

Advances in Mass Independent Isotopic Studies

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Since the first discovery of a chemically produced mass independent isotopic fractionation process by Thiemens and Heidenreich in 1983 the extent of applications of MIF in nature has expanded across a extensive range of applications that encompass much of terrestrial geochemistry, cosmochemistry, atmospheric science, and climate analysis. Time scales extend from the present to the origin of the solar system, more than 4.5 billion years ago to present. The creation of the INTRAMIF program exemplifies the extent of these investigations.

In the original work on ozone formation, it was shown there is not only a mass independent fractionation that duplicated the pattern observed in meteorites in oxygen and consequently has application in solar system evolution. A major follow up to that work is determining the actual physical chemical mechanism responsible for the effect, which remains elusive to this day. The role of chemical processes in the early solar system for the source of the anomaly in the early solar system is now agreed upon as compared to nuclear processes. Very recent experimental work has deepened understanding of processes will be presented.

The process of formation of isotopically anomalous ozone in the atmosphere has been used to trace chemical and dynamical processes in the atmosphere and has been applied to most major cycles. This includes SO_x, NO_x, CO₂, CO, N₂O, water, carbonates, chlorates, and O₂. The use of high sensitivity analysis of these species has been demonstrated to provide an analytical tool to decipher chemical reaction pathways which are otherwise identifiable by conventional technique as a consequence of using multiple isotope ratio measurements.

Through polar ice studies these processes have been studied through long time scales (present – Holocene). Sulfur isotope measurements have opened a new dimension in tracking the origin and evolution of oxygen in the earth's earliest environment. Recent work has shown that from Mars meteorite oxygen analysis of bulk silicate, water, and secondary minerals that the processes of Mars formation and evolution is less well understood than previously believed and will be discussed.

Modeling non-equilibrium uptake of Se(IV) upon calcite precipitation

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Selenium is relevant as a nutrient or poison for animal and human life, and as long-lived radionuclide ⁷⁹Se in the context of nuclear waste management. We investigated time-dependent Se uptake by growing calcite as a possible way of Se immobilization. Calcite precipitation from aqueous solutions in presence of Se(IV)O₃²⁻ was studied under the surface-controlled steady state conditions at low-to-moderate supersaturation in mixed flow reactor (MFR) experiments [1]. We then simulated MFR experiments using the GEM-Selektor v.3 geochemical code [2].

Calcite precipitation rates predicted using [3] were systematically higher than the rates observed in MFR experiments in Se(IV) - containing solutions. This corroborates the inhibiting effect of aqueous Se(IV) on calcite growth reported before [4]. To account for this effect, an inhibition term involving the Se(IV)O₃²⁻ ion activity was added to the rate equation [3].

Measured amounts of Se(IV) incorporated in calcite overgrowths are substantially higher than those predicted by the atomistic calculations for the solid solution- aqueous solution equilibrium [1]. This can be interpreted by invoking an extremely strong surface growth entrapment mechanism, accounted for in our unified uptake kinetics model [5]. This model was able to describe the observed concentrations of Se(IV) in calcite overgrowths by considering a very high Se surface enrichment factor (1.5·10⁷) with a rather low sub-surface diffusivity (10⁻¹⁰ nm²/s). These parameters for Se(IV) oxyanion differ significantly from those typically used in modeling entrapment effects for cations (Sr, Cd, Co) in calcite [5]. Possible reasons for this difference will be discussed.

[1] Heberling *et al.*, in prep. [2] <http://gems.web.psi.ch>; Kulik *et al.*, this conference. [3] Wolthers *et al.* (2012) GCA **77**, 121-134. [4] Renard *et al.* Chem. Geol. **340**, 151-161. [5] Thien *et al.*, in prep.