A NEW ISOTOPE EFFECT AND ITS POSSIBLE IMPORTANCE IN METEORITICS;
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Since the observation by Thiemens and Heidenreich (1) of a chemically produced mass
independent isotopic fractionation, essentially identical to Allende high temperature inclusions
(δ17O=δ18O) an important question has been: are meteoritic oxygen isotopic anomalies produced by
nuclear or chemical processes? Resolution of this question is of importance for definition of the
dynamics of the pre-nebula and its collapse. If, e.g., they derive from nuclear processes, then it
requires maintenance of several separate (time and/or space) isotopic reservoirs which respect to
16O excess, (defined against the terrestrial-lunar-enstatite chondritic) mass fractionation line. If the
oxygen reservoirs derive from a chemical fractionation, only one reservoir is required since both
positive and negative 18O reservoirs are simultaneously produced. To resolve this issue,
understanding how/why/when anomalous chemical isotopic fractionations occur is important, not
only for determining how the oxygen reservoirs were produced but also how individual isotopic
compositions were acquired, such as U.O.C. chondrules.

It is now reasonably well known that the chemically produced mass independent isotopic
fractionation reported by (1) occurs during the O + O2 combination reaction. The effect is not
restricted to ozone and has been observed in O + CO (2) and SF5 + SF5 (3). These experiments
are also consistent with a symmetry effect (4), as are tunable diode laser absorption measurements
demonstrating that the asymmetric isotopomer is the predominant carrier of the heavy isotope
enrichment (5). It is increasingly clear that recombination reactions, subject to symmetry
constraints, will produce mass independent isotopic fractionations and are likely to be important in
the early solar system. In order to understand all details of isotopic fractionation we have measured
the fractionation in a simple, gas phase thermal (O2) decomposition. The advantage here is that 1)
no excited states are involved; 2) all reactions and their rate constants are known; and 3) it is easily
and precisely controlled.

Ozone of known isotopic composition was decomposed a constant amount (~20%) as a
function of temperature. The product O2 is separated from O3 and both analyzed for yield and
isotopic composition as described previously (6,7). The results are shown in the Table and plotted
in the Figure. As reported, a mass independent fractionation is observed (7) in these experiments
which varies with temperature. At the 20% conversion chosen, the relevant reaction chemistry is
simple, only O3 + Δ → O2 + O and O + O2 are of importance since O + O2 + M is insignificant (8).
Therefore, this is apparently new effect since it is associated with decomposition, whereas the
previous effects were clearly during the formation step. At present, we might explain the data as
arising from two processes, one at "high" temperature with δ18O=δ17O=25% and a second at low
temperature with δ18O=16, δ17O=9, and a mixture of the two, intermediate. At temperatures
above 90°C, the measured rate of decomposition is in excellent agreement with published gas phase
decomposition rates (9), however, at lower temperatures (<70°C) the rate is several orders of
magnitude greater, which may be assumed to be due to catalytic wall decomposition. It is, in fact,
well known that at temperatures below 70°C wall decompositions are significant (9). We conclude
that the δ18O=δ17O fractionation is due to the gas phase decomposition, which is observed at
temperatures > 70°C.

It may not be unambiguously determined, yet, which of the two steps is responsible for the
anomalous effect. However, visible O3 photolysis experiments, which also produce ground state O
atoms, is nearly mass dependent, and produces light O2 rather than heavy (10). This also
qualitatively suggests that the isotopic structure of O3 (viz. 18O enrichment is the asymmetric
species) does not cause the effect since the same O3 is used for both visible and thermal
decompositions. It does not, however, rule out the importance of isotopic structure in a collision
and future experiments with O3 of different isotopic structure will resolve this.

There is no theoretical basis for this effect, through vibrational symmetry factors applied to
RRKM theory has been suggested (11). Levine (12) has suggested that there is a dependency of
rate for a molecular decomposition of isotopomers, depending upon the nuclei statistics for
equivalent nuclei (fermion or boson). Though it is not consistent with the present results, there is then at least some theoretical premise for a mass independent fractionation in a thermal decomposition reaction.

It is interesting to consider the possible importance of this effect in meteoritics. The effect clearly occurs during a thermal dissociation process; as such, chondrule formation may be important since it is a process clearly associated with a great deal of heat exchange. Size separated chondrules from Dhajala define a $\delta^{18}O=\delta^{17}O$ line, with the smaller chondrules nearest the terrestrial line, largest the most removed ($^{17}O, ^{18}O$ enriched) (13). If, during the chondrule forming event, aside from extensive evaporation there was thermal dissociation, then a $\delta^{18}O=\delta^{17}O$ fractionation might occur, as observed in our experiments. In that the general mechanism(s) for chondrule formation remains unclear, it is not certain how the isotopic signature was acquired and resolution of the chemical mechanism and further analysis of U.O.C isotopic components are obviously needed.

In summary, an apparently new isotope effect has been observed in a simple, thermal decomposition which produces isotopically heavy products with $\delta^{17}O=\delta^{18}O$ (at temperature $>70^\circ$C). There is no theory for the effect though it concerns the most fundamental chemical process: simple bond scission. The general nature of the process suggests its possible importance in nature and future experiments and theoretical development are needed.


Table. Experimental Results of the Ozone Thermal Decomposition at Various Temperatures. Isotopic measurements are normalized to a starting $O_2$ with $\delta^{17}O=\delta^{18}O=0\%_O$.

<table>
<thead>
<tr>
<th>$T$</th>
<th>Time Produced $O_2$</th>
<th>Residual $O_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\circ$C</td>
<td>min.</td>
<td>$\delta^{18}O$</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>20</td>
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