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An Investigation of Non-Spectral Matrix Effects on the Accuracy of Non-Traditional Stable Isotope Measurements by MC-ICP-MS

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Non-spectral matrix effects are an important cause of inaccuracy in non-traditional stable isotope ratio measurement by MC-ICP-MS because they affect the instrumental mass bias of analyte elements in matrix bearing samples. Instrumental mass bias corrections assume that drift in instrumental mass bias in the standards is representative of drift in samples. Where non-spectral matrix effects are present, any correction for instrumental mass bias based on pure standards will be inaccurate. The lack of any systematics to observed variations in these effects (e.g. Carlson et al., 2001) means they cannot be corrected for. At PCIGR we are undertaking a comparison of the non-spectral matrix effects on a range of non-traditional stable isotopes (e.g. Cu, Zn, Mo, Cd). Matrix elements investigated include alkali and alkali earth elements, Al, Zn, Lu, Ir and Pb.

For Cd (IP = 9.0eV; mass $\sim$ 112) all matrix elements, both lighter (Al, Rb, Zn) and heavier (Cs, Ba) than Cd, produced isotope results (Cd only data – i.e. correction by sample-standard-bracketing/SSB) that were negative (light) by up to -0.4‰/amu and varied systematically with the concentration of the added element. Of these elements only Zn has a first ionization potential greater than Cd (9.4eV). Comparison of SSB and Ag corrected data (i.e. external-normalisation-SSB and graphical methods) indicates that Al, Cs and Ba affect the instrumental mass biases of Cd and Ag differently.

For Mo (IP = 7.1eV; mass $\sim$ 96) matrix elements produced variations of between -0.27 and +0.40‰/amu (Mo only data - i.e. SSB correction). Addition of Ca, Cs, and Ba resulted in negative ‰/amu results, whereas addition of Li, Na, Rb, Mg, Sr, Zn, Ir and Pb resulted in positive ‰/amu results; no dependence on mass has been observed. However, all matrix elements with first ionisation potentials greater than that of Mo

(Pb, Mg, Ir, Zn) produced positive ‰/amu. Comparison of SSB and Zr corrected data (i.e. external-normalisation-SSB and graphical methods) indicates that Rb, Cs, Mg, Ca and Ba affect the instrumental mass biases of Mo and Zr differently.

Thus far, the data suggest that matrix elements with first ionisation potentials greater than the analyte element will produce only positive ‰/amu non-spectral matrix effects. Published data (e.g. Carlson et al., 2001) tend to support this observation, but there are exceptions. Further investigations are therefore needed before a mechanism can be proposed to explain this observation.