Instrumental mass fractionation overcome by total evaporation

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A select suite of isotopes, including Li, Cu, V, Lu, and Re, along with isotopic mixtures of unknown isotopic composition, require special analytical techniques to overcome instrumental mass fractionation (IMF). Generally, measurements subject to IMF are corrected using a known ratio either intrinsic to the system or externally added to the sample and measured simultaneously with the sample. For many systems, e.g. Os, and for many types of measurements, e.g. ICP-MS, internal ratios or doping works well. For other cases, e.g. NTIMS Re measurements, neither approach readily works. Therefore, following the work of Suzuki *et al* [1], an updated total evaporation (TE) technique is employed. In theory, if the entire sample is evaporated until exhaustion and all the ions collected, mass fractionation is overcome, thereby improving accuracy and precision, with less dependence on the analyst.

An experiment was designed to test TE against single-collector peak jumping and multi-collector static measurements using a variety of ^{185}Re/^{187}Re ratios (~0.6 standard; ~4 sample; ~37 spike) with the expectation of documenting differences in measured ratios due to variability caused by IMF. Preliminary results demonstrate, within statistical uncertainty, that TE provides equally accurate, equally precise data that is marginally less dependent on the analyst.

While the initial results did not indicate a drastic improvement in accuracy or precision, further optimization of the analytical procedure may result in better data. NBS peak jumping, and to a lesser extent Triton static collection, have undergone multiple filament warm-up, focusing, and centering optimizations during thousands of Re measurements. On the other hand, TE measurements are currently utilizing default parameters. Optimization of procedures and parameters including filament heating; ideal initial, final, and maximum intensities; heatslope (mA/cycle); integration time; and mathematical constants is on-going. Fine-tuning these parameters and procedures should result in higher quality data, surpassing other data collection techniques.

Total evaporation may be extended to other isotopic systems including Li, B, Cu, Ir, V, Br, and Lu. Additionally, total evaporation may provide improved accuracy and precision for artificial isotopic mixtures such as double spikes (e.g. Os, Mo, and Pb). In summary, TE provides an alternate method of data collection for samples subject to, but not internally or externally correctable for, IMF.

References

[1] Suzuiki K, Miyata Y, and Kanazawa N. (2004), *Int. Jour. Mass. Spec* **235** 97-101.

Formation of 4.5 Ga continental crust

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Geochemical models of crustal growth on early Earth have tended to favor mafic over felsic compositions for a variety of reasons including: lack of a mechanism to produce stable continental-type crust from a magma ocean (high ρ of feldspar w.r.t. hydrous melt, low feldspar growth rate w.r.t. convective vigor), problems reconciling Sm-Nd systematics, apparent inconsistency with Nb/Th/U ratios, and the absence of >4 Ga crust. However, Morse (1987) proposed a model that transcends most of these objections. He invoked a sinking, undercooled, two-phase plume that, upon reaching the base of a magma ocean, rapidly crystallizes olivine. The light, evolved liquid produced (assuming that the fluid in equilibrium with olivine is silica-rich at high P) ascends to shallow depths. Nucleation from sparse centers in the highly polymerized melt results in rapid crystallization of tonalitic rockbergs that coalesce into regions of stable, felsic crust. Recent Lu-Hf results on Hadean zircons tend to support the case for an early continental-type crust. Thus we have re-evaluated this proposal for the case of a ~250 km deep magma ocean using recent experimental data in conjunction with the MELTS program. Melting experiments in the CMAS system at 6.5 GPa and 1850°C (Asahara & Ohtani, 2001) yield liquid compositions characterized by 45-52% SiO_2. We modified the liquid composition by adding Fe to achieve MgO/(MgO+FeO)=0.8 and partitioning pyrolite levels of incompatible elements (e.g. K, Na) into the melt. Upon ascent to 0.2 GPa, the hygroscopic liquid containing 2% H_2O rapidly evolves during cooling to produce a dioritic (57% SiO_2) composition at 950°C. Thus an early felsic crust appears feasible even without the disequilibrium effects of the Morse model. He emphasized that a network-rich liquid would be characterized by a relatively high viscosity enabling the ‘pop-up’ crust to maintain sufficient mechanical integrity to resist remixing with the ultramafic magma ocean until rapid crystallization occurred. At the surface, proto-crust would tend to migrate to down-welling loci and be stabilized by the locally cooler conditions. As the base of the crust heats up in response to shutdown of the descending cell, felsic liquid produced would tend to ascend diapirically to shallow levels creating a feedback that sustains the presence of continental-type crust. Most of the arguments against an early continental-type crust described above lack rigor or have been transcended by recent evidence. Morse’s (1987) model provides a plausible mechanism to produce felsic crust in the earliest stages of Earth evolution. Subsequent re-working and eventual recycling of this proto-continental crust into the mantle provides an explanation for the isotopic characteristics of Hadean zircons and the apparent absence of pre-4 Ga continental crust.