The History of Chemically Produced Mass Independent Isotope Effects: Their Physical Chemical Basis and Applications to the Early Solar System, Planetary Atmospheres, and the Origin of Life

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Introduction: It was first suggested by Hulston and Thode (1) that meteoritic nuclear and physical/chemical processes isotopic sources may be distinguished by mass independencies in isotopic distribution. Deviation from mass dependent compositons was attributed to nuclear process as chemical are all mass dependent which they verified in sulfur isotopes. Clayton, Grossman and Mayeda (2) reported a mass independent oxygen isotopic composition in Allende calcium aluminum inclusions with a ^{16}O enrichment and attributed this to a nuclear process. Laboratory experiments by Thiemens and Heidenriech (3) demonstrated in O_3 formation there is a mass independent nearly identical to CAI.They suggested the source of the effect was isotopic self shielding, and in the early nebula shielding on CO was the source of the meteoritic oxygen isotopic anomalies. Subesequent experiments eliminated self shielding for the ozone isotopic anomaly and also for the meteoiritic anomalies though it remains a question of active research and discussion.

The quantitative quantum mechanical basis of the mass independent anomaly remains elusive but root of the effect is symmetry, with different formation rates for $^{16}O^{16}O^{16}O$ compared to equal enrichment in asymmetric $^{17}O^{16}O^{16}O$, $^{18}O^{16}O^{16}O$. This general aspect has broad conseqences for planetary science in space and time. The symmetry aspect renders oxygen a unique species, especially cosmochmeically as it generellay coordinates species resides and subject to symmetry rules, which makes oxygen unique. All oxygen species in the atmosphere possess mass independent isotopic compositions (including O_2) and vary in magnitude and have both positive and negative $\Delta^{17}O$ values (4). The oxygen and ozone record is recorded in polar across the Holocene. Measurements of carbonates and sulfates in Martian meteorites record both the past atmospheric oxgen-ozone levels and the signature of water. Experimental studies of the relevant processes have show that atmospheric records are recorded in both Earth (atmospheric) and Martian carbonates and capture various aspects of the global processes (5). Carbonaceous carbonate and sulfate anomalies allow additional parent body hydrothermal activites to be resolved.

The quest to understand the meteoritic oxygen anomlies continues. The general symmetry dependent nature of oxygen is of importance in the production of meteoritic anomalies. In the very earliest stage of solar syetm formation, the main Si bearing gas phase molecule SiO is oxidized an converted ulitmatley to silicate. The oxidation of SiO predominately proceeds via reaction with OH or O, leading to OSiO and issubject to symmetry rules, analogous to ozone. This was experimentally tested and the SiO oxygenation products measured and chemically modeled. The expected oxygen isotopic anomaly is produced. Further examination of this process and other non silicon elements will provide deeper reolution of this critical step in solar system formation. *There is a subtle but critical point to be made. In this symmetry driven process, the isotopic composition is determined by the short lived species alone. Thus even in a shielding regime, the oxidation process erases the original shielding isotopic effect in the transition state leading to the oxidized species (gas or solid).This creates both positive and negative $\Delta^{17}O$ values in the same space and time as in the present day atmopshere and does not require reservoir mixing.*

In the isotopes of sulfur, anomalies were reported in the atmosphere and Mars meteories (4). This lead to studies of samples from the earths Precambrium where MIF sulfur was observed and, as a consequence of lowered oxygen-ozone levels, UV SO_2 photolysis produces a MIF sulfur record (7). This reord requires low O_2 levels and as a result, the sulfur MIF has allowed the origin of oxygen to be traced from the earths earliest record until the Great Oxigenation event. This has led to the ability to quantify oxygen levels on the early Earth. This work has catalyzed a large community to employ sulfur anomaly measurements to trace global biogeochemical cycles through time. It has also prompted new measurements and models of the basic photophysics of isotopic effects in photodissociattion. These studies have lead to deeper quantum level understanding of the complexities of phtodissociation and to enhanced application to studies of nature

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