

High-precision isotopic analysis: Lessons from 'clumped isotope' geochemistry

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Several disciplines of geochemistry demand ppm-level precision in isotope ratio measurements (e.g., ^{142}Nd excesses in ancient terrestrial rocks; $\delta^{15}\text{N}$ in air from ice cores). 'Clumped isotope' geochemistry (the study of molecules containing more than one rare isotope) is one such field that presents several unusual analytical challenges, the solutions to which might inform high-precision isotopic measurements generally.

Clumped isotope measurements examine isotope ratios very far from 1 (10^5 to 10^6 is typical). Therefore, one must be concerned with the effect on minor ion beams of scattered ions from the major beams (i.e., abundance sensitivity is a significant factor) as well as isobaric interferences from trace contaminants. And, one must devise strategies for collecting vast numbers of ions in order to achieve the required precision for the minor species. The solutions to these problems are technically difficult but conceptually straightforward: samples must be exceptionally pure and unusually large, and ions must be collected for unusually long times.

A more complex problem arises from the fact that measurements must have ppm-level precision and accuracy over ranges of 10's of per mil in absolute isotope ratio. For example, carbonate clumped isotope thermometry demands that R^{47} (mass 47 / mass 44) ratios in CO_2 be measured with external errors of 0.005 ‰ (1s) over a range of up to ~100 ‰. This demands a firm control on or understanding of instrument linearity – i.e., how intensity ratios of registered ion beams vary with abundance ratios of isotopologues and/or absolute intensity of any given ion beam. Clumped isotope measurements address this problem by characterizing the apparent abundance ratios of all isotopologues in materials that are independently known to have a stochastic distribution of isotopes (such that measurement of one isotope ratio strictly predicts others). One can imagine using an analogous approach to precisely characterize the mass dependence of other methods of mass spectrometry, thereby improving precision.

Our presentation will also address the promise and challenges of emerging technologies for clumped isotope measurements (e.g., automated sample purification; spectroscopic analyses; high-efficiency electron bombardment ion sources).

Seasonal changes in chemical composition and organic activity in Lake Myvatn, Iceland

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Lake Myvatn is one of the most productive lakes on the Northern Hemisphere, despite the fact that it is covered with ice about 190 days per year on the average. Samples of the dissolved and suspended material from the outlet of the lake were collected regularly during the years 1999 to 2001. Lake Myvatn was covered with ice when the research began in Nov. 1999 and ice break-up began around middle of April. The Cyanobacteria *Anabena*, which is usually common during the summertime in Lake Myvatn, was not common in the summer 2000. The concentration of dissolved elements in Lake Myvatn is largely controlled by organic activity. The pH was 7.5 - 8 during the wintertime but when photosynthesis started, pH got as high as 9.86 in July 2000. Concentrations of dissolved organic nitrogen and phosphorus were up to 96% higher during summer than winter. Equally, dissolved organic carbon reached a maximum in the summer and was 81% higher than in winter. The concentrations of the macronutrients NO_3 , NH_4 and PO_4 which are essential for the primary production were up to 95% lower in summer than in winter. Similarly, there was a drawdown during summer in SiO_2 , the building material for diatom shells. The concentrations of the metals Mn and Cr showed similar behaviour as the macronutrients. The cations Na, K, Ca, and Mg were lower in the spring than the rest of the year and the same applied to the conductivity, probably because of snow- and ice-melt. The anions SO_4 , Cl and F did not have noticeable seasonal variations but the sulphur isotopes, $\delta^{34}\text{S}$, did and it increased during summer, likely because of reducing bacterias and formation of light sulphides. Oxygen- and deuterium isotopes were also strongly fractionated during the annual cycle and were lighter in winter than summer. The difference was 1 and 6‰, respectively. The concentration of Mo, an essential element for nitrogen fixation, was low in the spring, possibly because of snowmelt. Its concentration fell again from July to September. The nitrogen fixing Cyanobacteria *Anabena flos-aqua* was in blooms from late July to beginning of September, thus it is possible that it affected the concentration of Mo during that time. A few trace elements, Co, Al and Ti increased consistently during the summer but B, Sr, Ba, Cd, Cu, Ni, Pb and Zn showed little or no seasonal variations.