High Precision MC-ICPMS Measurement of Ag Isotopic Ratios

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The measurement of Ag isotopic ratios with ε-level (1 part in 10,000) precision is of cosmochemical interest because ^{107}Ag is produced by decay of the now extinct radionuclide ^{107}Pd ($t_{1/2}$ = 6.5 Myrs). Silver isotopic measurements are difficult, however, as Ag has only 2 naturally occurring isotopes and it shows unusual behaviour during chemical processing and analysis.

Silver has been analysed using a Nu-Instruments MC-ICPMS equipped with a desolvating nebuliser. Utilising both a Pd 'spike' to correct for instrumental mass bias and a standard bracketing technique[1], a reproducibility of 0.9ε (2σ) is obtained for ^{107}Ag/^{109}Ag (corrected using ^{108}Pd/^{105}Pd) for a pure Ag standard. Log plots of Ag vs. Pd ratios for single measurement sessions are linear, indicating that fAg/fPd (f = mass fractionation coefficient) remains constant, although the observed slopes are different to those predicted by the exponential law. Thus, the Maréchal method[2] can be used to effectively determine differences in the isotopic composition of Ag between samples and standards.

External normalisation does not remove the effects of mass-dependent fractionation generated in the laboratory. Experiments reveal several possible means by which isotopic 'anomalies' can be generated as analytical artefacts. (1) Isotopic compositions of standards vary subtly with time if they are stored (<5ε). (2) Drying down Ag in different acidic media can affect the measured isotopic ratios (<2ε). (3) If HCl is added to a Ag-standard in dilute HNO_3, the measured ^{107}Ag/^{109}Ag decreases. (4) Standards which have been processed via anion/cation exchange columns are isotopically lighter than unprocessed standards (<4ε); variable yields cannot be the only cause of these shifts.

Many of these problems can be accounted for, but accurate measurements of samples may only be possible by direct comparison with a standard of similar matrix processed in an identical manner. Thus, the ability to control isotopic artefacts generated in the laboratory, rather than precision of the instrumentation, is the limiting factor in accuracy of Ag isotopic measurements. Preliminary results suggest that the CV chondrite Allende, USGS reference material SCO-1 (Cody Shale) and a terrestrial sulphide have Ag isotopic compositions that are identical, within 2-3ε, to each other and to our JMC Ag standard.

References

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Constraints on Neoproterozoic ocean chemistry from δ^{13}C and δ^{11}B analyses of carbonates from the Witvlei and Nama Groups, Namibia

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High-resolution δ^{13}C data have been collected from shallow marine carbonates of the Witvlei and Nama Groups of south-central Namibia. The highest amplitude carbon isotopic excursion of the >600m composite section spans a range in δ^{13}C of over 12‰, with the lowest value of –9.4‰ at ~550-560 Ma. The δ^{13}C values preceding this most negative spike range from –2‰ to –6‰. Positive values of δ^{13}C (0-4‰) are indicated only for the uppermost ~250m of section. A duration of up to 10 Myr for the negative excursion is suggested based on estimates of sediment accumulation rates. The temporally equivalent Shuram Fm. of Oman provides a global correlation to the negative δ^{13}C record in Namibia by showing a light carbon anomaly over 100's of meters of section and minimum δ^{13}C values of –10‰ (Burns and Matter, 1993).

Unlike the short-lived (<1 Myr) negative excursion in δ^{13}C associated with the PC/C boundary (Grotzinger et al., 1995), the shallow-water, slowly accumulating, ordinary platform facies in Namibia and Oman show exceptionally long-lived, high amplitude δ^{13}C anomalies. This observation excludes the possibility that this negative δ^{13}C excursion represents a pulse from a light carbon reservoir, predicted by models invoking upwelling or release of methane hydrates. Additionally, the mechanism for generation of isotopically-depleted carbonates must differ from that of the "snowball earth" (Hoffman et al., 1998), due both to their significantly greater isotopic depletion and slow rather than unconventionally rapid sediment accumulation rates.

Preliminary analyses of δ^{11}B compositions in the Namibian carbonates show a positive correlation with δ^{13}C values. Because δ^{11}B in carbonate is a proxy for seawater acidity (lower δ^{11}B corresponds to lower pH), we infer that the ~550-560 Ma negative spike in δ^{13}C reflects a decrease in seawater pH.

References

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