**SPECIAL FEATURE: INTRODUCTION**

Introduction to Chemistry and Applications in Nature of Mass Independent Isotope Effects Special Feature

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Stable isotope ratio variations are regulated by physical and chemical laws. These rules depend on a relation with mass differences between isotopes. New classes of isotope variation effects that deviate from mass dependent laws, termed mass independent isotope effects, were discovered in 1983 and have a wide range of applications in basic chemistry and nature. In this special edition, new applications of these effects to physical chemistry, solar system origin models, terrestrial atmospheric and biogenic evolution, polar paleoclimateology, snowball earth geology, and present day atmospheric sciences are presented.

The use of stable isotopes has a long history of applications in physics and chemistry dating back to the discovery of isotopes themselves. Applications include processes that occur on Earth and in space, present and past, and their interpretation has been enriched by new theories and measurements of the fundamental physical chemistry. Application of relevant physical chemical laws to high precision isotope ratio measurements of controlled laboratory chemical and photochemical experiments develops a basis for interpreting measurements of a wide range of natural samples and enhances interpretations. Historically, development of thermodynamic theory for quantifying stable isotope variations (1, 2) and the ability to measure these variations in natural samples via isotope ratio mass spectrometry (3) lead to deeper understanding of natural phenomena. Measurement of oxygen isotope ratios in various geological materials has provided the ability to follow temperature variations of the world’s oceans over million years’ time scales, determine igneous rock crystallization temperatures, and track the earth’s hydrologic cycle, present and past (4–6). Isotope ratio measurements of ice core water has been the primary means by which temperature variations are determined. Quantifying the transfer of carbon between the Earth’s atmospheric and geological, biological, and hydrological systems is followed using carbon isotopes. Greenhouse gas sources and transport are recognized by isotopic measurements. Meteorite isotope measurements provide details of the origin and evolution of the solar system. The observation of isotope ratios of terrestrial sulfur isotopes in early earth minerals allows recognition of the origin and evolution of biological processes on Earth.

In this special issue, isotope ratio measurements are reported for a range of molecules in experiments and natural systems. By convention, the delta notation, is used, which for oxygen is

\[
\delta^{18} \text{O} \text{[per mil]} = \left( \frac{^{18}\text{O}}{^{16}\text{O}} \right) \text{sample} / \left( \frac{^{18}\text{O}}{^{16}\text{O}} \right) \text{SMOW} \times 1000.
\]

For oxygen, the standard is standard mean ocean water (SMOW). Stable isotope ratio measurements are typically reported in this manner, and a similar isotope ratio is reported for \(\delta^{17}\text{O}\).

In general, isotope ratio alterations are attributable to conventional thermodynamic, kinetic, translational, and gravitational phenomena (4–6). When changes are expressed in the delta notation, it is found that these different processes share the common feature that they are all ultimately related to differences in mass and in general:

\[
\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5\delta^{18}\text{O}.
\]

This relation arises from the mass dependence of isotope alteration processes, e.g., a process that varies the \(\delta^{18}\text{O}\) by 10 per mil (mass difference of two); the associated \(\delta^{17}\text{O}\) varies by a factor of approximately half that (5 per mil, for the mass difference of 1). A mass-dependent process by definition has \(\Delta^{17}\text{O} = 0\), and mass independent is nonzero and is referred to as a mass-independent fractionation (MIF). The coefficient varies between 0.50 and 0.53 and is dependent on the specific chemical process and the mass of the relevant molecular species. The variation in the coefficient is used to evaluate various processes and is discussed in several of the contributed papers.

The first application of multi-isotope measurements to detect mass-independent measurements was for sulfur (7) to identify nuclear processes, such as cosmic ray spallation effects in meteorites. The applications have subsequently expanded, particularly to oxygen isotopes, and in this special issue, many unique uses of both oxygen and sulfur isotopes are presented (8–18).

To identify mass-independent processes, two or more stable isotope ratios are required. It was assumed by ref. 7 that for meteorites, this deviation must reflect a nuclear process because no chemical process alters isotope ratios in a manner independent of mass. It was shown that cosmic ray spallation of iron and nickel by high energy galactic cosmic rays over billion year time scales produces excess \(^{32}\text{S}\) and \(^{34}\text{S}\). Oxygen isotopic measurements of calcium-aluminum rich inclusions (CAIs) from the Allende meteorite revealed a deviation from mass dependence (19). Fig. 1 schematically displays a collection of meteorite measurements including the relation of \(\delta^{17}\text{O} = \delta^{18}\text{O}\) for the CAIs. Based on the assumption that chemical processes cannot produce an isotopic composition that does obey mass relations, it was concluded that the data must be from a nuclear source, specifically addition of pure \(^{16}\text{O}\) from supernovae (19).

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The basic assumption that a chemical process may not produce a mass-independent isotopic composition was later experimentally demonstrated to be incorrect (20) and initiated the field of mass-independent isotopic chemistry and its applications. It was shown that the identical $\delta^{18}O/\delta^{16}O$ ratio observed in CAI is produced during the formation of ozone from dissociation of molecular oxygen. Fig. 2 shows that ozone is produced with equal $^{17}O$, $^{18}O$ enrichments. Thiemens and Heidenreich (20) interpreted this as arising from isotopic self-shielding on $O_2$, creating a fractionation pattern dependent on abundance rather than mass. Isotopic shielding by CO in the solar nebula might have suggested as a means to produce the observed meteoritic oxygen isotopic anomalies. Early measurements of the $^{18}O/^{16}O$ ratios in stratospheric ozone (21) suggested large heavy isotopic enrichment; however, they only measured a single isotope ratio and at least two are required to demonstrate a mass-independent process. A later reanalysis of the data led to the conclusion that these data are unreliable and should be disregarded, and subsequent return samples demonstrated the presence of mass-independent atmospheric ozone that were consistent with experimental observations (22).

Despite the simple isotopic fractionation pattern in the ozone formation process shown in Fig. 2, defining the basic physical chemical mechanism responsible for the process remains elusive (5). An early model attributed the isotope effect to the metastable transition state that arises immediately following the oxygen atom-molecule collision and its subsequent stabilization leading to stable ozone (23). In general, this stabilization process is determined by the lifetime of the metastable species, which is a function of a wide variety of parameters. It was suggested that the isotopic selective factor arises from the different number of states for asymmetric $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{17}O$, compared with the symmetric $^{16}O^{16}O^{16}O$ species resulting in an increased probability of stabilization for the asymmetric species. There have been numerous experiments directed toward identifying the source of the effect, with isotopically labeled ozone being particularly insightful (24–30) in defining the role of the isotopic structure of the ozone molecule on the ozone rate of formation, as well as pressure (27) and temperature (28). A full treatment of the chemical physics of the ozone formation process has been developed in refs. 29–33, using a modified statistical Rice–Ramsperger–Kassel–Marcus (RRKM) model for the recombination process. A key aspect was adoption of a new nonstatistical factor, termed the “$\eta$” effect that incorporates non-RRKM factors associated with the symmetry of the isotopically substituted isotopic species. In this special issue, Marcus (34) extends this work to fold in the effect of low pressure phenomena. At low pressures (less than the Lindemann fall-off region), the isotope enrichment decreases well ahead of the expected $O + \text{O}_2$ drop off and is directly treated (34). A potential source of this behavior is attributed to isotopomeric symmetry of overlapping resonances leading to a localized chaotic behavior, and potential testable experiments are suggested.

Alternate mechanisms have been developed (35–37) based on detailed inclusion of the potential energy surfaces of ozone, including the energy barrier region. A full quantum level treatment of the molecule-atom scattering process is used with a coupled channel model that allows incorporation of all states and their coordinates. The model includes resonances among the metastable states and the role of isotopic symmetry. In a contribution to this issue (38), the formation and stabilization steps are treated using mixed quantum/classical theory incurred during collisional energy transfer and passage of ro-vibrational energy. The involvement of scattering resonances and lifetime dependencies on rotational excitation, isotopic asymmetry, and the connection between differing reaction channels are included in the model.

After the unsuccessful first attempts to measure the isotopic composition of stratospheric ozone via in situ mass spectrometry, subsequent return sample measurements (39) revealed ozone isotopic compositions consistent with experimental observations of ozone formation (40–42). There now exists a substantial database of stratospheric ozone measurements (42, 43). An important application of atmospheric ozone isotopes takes advantage of the unique, identifiable isotopic composition of ozone and the ability to trace it through differing chemical reaction channels. It was suggested that the product of ozone dissociation, electronically excited atomic oxygen ($O^+$), may interact with carbon dioxide forming an excited $CO_3$ transition state that dissociates to ground state O ($^3P$) and

**Fig. 1.** Oxygen three-isotope plot of meteoritic and lunar materials. The slope 1 line was originally proposed to be nucleosynthetic and is now regarded as a mass independent chemical process. Figure from ref. 76.
During exchange, the ozone isotopic signature is transferred to CO₂ and serves as a measure of stratospheric ozone levels and degree of chemical interaction with electronically excited atomic oxygen (44, 45). From theoretical and experimental studies, CO₂ isotopic measurements have provided insight into the dynamics of the stratosphere–troposphere exchange (45–53) and a measure of upper atmospheric oxygen radical processes (54–56). Using balloons and National Aeronautics and Space Administration (NASA) ER-2 aircraft, CO₂ samples were collected in the winter of 1999–2000, as well as a 2004 balloon flight across an altitudinal and latitudinal range of the Arctic Polar vortex (15). As reported in this special issue, laboratory measurements coupled with atmospheric modeling may account for the observed CO₂ isotopic composition (15). Fig. 3 reveals the wide range in global variations in upper atmospheric CO₂ oxygen isotopes. The model and measurements reveal that the compositions are unlikely to be due to artifacts in measurement and resolve the complexity of upper atmospheric oxygen photochemistry and dynamics. A range in isotopic mass independence is observed that varies with latitude, altitude, and time (15) and is partly attributed to the position within and outside of the polar vortex, enhancing understanding of polar upper atmospheric oxidative processes. The work suggests that further measurements in tropical regions would further amplify understanding of the contributing factors. In this issue (17), a study of CO₂ photolysis in the actinic region 150–210 nm has documented the photo physical dynamics occurring in the Earth’s mesosphere that influence overall the upper atmospheric (stratosphere and mesosphere) isotopic cycle of CO₂-O₃-O₂, suggested as being important (17, 56).

The O₂-CO₂-O₃ isotopic interaction provides a means by which gross primary productivity may be measured from the very small, but significant, variation from mass dependence in atmospheric O₂ (57, 58). In this issue, measurements of the triple oxygen isotopic composition of barites from a post-Minoan (635 Ma) dolostone sequence at Wushanhu, in Southern China (16), have been shown to define the global biogeochemical system during a time period after the snowball earth period where this oxygen-ozone-carbon dioxide coupling is particularly perturbed. During this time period, global glaciation occurred, extending to low latitude equatorial regions and creating a snowball earth due to the drawdown of atmospheric carbon dioxide during intense geochemical weathering processes and producing a global temperature decrease. In a remarkable observation (59), a negative Δ¹⁷O anomaly in barite has been found in post-Minoan glacial diamictites at the time of the global melt-down of the global glacial ice cover (16, 59, 60). The existence of a negative Δ¹⁷O value is interpreted as deriving from enhanced CO₂ levels with elevated interaction with ozone photochemistry, which amplifies the negative effect on O₂. It is suggested that the CO₂ levels may have exceeded 25,000 ppm to account for the large barite negative isotopic anomaly. This observation represents one of the largest historical excursions in CO₂ levels, and confirmation of the process and understanding of its extent in amount and time are vital, particularly because this time period is associated with a period of major biodiversity expansion. A key aspect of this unique contribution is defining the time of the event

Fig. 2. Experimental results of Thiemens and Heidenreich (20) demonstrating a mass process in the formation of ozone along a slope one line, identically mimicking CAI in meteorites as shown in Fig. 1.

Fig. 3. A three-isotope oxygen isotopic plot of a wide range of stratospheric carbon dioxide samples. The samples have been obtained by balloon, stratospheric aircraft, and rocket borne whole air sampling. Plot taken from Wiegel et al. (15). The paper discusses the utility of understanding both the oxygen chemistry of the upper atmosphere as well as stratosphere-troposphere dynamics.
duration and (16) estimate it to be 0–0.99 million years using stable and radiometric isotopes. Consequences for global geochemistry as a consequence of this duration are discussed.

Mass-independent isotopic compositions are observed in a range of molecules, terrestrial and extraterrestrial. Mass-independent composition of water is reported in samples collected at Vostok, Antarctica (14). This signature captures stratospheric–tropospheric mixing and a stratospheric water source. The anomaly derives from methane oxidation as part of the stratospheric ozone cycle (14). Normally this magnitude would be too low to be recognized; however, the Vostok area is characterized by extremely low atmospheric water content and accumulation rate, allowing the stratospheric water to be distinguished. The measurements permits a measure of stratosphere–troposphere mixing in Antarctica and enhanced understanding of the role of anthropogenic methane sources on the global atmospheric water cycle.

Unique ice core sulfate measurements are reported in this issue (12) for samples retrieved from a high-resolution 22-y (1980–2002) snow pit at the South Pole. The oxygen isotopic variations record specific effects on the environment, including perturbations from volcanoes and El-Nino Southern Oscillations (ENSOs). From measurements of the variation in polar sulfate $\Delta^{17}$O values, tropical ozone variations in the upper troposphere/lower stratosphere have been detected at South Pole and are observed to be linked to the three largest ENSO events of the past 20 y. Fig. 4 schematically depicts the overall process, initiating with atmospheric upwelling driven at the equatorial Intertropical Convergence Zone (ITCZ) regions during ENSO events. It is observed that the sulfate anomaly coherently tracks with the Ozone ENSO Index (OEI) obtained from tropical latitude ozone satellite measurements. The El Nino OEI is thought to arise from variation of the tropopause height, itself a consequence of deviations of tropical deep convection and Brewer-Dobson circulation (12). As a consequence, an enhanced entrance to the stratosphere within the ITCZ is created, and tropospheric air enters the stratosphere and migrates poleward as shown in Fig. 4, allowing the El Nino perturbation to be recognized in Antarctic ice core samples. These measurements show that the sulfate oxygen isotopic measurements may be used to hemispherically track aerosol and trace gases along with their oxidative chemical processing. Along with the unique ENSO hemispheric record, the snow pit sulfate data also detected the El Chichon, Pinatubo, and Cerro Hudson volcanic eruptions.

With the special isotopic charater of ozone and its insertion into most atmospheric oxidation processes, it has developed into a useful probe of atmospheric chemical processes. An important aspect is the need to resolve the role of chemically reactive species. A significant amount of the ozone driven chemistry occurs within the tropical Marine Boundary Layer (MBL), where the process is driven by ozone sources [NOx and volatile organic compounds (VOCs)] and inadequately quantified ozone sinks. The total budget of NOx is inadequately known and limits resolution and quantification of the nitrogen cycle. Contributions from halogens (especially bromine), surface chemistry, and nighttime chemistry are confounding contributors to this complexity. From isotopic measurements of a yearly record of nitrates collected at the Cape Verde Atmospheric Observatory, a unique insight into MBL chemistry has been obtained (13). The measured nitrate oxygen isotopic variations are shown to fit nitrate chemistry, with bromine chemistry included. With application of two varieties of atmospheric models and inclusion of BrO, NO, NO$_2$, O$_3$, OH, HO$_2$, and dimethyl sulfide (DMS) with the $\Delta^{17}$O values, the complex chemistry was modeled. The work recognizes that aerosol transport time is approximatelly several days. More importantly, it was recognized that the role of N$_2$O$_5$ and its reaction products (ClNO$_2$) are likely insignificant in this environment, and high HNO$_3$ production rates from N$_2$O$_5$ hydrolysis is unlikely to be significant. The role of halogen in the MBL is consequently better established with the unique isotopic measurements facilitating diagnosis. Bromine nitrate is a significant sink, at a level of ~20% of total nitrate formation. The work illustrates that high precision multi-isotope ratio measurements coupled with appropriate concentration measurements and modeling provide a deeper understanding of complex atmospheric processes, particularly those that involve short lived, low concentration species.

Perhaps one of the most interesting applications of mass independent chemistry has been its amplification of understanding and detecting the rise and evolution of oxygen in the Earth’s atmosphere and the involvement of biological processes. For more than a half century, a quantitative record of the rise of
oxygen in the Earth’s atmosphere has been sought. Ironically, the best record of oxygen in the Earth’s earliest environment was captured in the mass-independent isotopic composition of sulfur isotopes (61). It was shown that mass-independent sulfur isotopic compositions are recorded in both sulfate and sulfide in a suite of the oldest rocks on earth until ~2.1 × 10⁹ y ago. Laboratory experiments and modeling efforts (61–65) demonstrated that the effect is reproduced in the photolysis of SO₂ in the UV region. Normally, this does not occur in the present earth’s atmosphere because UV light is required to produce the laboratory observed MIF isotope effect, and it is not available in the troposphere due to stratospheric ozone absorption of UV light. The observation of sulfur isotopic anomalies in the geologic record is due to the lowered O₂–O₃ levels that allow penetration of UV light to the troposphere permitting SO₂ photolysis. There now exists a massive dataset of observations of both negative and positive sulfur isotopic anomalies in the Archean, which is displayed in Fig. 5. This record has facilitated studies on the origin and evolution of oxygen on Earth and provided information sought for nearly a half century. With the extended studies using mass-independent sulfur isotopic composition observations of the geochemical record (oxidized and reduced sulfur species), detailed theoretical and experiment investigations and linkage to biological studies have facilitated advances in evolutionary biogeochemical systems. The photochemistry of SO₂ is complex, and modeling of the isotope effects, especially in the atmosphere, is challenging. In this issue, a unique photochemical photoexcitation mechanism that occurs in the stratosphere is presented (11). In Whitehill et al. (18), a creative series of experiments and trapping the photoexcited sulfur dioxide a new mass independent isotopic signature pattern was observed. The results imply that the effect is not from the excitation process but rather from isolate selective spin-orbit selection. The experiments demonstrate the complexity of photo processes and the possible importance in the early earth. The effect of oxidation reaction on the photochemistry is discussed. From the measurements and associated analysis, deeper insight into ice core isotopically anomalous sulfate records that are used to track massive volcanic eruptions (65) and during the Archean (66–68) has been provided. The role of OH oxidation is shown to be particularly important in controlling the magnitude of the sulfur isotopic anomaly, especially during volcanic events. The enhanced understanding of the combined oxidation mechanisms provides a test of the sensitivities of parameters, including photolysis altitude. The linkage between biology and the production and preservation of the mass independent sulfur isotopic composition is mediated by coupling of the geologic and oceanic processes. Quantifying this association is difficult; however, it is vital in interpreting the global mass-independent sulfur isotopic record. In this special issue, ref. 9 reports a model that quantifies linkages of the biogeochemical reservoirs. From analysis of the sulfur and iron cycles, constraints on the atmospheric sulfur photochemical cycle are placed, and the magnitude of the MIF signal following sulfur delivery to the oceans is better interpreted, particularly the fractionation associated with sedimentary preservation. The model results suggest that closer high-resolution isotopic studies of pyrites from shallow water environments would be fruitful and further understanding of the sulfur cycle in the early earth.

One of the most striking aspects of the Neoarchean is the observation that the atmospheric record has survived for billion year times scales and, despite mantle recycling, is preserved. The issue of preservation is addressed in ref. 8, specifically how the MIF signal may be maintained with the intervention of biological sulfate reduction over the original atmospheric mass-independent signature. The key to preservation is the need for at least two simultaneous oceanic basins for sedimentary pyrite. In one case, soluble sulfate permits uptake by biological organisms, sulfate reduction, and synthesis of isotopically normal pyrite. In a separate reservoir, insoluble sulfate is inorganically converted to pyrite with preservation of the atmospheric MIF signal (8). Mineral level sulfur isotopic analysis using a secondary ion MS (SIMS) has allowed data to be acquired on single grains of pyrite to provide identification of different populations of pyrite composition. The measurement of individual mineral phase sulfur isotopic composition has provided enriched understanding of biogeochemical evolution.

The field of chemical mass-independent chemistry began with the observation that in the production of ozone, an identical mass-independent isotopic composition to meteoritic high-temperature calcium aluminium-rich inclusions is included. It is commonly held that chemical processes, photochemical or chemical reactions, or both may be responsible for meteoritic oxygen isotopic anomalies. A deeper understanding of the relevant physical chemistry of photochemical processes enhances resolution of nebular processes. Meteoritic sulfur possesses mass-independent isotopic compositions,
including in organic molecules (70), and are suggested as arising from nebular photochemistry. There is a large database for SO$_2$ UV photolysis; due to experimental limitations, there are no short (vacuum) UV photolysis experiments relevant in the early solar system. To address the lack of photochemical data and explore the role of specific electronic states on photodecomposition and isotopic fractionation process, synchrotron experiments have been performed at narrow short UV wavelength bands, and the products have been isotopically analyzed. In ref. 10, vacuum UV photolytic decomposition of H$_2$S, a dominant sulfur species in the early solar system, was performed using the Advanced Light Source synchrotron facility (Lawrence Berkeley Laboratory). Wavelength-dependent mass-independent isotopic fractionations are observed and are presumably associated with resonance-assisted curve crossing dynamics. The results are discussed in the context of the photochemistry and application to meteoritic isotopic anomalies. These unique results emphasize that the field of mass-independent chemistry advances from concomitant understanding of fundamental physical chemistry and occurrence in nature.

Mass-independent isotope compositions occur in heavy elements, including Ba, Ca, Sr, Ti, Cr, and Hg (5). A special type of mass-independent isotope effect observed in heavy element chemistry known as the nuclear field effect (71, 72) has been suggested as a potential source of isotopic anomalies in meteoritic materials generally considered to be nucleosynthetic (71). This effect arises from an odd mass isotope effect observed in uranium (73, 74) and is suggested as being important in geo- and cosmochemical environments. The chemical basis is that in heavy element thermodynamic processes, nuclear field shifts become important as a consequence of effects on the electronic shape and size due to slight distortions from the interaction of the electron with the nucleus and the finite probability of a nonzero electron density within the nucleus (contact density). This effect occurs in odd number nuclei where a nuclear magnetic moment exists and produces a smaller electronic size. In ref. 75, the basic chemical physics of the nuclear volume effect, specifically for crystals, has been treated using density functional theory and applying a projector augmented wave method (DFT-PAW). This technique has the advantage in its computational ability, and the results are contrasted against other techniques that estimate nuclear volume. Using this computational technique, the nuclear volume effect is applied toward understanding the vapor-crystal isotope fractionation for cadmium and mercury where there exists a high-quality dataset. The results provide a unique and powerful computational technique for detailing isotope fractionations that derive from nuclear field shift–associated phenomena. The work has allowed comparison with a variety of other measurements, including Mossbauer and mass spectrometry.

**Conclusions**

Since the discovery of chemically produced mass independent isotope effects, a wide range of applications have emerged, ranging from basic physical chemistry studies, to observations in the atmosphere, planetary formation processes, the origin and evolution of oxygen on Earth, and paleo climatology. Fig. 6 is a plot of atmospheric species on Earth illustrating the range of oxygen isotopic compositions is large and that all oxygen-bearing atmospheric molecules are mass independent. In each case, specific insight into natural processes has been provided with observation of the mass independent isotopic compositions. Contributions to this special volume present a wide array of new applications. There will be new measurements made on other molecular species, terrestrial and extraterrestrial, and coupled with developments in basic physical chemistry (theory and experiment) and modeling, will continue to expand our understanding of nature.

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![Diagram](image_url)

**Fig. 6.** A plot of the oxygen isotopic composition of a variety of atmospheric species, including gaseous, aerosol sulfate and nitrate, and rain water peroxide. The small, but significant, negative mass independent isotopic composition of molecular oxygen is not observable in this expanded scale, but by mass, is the largest terrestrial mass independent isotopic reservoir. All oxygen atmospheric species measured to date are mass independent in composition. The ozone isotopic composition has been normalized to air oxygen at the intersection of the slope 0.5 and 1.0 slopes.
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