

OXYGEN ISOTOPIC FRACTIONATIONS IN SYMMETRY DEPENDENT CHEMICAL REACTIONS; S. K. Bhattacharya and M. H. Thiemens, Chem. Dept., B-017, Univ. of California, San Diego, La Jolla, California 92093-0317.

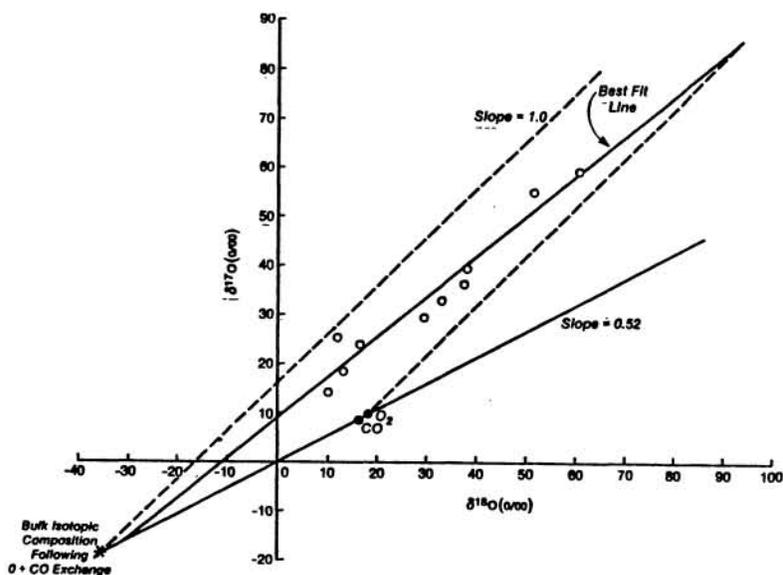
In order to specifically model the role of chemically produced mass-independent isotopic fractionations in the early solar system, it is necessary to develop a mechanistic physical-chemical understanding of the process. Heidenreich and Thiemens (1) have suggested that the  $\delta^{17}\text{O} \cong \delta^{18}\text{O}$  fractionation observed in ozone formation is due to the increased lifetime of the asymmetric isotopic species, e.g.  $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ ,  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$  with respect to symmetric  $^{16}\text{O}^{16}\text{O}^{16}\text{O}$  species, as a result of the doubling of rotational states. Thiemens (2) has suggested that, with regard to the early solar system, there are many potential reactions which may plausibly occur and which would produce a mass-independent isotopic fractionation. The reaction of atomic oxygen with  $\text{SiO}$ ,  $\text{FeO}$ ,  $\text{AlO}$  or  $\text{CO}$  should, for example, all produce a  $\delta^{17}\text{O} \cong \delta^{18}\text{O}$  fractionation and involve reaction components known to be present in various astronomical environments. Reactions involving more than three atoms should also produce the  $\delta^{17}\text{O} \cong \delta^{18}\text{O}$  signature provided the gas-phase reaction product possesses oxygen on each end of the molecule. Out of the wide range of possible reactions,  $\text{O} + \text{CO}$  was selected for study since (a)  $\text{CO}$  is a dominant oxygen-bearing molecule in a presolar environment, and (b) it is more tractable from an experimental consideration.

Techniques have been developed in the past year to more precisely study the fractionation process in  $\text{O} + \text{CO}$ , initially reported last year (3). Oxygen atoms are provided by UV photolysis of  $\text{O}_2$  in the presence of  $\text{CO}$  at two wavelengths, 185 and 130 nm, in a 5L spherical reaction chamber described elsewhere (4-6). The  $\text{CO}/\text{O}_2$  ratio is varied between ~200-400, with the initial  $\text{O}_2$  amount approximately 250 micromoles. Typical photolysis times are 20 hours, which is required to produce sufficient product  $\text{CO}_2$  for isotopic analysis. The  $\text{CO}_2$  yields vary between 16-63 micromoles. Irradiation of  $\text{CO}$  for >20 hours time at both wavelengths produced no  $\text{CO}_2$ . Oxygen isotopic analysis of the product  $\text{CO}_2$  was achieved by conversion to  $\text{CF}_4$  and  $\text{O}_2$  by reaction with  $\text{BrF}_5$ , as previously described (3). Background determinations for contamination were performed on each measurement to insure sample integrity following the  $\text{O}_2$  cryogenic clean-up. Initial  $\text{CO}$  isotopic composition was determined by conversion to  $\text{CO}_2$  in an electric discharge, followed by the same fluorination procedure. The results of the experiments are shown in the Figure, where a large mass-independent fractionation is observed. The best fit line for the data has a slope = .82,  $r = .97$ , and an intercept with the mass-fractionation line (determined by the starting  $\text{CO}/\text{O}_2$  composition) at  $\sim \delta^{18}\text{O} = -31$ ,  $\delta^{17}\text{O} = -16.2\%$ . Since the best fit line itself does not pass through the initial  $\text{CO}$  or  $\text{O}_2$  isotopic composition, more than one process is required to account for the data.

Following  $\text{O}_2$  photolysis, the kinetic fate of the  $\text{O}(^3\text{P})$  atom is to undergo isotopic exchange. Quantitative kinetic evaluation of the data with its high  $[\text{CO}]/[\text{O}_2]$  ratio demonstrates that  $\text{O} + \text{O}_2$  will not contribute to the fractionation (7). Isotopic exchange between an  $\text{O}$  atom and  $\text{CO}$  produces an isotopic composition for the atom 105.3% lighter in  $\delta^{18}\text{O}$  than  $\text{CO}$ , based on the reduced partition function ratios in Urey's paper (8). For a starting  $\text{CO}$  of  $\delta^{18}\text{O} = 16.1\%$ , this results in the atom acquiring an isotopic composition of  $\delta^{18}\text{O} = -89\%$ . Addition of this atom with the  $\text{CO}$  produces a bulk  $\text{OCO}$  isotopic composition at  $\sim \delta^{18}\text{O} = -36.5\%$ , as labelled in the figure. If in the subsequent  $\text{O} + \text{CO}$  reaction (slower than exchange by factors of ~17 to 33, as calculated

for the present experiments (7)) a mass-independent fractionation occurs, with  $\delta^{18}\text{O} \cong \delta^{17}\text{O}$ , the data would lie along the slope 1 line, shown in the figure with terminus at the labelled bulk. This is not observed in the present experiments. It is known that  $\text{CO}_2$  absorbs light and photodissociates at both 185 and 130nm. Photolysis would enrich the residual  $\text{CO}_2$  in the heavy isotopes in a mass-dependent fashion, superimposed upon the  $\delta^{17}\text{O} \cong \delta^{18}\text{O}$  fractionation. Two observations qualitatively support this: (a) the  $\delta^{18}\text{O}$  linearly correlates with the amount of  $\text{CO}_2$ , but not rate, and (b) the effect is significantly greater (~30%) for the 130nm photolysis experiments where the  $\text{CO}_2$  cross-section is  $\sim 10^3$  x larger than for 185nm. For the relevant lamp flux,  $\text{CO}_2$  concentrations and cross-section, as much as 50% of the product  $\text{CO}_2$  could be dissociated. Unfortunately, it is not possible to employ a cryogenic trapping system to immediately remove the product  $\text{CO}_2$  because the  $\text{O} + \text{O}_2$  reaction has a negative activation energy and would become dominant at the low temperatures required to trap the  $\text{CO}_2$ . Future experiments which determine the fractionation factor associated with  $\text{CO}_2$  photolysis will allow us to calculate the relevant fractionation factor.

The data might also be interpreted as deriving from a 2-fold mixture of  $\text{CO}_2$  produced by a mass-dependent means, with isotopic composition at the labelled bulk point, and a second, resulting from a  $\delta^{17}\text{O} = \delta^{18}\text{O}$  fractionation in  $\text{O} + \text{CO}$ , with the line originating at the  $\text{CO}$  and producing an isotopic composition for the  $\text{OCO}$  at the intersection of the  $m=1$  and best fit line ( $\delta^{18}\text{O} = 94$ ,  $\delta^{17}\text{O} = 86\%$ ). Such a mixture of fractionation processes might arise from differential lifetimes for the activated complex and the energy randomization process, as suggested by Bates (9). That model, however, predicts that the  $\text{O} + \text{CO}$  reaction, based on the known level density of vibrational states near the dissociation level, should produce a fractionation in  $\delta^{18}\text{O} \gg 230\%$ , though this is subject to large errors associated with the excited state lifetime. In addition, the effect on lifetime due to forbidden spin change required for reaction is unknown. At present, it may be concluded that the  $\text{O} + \text{CO}$  reaction definitely produces a large mass-independent fractionation. The effect appears to be due to symmetry, but further experimental and theoretical work is needed.



## References

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