Mass Bias in ICP mass spectrometers

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It is well known that the uncorrected isotopic ratio measured using ICP mass spectrometers differs from the true value in a time independent manner. Experimentally it has been shown in high precision studies using multiple collector magnetic sector instruments that the following formula often applies:

$$\frac{\text{True Ratio}}{\text{Observed Ratio}} = \left[\frac{M_1}{M_2}\right]^{\beta}$$

with the value of β being close to 2.

We suggest that the origin of this mass bias arises from two parts, each contributing a factor of one to the beta value. The first part comes from the supersonic expansion process at the sampler, and the second from the space charge repulsion at the rear of the skimmer, in the region where the ions experience their initial electrostatic acceleration.

During the supersonic expansion process in the sampler's throat, the ion's forward motion is converted into a narrow velocity distribution, centred at a common value, equal to the velocity of the bulk argon carrier gas. The transverse velocity distribution is also narrowed, but the average velocity in this direction maintains the normal mass dependent variation. The higher transverse speeds for the lighter ions results in the lower transport efficiency of these species to the next stage of the instrument interface.

Since the distribution of the species in the expansion cone at the rear of the sampler maintains a memory of the distribution in the flame (for standard geometry's) the mass bias will alter as the torch position is changed. Similarly different elements will be ionised differently in the flame, resulting in differing spatial ionic distributions. This can result in minor variations in beta values between elements.

If no charge separation occurred at the skimmer, the transmitted ions would continue in an extremely narrow cone into the mass spectrometer, defined by the geometry of the sampler and skimmer orifices. However, the extraction voltage on the first ion optical element repels the electrons in the plasma, and accelerates the ions. These ions then experience a mutual repulsion, in this region of low acceleration potential. The heavier ions, which have a higher energy (since the forward velocity of all the species present is the same), will experience less repulsion than the lighter ions. This results in the second major contribution to the mass bias. It is to be expected that it should be possible to design an interface such that this repulsion is kept at a low enough level so that all ions which pass through the skimmer tip are transmitted into the mass spectrometer. In such a case, the overall beta value would approach unity.

Re-Os, Sm-Nd isotope- and REE systematics on komatiites and pillow basalts from the Earth's oldest oceanic crustal fragments (Isua Supracrustal Belt, W Greenland)

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Komatiites and pillow basalts from the Western and Northwestern sector of the Isua Supracrustal Belt (ISB) reveal a complex pattern of trace elements, mainly with respect to their rare earth elements (REE). The heterogeneity of LREE patterns, in combination with widely scattering εNd[T=3.81 Ga] values, indicate that the REE systematics of the samples were disturbed by one (or more) metamorphic events which took place some considerable time after the original crystallization of the Isua belt. Furthermore, LREE-rich metasomatic fluids associated with the emplacement of tonalites into the supracrustals may have significantly altered the primary trace element budget. Extreme variations in whole rock γOs[T=3.81 Ga] values of these rocks are favorably interpreted to derive from major metamorphic losses of Os, rather than from Re additions during fluid hydrothermal alterations. In contrast, the Re-Os isotope system remained intact in komatiite-hosted chromites from Isua and an average γOs[T=3.81 Ga] value of +1.3 +/-0.9 indicates that these komatiites were derived from a mantle source with a time-integrated slightly suprachondritic Re/Os ratio. Our data are the first to show early Archean mantle rocks with radiogenic initial ^{187}Os/^{188}Os isotopic compositions. Our data do not allow to further impinge on the petrogenesis of the ISB mantle-derived rocks. Similarities of unaltered pillow basalts with Phanerozoic boninites (Polat et al., 2002) may indicate a formation in an intra-oceanic subduction zone like geodynamic process, in which extreme early (Hadean?) depletion of a mantle source by melt extraction was followed by a second stage of melting induced by enriched subduction components. Alternatively, core-mantle interaction as a plausible mechanism for the ^{187}Os enrichments in these rocks remains a valid hypothesis.

References

Polat, A., Hofmann, A.W. and Rosing, M.T., (2002), *Chem. Geol.* **184**, 231-254.