Mass-independent isotope effects

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Mass-independent isotope effects (equal enrichment of ^{17}O and ^{18}O) have been observed in the formation of ozone in the stratosphere and in the laboratory, and in some other molecules. A theory of these previously unexplained and highly unusual effects is described, based on three features: (1) A small nonstatistical correction ("non-RRKM") for the dissociation of molecules newly formed in the recombination step $O + O_2 = O_3$, the correction being larger for symmetric ozone isotopomers. (2) Under special experimental conditions very large isotope effects occur and arise from small differences in zero-point energy for the dissociation of an asymmetric molecule OOQ via the two exit channels, OOQ $\rightarrow$ OO + Q or O + OQ, where Q = ^{17}O or ^{18}O. (3) Weak collisions in the deactivation of the newly formed energetic ozone molecules restrict the reaction at low pressures to relatively small energies above threshold (about 150 cm^{-1}), so emphasising the effect of small differences in zero-point energies in the two exit channels. The latter difference yields dramatic differences in numbers of accessible quantum states in the transition state of each exit channel, leading to large differences in the two competing dissociation rates. The effects begin to disappear at pressures > 1 atm *ca.*

With these ideas the large existing body of mass-independent and mass-dependent experimental data on ozone can be understood. Similar applications can be made to other molecules in the upper atmosphere, though more laboratory experiments for such systems, similar to those undertaken for ozone, are needed to test the predictions. The robustness of the theory towards different descriptions of the "transition state" for the dissociation strengthens the conclusions drawn. The different types of experiments illuminate the different features of the theory. In particular, the three features outlined above serve to explain the paradox of observing mass-independent and mass-dependent effects, depending on the experiment.

In a pioneering article Clayton *et al.* analysed the oxygen isotopic composition of the earliest processed materials in the solar system, the CAI's in meteorites. Understanding whether or not a credible chemical mechanism may explain such phenomena would be facilitated by the kinds of experiments used in the ozone system. It would involve the controlled gas phase recombination of constituents such as CaO, AlO, SiO and SiO_2 molecules, which ultimately may lead to the formation of CAI's. Such studies fall between the standard disciplines of cosmo/geochemistry, inorganic chemistry and chemical physics, and remain almost entirely unexplored. Collaborators in the ozone research are Drs.Y. Gao and B. C. Hathorn. Cf *Science* **293**, 259-263 (2001), *J. Chem. Phys.* **116,** 137-154 (2002), and in press.

Isotopic fractionation of Cu and Zn between chloride and nitrate solutions and malachite or smithsonite at 30° and 50°C

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Interpretation of the isotopic variations in natural Cu systems (~9 permil) and, to a much lesser extent, Zn systems (~1 ‰) requires experimental fractionation data.

Malachite ($CuCO_3.Cu(OH)_2$) and smithsonite ($ZnCO_3$) were synthetised using a slightly modified experimental protocol of the slow precipitation method of Melchiorre et al. [1]. Powdered calcite was replaced by malachite or smithsonite by reaction with a copper or zinc salt solution. Solutions of 0.05 M, 0.1 M and/or 0.5 M $CuCl_2$, $Cu(NO_3)_2$, $ZnCl_2$ and $Zn(NO_3)_2$ were prepared from reagent-grade solids and distilled water, and isotopically ($^{18}O/^{16}O$, $^{65}Cu/^{63}Cu$, $^{66}Zn/^{64}Zn$) characterised. After reacting in a closed tube for 3 to 4 weeks in a constant temperature bath at 30°C and 50°C, the solid products were separated from the solution. Before isotopic analysis, the presence of Ca in the solid phases was measured by ICP-MS and found to be negligible. In the absence of possible interference from Ca, Cu and Zn were analysed without purification by MC-ICP-MS. All experiments were run in duplicate. The analytical precision of $\delta^{65}Cu$ and $\delta^{66}Zn$ is $\pm$ 0.04 ‰ (2 σ level). The delta values are expressed with respect to Cu NIST 976 and to an in-house solution of Zn JMC 30749L. [Note: $\alpha_{solution-mineral} = (^{65}Cu/^{63}Cu)_{solution}/(^{65}Cu/^{63}Cu)_{mineral}$].

Measured chloride and nitrate solution-mineral fractionations factors at 30°C are 1.00038 and 1.00020 for malachite and 1.00004 and 1.00011 for smithsonite respectively. Minerals are thus depleted in ^{65}Cu and ^{66}Zn relative to the solutions. Compared to the 30°C data, fractionation factors at 50°C are slightly smaller for malachite (chloride: 1.00031 and nitrate: 1.00017) but indistinguishable for smithsonite. For Cu, fractionation factors are the same for 0.05 M, 0.1 M and 0.5 M solutions but those for chloride solutions are systematically larger than those for nitrate solutions, as observed for chromatographic experiments [2].

Similar to observations on natural systems [3, 4] and ion exchange experiments [2], the Cu-isotope fractionations are substantially larger than those for Zn. The experimental fractionations are small and rather insensitive to temperature variations and cannot simply account for the 6 ‰ range of variations in natural malachites [5]. Changes in solute chemistry and/or distillation type processes are probably important during malachite formation.

References

[1] Melchior et al. (1999) *Econ. Geol.*, 94, 245. [2] Maréchal and Albarède (2002) *GCA*, 66, 1499. [3] Maréchal et al. (1999) *Chem. Geol.*, 156, 251. [4] Zhu et al. (2000) *Chem. Geol.*, 163, 139. [5] Maréchal (1998) thesis.