

FIRST OBSERVATION OF A MASS INDEPENDENT ISOTOPIC FRACTIONATION IN A CONDENSATION REACTION; M.H. Thiemens, R. Nelson and Q.W. Dong, ¹Department Of Chemistry, UCSD, La Jolla, CA 92093-0356. J. A. Nuth, III, ²Astrochemistry Branch, Goddard Space Flight Center, Greenbelt, MD.

Thiemens and Heidenreich (1983) first demonstrated that a chemically produced mass independent isotopic fractionation process could produce an isotopic composition which is identical to that observed in Allende inclusions. This raised the possibility that the meteoritic components could be produced by chemical, rather than nuclear processes. In order to develop a mechanistic model of the early solar system it is important that relevant reactions be studied, particularly those which may occur in the earliest condensation reactions. This abstract reports the isotopic results for isotopic fractionations associated with condensation processes. A large mass independent isotopic fractionation is observed in one of the experiments.

The condensate smokes were produced utilizing the Goddard Space Flight Center condensation flow apparatus, which has been described by Nelson et al. (1989). The silicon oxide condensates were prepared from mixtures of molecular hydrogen, silane and molecular oxygen. The total pressure was approximately 60 torr with silane and molecular hydrogen in excess of molecular oxygen by approximately a factor of 10. Reaction temperature was about 800 K. The oxygen was obtained from the samples by reaction with bromine pentafluoride as previously described (Nelson et al, 1989). After oxygen extraction all samples were additionally purified by passage through a molecular sieve powder at -122 degrees centigrade. Measurement of the sample background demonstrated that the samples contained no impurities. The measured stoichiometry for the samples was approximately $\text{SiO}_{1.5}$ - $\text{SiO}_{1.8}$.

From the data it is observed that experimental runs II and III produced samples which were essentially isotopically identical, -12.54 and -12.57 per mil ($\delta^{18}\text{O}$), respectively. These particular samples were obtained from within the furnace of the flow condensation apparatus. For runs II and III, which were obtained from the collection foils outside the furnace exit, the fractionation is somewhat greater, -16.15 and -15.09 per mil, respectively. The modest difference between the foil and furnace samples likely results from the temperature difference between the furnace and collection surface exterior to the furnace. The magnitude of the observed fractionation reflects the isotopic fractionation associated with the condensation reaction at temperatures of approximately 800 degrees K. For all samples from runs II and III the fractionation is strictly mass dependent.

Sample I reveals a striking and important isotopic difference. The four samples which were collected from the furnace define a straight line with a slope of 0.73 and a correlation coefficient of 0.99, clearly mass independent. This is the first observation of a chemically produced mass independent fractionation in a condensate. At present we may make the following observations. The anomalous composition does not derive from contamination. As described, all samples were processed through a second purification step and the background measurements demonstrated that all were clean. The ratio in the experiments of reduced (silane+hydrogen) to oxidized (molecular oxygen) were similar, with the anomalous samples having a value between samples from runs II and III. The total pressure for run I was approximately 15% higher (70 torr total), thus there could be a different kinetic reaction mechanism though at present we cannot resolve this from the limited data. The greatest difference between the experiments was reaction time. Experiment I was only 13 minutes duration whereas II and III were significantly longer; up to 2 hours for experiment III. It may be possible that secondary reaction between the flow molecular oxygen and the condensate alters the primary condensation isotopic signature. Future studies which determine the temporal characteristics will be of importance in addressing the possible extent of secondary isotopic exchange.

The best fit line determined by experiment I does not pass through the initial molecular oxygen isotopic composition. This requires that there are at least two isotopic fractionation

processes occurring. For the reaction conditions, it is reasonable to presume that gas phase reaction between oxygen and silane produces an isotopic fractionation. If this is the case, then the magnitude of the observed isotopic fractionation (in all three experiments) would be larger since the residual molecular oxygen which reacts to form a condensate would be isotopically heavier. There is also no reason to presume that this does not happen in all three experiments, in which case we would conclude that this initial reaction between silane and oxygen in the flow stream is a mass dependent process as experiments I and II are strictly mass dependently fractionated. This then suggests that the source of the anomalous fractionation could be in the reaction leading to condensation and which is secondarily lost by exchange during passage of molecular oxygen over the solid product. The observed difference isotopically between the foils and the furnace may be a reflection of this as greater extent of exchange would be expected in the furnace.

A most important observation in the products of experiment I is that they are enriched in ^{16}O with respect to the make up gas. In other gas phase reactions which have previously been studied, and where mass independent isotopic fractionations are observed, the stable products have been enriched in the heavy isotopes. This is the first example of a ^{16}O enrichment. Wen and Thiemens (1993) have shown that exchange between atomic oxygen and CO_2 produces a mass independent fractionation, with $\delta^{17}\text{O}=\delta^{18}\text{O}$. In this instance, the CO_2 is enriched in the heavy isotopes and the atomic oxygen depleted. It appears that the present results are unlike any previous experiments. We rule out ozone formation as being responsible for the observed mass independent component as 1) at these temperatures it is unstable and would not form 2) the conditions are too reducing and 3) ozone is enriched in the heavy isotopes whereas the product is depleted in the heavy isotopes. Thus, it is unlikely that ozone formation is relevant to the present experiments.

In conclusion, the first mass independent fractionation in the formation of a solid has been observed. The fractionation is unlike those observed in gas phase reactions in the laboratory and the atmosphere and may be a new type of isotope effect. Future experiments which control the reaction kinetics and define the reaction mechanisms will be crucial in resolving the source of this isotopic fractionation process.

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