PERSPECTIVES: ATMOSPHERIC SCIENCE

The Mass-Independent Ozone Isotope Effect

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Many elements exist as mixtures of stable isotopes. These isotopes are all incorporated into molecules, but the isotopic composition of a molecular species does not always reflect the background isotopic composition. The reason for this has long been known (*1*, *2*): Equilibrium chemical processes—such as isotopic exchange, diffusion, evaporation, and condensation—are sensitive to isotopic mass, and different isotopes may thus be incorporated into the molecules at different rates.

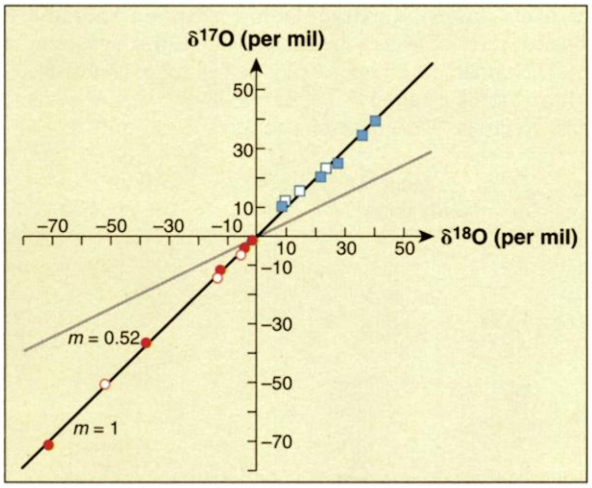
The resulting changes are small but measurable. They are usually reported in the δ notation, which for oxygen is

$$\delta^{18}O\ (‰) = (R^{18}_{sample}/R^{18}_{std} - 1) \times 1000$$
$$\delta^{17}O\ (‰) = (R^{17}_{sample}/R^{17}_{std} - 1) \times 1000$$

where $R^{17} = {}^{17}O/{}^{16}O$, $R^{18} = {}^{18}O/{}^{16}O$, and std refers to standard. For a process independent of isotopic mass, $\delta^{17}O/\ \delta^{18}O = 0.5$, which reflects the background isotopic composition. Conventional mass-dependent fractionation processes produce small variations in this ratio because the mass difference between ^{18}O and ^{16}O is 2 atomic mass units (amu), whereas for ^{17}O it is 1 amu. Such compositions are termed mass dependent.

The first exception to this was found by Clayton *et al.* (*3*), who observed that in the calcium-aluminum–rich inclusions in the Allende meteorite, $\delta^{17}O = \delta^{18}O$. At the time, no chemical process were known that could produce such an anomalous composition, and it was therefore argued that a nuclear process such as helium burning or explosive carbon burning must be responsible. But a decade later, Thiemens and Heidenreich (*4*) demonstrated that a simple chemical process can produce a mass-independent isotopic composition. They showed that ozone formation yields a product enriched in both ^{17}O and ^{18}O, with $\delta^{17}O = \delta^{18}O$. This $\delta^{17}O/\delta^{18}O$ ratio is essentially the same as in the calcium-aluminum–rich inclusions in the Allende meteorite.

Many modeling studies have attempted to reproduce these observations, but no satisfactory explanation for the ozone isotopic fractionation process has emerged. On page 259 of this issue, Gao and Marcus (*5*) finally report a mechanism that can account for all laboratory measurements, including studies of pressure and temperature dependencies (*6*, *7*) and kinetic measurements with isotopically enriched oxygen (*8*–*11*).



Plot of the first demonstration of a chemically produced mass independent isotope effect. Square symbols, ozone samples; circles, molecular oxygen reservoirs; $m = \delta^{17}O/\delta^{18}O$. The report Gao and Marcus successfully explains these observations.

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The work is based on an intramolecular theory of the mass-independent isotope effect in the formation of ozone (*12*, *13*). In this theory, the formation of the asymmetric ozone species ($^{16}O^{16}O^{18}O$ and $^{16}O^{16}O^{17}O$) is favored because it can proceed through a greater number of reactive quantum states than the formation of the symmetric isotope ($^{16}O^{16}O^{16}O$).

The model works as follows. The collision of atomic and molecular oxygen leads to the formation of a vibrationally excited O_3 transition state. The latter can either dissociate or lose or gain energy by collision to form a stable ozone molecule. The symmetric isotopic species ($^{16}O^{16}O^{16}O$) is less likely to form a stable molecule than the asymmetric species ($^{16}O^{16}O^{18}O$ and $^{16}O^{16}O^{17}O$) because some vibrational-vibrational and some vibrational-rotational coupling terms are not allowed for the symmetric species. Hence, the asymmetric species can distribute energy better and is more likely to couple to the exit channel that leads to a stable molecule. In this model, there is no mass dependency but rather a subtle symmetry factor that produces the anomalous ozone.

Using this model, Gao and Marcus have calculated rate constants and isotopic enhancements for 26 of the 54 isotopically substituted ozone molecules that can be constructed from ^{16}O, ^{17}O, and ^{18}O. The agreement of the calculations with a broad array of experimental results is spectacular. The isotopic enrichments for nine isotopic species are in excellent agreement with experiment. The calculated rate constant ratios also agree remarkably well with the measurements.

The new model not only accounts for the ozone isotopic measurements, it also extends fundamental understanding of gas phase reaction and collisional processes.

The development of this theory is timely. Many natural species are now known to have unusual mass-independent isotopic compositions. In Earth's atmosphere, O_3, O_2, CO_2, CO, N_2O, H_2O_2, sulfate, and nitrate aerosols all have mass-independent compositions (*14*, *15*). Carbonates and sulfates from Mars are also mass independent, as are sulfates from the Namibian Desert and the dry valleys in Antarctica. Sulfur from sulfides and sulfates in the Precambrian have mass-independent sulfur isotopic compositions (*16*). This isotopic signature has been used to follow the evolution of atmospheric oxygen between 3.8 and 2.2×10^9 years ago (*17*). In all of these examples, the specific mass-independent isotopic compositions have afforded new insights, but understanding of the underlying processes has been limited. The latest report from Gao and Marcus enhances our ability to understand these observations considerably.

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