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Optimisation of sample preparation protocols for measurement of PGE and Re-Os in organic-rich shales by isotope dilution ICP-MS

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Platinum-group elements (PGE) and Re-Os isotopes, which are variably redox-sensitive and fluid-soluble, have potential as proxies for the oxygenation of the atmosphere and oceans (e.g. [1]). However, analysis of these elements in organic rich shales (ORS) is challenging due to abundances of <1 ng/g and the presence of interfering isotopes or molecules of matrix elements. Furthermore, PGE-ReOs systematics in detrital and hydrogenous components may vary, and the choice of digestion parameters (reagents, temperature and pressure) during decomposition of rock powder affects the ratio of digested components [2,3]. Additional treatment to remove the matrix and pre-concentrate PGE-Re by column chromatography is necessary to minimise the effects of interfering elements, but presents its own challenges.

We are in the process of conducting variations of acid digestion and column chromatographic protocols on reference sample SDO-1 (Devonian Ohio Shale, USGS). We aim to identify the optimum protocol to investigate PGE-Re-Os systematics of ORS that were sampled as part of the Barberton Drilling Project BARB5 drill core, in order to constrain the changes in detrital and hydrogenous contributions to the sediment with time, to assess the extent of euxinity in the sedimentary basin and to look for evidence of transient “whiffs of oxygen” [1]. The following digestion methods were tested: (1) 4h acid digestion in High Pressure Asher (HPA) apparatus with reverse aqua regia at 300°C and 130 bar (only this digestion allows extraction of volatilised Os in CHCl3 followed by HBr); (2) 3h reverse aqua regia digestion in centrifuge vials on hotplate at 80°C; (3) 48h reverse aqua regia digestion in closed Teflon beakers on hotplate at 140°C followed by a HF/HNO_3 digestion step; (4) 48h HF/HNO_3 digestion of ashed sample powder in closed Teflon beaker at 140°C on hotplate followed by an aqua regia digestion step. Column chromatographic approaches to decrease the concentrations of interfering elements (Y, Zr, Mo, Cd, Hf, Hg) include the use of cation- and anion resins, and variations of the molarity and composition of the eluent.

Preliminary results show that digestion method (1) leaves behind small amounts of presumably PGE-free silica gel; (2) yields consistently higher Re concentrations with an expectedly large amount of solid residue; (3) produces an insoluble sludge; (4) allows complete digestion, but precludes the collection of Os. Column calibrations show the best recovery of PGE-Re in cation resin using 0.2 mol/l HCl as eluent, but intolerably high ratios of interfering over elements of interest, whereas the best matrix separation is achieved using 0.05 mol/l HCl as eluent, but is accompanied by low PGE-Re yields presumably due to the instability of Cl complexes in this medium. They also show that U elutes separately from PGE-Re in 6 mol/l HCl and could be collected with a view to analysing U isotopes as an additional redox proxy. Further tests will be carried out using alternative high-pressure digestion systems.

[1] Anbar, et al. (2007) Science 317:1903-1906; [2] Meisel et al. (2003) JAAS 18:720-726; [3] Xu et al. (2012) CG 324:132-147