Analysis of inclusion μ-environments in cryo-biological systems

R.E. BARLETTA[1]*, C.H. ROE[1] AND C.W. BROWN[2]

[1]Chemistry Dept., Univ. of South Alabama, Mobile, AL 36535, USA
(*correspondence: rbarletta@southalabama.edu)
[2]Chemistry Dept., Univ. of Rhode Island, Kingston, RI 02881, USA (cbrown@chm.uri.edu)

There is much evidence for the viability microbes isolated from glacial ice. Price [1] and Mader *et al.* [2] have proposed that liquid veins found in glacial ice could support life at depth using trapped oxyanions as a nutrient source. Mader *et al.* have recently proposed a prototypic vein mixture based on core analyses (Mix-1). They have cultured Antarctic microbes in this mixture, and shown that bacteria congreagte in fluid veins of ice crystals. To date, however, microbial respiration under typical glacial conditions has not been observed, in part because the characterization of these vein micro-environments have not been performed since traditional analystical methods require thawing of the ice.

We are developing micro-analysis methods for *in situ* characterization of ice vein chemistry using Raman spectroscopy. Barletta *et al.* [3] reported sensitivities for biogenic sulfur compounds far above the concentrations expected for the major molecular ions expected in the veins. To evaluate the potential of Raman for quantitative anlysis of vein microhabitats, a series of laboratory experiments have been conducted, including physico-chemical analyses of the sulfate water phase diagram [4] and Mix-1 using calorimetry and Raman senstivitiy studies of Mix-1 ions. Based on these studies, it was concluded that Mix-1 vein mixtures would be solid at temperature of relavance to deep glacial ice (-20 to -40°C) and that the vein concentrations are likely closer in sulfate concentration to the H_2SO_4-water eutectic, i.e. 30-40 wt % H_2SO_4. Using this eutectic as a starting point, test mixtures were prepared with varying amounts of the other Mix-1 anions. Raman spectra were obtained at temperatures ranging from +15°C to -20°C and the spectra analyzed to provide a methodolgy for μ-Raman characterization of vein habitats. The results of these analyses will be presented as well as the implications for *in situ* characterization.

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[1] Price (2000) *PNAS* **97**, 1247–1251. [2] Mader *et al.* (2006) *Geology* **34**, 169–172. [3] Barletta *et al.* (2009) *J. Raman Spectr.* **40**, 972–981. [4] Beyer *et al.* (2003) *J. Phys. Chem.* **107**, 2025–2032.

Mass dependent fractionation of Pb and Tl isotopes in an inductively coupled Argon plasma

JANE BARLING* AND DOMINIQUE WEIS

PCIGR, EOS, University of Bristish Columbia, Vancouver, BC V6T 1Z4, Canada
(*correspondence: jbarling@eos.ubc.ca)

Instrumental mass bias in (MC)-ICP-MS results from a combination of space charge effects during sample introduction and transport through the interface, and processes in the plasma [1]. To investigate the latter we measured variations in Pb and Tl isotope ratios with axial sampling depth in the plasma. Six axial sampling profiles were sampled incrementally at depths between 3.4 and 9.4mm from the load coil in a plasma tuned at a sampling depth of 5.9mm. Isotopic (e.g. $^{208}Pb/^{206}Pb$) and elemental (e.g. $^{208}Pb/^{205}Tl$) heavy/light isotope ratios vary linearly with sampling depth. Isotopic ratios decrease with increasing sampling depth (e.g. $^{208}Pb/^{206}Pb$ from 2.216 to 2.194 = exponetial mass bias -2.28 to -1.26) whereas the elemental ratio ($^{208}Pb/^{205}Tl$) increases (from 2.516 to 2.825). We suggest that the variation in the isotopic ratios reflects a mass dependent process whereas a different process must be responsible for the $^{208}Pb/^{205}Tl$ variation, perhaps one dependent on the relative magnitude of the first ionization potentials of Pb and Tl. Model data generated from the measured profiles, reveal that the locations of signal maxima (Imax) for the individual Pb isotopes vary in a mass dependent fashion along the sampling profile, with the ^{208}Pb reaching Imax closest to the load coil and ^{204}Pb reaching Imax furthest from the load coil. Signal maxima separation varied from fire-up to fire-up, ranging between 2.25 – 4.75μm/amu. A similar range of μm/amu separation was observed for Tl isotopes, however the Tl Imax were displaced relative to the Pb Imax. Separation of ^{205}Tl Imax from ^{208}Pb Imax varied from -9 to -23.5μm/amu (i.e. closer to the load coil). With matrix present, the separation of isotopes is less variable from fire-up to fire-up (e.g. Pb: 2.88 to 3.88 μm/amu) while the reverse is true for the separation between ^{208}Pb and ^{205}Tl Imax (-6.7 to -39.2μm/amu). Furthermore, the location of the Imax relative to the load coil changes dramatically (e.g. ^{208}Pb Imax shifted from up to ~500μm nearer to ~200μm further from the load coil). These shifts in Imax correspond to significant mass bias variations between matrix-free and matrix bearing solutions sampled at the same distance from the load coil. This suggests that significant inaccuracies may result from the use of matrix-free standard data to normalize data from matrix bearing samples.

[1] Andrén *et al.* (2004) *JAAS* **19**, 1217–1224.