

## Capabilities of LA-ETV-MC-ICPMS for the measurement of Sr isotope ratios in Rb-rich samples

R. BROGIOLI, L. DORTA, B. HATTENDORF\* AND D. GÜNTHER

<sup>1</sup>Laboratory of Inorganic Chemistry, ETH Zurich, Wolfgang-Pauli Strasse 10, 8093, Zürich, Switzerland

The successful use of LA-MC-ICPMS for the determination of Sr isotope ratio in the field of geochronology has been demonstrated for samples with relatively low Rb concentration [1, 2]. Its applicability for samples with higher Rb content is however still a challenge, mainly because mathematical correction of the isobaric interference of <sup>87</sup>Rb on <sup>87</sup>Sr affects the accuracy of the method [3, 4].

In an earlier study we investigated the effect of heating laser generated aerosols within an Electrothermal Vaporizer (HGA600 MS, Perkin Elmer, CAN) prior to the introduction into the ICPMS. Passing the laser generated aerosol through a commercial electrothermal vaporizer heated to 2000°C before the ICP allowed to attenuate the Rb interference by almost two orders of magnitude [6] for a silicate glass reference standard (NIST SRM610, Rb/Sr ~1). This same approach was now used for the measurement of Sr isotope ratios by LA-MC-ICPMS. To benchmark the Rb removal efficiency and the accuracy of Sr isotope ratio, a wide range of reference standard material were tested: NIST SRM610 (Silicate glass, Rb/Sr = 1), MPI-DING ATHO-G (rhyolite glass, Rb/Sr = 0.54), MPI-DING TIG (diorite glass, Rb/Sr = 0.28), USGS BCR-2G (basalt glass, Rb/Sr = 0.14) and Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fused disks of NIST 607 (potassium feldspar, Rb/Sr = 8). Depending on crater size adopted for the analysis and the ETV heating temperature, Rb signal was decreased by factor ~5 (for NIST SRM 607) to 100 (for NIST 610 and BCR-2G) resulting in an improved accuracy for the measured <sup>87</sup>Sr/<sup>86</sup>Sr ratio.

Rb is not the only element interfering with Sr isotope analysis, doubly charged rare earth elements, metal oxides or calcium polyatomic ions are known to affect results accuracy [3]. For this reason Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fused disks of NIST SRM987 (Sr carbonate) were spiked with Er, Yb, Hf, Ca, Fe, Ga, Zn to investigate the formation of potential interferences and the applicability of mathematical corrections. This study will show that the use of electrothermal vaporization coupled to LA sampling has the potential to widen the range of samples suitable for accurate *in-situ* determination of Sr isotope ratio.

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## Biogeochemistry of mercury in contaminated sediments of East Fork Poplar Creek

SCOTT C. BROOKS<sup>1\*</sup>, DAVID KOCMAN<sup>2</sup>, CARRIE MILLER<sup>1</sup>, XIANGPING YIN<sup>1</sup>, AMI RISCASSI<sup>1</sup>

<sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, TN, USA, brookssc@ornl.gov (\* presenting author)

<sup>2</sup> Jožef Stefan Institute, Ljubljana, Slovenia, david.kocman@ijs.si

Mercury use at the Oak Ridge Y-12 National Security Complex (Y-12 NSC) between 1950 - 1963 resulted in contamination of the East Fork Poplar Creek (EFPC) ecosystem. Hg continues to be released from point sources and diffuse contaminated soil and groundwater sources within the Y-12 NSC and outside the facility boundary. In general, methylmercury (MeHg) concentrations in water and in fish have not declined in response to improvements in water quality and exhibit trends of increasing concentration in some cases.

Therefore, our study focuses on identifying ecosystem compartments and/or characteristics that favor the production, as well as degradation, of MeHg in EFPC. Detailed geochemical characterization of the surface water, interstitial pore water, and creek sediments were performed during quarterly sampling campaigns in 2010 and 2011 at two locations. One site is 3.7 km (NOAA) and the other 20 km (NH) downstream of the headwaters and source of the point discharges. Vertical profiles of interstitial pore water collected from fine-grained deposits at the creek margin showed decreases in nitrate, sulfate, and oxidation-reduction potential (ORP) with depth as well as increases in dissolved manganese, iron, and small increases in sulfide. The results indicate the progression of terminal electron accepting processes with depth in the upper 30 cm of these fine grained sediments. Dissolved (passing 0.2 µm pore) MeHg concentration was positively correlated with depth suggesting these areas served as a source of MeHg. MeHg in the surface water is associated with phases small enough to pass a 3 kiloDalton filter. In contrast, interstitial water collected from the cobbly center channel of the creek did not exhibit these redox gradients. The observed constant or decreasing MeHg concentrations with depth suggest that the interstitial water in the fast flowing sections of the creek is rapidly exchanging with the surface water and these sections do not serve as MeHg sources. Total Hg concentration in sediment cores from the creek margin was variable, 0.057-24 mg/kg and 0.02-155 mg/kg, at NH and NOAA respectively. MeHg measured on a subset of these sectioned cores ranged from 0.71-17.5 µg/kg at NH and 1.08-46.7 µg/kg at NOAA. Large intra- and inter-site variability of Hg distribution in these samples is partly attributed to the very heterogeneous sediment texture that ranged from coarse- to fine-grained. Methylation potential, measured using enriched stable isotopes of Hg on intact sediment cores, was significantly correlated with ambient MeHg concentration at both sites.