A survey of mass independent isotope effects in nature

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It has been over 20 years since the first discocvery of a chemically produced mass independent isotope effect by Thiemens and Heidenreich (1983). In spite of the simplicity of the data from those experiments, with equal ^{17}O and ^{18}O enrichment in the product ozone, it required more than 15 years of experiments and theory before a quantum level description of the fractionation process developed.

Along with the continued development of the physical chemical theory, a spectacular range of applications and observations of mass independent isotopic compositions has developed in the same years. It is know that with the exception of water, ***EVERY*** oxygen bearing molecule in the atmosphere posseses a mass independent oxygen composition. This includes O_2,O_3, H_2O_2, $HClO_4$, CO, N_2O, CO_2, solid sulfate and nirate aerosols. In addition, sulfur isotopes in the atomsphere possess variable mass independent isotopic compositons. Work by Alexander and Savarino has shown that the stability of the oxygen isotopes in sulfate and nitrate in ice core samples provides a mechanism to observe the oxidative capacity changes of the atmosphere from yearly time scales to Holocene changes and glacaiation periods. Work by Micahlski on nitrates in many environments, aqueous, atmospheric, and geological, has proven to be a powerful technique to resolve environmental changes and biogeochemical processes.

Mass independent sulfur isotopic varaitions in the Archean have lead the way in developing a new technique to track molecular oxygen and ozone level varaitions following the work of Farquhar. Combined laboratory photochemical investigations and Martian SNC measurements have allowed for the atmospheric chemistry and its coupling to the Martian regolith to be explored. Sulfur isotopic measurements are also now providing details of climate perturbations from a variety of samples (work by e.g. Savarino and Cole Dai) Finally, the application in solar system evolution is now particualrly important since the nuclear model has been abandoned. Furthermore, development of a physical chemical model by Marcus and colleagues is now providing a basis to develop key experiments to study the role of mass independent chemistry in the early solar system and the evolution of the most abundant element on stony planets.

Oxygen-17 anomaly in terrestrial minerals: An update

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There exist a few albeit rare minerals on Earth that bear an ^{17}O anomaly, a measure of the deviation from the terrestrial fractionation lines defined by the overwhelming majorities of mineral and water samples. The anomalous minerals that we know so far are sulfates, nitrates, and perchlorates found in arid and hyperarid settings, where oxyanion acids or salts produced in the atmosphere accumulate and recrystallize over time and become massive ^{17}O-anomalous deposits.

So far, all the oxyanions' ^{17}O anomalies appear to derive from atmospheric ozone during the oxidation reactions in which ozone's anomalous oxygen(s) are transferred to oxyanions. Non-labile oxyanions such as sulfate, nitrate, and perchlorate could hold portions of the ozone's ^{17}O anomaly without exchanging with water after deposited in the surface environments.

Multiple stable isotope analyses (including ^{17}O anomaly) of atmospheric salts have brought in new insights in at least four major research areas: atmospheric chemistry, soil processes in arid settings, forensics of contaminants, and Mars exploration. New sources and oxidation pathways of atmospheric S, N, and Cl species have been revealed. Passively accumulated atmospheric salts over millions of years provide ample samples for studying long-term atmospheric processes. Transient yet unusual atmospheric events may have left behind geological records. Multiple isotope profiles of salts have uncovered extremely slow leaching, volatilization, or biological processes in hyperarid deserts that are otherwise unrecognizable. The finding that natural (atmospheric) perchlorate bears an ^{17}O anomaly has provided a powerful forensic tool for perchlorate contamination in environments. On Mars, atmospheric deposition is probably the only currently active and ever-lasting process on the surface. Salt isotope profiles from Martian regolith are predicted to hold rich information on Mars atmosphere and climate history.

Traditional isotope ratio measurements have been focusing on either solids or gases. Analytical demands (high spatial resolution, small sample sizes, or pure phases) have led to laser or microprobe analysis for solids and gas chromatograph separation and purification for gases. Precise and multiple stable isotope measurements for oxyanions, which often go through an aqueous phase during separation and concentration, have created new challenges for the use of ion chromatograph and column separations in geological applications.