

S1. Supplementary text

Element fractionation during storage in a mixed gravimetric Lu-Hf solution

Standard and spike solutions can also be unstable in long-term storage. The concentration of elements in solution can increase due to loss of water by evaporation, and decrease due to absorption on the walls of the container, or formation of particles (either macroscopic or colloidal) that can precipitate over time. Evaporation can only change concentrations, but not the abundance ratios of the elements, whereas absorption and precipitation are element-specific and can change element ratios. Long-term changes of the element ratios due to absorption or precipitation can possibly affect any solutions, including mixed spikes, gravimetric reference solutions used for spike calibration, and synthetic age reference solutions, and, if left unchecked, can pose a serious problem to the accuracy of U-Pb dating by ID-TIMS. During re-calibration of Lu-Hf spikes at the Geological Survey of Canada in 2006, we observed a large discrepancy in the Lu/Hf ratios in gravimetric reference solutions that is clearly related to Hf absorption during storage. Calibration of the spike against fresh Lu-Hf gravimetric reference solution, and an aliquot of similar solution prepared in 1990 and diluted in 2006 yielded consistent $^{176}\text{Lu}/^{180}\text{Hf}$ ratios in the spike within 0.2%, whereas calibration against an aliquot of the same 1990 reference solution diluted with water shortly after preparation indicated a 7% deficiency of Hf in the reference solution. The discrepancy disappeared after long ultrasonication of the 1990 dilute reference solution. This example indicates that multi-element solutions are prone to absorption-related changes of the element ratios if the solution acidity is insufficient to suppress absorption, but these changes can be reversed by ultrasonication. In order to prevent similar problems, all standard and spike solutions in this study were ultrasonicated in their storage containers before taking aliquots after prolonged storage.

Cup efficiency

In a perfectly operating Faraday cup, the charge of the incoming ions is completely absorbed and is registered by the electrometer amplifier. However, interaction of ion beam with the interior of the cup causes emission of secondary ions and electrons, and if any of these ions charged particles escape the cup, the measured charge would differ from the charge of the incoming ion beam. Design of Faraday cups in modern mass spectrometers, e.g.,

increased depth, using graphite as material for internal cup liners, and using suppressor plates, helps to maintain cup efficiency close to unity, but these measures are imperfect: efficiency varies between individual cups, and can degrade over time due to build up of surface coatings on the graphite liners^{1, 2}. If cups in an array have different efficiencies, then isotope ratios measured with these cups will contain systematic uncertainty proportional to the deviation of the ratio of cup efficiencies from unity. Long-term stability of isotope ratios measured in static multicollector mode requires stability of cup efficiencies, and calculating accurate isotope ratio values from such measurements would rely on knowing cup efficiencies and including them as correction factors in intensity calculation. An alternative approach is to use a multi-dynamic measuring algorithm where cup efficiencies cancel out almost completely^{3, 4}.

References

1. C. Holmden and N. Bélanger, *Geochimica et Cosmochimica Acta*, 2010, **74**, 995-1015.
2. Y. K. Di, E. Krestianinov, S. Zink and Y. Amelin, *Chemical Geology*, 2021, **582**.
3. M. Thirlwall, *Chemical Geology: Isotope Geoscience Section*, 1991, **94**, 85-104.
4. M. Garçon, M. Boyet, R. W. Carlson, M. F. Horan, D. Auclair and T. D. Mock, *Chemical Geology*, 2018, **476**, 493-514.