Oxygen Isotope Fractionation by CO-self-shielding and UV photodissociation of CO: Theoretical Calculations, Experiments, and Observations. M.H. Thiemens , Department of Chemistry and Biochemistry, University of Calfironia San Diego. La Jolla, California. 92093-0356. mthiemens@ucsd.edu

Introduction:

Since the discovery by Clayton el at (1) of the presence of a $\delta^{17}O = \delta^{18}O$ relation of oxygen isotopes contained within Allende calcium aluminum inclusions it has been recognized that definition of the source of this anomaly presents a major component in the ultimate resolution of the physical chemical processes responsible for the formation of the solar system. This recognition is amplified by the finding that bulk meteoritic classes possess unique identifiable isotopic compositions in three isotope space. It was originally suggested that the anomalies could only derive from a nuclear effect, such as a supernova based upon know laws of physical chemistry at that time. With the discovery of a mass independent isotope effect by Thiemens and Heidenreich (2) of an isotopic fractionation process that duplicates the $\delta^{17}0=\delta^{18}O$ pattern observed in CAI, it was recognized that chemical production of the meteoritic oxygen isotopic compositions is possible. It was suggested by Thiemens and Heidenreich that isotopic self shielding of CO could be a mechanism by which the anomalies could be produced. The concept of self shielding as a mechanism by which meteoritic isotopic anomalies could be produced by self shielding has subsequently been adopted by others (e.g. 3-5). It is now known that the chemically prodced mass independent isotopic effect first observed in ozone formation by (2) is a genral phenomena and arises as a concequence of symmetry effects during chemical reactions. It has been suggested also that this effect arises from this general feature (e.g. review by 6), or is catalyzed by the presence of grain surfaces (7).

In spite of decades of intensive observational, experimental, and theoretical investigations, the source of the meteoritic oxygen isotopic compositions remanins unresolved. For this workshop, the intent of this presentation is to provide an overview of the various observations, experiments and observations with the focus upon development of future tests to enhance insight into this most basic question: how were the observed meteoritic oxygen isotopic compositions produced.

Topical Overview:

CO Self Shielding: There exist a number models at present that suggest that CO self shielding may be the the primary mechanism by which meteoritic oxygen isotopic anomalies may be produced. They differ in where the occur (cold vs hot nebular regions), or, even outside the solar system. This is an issue as preservation of the oxygen isotopic anomaly post photolysis is a major issue and, the same is true for the provision of how these anomalies stored as water ice are converted into silicate material. There also exist questions as to experimental testing of the actual self shielding model and whether it is viable. The first test of self shsielding produced results inconsistent with self shielding (9). New unpublished experimental work (10) has also begun to experimentally probe the CO self shielding mechanism. A general assumption of self shielding is that following isotopic self shielding of incoming UV radiation there will be no subsequent isotopic fractionation associated with the photodissociative process. Recent quantum mechanical calcutions of the photochemical dissociation process have shown that this assumption may be wrong and, isotope effects not captured in photochemical cross sections may not incorporate these associated isotope effects (11,12).

Recent work on non equilibrium isotope effects on cold inter stellar grain surfaces has lead to a new, testable model for production of oxygen isotopic anomlaies (13). In this theoretical model it is found that photolytic effects of ice grains leads to formation of ozone within the grain and a series of radical oxidation reactions leading to build up of anomalous oxygen isotopic reservoirs. The results are seemingly counter intuitive thermodynamically, however, the production of the anomalies on cold grain surfaces, with loss of hydrogen may lead to production of ozone in an otherwise highly reducing environment. It has also been suggested that symmetry effects in oxygen with the relevant associated symmetry reactions of SiO and O on grain surfaces may lead to production of the CAI by a purely chemical reaction sequence (7). In both of these scenarios, the specific role of grain surface chemistry play a fundamental rle and irrespective of the correctness of either model, resolution of the role of gas-surface chemstry, surface reactions, as wewll as secondary photochemical reactions are all relevant processes which merit further study.

Summary: The prevailing models and experiments relevant to production of the meteoritic oxygen isotopic anomalies is intellectual broad and, unresolved. The purpose of this presentation is to provide a backdrop to facilitate discussion of what relevant future experiments and models might be rather than to assess current models.

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