
Isotopic studies of meteoritic materials have been instrumental in determining the isotopic composition of early solar system processes. A significant observation in the isotopic distribution of oxygen was made by Clayton et al. (1). It was shown that, in the "high temperature" minerals of carbonaceous chondrites, a plot of $\delta^{17}O$ vs. $\delta^{18}O$ produced a slope 1 line. This was interpreted as representing the admixture of a component of essentially pure $^{16}O$ into the presolar nebula. Since then, there have been extensive studies of the isotopic distribution of elements such as Si, Mg, Ca, Ba, Nd, Sr, U and Ag (cf. 2). Lively debates have ensued regarding their interpretation; however, there is general agreement on one point; deviations from mass fractionations must be due to nuclear processes. Only Arrhenius (3) has considered the possibility that chemical processes may be responsible for non-linear fractionations.

We have recently reported a chemically produced, mass independent fractionation of oxygen isotopes (4, 5). The chemical fractionation, in a $\delta^{17}O$ vs $\delta^{18}O$ plot, produces a slope 1.00 line ($\pm .01$), essentially the same as the C2-C3 "mixing" line. Briefly, the experiments involve generation of ozone by electrical (Tesla coil) discharge in pure molecular oxygen (pressure range 1-15 cm). Ozone is cryogenically removed following its synthesis at liquid nitrogen temperatures. Following reaction (run to various completion), the residual O$_2$ is analysed for $\delta^{18}O$ and $\delta^{17}O$ by isotope ratio mass spectrometry. Ozone is converted to O$_2$ on warm (300°C) molecular sieve and analysed for $\delta^{18}O$ and $\delta^{17}O$. It is felt that the slope 1 is probably a result of optical shielding by the major isotopic species $^{16}O$. Selective removal of the well known $^{16}O$ lines in the Schumann-Runge region, which are wavelength shifted from the heteronuclear lines, results in preferential dissociation of $^{18}O^{18}O$ and $^{18}O^{17}O$ with subsequent formation of isotopically heavy ozone. Since the heteronuclear species are significantly less abundant than $^{16}O_2$ (<.5%), their photolysis scales strictly with their isotopic abundance, producing a slope 1 fractionation line. We have performed numerical solutions which show that path length, pressure and optical path length of reaction do not alter the fractionation results. We are also considering the role of molecular symmetry which may be of importance due to the appearance of alternate rotational lines for the heteronuclear species in the absorption spectra.

It is felt that, since the photochemically produced fractionation strikingly resembles the meteoritic oxygen isotopic distribution, a similar photochemical process may have been operative in the presolar nebula. A compelling piece of evidence is the observed large variations in the abundance ratio of CO isotopes in molecular clouds which are also a result of isotopically selective self-shielding (6). Although our experiments utilize O$_2$, this is not a requirement for the early solar system, since oxygen only need be contained in a gas phase molecule such as CO, SiO, OH, H$_2$O or O$_2$. We have now produced the same effect (slope 1) in CO$_2$ and possibly SO$_2$, which indicates the general nature of our effect.
As concerns dissociative energy sources, two are under immediate consideration. Young T-Tauri stars (<10^6 yr) are enhanced in the UV region by factors of at least 10^4 (7). External UV sources from interstellar space, such as produce the observed CO isotopic variations, may also be of importance.

One of the significant aspects of the photochemical process in the presolar environment is that, besides its ability to produce the C2-C3 "mixing" line, it only requires one reservoir, whereas the nuclear admixture requires, at the very least, two. A problem with ^16O admixture is the lack of correlated isotope effects in other elements. As discussed by Clayton et al. (1), one would expect effects in a-integral light Z elements, particularly ^24Mg and ^28Si. With the exception of two inclusions, there have been no nuclear anomalies reported for silicon, much less the wide spread "anomalies" (positive and negative) observed in oxygen. The photochemical process, as we may show by calculation, will not produce non-linear fractionations in Si or Mg, since their minor isotopic abundances are too large (and for symmetry, they have no diatomic progenitors). The elements where one would expect significant photochemical fractionations would be species with large isotopic abundance differences (and/or diatomic precursors) such as nitrogen and hydrogen. We regard the extraordinarily large reported meteoritic isotopic fractionations for these elements (8, 9) as potential evidence for photochemical processing in the early solar system.

Obviously a great deal of work remains to be done in the future. Energy sources, chronology of events, kinetics of reaction and speciation are all areas of immediate interest. However, the astrophysical observation of a similar process in molecular clouds may provide us with a direct link between early solar system processes and presently observed astrophysical processes.


Fig. 1: Three isotope plot of the isotopic composition data. Solid squares represent ozone samples, open circles are ozone samples measured at the Univ. of Chicago, solid squares are reservoir samples and open circles are reservoir samples measured at the Univ. of Chicago.