The first multiple sulfur isotope evidence for a 2.9 Ga Mesoarchean sulfate reservoir

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The relationship between the evolution of Earth's atmosphere and hydrosphere during the Archean are important and mass-independent fractionation (MIF) of multipe sulfur isotopes caused by ultrviolet photolysis of atmospheric SO_2 is a key contribution to this when the atmosphere was oxygen poor and ocean was sulfur poor. In particular understanding why there are significant variations in the degrees of mass independent fractionation during the Archean and why it was lowest in the Mesoarchean (from 3.3 to 2.8 Ga) is important. This had been suggested to be a result of an early rise of oxygen. However, more recent studies show there is no clear evidence that oxygen rose then and the strongest Mesoarchean $\Delta^{33}S$ MIF values ranged from -0.13 to 1.31 between 2.96 Ga and 2.9 Ga [1] that coincide with volcanic events during this period that erupted volcanic gasses to the atmosphere for development of MIF and the most abundant Mesoarchean sulfur. Because prior to 2.7 Ga there is a limited rock record and most samples analysed from the Mesoarchean are from continental margin sedimentary ocean basins, the lack of significant negative $\Delta^{33}S$ values has provided no evidence for oceanic sulfate during this period. However, the ~2.9 Ga Lake Johnston Greenstone belt in the Yigarn Craton is a marine rift with submarine volcanic rocks (basalts, felsic volcanics and komatiites) shales and banded iron formations (BIFs) with a significant amount of low temperature volcanogenic massive sulfides (VMS) and the Maggie Hays komatiite-hosted Ni sulfide deposit. The $\Delta^{33}S$ values we recently obtained from this belt range from -1.7 to 0.1 providing the first strong negative $\Delta^{33}S$ data from the Mesoarchean consistent with inorganic sulfate reduction similar to that observed in the Neoarchean VMS, komatiite-hosted Ni sulfides and BIFs. This provides evidence for a Mesoarchean sulfate reservoir linked to a subaerial volcanic plume and oceanic volcanic island eruptions.

[1] Farquar *et al.* (2007) *Nature* **449**, 706-709.

An isotopic perspective on mass bias and matrix effects in MC-ICP-MS

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Precise and accurate correction for instrumental mass bias is required to achieve the level of precision and accuracy needed for isotope ratio measurements by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, instrumental mass bias and the causes of its variation are not well constrained. With the excellent internal precision of isotope ratio measurements by MC-ICP-MS, we can investigate mass bias variation at an isotopic as opposed to elemental level in order to shed light on the processes underlying mass bias variation in the plasma. For this study we measured the spatial variation of Pb and Tl isotope ratios in dry plasma and their response to the presence of matrix.

Mass dependent radial variation of Pb isotope ratios indicates that lighter isotopes show greater dispersion from the axis of the plasma than heavier isotopes, in agreement with elemental observations by ICP-MS [1]. Axial variations in Pb and Tl isotope ratios show that isotopic signal maxima (I_{max}) are distributed in a mass dependent manner (Pb I_{max} separation: 3.47±2.07μm/amu), with I_{max} for heavier isotopes closer to the load coil than I_{max} for lighter ones; the reverse of the elemental mass dependence observed in ICP-MS [2]. This difference in mass dependent behaviour may be due to processes in the interface related to, for example, the high acceration potentials (4-10kV) used in MC-ICP-MS.

Addition of a low first ionization potential (1.IP) element to the plasma promotes ionization of Pb and Tl closer to the load coil, whereas a high 1.IP element results in ionization further from the load coil. Elements with low second ionization potential and those forming refractory oxides may also promote ionization further from the load coil. In addition to shifting the position of Pb and Tl I_{max}, the presence of matrix also reduces run-to-run variations in the mass dependent separation of isotope I_{max} (Pb I_{max} separation: 3.50 ± 0.54μm/amu). This reduced variability in mass dependent isotope separation under matrix-loaded conditions may provide an explanation for improved accuracy and external reproducibilty of dry plasma Pb isotope ratio measurements in the presence of a common matrix [3].

[1] Dziewatkoski *et al.* (1996) *Anal. Chem.* **68**, 1101-1109. [2] Vanhaecke *et al.* (1993) *JAAS* **8**, 433-438. [3] Barling & Weis (2008) *JAAS* **23**, 1017-1025