Improved $^{27}Al/^{24}Mg$ ratio measurement using a modified isotope-dilution approach

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With its half-life of ~0.73 Myr, the decay of (now extinct) ^{26}Al to ^{26}Mg is capable of providing extremely precise relative ages, and as a result the ^{26}Al–^{26}Mg system is widely employed in constraining the timing of events in the early solar system. The popularity of ^{26}Al as a chronometer has stimulated a continual refinement in the analytical methods of Mg-isotope determination, resulting in a present day reproducibility for $^{26}Mg^*$ values of better than 3 ppm [1]. However, methods for the measurement of $^{27}Al/^{24}Mg$ ratios (as a proxy for parent/daughter ratios) have seen little improvement, and the present accuracy of ±2% [2] is no better than it was a decade ago [3]. As a result, the uncertainties in Al/Mg isochrons are now dominated by uncertainties in the measured $^{27}Al/^{24}Mg$ ratio.

By modifying conventional mixed-spike isotope-dilution methods we have developed a technique using a spike consisting of isotopically enriched ^{25}Mg and isotopically normal Al, which incorporates an approach analogous to standard-sample bracketing. The method employs isotope dilution to determine the spike to sample ratio for magnesium, but utilises bracketing of spiked and unspiked sample solutions to obtain the spike to sample ratio for aluminium. A typical run consists of four spiked measurements, bracketed by five unspiked measurements, and consumes < 2 μg of Mg.

This technique overcomes the problem of aluminium being monoisotopic, and measurements of international rock standards, as well as a gravimetric calibrant solution, indicate a reproducibility approaching conventional mixed-spike isotope dilution (i.e. 2 s. d. of <0.5%). Measurements are made on a single unpurified aliquot of the sample, so no chromatographic separation is required, and the method is less susceptible to biases generated by differences in sample matrix composition.

[1] Bizzarro *et al*. (2011) *Journal of Analytical Atomic Spectrometry* **26**, 565–577. [2] Schiller *et al*. (2010) *Geochimica et Cosmochimica Acta* **74**, 4844–4864. [3] Galy *et al*. (2000) *Science* **290**, 1751–1753.

Concentration of chalcophile and siderophile elements in MORB sulphide droplets: New sulphide melt-silicate melt partition coefficients

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We have determined the concentrations of chalcophile and siderophile elements by LA-ICP-MS from sulphide droplets and fresh glass in contact with them from MORB pillow rims. MORBs play an important role in the understanding of mantle petrogenesis, providing information on chemical fractionation of elements in the mantle. However, chalcophile element behaviour is not completely understood, partly due to the lack of data for partition coefficients between sulphide and silicate melts.

Some droplets present homogenous textures and others portions rich in monosulphide solid solution (Mss) and intermediate solid solution (Iss) indicating that they have undergone crystal fractionation. For homogenous droplets, concentrations of Ni and Cu are 10 to 1%; Co and Zn 1000 to 100 ppm; Se, Te, Ag and Pb 100 to 10 ppm; Cd, Sn, Pd, Bi and Pt 10 to 1 ppm; Au, Ru and Re 1 to 0.1 ppm. For some of these elements it was also possible to obtain data in fresh glass allowing the calculation of partition coefficients. These were calculated for Ni (745± 252), Cu (1219 ± 381), Co (42 ± 5.5), Zn (3.4 ± 0.9), Sn (10.4 ± 1.8) and Pb (55.6 ± 9.3). Values for Ni, Cu and Co are in agreement with literature [1], suggesting that values for Zn, Sn and Pb are realistic.

[1] Peach *et al*. (1990) Sulfide melt-silicate melt distribution coefficients for noble metals & other chalcophile elements as deduced from MORB, Implications for partial melting, *Geochimica et Cosmochimica Acta* **54**, 3379–3389.