

## Accuracy and long-term precision of MC-ICP-MS isotope ratios

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The use of internal mass fractionation corrections in thermal ionization mass spectrometry (TIMS), e.g. using  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  to correct  $^{143}\text{Nd}/^{144}\text{Nd}$ , has led to long-term reproducibility of  $\pm 20$  ppm or better over several years. This level of reproducibility has not so far been demonstrated for MC-ICP-MS with several studies showing significant variation in internally-normalized ratios on day to month timescales. This problem is usually overcome by correcting to bracketing standards, but this substantially decreases analytical throughput and worsens precision, as the internal errors of sample and standard must be combined.

We investigate possible causes of drift in normalized MC-ICP-MS ratios using static and multidynamic analyses of Nd, Yb, Hf and Pb on a Micromass IsoProbe. Multidynamic Nd and Hf ratios have 1.1 to 3x better external precision than static data with systematic differences reflecting non-unity cup efficiencies, and possible change in these with time. From a more limited database,  $^{207}\text{Pb}/^{206}\text{Pb}$  shows 6x improvement. Drift in multidynamic  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  is strongly correlated with non-radiogenic ratios  $^{142}\text{Nd}/^{144}\text{Nd}$  and  $^{180}\text{Hf}/^{177}\text{Hf}$  respectively. For Nd, we have shown<sup>1</sup> that this results from a non-exponential component to mass bias resulting in greater deviations from TIMS isotope ratios the more divergent the average mass of the ratio is from 145. Correction for these effects results in longterm 2sd reproducibility of  $<20$ ppm for  $^{143}\text{Nd}/^{144}\text{Nd}$  and ca. 30ppm for  $^{176}\text{Hf}/^{177}\text{Hf}$ . Since the difference in average mass between radiogenic and normalizing ratio is the same for Hf and Nd, we would expect to measure  $^{176}\text{Hf}/^{177}\text{Hf}$  120ppm low, that is 0.282125, prior to this correction, but in reality we obtain slightly higher than the conventional value of 0.282160 on uncorrected multidynamic data.

To investigate whether the magnitude of non-exponential mass bias reduces with increasing mass, we have also analysed Yb using multidynamic methods on both TIMS and IsoProbe. For  $^{171}\text{Yb}/^{172}\text{Yb}$  normalized to  $^{174}\text{Yb}/^{172}\text{Yb}$ , which is analogous in relative mass difference to  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$ , IsoProbe ratios are only  $48 \pm 36$ ppm lower than TIMS results, while  $^{176}\text{Yb}/^{172}\text{Yb}$  is  $120 \pm 60$ ppm low. Compared with 124 and 234ppm for the equivalent Nd ratios this suggests that the accuracy of our IsoProbe Hf and Pb<sup>2</sup> isotope ratios reflects a reduction in non-exponential mass bias with increasing mass.

### References

- 1 Vance D., and Thirlwall M.F., (2002), *Chem. Geol.* **185**, 229-242.
- 2 Thirlwall M.F., (2002), *Chem. Geol.* **184**, 255-279.

## The Nagra/PSI Chemical Thermodynamic Data Base

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The Nagra/PSI Chemical Thermodynamic Data Base has been updated from version 05/92 to 01/01 to support the ongoing safety assessment of a planned Swiss repository for high-level radioactive waste. Database version 05/92 distinguished between "core data" and "supplemental data". Core data are for elements commonly found as major solutes in natural waters. These data are well established and have not been changed to any significant degree. Supplemental data comprise actinides and fission products, as well as Mn, Fe, Si and Al. The update involved major revisions for most of these data. Altogether, more than 70% of the database contents have been updated.

Most data for U, Np, Pu, Am and Tc recommended by the internationally recognized NEA TDB project were accepted for the update. Deviations from several NEA recommendations are documented in detail. Thermodynamic data for Th, Sn, Eu, Pd, Al, and the solubility and metal complexation of sulfides and silicates were extensively reviewed. Data for Zr, Ni and Se were examined less rigorously, as these elements are currently being reviewed in phase II of the NEA TDB project.

The update is documented in Hummel et al. (2002) and electronic versions of the database for use with PHREEQC-2 and GEM-Selektor are available for download from <http://les.web.psi.ch/>.

Our experiences from this two year team effort can be summarized as follows. (1) Detailed in-house reviews and critical appraisal of NEA recommendations greatly improved the chemical consistency and quality of the selected data, as shown e.g. by comparison of complexation constants for the M(III) and M(IV) oxidation states of actinides and fission products. (2) On the other hand, major gaps in the data could be discerned, especially with respect to missing carbonate complexes. (3) In some systems, e.g.  $\text{ThO}_2 - \text{H}_2\text{O}$  and  $\text{UO}_2 - \text{H}_2\text{O}$ , experimental data cannot be described by a unique set of thermodynamic constants. In these cases a pragmatic approach based on solubility data was chosen to provide data for application to performance assessment.

### Reference

- Hummel W., Berner U., Curti E., Pearson F.J. and Thoenen T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida, USA. In press.