## Past,Present and Future of Mass Independent Isotope Measurements

## MARK H. THIEMENS<sup>123</sup>

<sup>1</sup>Department of Chemistry and Biochemistry 0356 <sup>2</sup>MC 0356 <sup>3</sup>UCSD La Jolla Ca.

The first application of mass independent isotope ratoo measurements was nearly 50 years ago when multi sulfur isotope ration measuremnts were used to quantify billion year cosmic ray effect spallation effetcs in iron meteorite based upon the premise that only nuclear effects can produce isotope ratio alteartions that are independent mass differences. The subsequent observation of mass indendent oxygen isotopic compositions in the primitive Allende calcium inclusion inclusions was interpreted as requiring a nuclear process to account for the mass indpendent isotopic composition. The Thiemens and Heidenreich ozone experiment in 1983 was the first demonstration that a chemical process was capable of simultaneously producing a mass indenent isotopic compsoition, but one that also duplicates the pattern observed in the calcium aluminum inclusions.

The identification of the quantum mechanical basis of the production of the mass independent isotopic composition remains elusive to this date and in chemical physics has been a subject of interse theroetical and experimental measurements. Likewise, the chemical process responsible for the metoritic components is a subject of theroetical and physical chemical study to define its role in the early solar system.

In atmopsheric molecules it is known that every oxygen bearing molecule has a mass independent, ranging from the second most abundant molecule  $(O_2)$  through H<sub>2</sub>O, CO<sub>2</sub>, CO, N<sub>2</sub>O, H<sub>2</sub>O2, O<sub>3</sub>, SO<sub>4</sub>, NO<sub>3</sub>, and ClO<sub>4</sub>.This encompasses a range of applications, including global primary prodictivity quantification present and past (ice core), ozone chemistry and interactions in the tropopshere and stratosphere, post Snowball Earth atmopsheric chemistry, paleo ozone levels, El Nino global atmopsheric chemistry and the record in at the South pole, greenhouse gas source identification and troposopheric chemistry of nitrate and sulfate and the oxygen cycle.

The observation of mass indpendent sulfur isotopic anomalies in the Archean permits definition of the origin and evolution of oxygen from the oldest rocks through the great oxygenation event and the beginning of defining the total biogeochemical system of sulfur across that time span.