius tubes followed by a desilicification step with HF in order to liberate HSEs contained in residual silicates. Although the method has already been introduced for determining Ir, Ru, Pt and Pd concentrations of mid-oceanic ridge basalt (MORB) glasses by Bezos et al. (2005) and Tongan arc basalts by Dale et al. (2012), we extend the application to the Re-Os isotope systems which are not fully evaluated in previous studies. The importance of the desilicification step for different sample type was examined by comparing the results of replicate analyses of basaltic (TDB-1 and BIR-1), ultramafic (UB-N and JP-1) and sedimentary (SCO-1 and SDO-1) rock reference materials digested with and without HF. Resultant analytical values for the reference materials, which are compared to literature values, support the previous notion that HF treatment is necessary for some basaltic materials but not for typical ultramafic and sedimentary samples.

Keywords: highly siderophile elements, Re-Os isotopes, isotope dilution analysis, ICP-MS, N-TIMS