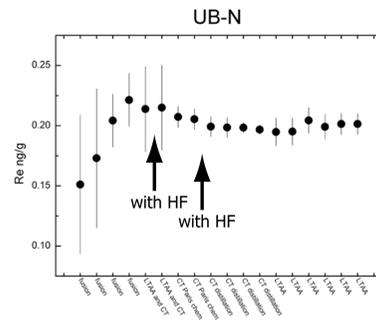
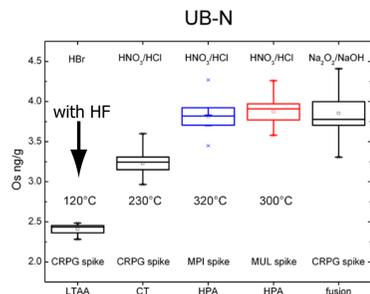




Introduction

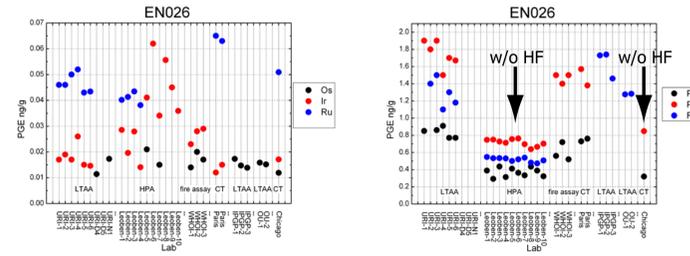
Complete digestion and dissolution as well as complete recovery of an element of interest are essential for accurate measurement. Early Re and Os analysis, in the mid-late 1950's utilised alkali fusion to liberate Os-containing mineral phases without oxidising Os to a volatile species. Acid digestion under reducing conditions (HCl, HF and ethanol) was considered to be the way forward in the 1980's. The rediscovery of Carius tubes applying concentrated HCl and HNO₃ only, which were used in the 1940's for platinum group element dissolution, was thought to be a major step forward toward complete digestion and spike – analyte equilibration for Re as well as for Os in the 1990's. It was observed that Carius tube (CT) digestion at ca. 230°C was not sufficient for complete Os dissolution, particularly in harzburgites. At the end of the 1990's it was demonstrated that a minimum temperature of 300°C was essential in the case of harzburgites. These conditions were achieved either with a High Pressure Asher (320°C) or with high temperature Carius tubes (350°C). This digestion method was validated with various kinds of peridotites and complete recovery of Re and Os was demonstrated by also applying fusion as an independent method of sample digestion. Thus acid digestions under high pressure and temperature are currently assumed to be the state of the art for isotope analysis within Re-Os isotope system.

peridotite studies

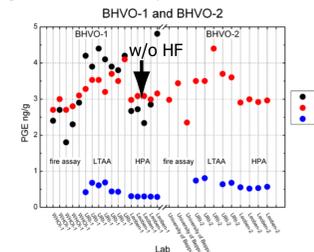


Based on the UB-N peridotite studies:
Acid digestions at temperatures above 270°C are assumed to be the best sample preparation technique for PGE analysis

Observations on basaltic reference materials from previous studies



PGE and Re results for the interlaboratory comparison of MORB EN026 10D3, an in house RM from the University of Rhode Island (URI). Other participants were WHOI Wood Hole Oceanic Institution, Natural History Museum of Paris, the IGP Institut de Physique du Globe de Paris, the OU Open University, The University of Chicago and the Montanuniversität Leoben. LTAA stands for low temperature acid attack with HBr and HF, HPA for high pressure asher digestion without HF, fire assay for NIS bead formation in LITB, Carius tube digestion for acid digestion at ca. 230°C.



PGE and Re results for the interlaboratory comparison of BHVO-1 and its successor BHVO-2 an Hawaiian basalt reference material provided by the USGS.

From about 10 years ago, it was apparent that for basaltic materials the use of hydrofluoric acid (HF) had a significant effect on the yields of Re and in the case of EN026 also on Pd and Pt concentrations. Difference at that time were attributed to different batches of the sample powder provided for the interlaboratory comparison.

Based on these previous studies it is accepted that a low temperature acid attack (LTAA) with HF is not sufficient to liberate all Os, Ir and Ru from peridotites and on the other hand that high temperature - high pressure digestions (e.g. with HPA) w/o HF yields low Re, Pd and Pt results for some basaltic materials.

Conclusion:

While for peridotites complete PGE and Re liberation with acid digestion without hydrofluoric acid (HF) can be achieved, basaltic materials, including MORB, can only be digested in the presence of HF.

Observations on basaltic reference materials new systematic studies

Methods:

High Pressure Asher digestion:

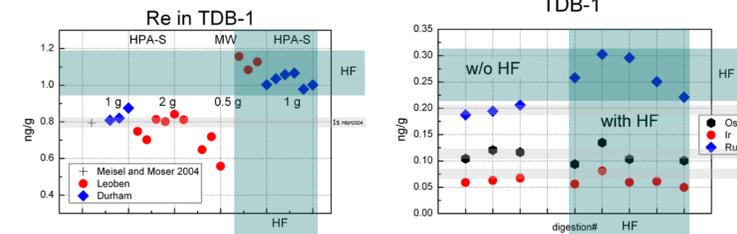
Test portions (1g) of reference material TDB-1 were spiked and digested using inverse aqua regia (2.5ml 12 mol l⁻¹ HCl and 5 ml 16 mol l⁻¹ HNO₃) in an Anton-Paar HPA-S at 300 °C for at least 12 hours. Five aliquots were also digested with 29 mol l⁻¹ HF either prior to HPA digestion (with 12 mol l⁻¹ HCl), or following Os extraction after HPA digestion. Os was extraction from the aqua regia, purified and analysed by N-TIMS on a ThermoFinnigan Triton at Durham University. Re, Ir, Ru, Pt and Pd were separated and purified using AG1X-8 (100-200#) anion-exchange resin, and were measured on the ThermoScientific Element 2 ICP-MS at Durham University.

At **Leoben** 2 g sample test portions of TDB-1 were spiked and digested with 2 ml 12 mol l⁻¹ HCl and 5 ml 16 mol l⁻¹ HNO₃ in an Anton-Paar HPA-S at 300 °C for at least 4 hours. PGEs and Re concentrations were determined on-line via isotope dilution with a cation exchange resin (AG50wx8) colum coupled to an ICP-QMS (Agilent 7500). Osmium concentrations were determined via sparging of OsO₄ directly into the ICP torch.

Microwave digestions:

All test portions of TDB-1 were 0.5 g only. After spiking, a mixture of 29 mol l⁻¹ HF, 12 mol l⁻¹ HCl 16 mol l⁻¹ HNO₃ was added to TFM vessels. The digestion was performed in a Multiwave microwave oven from Anton-Paar at 220 °C for ca. 30 minutes. After drying and driving off most of the HF, chromatographic separation was performed as mentioned above in the **Leoben** method.

Results:



PGE and Re results on TDB-1, a basaltic PGE reference material from CANMET, of this work. Only the use of HF increases and not the applied temperature yields higher results for this material.

Overall, it is now clear that a low temperature acid attack (LTAA) with HF is not sufficient to liberate all Os, Ir and Ru from peridotites and on the other hand that high high temperature - high pressure digestions (e.g. with HPA) w/o HF yields low Re, Pd and Pt results for some basaltic materials.

For magmatic rocks formed under sulphide-undersaturated conditions, HF is even more important for complete PGE and Re extraction, as a significant proportion of the PGE may be hosted by silicates, as demonstrated for Tongan arc lavas (Dale et al., in prep).

