The effect of sample matrix on the precision and accuracy of radiogenic isotope ratio measurements by MC-ICP-MS

J. BARLING, I. NOBRE SILVA AND D. WEIS

Pacific Centre for Isotopic and Geochemical Research, Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, B.C. V6T 1Z4, Canada (jbarling@eos.ubc.ca, inobre@eos.ubc.ca, dweis@eos.ubc.ca)

Introduction

Residual sample matrix is known to cause non-spectral matrix effects that adversely influence the accuracy of non-tradional stable isotope ratio determinations by MC-ICP-MS (e.g. Carlson et al., 2001). It is commonly assumed however, that matrix effects do not significantly influence the accuracy and precision of radiogenic isotope determinations by MC-ICP-MS (e.g. Nd, Hf, Pb). The external normalisation method (Tl) used to correct Pb data for instrumental mass bias means that Pb data are potentially susceptible to matrix effects if matrix causes different instrumental mass bias responses for Pb and Tl. We have therefore investigated the significance of matrix effects on the precision and accuracy of MC-ICP-MS radiogenic isotope data.

Observations and experiments

In the case of Hf, subtle differences have been observed between measured stable isotope ratio correlations (i.e. 178/177, 179/177, 180/177) for mafic and felsic sample material (Weis et al., 2007), raising the spectre that instrumental mass bias for samples may not follow the same empirical fractionation law as for standards. Preliminary experiments with Nd however, suggest that internal normalisation is effective in compensating for matrix effects.

In purified Pb samples, residual sample matrix decreases with increasing SiO_2. Ca is the dominant matrix element, followed by Al, Fe and Mg; organics derived from ion exchange resin may also be present. This matrix causes changes in instrumental mass bias and signal enhancements of up to 80%. Experiments carried out on standards doped with Ca, Al, Fe and Mg, demonstrate that these four elements can account for Pb and Tl signal enhancements of up to ~50% and that enhancement of Tl > Pb. Pb and Tl instrumental mass biases also respond differently to matrix elements; both effects are greatest in the presence of Ca. Samples passed twice through chemistry show significant reduction in matrix effects and better reproducibility. Sample matrix must therefore be reduced to negligible levels for high precision and accuracy radiogenic isotope data.

References

Carlson R., Hauri E. and Alexander C. (2001) In: Plasma source mass spectrometry: The new Millenium. *Roy. Soc. Chem.* 288-297.
Weis D., Kieffer B., Hanano D., Nobre Silva I., Barling J., Pretorius W., Maerschalk C. and Mattielli N., (2007) , *Geochemistry, Geophysics, Geosystems* (in press).

Chlorine stable isotopes as a geochemical tracer along the Central American and the Izu-Bonin-Mariana arcs

J.D. BARNES, Z.D. SHARP AND T.P. FISCHER

Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131 (jdbarnes@unm.edu; zsharp@unm.edu; fischer@unm.edu)

Chlorine stable isotope ratios of different potential sources of Cl to subduction zones (sediments (~ -2‰?), pore fluids (–8 to –0.1‰), mantle (0‰), subducted oceanic crust, *e.g.*, serpentinites (–1.8 to +0.5‰)) are distinct, thereby providing a geochemical tracer of the fluid source responsible for melts and arc volcanism. We have analyzed volcanic gases (collected in Giggenbach flasks), volcanic gas condensates, aqueous fluids from crater lakes, streams, geothermal wells, tephras, lavas, sediments from the subducting plate, backarc basalts, and clasts and muds from serpentinite seamounts to help identify the sources of Cl in the Central American (CA) and Izu-Bonin-Mariana (IBM) subduction zones.

$\delta^{37}Cl$ values of volcanic gases from along the CA arc range from –4 to +12‰. Gas samples from Poás (Costa Rica) have the most positive $\delta^{37}Cl$ values (+5.2 to +12.1‰) of all volcanoes analyzed. However, the lake and streams in the Poás crater have near zero $\delta^{37}Cl$ values with little to no variation over time. Gases from nearby, Turrialba and Irazu (Costa Rica) have negative $\delta^{37}Cl$ values (averaging ~ –2‰). Santa Ana (El Salvador) and Momotombo (S. Nicaragua) have $\delta^{37}Cl$ values of +6.3 and +4.0‰, respectively. San Jacinto, San Cristobal, and Cerro Negro (N. Nicaragua) have negative $\delta^{37}Cl$ values (averaging ~ –2‰). Fuego (Guatemala) also is isotopically negative, –0.6‰. Tephra and lava samples from six Nicaraguan volcanoes range from –3.0 to +1.6‰.

$\delta^{37}Cl$ values of volcanic gases from along the IBM arc are generally negative (averaging –2.2 ± 1.2‰). Serpentinite clasts from the Conical and South Chamorro seamounts have bulk $\delta^{37}Cl$ values of 0.33 and 0.31‰, respectively. Serpentine muds from both seamounts have bulk $\delta^{37}Cl$ values of 0.12‰. Backarc basalts from the Guguan cross-chain also average 0.12‰. Sediments from ODP Leg 129 have negative bulk $\delta^{37}Cl$ values, ranging from –0.3 to –1.2‰ (n = 3).

The consistently negative $\delta^{37}Cl$ values of volcanic gas samples from along the IBM arc indicate that chlorine is likely sourced from subducting sediments, isotopically negative serpentinites, and/or pore fluids. Similar conclusions may be drawn from isotopically negative volcanoes from N. Nicaragua, Guatemala, and some volcanoes in Costa Rica. Additional ODP sediment samples from the Pacific plate will be analyzed to better define the $\delta^{37}Cl$ value of the sediment source, which is not well known at present. The high $\delta^{37}Cl$ values from Poás, Santa Ana, and Momotombo may be due to volatilization of acidic fluids at high temperatures, where extreme fractionations have been observed experimentally.