REVIEW: ATMOSPHERE SCIENCE

Mass-Independent Isotope Effects in Planetary Atmospheres and the Early Solar System

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A class of isotope effects that alters isotope ratios on a mass-independent basis provides a tool for studying a wide range of processes in atmospheres of Earth and other planets as well as early processes in the solar nebula. The mechanism for the effect remains uncertain. Mass-independent isotopic compositions have been observed in O_3, CO_2, N_2O, and CO in Earth's atmosphere and in carbonate from a martian meteorite, which suggests a role for mass-independent processes in the atmosphere of Mars. Observed mass-independent meteoritic oxygen and sulfur isotopic compositions may derive from chemical processes in the presolar nebula, and their distributions could provide insight into early solar system evolution.

The variations of the stable isotope compositions of elements of the Earth, Mars, moon, and meteorites have led to major discoveries in the fields of geochemistry, cosmochemistry, atmospheric sciences, and oceanography. The potential for these applications was first presented by Urey (*1*), who showed how parameters such as temperature produce variations in the position of chemical equilibria in an isotope exchange reaction of a molecule and atom. Simultaneously, Bigeleisen and Mayer (*2*) showed how reaction rates and the position of chemical equilibrium are affected by isotopic substitution. In the same year (1947), Nier *et al.* (*3*) developed the double collector mass spectrometer that simultaneously collects two beams of ions corresponding to isotopic species and allows high isotopic precision by eliminating effects such as beam intensity variations. Further precision can be obtained by sequentially measuring a standard of known isotope ratios and sample (*4*). With the technological development of high-precision isotope ratio mass spectrometry and a quantitative treatment of isotopic thermodynamic properties, the field of stable isotope geochemistry emerged. Along with thermodynamic equilibrium effects in isotopic exchange processes, isotope ratios may also vary from kinetic effects, such as velocity and gravity. For example, the observed $^{15}N/^{14}N$ enrichment in the martian atmosphere arises from the preferential gravitational escape of ^{14}N, of greater velocity than ^{15}N, over geologic time (*5*).

Although the magnitude and direction of variation of the isotope ratios for these processes vary, they have one common feature—they all depend on mass. In a three-isotope (or more) system, it is particularly useful to observe isotope variations in a three-isotope plot. Oxygen, the most abundant element on Earth and common in most planetary atmospheres, has three stable isotopes—^{16}O, ^{17}O, and ^{18}O. In a three-isotope plot of the oxygen isotopic composition of terrestrial and lunar materials, most materials lie along a line with a slope (~0.50) as shown in Fig. 1. For small chemical isotopic fractionations (<20 per mil) the isotope ratios in a three-isotope system are an approximate linear function of the differences in the reciprocal masses of the isotopic species (*6*). In the case of molecular oxygen, with isotopic species $^{16}O^{16}O$, $^{16}O^{17}O$, and $^{16}O^{18}O$, the fractionated ratios expressed as per mil deviations $\delta^{18}O$ and $\delta^{17}O$ are related as follows:

$$\delta^{17}O/\delta^{18}O \cong \left(\frac{1}{32} - \frac{1}{33}\right)\Big/\left(\frac{1}{32} - \frac{1}{34}\right)$$

or $\delta^{17}O = 0.516\ \delta^{18}O$. Thus, a 6 per mil fractionation in $\delta^{18}O$ is accompanied by a 3.1 per mil change in $\delta^{17}O$. The value of the coefficient depends on molecular mass, which for oxygen may range from 0.529 for atomic oxygen to 0.500 for higher molecular weight species.

Here I discuss recent progress in the study of a class of isotope effects that is found to alter stable isotope ratios on a mass-independent basis. Development of a quantitative model for the mechanism of these effects has presented a formidable challenge to the chemical physics community. Mass-independent isotopic compositions have been observed in a range of atmospheric molecules, including O_3, CO_2, N_2O, CO, and sulfate aerosols. In all cases, insights into their atmospheric chemistry have been provided that could not have been acquired by concentration or single isotope ratio measurements. Mass-independent chemistry has also been found in the martian atmosphere and in meteoritic measurements, which suggests that mass-independent chemical processes operated in the early solar system.

Recognition of Mass-Independent Isotope Effects

On the basis of the assumption that any deviation from mass dependence must reflect intervention of a nuclear (nucleosynthetic, spallogenic, or radiogenic) process, Hulston and Thode (*6*) suggested that deviations from mass-dependent isotopic compositions may be used to distinguish nuclear from chemical and physical processes in meteoritic measurements. The observation by Clayton *et al.* (*7*) of a non–mass-dependent isotopic composition in calcium-aluminum–rich inclusions (CAIs) from the Allende meteorite was thus interpreted as indicating that the meteorite contained residual primary grains from a nucleosynthetic process. When plotted in a three-isotope plot, the anhydrous, high-temperature CAIs define a line with a slope of about 1, rather than 0.5, with equal depletions of ^{17}O, ^{18}O with respect to ^{16}O, and the terrestrial fractionation line. It was concluded that the stellar nucleosynthetic processes of He burning or explosive C burning produce copious ^{16}O and little ^{17}O and ^{18}O; thus, admixture of essentially pure ^{16}O would produce a slope of 1 in a three-isotope plot. This isotopic anomaly is remarkably large. The ^{16}O enrichments observed in CAI oxygen, the major element, are as great as 40 per mil. Additionally, bulk meteoritic oxygen isotopic measurements demonstrate that the effect is on the scale of meteorites, asteroids, and planets. Thus, whatever process generates the observed composition is a major event in the formation of the solar system.

Subsequently, Thiemens and Heidenreich (*8*) reported a chemically produced mass-independent isotopic composition in the formation of ozone (O_3) from molecular oxygen. The product O_3 was significantly enriched in ^{17}O and ^{18}O, so that $\delta^{17}O\delta^{18}O \cong 30$ per mil (*8*) as shown in Fig. 2. The observed fractionation pattern is the same as observed in the Allende CAIs ($\delta^{17}O/\delta^{18}O = 1$), and thus it was suggested that

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the observed isotopic composition in Allende could reflect a chemical instead of a nuclear process.

Mass-Independent Mechanism

Currently, the chemical origin of mass-independent isotope effects is uncertain. In a recent thorough review, Weston (*9*) critically evaluates theoretical models in light of available experimental information. It was initially suggested that the $\delta^{17}O = \delta^{18}O$ fractionation observed in the O_3 formation process might derive from isotopic self shielding by $^{16}O^{16}O$ (*8*). However, the rapidity of isotopic exchange of atomic oxygen produced in O_2 photolysis (*10*), and the difficulty in sequestering the isotopic product at a sufficiently rapid rate in a stable species (*11*), ruled out this theory. Later, it was suggested that the isotopic effect arises as a result of the differential symmetries of $^{16}O^{16}O^{17}O$ and $^{16}O^{16}O^{18}O$ compared with $^{16}O^{16}O^{16}O$ (*12*). The symmetry dependency might arise because the stability or lifetime of the asymmetric metastable O_3 species is enhanced as its state density is increased from the appearance of alternative rotational states. Subsequent experiments demonstrated that the isotopic enrichment decreased at higher pressures and disappeared at about 54 atm (*13*), contrary to that expected from the pressure dependency of the macroscopic rate constant. Although a lifetime effect from the appearance of rotational states may be incorrect, a role of differential lifetimes is not strictly eliminated. Other experiments have reported that the asymmetric isotopomer possessed 80% of the isotopic enrichment (*14*), consistent with symmetry as a basis for the mass-independent effect. Studies with isotopically enriched oxygen and O_3 analysis lead to the conclusion that symmetry controls the fractionation process, but other processes may also influence the enrichment (*15*). A recent model for symmetry-induced kinetic isotope effects (*16*) suggests that the formation rate of O_3 deriving from collisions of O and isotopically homonuclear O_2 is a function of the parity label state of O_2—that is, whether it is in an *f* (allowed) or an *e* (restricted) parity label state. In this model, heteronuclear O_2 ($^{16}O^{17}O$, $^{16}O^{18}O$) in its electronic ground state will correlate in all quantum states with O_3 in its electronic ground state (*17*). Another hypothesis suggests that the isotopic fractionation arises from differential collision cross sections in nonthermal exchange processes (*18*).

A model based on a selection dissociation channel for asymmetric O_3 has also been suggested (*19*). The model is based on experiments (*20*) that demonstrated that photolysis of O_3 produces a significant fraction of O_2 of sufficient vibrational energy ($v \geq 26$) to react with O_2 to form O_3. Isotopically selective dissociation of heavy O_3 could produce enriched oxygen atoms that are subsequently incorporated into new O_3, thus distilling heavy oxygen atoms into O_3 (*19*).

A recent study of rate coefficients for the reactions $O + O_2$, $Q + O_2$, $O + Q_2$, and $Q + O_2$ ($O = {}^{16}O$, $Q = {}^{18}O$) has further emphasized the complexities of the mass-independent processes (*21*). The production of enriched O_3 permits measurement of the relative formation rates of the different isotopomers, such as $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{18}O$, $^{16}O^{16}O^{16}O$, and $^{18}O^{16}O^{18}O$. The rate k_{Q+O_2} is similar to k_{O+O_2}, whereas k_{O+Q_2} (where $Q = {}^{18}O$) is about 50% greater. These observations require that, to account for laboratory observations, k_{O+OQ} must be about 20% greater than k_{Q+OQ} (*20*). These rate measurements, as well as the enriched studies (*22*), suggest that symmetry alone is not sufficient to account for the mass-independent process in O_3. The nature of the third body involved in the reaction also appears to be a mitigating factor (*22*). Symmetry-induced kinetic isotope effects (SIKIEs) are, however, well documented in termolecular reactions. SIKIEs have been observed in $CO_2^+ + CO_2$ to produce $(CO_2)_2^+$ (*23*) and in the termolecular association reaction of Ar and CO_2^+ to produce $ArCO_2^+$, the first system where a SIKIE is observed in which the reactants have no atoms in common (*24*). The clustering reaction of O_2^+ and O_2 produce O_4^+, which preferentially incorporates the heavy isotopes of oxygen at a concentration about 100 times their natural abundance (*24*). The explanation of these spectacular SIKIEs entails a symmetry correlation scheme that connects symmetry distinct rovibronic states of the isolated reactants with specific electronic symmetries of the system in the interaction region (*23–25*).

Currently, in spite of 15 years of intensive experimental and theoretical investigation after the first observation of a chemically produced mass-independent process (*9*), the mechanism that is responsible remains unidentified. In addition, other classes of mass-independent effects involving sulfur isotopes in a gas-phase photopolymerization, solid reaction production have been reported (*26*).

Applications

Atmospheric ozone. In situ mass spectrometric measurements have shown that the isotopic composition of O_3 varies with altitude. From 22 to 38 km, stratospheric O_3 is greatly enriched in ^{18}O, as high as $\delta^{18}O \cong 400$ per mil at 32 km (*27, 28*) with approximately equal $\delta^{17}O$, $\delta^{18}O$ enrichments. Optical meth-

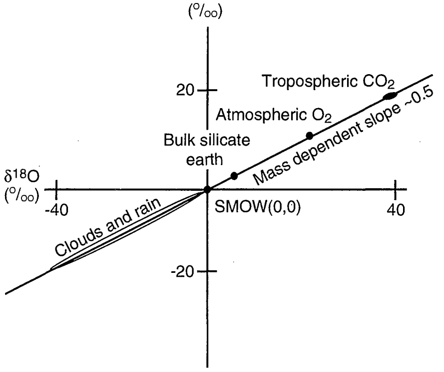

Fig. 1. Oxygen three-isotope plot showing the mass-dependent relation for a variety of terrestrial materials. Range in allowed mass fractionation values extends from 0.500 to 0.526.

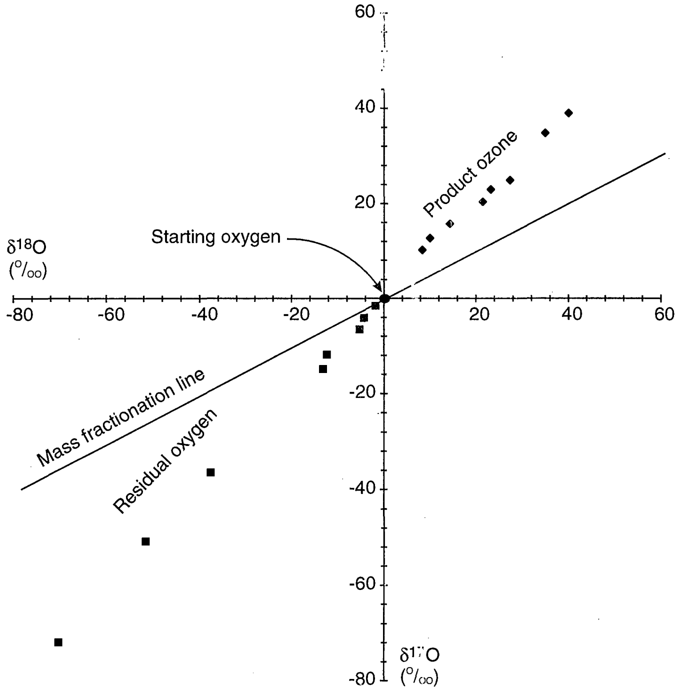

Fig. 2. Isotopic composition of O_3 formed in laboratory experiments from oxygen with an isotopic composition at $\delta^{17}O = \delta^{18}O = 0$. Heavy O_3 is complemented by isotopically light residual oxygen. Errors associated with measurements are smaller than the symbols.

ods, including absorption (*29*), far infrared emission (*30*), and Fourier transform infrared spectroscopy measurements, including in situ (*31*) ground-based (*32*), and have confirmed the stratospheric O_3 isotopic enrichments.

The origin of this enrichment remains paradoxical. The magnitude of the heavy isotope enrichment at times far exceeds that expected on the basis of laboratory measurements, though return sample O_3 isotopic analysis displays $\delta^{18}O$ values between 81 and 161 per mil. In contrast, the oxygen isotopic composition of ground level O_3 is consistent with laboratory measurements (*33, 34*). The inability to quantitatively account for the stratospheric O_3 isotopic enrichment and variability represents a significant inadequacy in our understanding of upper atmospheric O_3. Measurement of these isotopic variations, however, presents a new tool to monitor tropospheric O_3 chemistry and variability and may afford a new way to track O_3 transport and transformation.

Stratospheric and Mesospheric CO_2

Stable isotope ratio measurements ($\delta^{18}O$ and $\delta^{13}C$) have been used for more than four decades to identify sources and sinks of atmospheric CO_2 and to enhance understanding of the carbon cycle. Recent $\delta^{17}O$ measurements have provided additional new information.

Like O_3 in the altitudinal region between 26 and 35.5 km, stratospheric CO_2 possesses a large, mass-independent isotopic composition (*35*) that exceeds mass-dependent tropospheric CO_2 by as much as 15 per mil. The $\delta^{17}O$ values are inconsistent with models that had been suggested to explain the observed $\delta^{13}C$, $\delta^{18}O$ measurements, such as transport from lower latitudes (*36*). Instead the CO_2 could be related to O_3 by isotopic exchange between $O(^1D)$, produced from O_3 photolysis. This provides a mechanism for creating an ^{18}O, ^{17}O enrichment in CO_2 (*37*). The relevant reaction is as follows:

$$^{17,18}O(^1D) + CO_2 \rightarrow C^{17,18}O_3^* \rightarrow C^{17,18}O_2 + O(^3P)$$

where CO_3^* is a short-lived transition state, $O(^1D)$ is electronically excited oxygen, and $O(^3P)$ is ground state. Stratospheric and mesospheric CO_2 measurements of rocket-borne cryogenic whole air samples confirmed the mass independence and the relation to stratospheric O_3 (*38*). Simultaneous CO_2 isotopic and N_2O, CH_4 concentration measurements revealed an inverse correlation between the degree of isotopic enrichment and N_2O, CH_4 concentrations, both arising from the interaction with $O(^1D)$. Reaction with $O(^1D)$ simultaneously increases the $\delta^{17}O$ and $\delta^{18}O$ of CO_2 and reduces N_2O and CH_4 concentrations. Consequently, stratospheric CO_2 is mass independently fractionated whereas tropospheric CO_2 is mass dependent (its composition is established by conventional mass-dependent CO_2-H_2O exchange), and $\delta^{17}O$, $\delta^{18}O$ measurements provide an ideal tracer of stratosphere-troposphere mixing. Any mass-independent CO_2 observed in the troposphere must be stratospherically derived and, unlike ^{14}C, the tracer is stable. Second, because the mass-independent anomaly arises from $O(^1D)$ exchange, a measure of stratospheric $O(^1D)$ activity is available from the magnitude of deviation from mass dependence (or tropospheric). Concentrations of N_2O and CH_4 are conventionally used as air mass tracers; however, with increasing stratospheric altitude, these concentrations become unmeasurable. The magnitude of the $\delta^{17}O$, $\delta^{18}O$ isotopic composition and mass independence of CO_2 increases with altitude; thus, the isotopic measurements become a tracer of air motion, particularly in the upper stratosphere and mesosphere (*33*).

Currently, there remains a need for further measurements and theoretical considerations. As Fig. 3 shows, the CO_2 isotopic data are shifted from the values of tropospheric CO_2. On the basis of laboratory experiments (*39*), the isotopic composition is not that expected for pure isotopic exchange. The data require that there must be another unrecognized fractionation process occurring in the upper atmosphere. This represents a significant deficiency in understanding upper atmospheric CO_2 isotopic systematics. The magnitude of the isotopic offset is sufficiently great that a large-scale fractionation process is required to produce the observed isotopic compositions. Further experimental and theoretical work is needed to determine the isotopic mechanism of the $O(^1D)$-CO_2 exchange process. A recent theoretical model suggests that there is a statistical transfer of the ^{18}O from O_3 to CO_2 (*40*), rather than a CO_3^* transition state effect (*39*). However, there remains a discrepancy between experimental and model results.

Nitrous oxide. Atmospheric nitrous oxide is an effective greenhouse gas that also destroys catalytic stratospheric O_3. Photooxidation is the dominant source of stratospheric nitric oxide (*41*). Tropospheric N_2O mostly comes from biogenic processes, although the observed increases derive from anthropogenic activities. Currently, there is a significant deficiency in our understanding of the global N_2O budget; the mismatch between sources and sinks is about 30% (*42*). $\delta^{18}O$ and $\delta^{15}N$ measurements of atmospheric N_2O (*43–47*) have enhanced our understanding of atmospheric N_2O. Recent $\delta^{17}O$, $\delta^{18}O$ measurements of N_2O (*48*) collected from four ground level locations reveal that it possesses a large, variable mass-independent isotopic composition. Biologic, combustion, and anthropogenic sources of the mass-independent isotopic composition have been ruled out from laboratory measurements and theoretical considerations. The two known atmospheric reactions of N_2O, photooxidation and photolysis, have also been shown to be mass dependent and incapable of accounting for the observations (*49*). Isotopic fractionation associated with the photolytic destruction of N_2O (*50*) could account for the stratospheric isotopic observations (*47, 51*); however, this effect is based on relative differences in isotopic zero point energy differences that are mass dependent, arising from vibrational energy differences. Thus, the $\delta^{17}O$, $\delta^{18}O$ N_2O measurements apparently require a new atmospheric mass-independent process—a source, sink, or exchange reaction. A number of possible atmospheric reactions have been suggested (*52*), such as the reaction of electronically excited O_3 with N_2 to form N_2O. Laboratory $\delta^{17}O$, $\delta^{18}O$ isotopic measurements of N_2O produced by such processes would confirm the role of such reactions.

Carbon monoxide. Atmospheric CO is predominantly produced by combustion, biomass burning, and nonmethane oxidation. In the atmosphere, CO controls more than 70% of the OH budget (*53*). In turn, OH dominates the oxidation of numerous species (such as H_2S, SO_2, CH_4, CH_3Cl, and CH_3Br). Increasing CO concentrations decrease the OH number density and, consequently, increase the lifetime of CO. This increase in lifetime is sufficient to mix CO into the stratosphere where it simultaneously serves as a greenhouse gas and destroys stratospheric O_3. Carbon monoxide is also a dominant source of tropospheric O_3, a well-known health and agriculturally destructive agent. In spite of decades of concentration measurements, the global CO budget remains unbalanced by as much as 30% (*54*). Recent $\delta^{13}C$, $\delta^{18}O$ measurements have, however, refined understanding of atmospheric CO (*55*). Carbon monoxide is now known to possess a mass-independent isotopic composition that ranges from 0 to 7.5 per mil excess ^{17}O (*56–58*). On the basis of laboratory observations, it was suggested that the mass-independent anomaly arises from the ozonolysis of unsaturated hy-

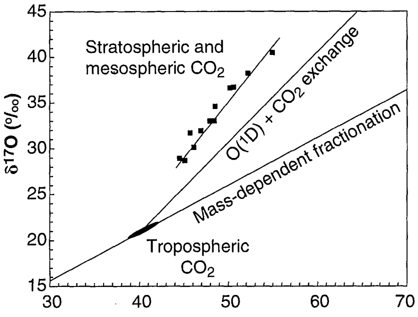

Fig. 3. Oxygen isotopic composition of stratospheric and mesospheric CO_2. Data are from Thiemens *et al.* (*36*).

drocarbons, which transfers the isotopic anomaly from O_3 to CO (*55*). Recent field (*57, 58*) and laboratory observations (*59*) show instead that the source of the mass-independent anomaly is the CO + OH reaction. The deviation from a mass-dependent fractionation is conventionally defined by $^{17}\Delta = \delta^{17}O - (0.517)\ \delta^{18}O$; a mass-dependent composition is then $^{17}\Delta = O$. As shown in Fig. 4, the observation that $^{17}\Delta$ values increase as concentrations approach zero indicates that the source of the $^{17}\Delta$ is likely a sink reaction (*57, 58*). This inference is supported by laboratory experiments and observations of the seasonal character of $^{17}\Delta$; the greatest values occur in summer months during peak OH concentration (*58*). These measurements demonstrate the resolution capability afforded by the mass-independent signature. First, the source of the $^{17}\Delta$ arising from the OH reaction provides a new measure of the extent of reaction of a CO-bearing air mass with OH. Second, the $\delta^{17}O$, $\delta^{18}O$ measurements permit resolution of different sources with identical $\delta^{18}O$ values. For example, biomass burning ($^{17}\Delta = O$) and transported CO ($^{17}\Delta \cong 2‰$) may be resolved even though both possess $\delta^{18}O \cong 20$ per mil (*57*).

Currently, to resolve the outstanding budgetary issues global CO observations of $\delta^{17}O$, $\delta^{18}O$, $\delta^{13}C$, and ^{14}C isotopes are needed. The observed isotopic fractionation factor associated with the CO + OH reaction, which produces a mass-independent ^{17}O excess in the residual CO (*59*), is not explained by existing theory.

Mars

The isotopic compositions of the present-day martian atmosphere has been measured by in situ mass spectrometry (*60*). Measurements of minerals and gases (SNC) in martian meteorites have been used to constrain the isotopic and chemical composition of the past martian atmosphere (*61*). The physical and chemical processes (isotopic exchange, atmospheric escape, impact erosion, and planetary outgassing) that have been invoked to explain the present and past compositions (*62*) all produce mass-dependent isotopic compositions. For example, solar wind–induced sputtering of oxygen followed by atmospheric escape from the martian exosphere is mass dependent (*63*). The $\delta^{18}O$ and $\delta^{17}O$ composition of water extracted from hydrated minerals (*64*) and CO_2 extracted from carbonate in one SNC meteorite, ALH 84001 (*65*), indicates that at least one component of the martian atmosphere is mass independently fractionated, so that $^{17}\Delta$ is at least 0.5 per mil. The magnitude of the mass-independent fractionation may have varied throughout martian history (*65*). The $\delta^{18}O$ and $^{17}\Delta$ of carbonate from ALH84001 are not consistent with an origin from solar wind mass–dependent induced escape, and it has been suggested that the mass-independent fractionation reflects photochemistry and exchange of CO_2 with $O(^1D)$ initiated by photolysis of O_3 and uptake of low $^{17}\Delta$ molecular oxygen by the martian regolith (*65*). If this mechanism is responsible for the observed oxygen isotopic signature, mass-independent processes and observations may provide a mechanism by which martian atmosphere-regolith chemistry and atmospheric evolution may be further understood. At present, the specifics of the evolution of $\Delta^{17}O$ in the martian atmosphere are not well understood. Further measurements of $\delta^{17}O$ and $\delta^{18}O$ of martian carbonates, water, and sulfate are needed to constrain atmosphere-regolith exchange and atmospheric chemistry on Mars. Return samples of the martian atmosphere, ice, and regolith for high-precision isotopic analysis would greatly enhance our understanding of global martian processes.

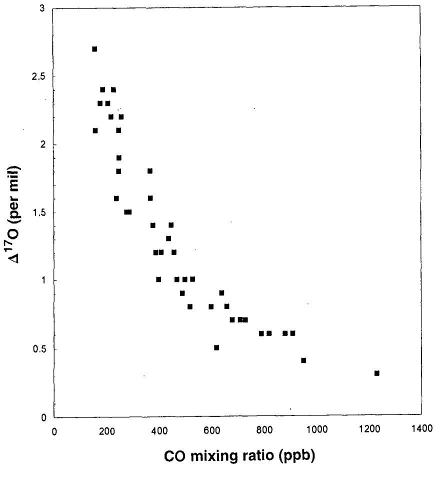

Fig. 4. Relationship between atmospheric CO concentration and the magnitude of the mass-independent oxygen isotopic composition $^{17}\Delta$. Data are from samples collected at sea level in La Jolla, California (*54*).

The Early Solar System

Because the fundamental assumption about the use of mass-independent isotopic composition as a means to detect nucleosynthetic anomalies has been shown to be incorrect, the source of the meteoritic anomalies needs to be reexamined, particularly since the observed chemical isotopic fractionation factor produces the same $\delta^{17}O/\delta^{18}O$ ratio observed in CAI and chondrules. The magnitude of the observed oxygen isotopic anomaly is so large that correlated effects should be isotopically identifiable in other elements, such as magnesium and silicon. After more than 25 years of measurements, meteoritic oxygen isotopes have not been observed to correlate with any other isotope. Relict interstellar grains, however, have now been detected in meteoritic material. These oxide grains (Al_2O_3) form four isotopically distinct groups (*66*). The group 1 and 3 grains possess large ^{17}O excesses and slight ^{18}O depletions, group 2 are characterized by large ^{18}O depletions, and group 4 have large ^{18}O excesses and little or no ^{17}O excess [see (*67*) for a review]. None of these populations possesses the excess ^{16}O expected from supernova and the near total lack of highly enriched ^{16}O grains has led to the conclusion that nonnucleosynthetic processes may be needed (*68, 69*). Several observations regarding the occurrence of mass-independent processes are relevant. It is known that the mass-independent processes are not restricted to O_3 formation. Mass independence has also been observed in the reactions $O + CO \rightarrow CO_2$ (*70*), $SF_5 + SF_5 \rightarrow S_2F_{10}$ (*71*), isotopic exchange $O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$ (*39*), and $OH + CO \rightarrow CO_2 + H$ (*59*). These observations all involve symmetric molecular products. Although the recent rate-constant measurements underscore the lack of a suitable mechanism accounting for mass-independent processes (*20*), the experimental observations demonstrate that the effect is not restricted to O_3 and that there is some reliance on symmetry. Symmetry-dependent kinetic isotope effects are now well established in ion-molecule reactions (*23–25*). It is also known that excitation of the reactants is not required and the fractionation is a consequence of gas-phase reactions (*13*).

A number of reactions in a nebular environment could produce the CAI isotopic composition, such as $O + SiO$, $O + Si_2O_2$, $O + FeO$, or $O + AlO$. In addition, with the recent observation of a mass-independent fractionation in the OH + CO reaction (*59*), nebular OH reactions could be important.

Another potentially important process is gas-phase isotopic exchange. For example, the exchange process

$$^{17,18}O(^1D) + CO_2 \Leftrightarrow {}^{17,18}CO_2 + O(^3P)$$

produces a mass independence in upper atmospheric CO_2 (*36, 38, 39*). It has been observed experimentally that this process depletes the reactive product atomic oxygen in the heavy isotopes (*39*) independent of the atomic oxygen isotopic composition. Furthermore, the final isotopic composition of the oxygen is equally depleted in ^{17}O and ^{18}O by 40 per mil with respect to the bulk CO_2, remarkably similar to the Allende CAI in slope and magnitude. The mean isotopic composition of the dust in the nebula is suggested as being similar to that observed in most ^{16}O-rich minerals in CAI ($\delta^{18}O = -40$ per mil, $\delta^{17}O = -42$ per mil) (*72*). Oxygen exchange processes could produce the CAI isotopic reservoir if the bulk nebular oxygen isotopic composition resembles that of terrestrial oxygen. Subsequent sequestering of the atomic oxygen in a mineral phase would then produce the $\delta^{17}O = \delta^{18}O$ values of correct magnitude (about 40 per mil). In the nebula, exchange reactions involving, for example, CO and O, could produce similar $\delta^{17}O$ and $\delta^{18}O$ compositions and, simultaneously, different isotopically distinct reservoirs.

In a chemical production model, the advantage is that only one nebular reservoir is required to account for all meteoritic oxygen isotopic compositions (*69*). Nucleosynthetic models require several distinct oxygen isotopic reservoirs that do not correlate with anomalies in other elements. In addition, the issue of why oxygen is the only element that exhibits bulk level isotopic anomalies is addressed as the reactions involve the bulk oxygen isotopic reservoir. Oxygen is the only element on the periodic chart that could produce a symmetry-dependent isotopic fractionation. Essentially all other elements are coordinated by oxygen and thus are incapable of producing a symmetry-dependent isotopic fractionation. Carbon and hydrogen could also be fractionated by symmetry-dependent processes, but with only two stable isotopes mass independence would be unobservable.

Experimental studies of relevant nebular reactions involving metal oxides are needed to enable modeling of chemical isotopic processes in the presolar nebula. Reactions involving SiO_x, AlO_x, and MgO_x are of particular interest as initiating reactions in the early solar system and would further general understanding of the chemical physics of mass-independent isotope effects.

Concluding Comments

Mass-independent chemical processes are now known to be pervasive in the Earth's atmosphere. These compositions have been useful in resolving processes that are unobservable by other techniques, including single isotope ratio measurements. It is apparent that the atmosphere of Mars may be subject to mass-independent processes.

There are many atmospheric oxygen- and sulfur-bearing species that remain to be measured that might have their atmospheric roles clarified by isotopic analysis. In particular, atmospheric sulfates and nitrates are ideal candidates. Measurement of sulfate from SNC meteorites could also provide enhanced details of martian atmosphere-regolith interaction and evolution.

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