# Mass-Independent Isotopic Compositions in Terrestrial and Extraterrestrial Solids and Their Applications

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## ABSTRACT

In 1983, Thiemens and Heidenreich reported the first chemically produced mass-independent isotope effect. This work has been shown to have a wide range of applications, including atmospheric chemistry, solar system evolution, and chemical physics. This work has recently been reviewed (Weston, R. E. *Chem. Rev.* **1999**, *99*, 2115–2136; Thiemens, M. H. *Science* **1999**, *283*, 341–345). In this Account, observations of mass-independent isotopic compositions in terrestrial and Martian solids are reviewed. A wide range of applications, including formation and transport of aerosols in the present atmosphere, chemistry of ancient atmospheres and oceans, history and coupling of the atmosphere—surface in the Antarctic dry valleys, origin and evolution of oxygen in the Earth's earliest environment, and the chemistry of the atmosphere and surface of Mars, are discussed.

## I. Introduction

It has been known for more than a half century that the alteration of the position of equilibrium by isotopic substitution[1,2] provides a quantitative mechanism by which an enormous range of processes may be resolved. These applications include chemical reaction mechanistic

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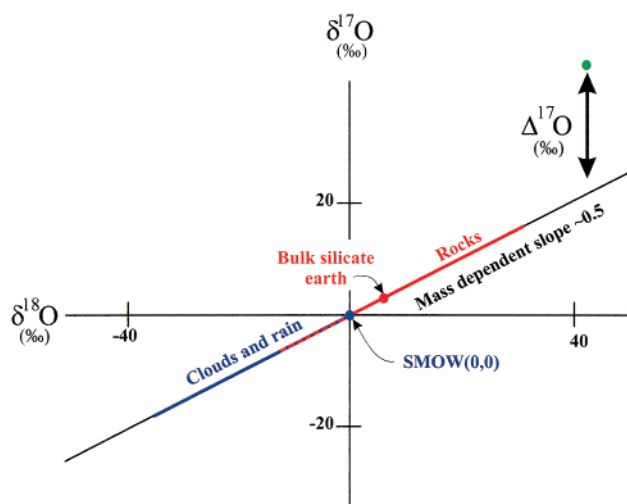
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**FIGURE 1.** Three isotope plots for oxygen, illustrating mass-dependent slope and $\Delta^{17}O$.

studies, paleothermometry, igneous thermomometry, atmospheric chemistry, and the resolution of origin of the solar system. Although these isotopic shifts are modest, they are readily measurable.[1] Stable isotopes in gaseous species are measured on multiple collector mass spectrometers. The simultaneous collections afford extraordinarily high precision. Further precision is attained by sequentially measuring a standard of known isotope ratio and sample. For a species such as oxygen, the ratio of $^{18}O/^{16}O$ (or mass 34/23) may be measured at a precision and accuracy better than 0.1 parts per thousand, or per mil (‰). These isotopic ratios are reported in the conventional delta notation, which for oxygen isotopes is given by

$$\delta^{18}O\ (‰) = (R^{18}{}_{sample}/R^{17}{}_{STD} - 1) \times 1000 \qquad (1)$$

$$\delta^{17}O\ (‰) = (R^{17}{}_{sample}/R^{17}{}_{STD} - 1) \times 1000 \qquad (2)$$

$R^{17} = {}^{17}O/{}^{16}O$, $R^{18} = {}^{18}O/{}^{16}O$, and "STD" refers to standard mean ocean water (SMOW). It is well known that the variation of these isotope ratios produces a highly correlated array, with $\delta^{17}O \approx 0.52\ \delta^{18}O$. This arises from the mass dependency of conventional isotope effects such as isotope exchange from the mass dependence of vibrational frequencies, kinetics, evaporation/condensation, and velocity. A plot of isotopic measurements of a broad range of terrestrial samples displays the coherence of this $\delta^{17}O = 0.52\ \delta^{18}O$ relation (Figure 1). Note that $\Delta^{17}O$ expresses the deviation, in parts per thousand, from the mass fractionation line. The Earth—moon system was formed from a common oxygen reservoir and subsequent partitioning by mass-dependent processes, thus producing the array depicted in Figure 1.

The first exception to this observation was reported by Thiemens and Heidenreich.[3] It was observed that, in the production of ozone by molecular oxygen, ozone was equally enriched in the isotopes $^{17}O$ and $^{18}O$, or $\delta^{17}O = \delta^{18}O$, rather than $\delta^{17}O = 0.52\ \delta^{18}O$. Aside from the inherent importance to chemical physics, precisely the same

isotopic composition had been observed in meteorites.[4] In this work, it was assumed that, since no chemical processes could produce a $\delta^{17}O = \delta^{18}O$ composition, the observations must reflect a nuclear process. Further, it was suggested that it was exotic supernova nucleosynthetic debris, admixed with the proto solar nebula. With the laboratory observations,[3] this assumption was demonstrated to be invalid, and it now appears likely that the meteoritic compositions derive from chemical processes. Given that stony planets are predominantly composed of oxygen, the event responsible for production of the isotopic anomalies is a major process in the formation of the solar system.

An intriguing aspect of the mass-independent isotope effect has been the difficulty in determining the physical–chemical basis for the effect. Two recent reviews thoroughly document this history.[5,6] In the time since those reviews were published, new experimental data have emerged which have further examined the relative formation rates of $^{50}O_3$ and $^{52}O_3$ in $^{16}O-^{18}O$ mixtures[7] and the third-body dependence of rate coefficients for ozone formation in $^{16}O-^{18}O$ mixtures.[8] The isotopic selectivity is suggested as being explicable within the context of the Lindemann–Hinshelwood mechanism, coupled with an isotopic selectivity derived from the $O-O_2$ collision and production of the activated $O_3{}^*$ complex.[8] This model does not invoke molecular symmetry. Hathorn and Marcus[9] have produced a theoretical model which accounts for the observed isotope effects. The treatment utilizes a loose transition state theory and a phase space partitioning with the activated $O_3{}^*$ complex, coupled with a modest non-Rice–Ramsperger–Kassel–Marcus effect for the symmetric isotopomers. The model demonstrates reasonable agreement with experimental results. At present, there remains a need for further theoretical and experimental exploration of the mass-independent isotope effect.

Despite the difficulty in determining the physical–chemical basis of the effect, it is now known that the effect is pervasively observed in nature. The atmospheric molecules $O_3$, $CO_2$, CO, aerosol sulfate, and nitrous oxide all possess mass-independent isotopic compositions (for reviews, see refs 5 and 6). In each particular case, insights into their source, transport, and chemical transformations have been derived which could not have been obtained by any other observation. Recently, the striking observation has been made that atmospheric $O_2$, the second most abundant molecule, is mass-independently fractionated.[10] This signature is acquired from $O_2-O_3-CO_2$ isotopic coupling in the stratosphere via $O(^1D)$ transfer from $O_3$ to $CO_2$, at the ultimate expense of $O_2$. The magnitude of the tropospheric $^{17}O$ anomaly in $O_2$, which is returned to "normal" isotopic $O_2$ by photosynthesis and respiration in the oceans, provides a new and unique tracer of global biospheric production. Isotopic measurements of $O_2$ trapped in polar ice are used to estimate global biospheric productivity over the past $\sim$80 000 years.[10]

Most recently, for the first time, mass-independent isotopic compositions have been detected in terrestrial solids (sulfur and oxygen isotopes). These observations

have opened an enormous vista into widely ranging processes, which occurred as long ago as $3.9 \times 10^9$ years, and as far away as Mars. In this Account, these new observations are reviewed. These measurements begin with present-day observations and then look to the past, as far as $3.9 \times 10^9$ years back in the Earth's history, and end up on the surface of Mars. As in the atmospheric observations, new insights, otherwise unobtainable, have been gleaned from these mass-independent isotopic compositions.

## II. Oxygen Isotopic Study of Sulfur(IV) Oxidation

The first simultaneous $\delta^{17}O$ and $\delta^{18}O$ measurements of atmospheric sulfate aerosol particles have demonstrated that these particles possess a clear mass-independent composition, ranging from $\Delta^{17}O = 0.1$ to 2‰.[11,12] In light of this discovery and the wide range of applications in atmospheric and paleo sciences, the question of the origin of these oxygen-17 anomalies arises. Any interpretation of the sulfate anomaly is dependent upon the resolution and quantification of the source of these natural isotopic anomalies. Recently, Savarino et al.[13] performed a series of experiments which identified the source of the mass-independent isotopic composition. There are three reaction sequences which may give rise to the observed isotopic anomaly:

(1) The precursor of sulfate, $SO_2$, may possess an anomaly associated with its formation.

(2) The sink processes responsible for removal of sulfate from the atmosphere are mass-independent.

(3) The oxidation pathways transforming the S(IV) to the S(VI) may have an associated mass-independent fractionation process.

Equilibrium isotopic exchange between $SO_2$ and water is rapidly attained in the atmosphere.[14] The exchange mechanism is a mass-dependent process, and the oxygen isotopes of water are known to possess a mass-dependent composition; hence, the oxygen isotopic composition of sulfur(IV) has no influence on the generation of a mass-independent anomaly in the atmosphere. Sink processes for sulfate in the atmosphere cannot account for the observations since sulfate is exclusively removed from the atmosphere by physical processes (dry and wet deposition), which are strictly mass-dependent. Therefore, the question focuses upon which oxidation pathway generates the observed sulfate anomaly. The relevant mechanisms that may lead to a mass-independent oxygen composition of sulfate are

*oxygen isotopic reaction selection*

$$\text{S(IV) (MD)} + \text{oxidant (MD)} \rightarrow SO_4{}^{2-}\text{ (MI)} \quad \text{(A)}$$

*oxygen isotopic transfer*

$$\text{S(IV) (MD)} + \text{oxidant (MI)} \rightarrow SO_4{}^{2-}\text{ (MI)} \quad \text{(B)}$$

where MD and MI stand for mass-dependent and mass-independent oxygen compositions, respectively, and sul-

**Table 1. Summary of Isotopic Results from Gas- and Aqueous-Phase Sulfur(IV) Oxidation Experiments**[a]

| | | reactants | | | |
| | | sulfur species | oxidant | product sulfate | $\Delta^{17}O$ slope S(IV)/oxidant |
| reactions | phase | | | | |
| --- | --- | --- | --- | --- | --- |
| $SO_2$ + OH | gas | MD | MD[b] | MD | na[c] |
| $SO_3$ + $H_2O$ | gas | MD | MD | MD | $0.21 \pm 0.01$ |
| S(IV) + $H_2O_2$ | aqueous | MD | MD | MD | $0.47 \pm 0.04$ |
| | | MD | MI | MI | |
| S(IV) + $O_3$ | aqueous | MD | MD | MD | $0.24 \pm 0.02$ |
| | | MD | MI | MI | |
| S(IV) + $O_2$ (with metal catalysts) | aqueous | MD | MD | MD | na |

[a] MD and MI represents mass-dependent and mass-independent isotopic composition, respectively. $\Delta^{17}O$ slopes and their standard deviations are calculated using the method of least squares. [b] Not directly measured but presumed. [c] Not applicable.

fur(IV) represents sulfur species such as $SO_2$, $HSO_3^-$, $SO_2 \cdot H_2O$, and $SO_3^{2-}$. In the case of reaction A, the isotopically selective oxidation mechanism is responsible for the production of a mass-independent composition, as observed in the CO + OH reaction[21] or ozone formation.[3] In the second case (reaction B), the mass-independent anomaly is the result of a transfer of anomalous oxygen from the oxidant to the final product.

Laboratory experiments were carried out to identify a chemical/oxidative source for the aerosol sulfate oxygen-17 anomalies. The major and well-established oxidation reaction pathways in the aqueous phase involve $H_2O_2$, $O_3$, and $O_2$ by a transition-metal-catalyzed reaction.[15]

Atmospheric $O_3$ and $H_2O_2$ possess mass-independent oxygen isotopic compositions[18-20] and undergo gas-phase oxidation by the OH radical. Recent work has proposed other oxidant and oxidation pathways as the main oxidation pathway for sulfur(IV).[16,17] However, these new pathways are significant only in highly perturbed environments.

Isotopic measurements of aqueous-phase S(IV) oxidation experiments are reported (Table 1). The results demonstrate that reaction A does not produce a mass-independent isotopic composition. Only mass-dependent oxygen isotopic compositions are observed in the product sulfate for aqueous-phase experiments with MD reactants, regardless of the presence or absence of catalysts. This result is expected as only gas-phase reactions generate anomalous isotopic compositions. The catalytic oxidation of sulfur(IV) may be significant for groundwater, and recent studies speculate on its relative importance in droplet chemistry.[16] However, this does not generate mass-independent sulfate. For the primary aqueous oxidation by $H_2O_2$ and $O_3$, the conclusion is the same. Gas-phase oxidation by H also does not produce a mass-independent fractional (MIF). This result is somewhat surprising, as the CO + OH reaction[21] produces a mass-independent fractionation. This discrepancy underlines the complexity of predicting results a priori. In the absence of a global theory of mass-independent fractionation, experimental observations for relevant reactions are needed. The $SO_3$ + $H_2O$ + M reaction is an important step in the production of sulfate in the gas phase in the atmosphere.
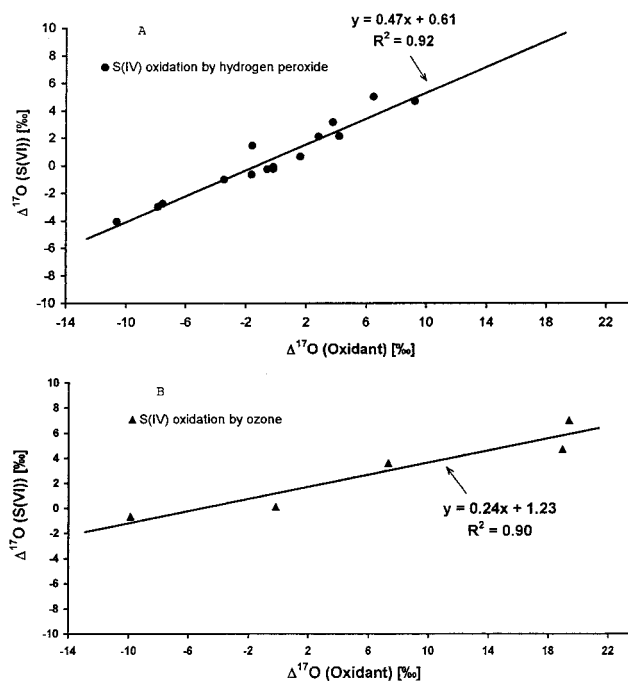


**FIGURE 2.** Correlation plot between $\Delta^{17}O(SO_4)$ and $\Delta^{17}O(H_2O_2)$ (A) and between $\Delta^{17}O(SO_4)$ and $\Delta^{17}O(O_3)$ (B) from laboratory experiments in the aqueous phase. Oxygen isotopic analysis of the experiment indicates a strong linear correlation. The slope indicates the relative number of $SO_4^{2-}$ oxygen atoms coming from the oxidants, ~2/4 and ~1/4 for respectively $H_2O_2$ and $O_3$.

The experimental results show that the hydration of sulfur trioxide is a strictly mass-dependent process. The ratio of $\Delta^{17}O_{S(VI)}/\Delta^{17}O_{H_2O}$ for this reaction approaches the ideal statistical mixing value of 0.25; thus, mass-independent compositions are not generated by these reactions, and the production of anomalous sulfate by oxygen isotopic reaction selection may be dismissed. For the isotopic transfer route, only relevant mass-independent isotopic compositions of oxidants have been tested. Molecular oxygen, OH, and $H_2O$ possess mass-dependent isotopic compositions on Earth. The only two oxidants of sulfur-(IV) known to possess mass-independent isotopic composition are $H_2O_2$ and $O_3$,[18-20] and the transfer route was studied for these two oxidants. The results are displayed in Figure 2. For hydrogen peroxide, the experiments demonstrate that half of the peroxide anomaly is transferred to the final sulfate.

The experimental isotopic results of the aqueous-phase sulfur(IV) oxidation by $H_2O_2$ agree with previous investigations, which proposed that the reaction proceeds via a nucleophilic displacement on bisulfite by $H_2O_2$, whose two oxygen atoms are transferred from the peroxide to the sulfuric acid[22-24] product. Using the reported anomaly measured for hydrogen peroxide of N 20/1000,[18] a maximum value of 0.5‰ is obtained for $\Delta^{17}O_{S(VI)}$ if $H_2O_2$ is the only oxidant transferring its anomaly. This value is well below the maximum anomaly reported for sulfate ($\Delta^{17}O$ = 4.6‰[25]). Therefore, hydrogen peroxide cannot entirely account for the observed sulfate anomaly. The results obtained from the ozone experiments (Figure 2b) are similar to those for peroxide, but with a slope of 0.24,
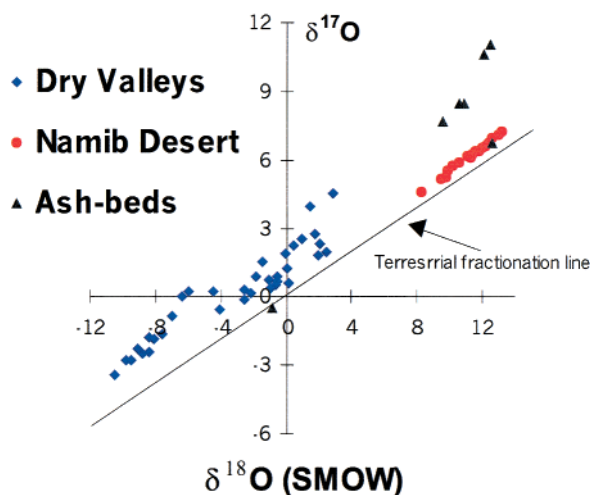
## Anomalous Sulfate Minerals



**FIGURE 3.** Examples of terrestrial sulfate minerals that possess anomalous oxygen-17 compositions.

suggesting that only one of the four sulfate oxygens comes from ozone. This result rules out the free radical mechanism involving $OH^{\bullet}$, $HSO_3^{\bullet}$, and $HSO_5^{\bullet}$ as principal radicals proposed by Penkett et al.[24] However, it confirms a nonradical mechanism, proceeding via an electrophilic displacement reaction of $O_3$ on sulfur atoms (sulfur(IV) species) in the aqueous phase, as suggested by Erickson et al.[26] Given the large $O_3$ isotopic anomaly ($\Delta^{17}O = 20‰$[20]), even a small relative contribution of ozone to the overall oxidation of sulfur(IV) accommodates the sulfate anomaly. These experiments demonstrate that, provided $H_2O_2$ and $O_3$ are the principal oxidants of sulfur(IV) in the liquid phase (the normal occurrence in the atmosphere), the $\Delta^{17}O$ of sulfate is a measure of the atmospheric origin of sulfate and is a tracer of the relative contribution of aqueous-phase oxidation to the overall oxidation pathways.

## III. Oxygen-17 Anomalies in Terrestrial Sulfate Minerals

It was thought that $\delta^{17}O$ and possibly $\delta^{18}$ in the rock record on Earth have followed a mass-dependent relationship since at least 3.7 billions years ago.[28] However, several recent studies have revealed that sulfate minerals in many arid environments, as well as in a few ancient volcanic ash beds, possess a range of positive $\Delta^{17}O$ values[25,29,30] (Figure 3).

The central Namib Desert hosts one of the most extensive gypsum ($CaSO_4 \cdot 2H_2O$) accumulations in Africa. The gypsum crust occurs extensively near the coast and gradually thins off and disappears $\sim50-70$ km from the coast, covering an area of about 30 000 $km^2$. Most of the gypsum's $\Delta^{17}O$ values are in the range of $0.2-0.5‰$. A similarly old and dry but much colder desert environment is found in the Antarctic dry valleys, where the salt content is extremely high. Recent measurements show that all the soil sulfates have highly positive $\Delta^{17}O$ values, ranging from 0.5 to 3.4‰, significantly higher than those found in the central Namib Desert. There are intriguing correlations between sulfate oxygen isotopic compositions and climatic region or soil depths, indicating that the differences in particle size, transport mode, and local precipitation pattern between sea salt aerosols and biogenic aerosols determine the sulfate distribution in the Antarctic dry valley regions. It is also found that sulfate minerals with positive $\Delta^{17}O$ values are widespread in other arid regions on Earth. For example, all water-soluble sulfates extracted from desert varnishes, which are thin coatings composed of mostly clays and Mn$-$Fe minerals on rock surfaces, exhibit positive $\Delta^{17}O$ values, ranging from 0.4 to 1.3‰. So far, the most mysterious sulfate oxygen-17 anomalies were found in ancient (Miocene, >15 million years old) volcanic ash beds in Nebraska and South Dakota, where the highest $\Delta^{17}O$ value reaches 4.6‰.

Since all other sulfate processes on the Earth, such as reduction, sulfide mineral oxidation, and evaporation, are mass-dependent,[25] it was concluded that these anomalous oxygen-17 signatures derive from the oxidation of sulfur gases in the atmosphere by $O_3$ or $H_2O_2$, which are known to have positive $\Delta^{17}O$ values.[18-20] At present, the main sources of reduced sulfur gases are anthropogenic, marine biogenic, and volcanic emissions. It is, therefore, not surprising to find large atmospheric sulfate deposits in the vicinity of these sources. For example, both Antarctica and central Namibia have high dimethyl sulfide (DMS) emissions into the atmosphere from nearby oceans, and $SO_2$ is the main component of volcanic gases. Once oxidized, atmospheric sulfate is transported to Earth's surface via wet and dry deposition. Provided suitable depositional conditions exist (such as arid climates), and that there are minimal sources of other sulfate and a lack of biological alteration, the atmospheric sulfate accumulates and becomes the dominant geological record which tracks ancient atmospheric$-$oceanic interactions. The rock record can offer new clues to ancient atmospheric conditions on Earth as well as on other planets, such as Mars. Recently, a new analytical method has been developed for an efficient analysis of both oxygen-18 and oxygen-17 isotopic composition for sulfate,[31] which will greatly expedite these studies.

## IV. Sulfide and Sulfate in Ancient Terrestrial Sedimentary Rocks

Measurements of sulfur $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ and the observed mass-independent composition in sulfide and sulfate sedimentary and metasedimentary rocks[32] point to a major change in the terrestrial sulfur geochemistry that occurred between 2090 and 2450 Ma (million years ago) (Figure 4). For sulfur, $\delta^{33}S$ is the $^{33}S/^{32}S$ ratio, and $\delta^{34}S$ is $^{34}S/^{32}S$, reported in per mil variations. The deviation from mass fractionation is given as $\Delta^{33}S \cong \delta^{33}S - 0.515\,\delta^{34}S$. The sulfur isotope compositions in samples older than 2450 Ma are mass-independent, with $\Delta^{33}S$ varying between 2.04 and $-1.29‰$. Samples older than 2090 Ma but younger than 2450 Ma exhibit a range of $\Delta^{33}S$,
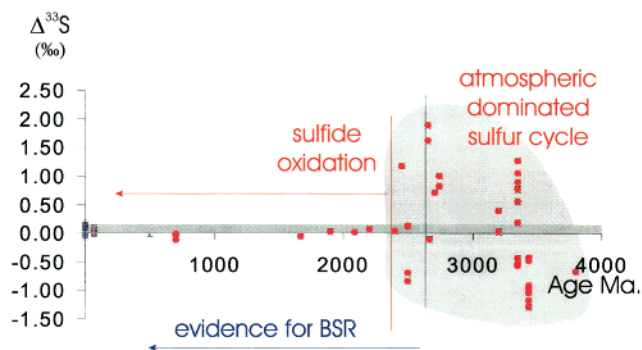
**FIGURE 4.** Sulfur multiple-isotope data for sedimentary sulfide and sulfate as a function of age. The large range for $\Delta^{33}S$ in samples older than 2500 Ma reflects a change in the role of atmospheric chemistry relative to oxidative weathering and bacterial sulfate reduction in the sulfur cycle.

varying between 0.02 and 0.34‰ and are considered to exhibit smaller-magnitude mass-independent fractionations. Samples younger than 2090 Ma exhibit a range of $\Delta^{33}S$ from −0.11 to +0.02‰ and are considered to be consistent with fractionation by mass-dependent processes.

The sulfur isotopic data appear to represent a global isotopic signature because the signature is present in a wide variety of different hydrothermal and sedimentary rock types older than 2500 Ma.[32] A characteristic of massive barite ($BaSO_4$) samples that are composed primarily of sulfate is that they are $^{33}S$-depleted relative to the terrestrial mass fractionation line. Samples that are composed primarily of reduced sulfur are $^{33}S$-enriched relative to the terrestrial mass fractionation line. This has been interpreted as indicating that these samples record the isotopic signatures of two different global sulfur reservoirs in the Archean (2500−3800 Ma). The sulfate samples are inferred to record the systematics of the dissolved oceanic sulfate reservoir, and the reduced samples are inferred to record the processes of an insoluble reduced reservoir.

In the present-day terrestrial sulfur cycle, two dominant pathways are oxidative weathering (oxidation of continental sulfide to sulfate) and bacterial sulfate reduction (reduction of sulfate to sulfide). Walker and Brimblecombe[33] suggest that the role played by these pathways may have been limited on a primitive Earth if the atmosphere had low oxygen content and the role of bacterial sulfate reduction was limited. In this model, the balance between atmospheric sulfur chemistry, volcanic sources, and hydrothermal sinks would control the terrestrial sulfur cycle. The data in Figure 3 are consistent with the model and can be used to constrain the oxygen partial pressures in the Archean atmosphere, an index sought for decades. In the absence of $O_2$ and $O_3$ in the early atmosphere, UV light penetrates to the Earth's surface, where photochemistry of S-bearing atmospheric species produces the observed mass-independent isotopic signatures.[32] As $O_2/O_3$ levels grow in the atmosphere, UV is optically shielded, and this photochemistry no longer occurs. By ∼2200 Ma, the isotopic signature disappears,

reflecting the buildup of atmospheric oxygen and, in turn, the biomass of photosynthetic bacteria. The use of the mass-independent character has permitted these assignments, which could not be done by any other measurement technique.

## V. Oxygen and Sulfur Isotopes in Martian Meteorites

The Shergottite−Nakhlite−Chassignite (SNC), or Martian, meteorites are a group of evolved meteorites that share several features. They crystallized from silicate melts (some may be melting residues as well) and are made up of minerals such as olivine (($Mg,Fe)_2SiO_4$), pyroxenes (($Ca,Mg,Fe)SiO_3$), and feldspar (($Ca,Na)_{1-2}Al_{1-2}Si_{2-3}O_8$) in varying proportions. The crystallization ages of the igneous rocks that form these meteorites have been determined by radiometric age-determination techniques to range from approximately 160 Ma to greater than 4000 Ma.[34−40] The SNC meteorites also contain secondary minerals such as hydrated silicates, sulfates, carbonates, and salts that formed at low temperature as a result of interactions between the already-present igneous minerals and their environment during weathering and episodes of hydrothermal activity.[41−44] The compositions of these secondary minerals have been used to gain insight into the environments in which they formed. Young igneous crystallization ages and evidence for low-temperature alteration suggest a geologically active parent body, which narrows the candidates to Venus and Mars.[35−37,45,46] The strongest evidence for a Martian origin comes from an observed close correspondence between on-site measurements of Martian atmospheric noble gas abundances by the Viking Landers and the abundances of noble gases that are trapped in shock-related silicate glasses.[47,48]

## VI. Martian Oxygen Isotopes in SNC Meteorites

A number of secondary minerals, that is, minerals formed in situ by aqueous activities on Mars, have oxygen isotope compositions that do not fall on the same oxygen isotope mass fractionation line as that defined by coexisting igneous silicate minerals.[49−52] Karlsson et al.[52] extracted water from a number of SNC meteorites and demonstrated that waters from Nakhla, Lafayette, Zagami, and Chassigny were more $^{17}O$-enriched than their coexisting igneous silicate minerals. Farquhar et al.[50,51] demonstrated that carbonates from ALH 84001, Nakhla, and Lafayette as well as sulfate from Nakhla were $^{17}O$-enriched relative to coexisting igneous silicate minerals. The mass-independent oxygen isotopic compositions are in the wrong direction to be explained by terrestrial contamination and have been interpreted in the context of a mass-independently fractionated reservoir (or reservoirs) in the Martian atmosphere−hydrosphere system.

An important signature of chemical mass-independent isotopic fractionation processes is a variable mass-independent signature in different phases, since secondary phases form by different reaction pathways and some
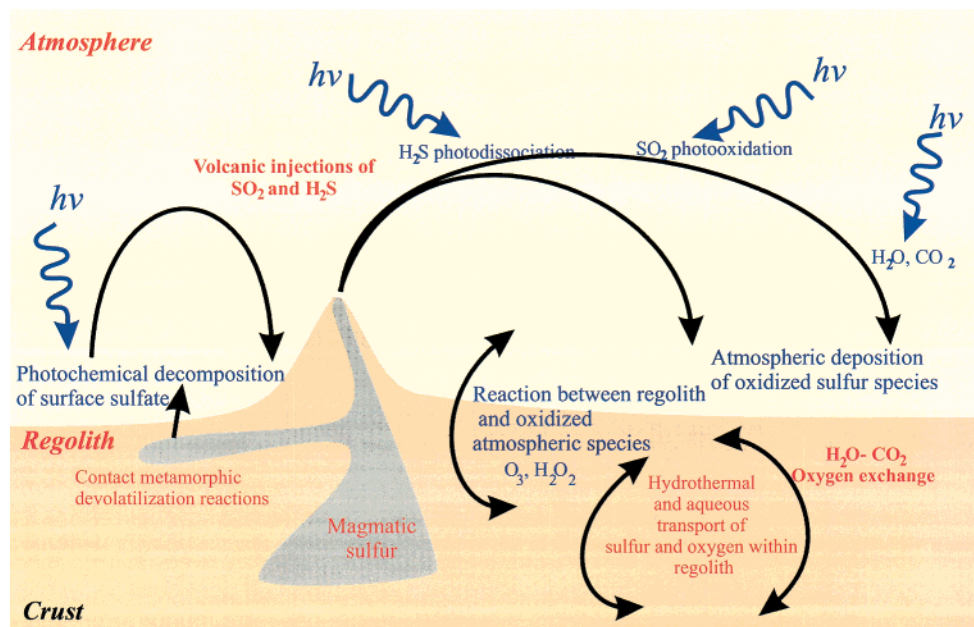
**FIGURE 5.** Synthetic model of the Martian cycles of oxygen and sulfur that is obtained by consideration of mass-independently fractionated sulfur and oxygen in Martian (SNC) meteorites.

species exchange oxygen more readily than others. As a consequence, some secondary minerals may carry large mass-independent signatures, while others do not. Different $\Delta^{17}O$ values for sulfate (1.33‰) and water (0.95‰) are inconsistent with mass-dependent equilibria. This observation is, however, consistent with a mass-independent chemical system where water and sulfate acquire their respective isotopic composition through different isotopic fractionation processes. This is feasible, given the slow rates of oxygen isotope exchange between sulfate and water in solutions that are not strongly acidic (pH < 2), and given that sulfate produced by oxidation may acquire part of its oxygen from mass-independently fractionated species such as $H_2O_2$ and $O_3$.[13,25] Carbonate precipitated from water must lie on a mass fractionation line because carbon dioxide and liquid water undergo rapid oxygen isotope exchange through the formation of $H_2CO_3$. Equilibrium $CO_2-H_2O$ exchange predicts $\ln(^{17}\alpha)/\ln(^{18}\alpha) \approx 0.524$ at 25 °C.[53] The term $\alpha$ is the conventional fractionation factor reflecting the isotopic difference between two phases, in this case $CO_2$ and $H_2O$. The fractionations between carbonate and water extracted from Nakhla yield $^{17}\alpha = 1.01797$ and $^{18}\alpha = 1.03460$, and the quantity $\ln(^{17}\alpha)/\ln(^{18}\alpha)$ is within error of that calculated for $CO_2-H_2O$ isotopic exchange. This is consistent with mass-dependent carbonate−water equilibrium. A similar relationship is defined by carbonate and water from Lafayette.

The carbonates in Nakhla and Lafayette, however, are not in mass-dependent equilibrium. Since Nakhla and Lafayette are believed to be related and also to originate in the same volcanostratigraphic sequence, the variable $\Delta^{17}O$ values therefore indicate that geochemical exchange of oxygen between water and rock at the time of formation of secondary minerals in these meteorites was highly active and contributed to heterogeneous $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$. The additional observation of similar $\Delta^{17}O$ values

for significantly older carbonate from ALH 84001 indicates that the process responsible for the generation of mass-independent compositions persisted throughout a significant part of Mars's evolution and attained equilibrium. This also requires that the chemistry in the Martian regolith has been coupled to Martian atmospheric chemistry throughout much of Mars's history. This had not been quantified prior to these isotopic measurements.

While the $\Delta^{17}O$ signature in secondary phases originates in the Martian atmosphere, the chemical reactions responsible for its transfer to minerals remain unresolved. This is, in part, a result of the limited number of samples available. It has been speculated that the signatures may reflect reactions such as isotopic exchange between $CO_2$ and $O(^1D)$ produced by photolysis of $O_3$, $CO_2$ photodissociation in the Martian atmosphere,[54−56] or exchange between $CO_2$ and isotopically anomalous water that itself inherited anomalous $\Delta^{17}O$ through exchange with compounds in the soil that have been oxidized by isotopically anomalous atmospheric oxidizing agents (e.g., $O_3$ and $H_2O_2$). Such oxidized compounds are thought to be common in the soil (e.g., iron oxides and oxidized organic acids).[57] Sulfate forms by a different process that may include oxidation of $SO_2(aq)$ by $H_2O_2$ or $O_3$ and $SO_2 + OH$ or $SO_2$ photooxidation. This oxygen mass-independent isotopic signature has been utilized to significantly enhance understanding of Martian processes.

## VII. Martian Sulfur from SNC Meteorites

The SNC meteorites also contain sulfides and sulfate with negative $\Delta^{33}S$ values.[58] These data have been interpreted in the context of previously described results for ancient terrestrial sedimentary sulfide and sulfate and gas-phase photochemical experiments involving $CS_2$, $SO_2$, and $H_2S$ that have produced mass-independent sulfur isotope

fractionations during photolysis by deep UV and visible radiation.[58,59] Because of low oxygen pressures, the Martian atmosphere has been optically thin throughout Mars's history.

Oxygen and sulfur isotope systematics of SNC meteorites can be used to form a synthetic model of the Martian geochemical oxygen and sulfur cycles (Figure 5). The model provides a conceptual framework for targeting future return sampling missions. Such models and multiple isotopic measurements also provide insights into, and may ultimately address, a number of longstanding questions pertaining to the origin of oxidized sulfur species observed by both Pathfinder and Vikings, and to the role of highly oxidized compounds such as $O_3$ and $H_2O_2$ in the Martian regolith. These atmospheric compounds may also be an energy source for potential Martian biota. As such, their isotopic composition/memory will be an important tracer.

## VIII. Concluding Comments

With the discovery by Thiemens and Heidenreich in 1983 of a chemically produced mass-independent isotopic process, a realm of applications in atmospheric chemistry, solar system evolution, and atmospheric chemistry was opened. In the past few years, mass-independent isotopic compositions have been observed in an extensive range of terrestrial solids. These new observations have been shown to enhance understanding of an extraordinary range of natural processes which include origin and transport of aerosol sulfates in the present atmosphere, the past history of the atmosphere and ocean in west Africa, the interaction between the atmosphere and the Antarctic dry valleys over geologic time scales, the origin and evolution of the sulfur cycle in the earliest Earth's history as well as the origin and evolution of oxygen, and finally, the chemistry of the Martian atmosphere and its coupling to the surface of Mars and the consequences for life on Mars. These new studies have opened new fields and made significant new advances where no other technique could have provided such insights. There is likely a much wider range of applications of mass-independent signatures on Earth as well as throughout the solar system.

## References

(1) Urey, H. C. Thermodynamics of Isotopic Substances. *J. Chem. Soc.* **1947**, 562−581.

(2) Bigeleisen, J.; Mayer, M. Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *J. Chem. Phys.* **1947**, 15261−15267.

(3) Thiemens, M.; Heidenreich, J. E., III. The Mass Independent Fractionation of Oxygen: A Novel Effect and Its Possible Cosmochemical Implications. *Science* **1983**, *219*, 1073−1075.

(4) Clayton, R. N.; Grosman, L.; Mayeda, T. K. A Component of Primitive Nuclear Composition in Carbonaceous Meteorites. *Science* **1973**, *182*, 485−488.

(5) Weston, R. E. Anomalous or Mass-Independent Isotope Effects. *Chem. Rev.* **1999**, *99*, 2115−2136.

(6) Thiemens, M. H. Mass Independent Isotope Effects in Planetary Atmospheres and the Early Solar System. *Science* **1999**, *283*, 341−345.

(7) Janssen, C.; Guenther, J.; Krankowsky, D.; Mauersberger, K. Relative Formation Rates of $^{50}O_3$ and $^{52}O_3$ in $^{16}O-^{18}O$ Mixtures. *J. Chem. Phys.* **1999**, *111*, 7179−7182.

(8) Guenther, J.; Krankowsky, D.; Mauersberger, K. Third-Body Dependence of Rate Coefficients for Ozone Formation in $^{16}O-^{18}O$ Mixtures. *Chem. Phys. Lett.* **2000**, *324*, 31−36.

(9) Hathorn, B. C.; Marcus, R. A. An Intramolecular Theory of the Mass-Independent Isotope Effect for Ozone I. *J. Chem. Phys.* **1999**, *111*, 4087−4100.

(10) Luz, B.; Barkan, E.; Bender, M. L.; Thiemens, M. H.; Boering, K. *Nature* **1999**, *400*, 547−550.

(11) Lee, C. W. In *AGU Fall Meeting*; Union, A. G., Ed.; EOS Supplement Transaction, San Francisco, 1997; Vol. 78, p F111.

(12) Lee, C. W.; Savarino, J.; Thiemens, M. H. In *AGU Fall Meeting*, Supplement, E; EOS Supplement Transaction, San Francisco, 1998; Vol. 79, p F91.

(13) Savarino, J.; Lee, C. W.; Thiemens, M. H. Laboratory oxygen isotopic study of atmospheric Sulfur (IV) oxidation: Origin of the mass independent oxygen isotopic anomaly in atmospheric sulfates and other sulfate deposits. *J. Geophys. Res.* **2000**, *105*, 29079−29088.

(14) Holt, B. D.; Cunningham, P. T.; Engelkemeir, A. G.; Graczyk, D. G.; Kumar, R. Oxygen-18 study of nonaqueous-phase oxidation of sulfur dioxide. *Atmos. Environ.* **1983**, *17*, 625−632.

(15) Seinfeld, J. H.; Pandis, S. N. *Atmospheric chemistry and physics*; John Wiley & Sons: New York, 1998; Vol. 1.

(16) Herrmann, H.; Ervens, B.; Jacobi, H.-W.; Wolke, R.; Nowack, P.; Zellner, R. CAPRAM2.3: A chemical aqueous phase radical mechanism for trophoseric chemistry. *J. Atmos. Chem.* **2000**, *36*, 231−284.

(17) Liang, J. Y.; Jacobson, M. Z. A study of sulfur dioxide oxidation pathways over a range of liquid water contents, pH values, and temperatures. *J. Geophys. Res.* **1999**, *104*, 13749−13769.

(18) Savarino, J.; Thiemens, M. H. Analytical procedure to determine both $\delta^{18}O$ and $\delta^{17}O$ of $H_2O_2$ in natural water and first measurements. *Atmos. Environ.* **1999**, *33*, 3683−3690.

(19) Savarino, J.; Thiemens, M. H. Mass-independent oxygen isotope ($^{16}O$, $^{17}O$, $^{18}O$) fractionation found in $H_x$, $O_x$ reactions. *J. Phys. Chem.* **1999**, *103*, 9221−9229.

(20) Johnston, J. C.; Thiemens, M. H. The isotopic composition of tropospheric ozone in three environments. *J. Geophys. Res.* **1997**, *102*, 25395−25404.

(21) Röckmann, T.; Brenninkmeijer, C. A. M.; Saueressig, G.; Bergamaschi, P.; Crowley, J. N.; Fisher, H.; Crutzen, P. J. Mass-Independent Oxygen Isotope Fractionation in Atmospheric CO as a Result of the Reaction CO + OH. *Science* **1998**, *281*, 544−546.

(22) Halperin, J.; Taube, H. The transfer of oxygen atoms in oxidation−reduction reactions. IV. The reaction of hydrogen peroxide with sulfite and thiosulfate, and of oxygen, manganese dioxide and of permanganate with sulfite. *J. Am. Chem. Soc.* **1952**, *74*, 380−382.

(23) McArdle, J. V.; Hoffmann, M. R. Kinetic and Mechanism of Oxidation of Aquated Sulfur Dioxide by Hydrogen Peroxide at Low pH. *J. Phys. Chem.* **1983**, *87*, 5425−5429.

(24) Penkett, S. A.; Jones, M. R.; Brice, K. A.; Eggleton, A. E. The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rainwater. *Atmos. Environ.* **1979**, *13*, 123−137.

(25) Bao, H.; Thiemens, H. M.; Farquhar, J.; Campbell, A. D.; Lee, C. W. C.; Heine, K.; Lope, D. D. Anomaly $^{17}O$ compositions in massive sulphate mineral deposits on the Earth. *Nature* **2000**, *406*, 176−178.

(26) Erickson, R. E.; Yates, L. M.; Clark, R. L.; McEwen, D. The reacion of sulfur dioxide with ozone in water and its possible atmospheric significance. *Atmos. Environ.* **1977**, *11*, 813−817.

(27) Robert, F.; Rejou-Michel, A.; Javoy, M. Oxygen isotropic homogeneity of the Earth: new evidence. *Earth Planet. Sci. Lett.* **1992**, *108*, 1−9.

(28) Clayton, R. N.; Mayeda, T. K. Oxygen isotope studies of achondrites. *Geochim. Cosmochim. Acta* **1996**, *60*, 1999−2017.

(29) Bao, H.; Campbell, D. A.; Bockheim, J. G.; Thiemens, M. H. Origins of sulphate in Antarctic dry valley soils as deduced from anomalous $^{17}O$ compositions. *Nature* **2000**, *407*, 499−502.

(30) Bao, H.; Michalski, G. M.; Thiemens, M. H. Sulfate oxygen-17 anomalies in desert varnishes. *Geochim. Cosmochim. Acta* **2000**, in press.

(31) Bao, H.; Thiemens, M. H. Generation of $O_2$ from $BaSO_4$ using a $CO_2$-laser fluorination system for simultaneous analysis of $\delta^{18}O$ and $\delta^{17}O$. *Anal. Chem.* **2000**, *72*, 4029−4032.

(32) Farquhar, J.; Bao, H. M.; Thiemens, M., Atmospheric influence of Earth's earliest sulfur cycle. *Science* **2000**, *289*, 756−758.

(33) Walker, J. C. G.; Brimblecombe, P. Iron and sulfur in the Pre-biologic ocean. *Precambrian Res.* **1985**, *28*, 205–222.

(34) Borg, L. E.; Connelly, N. J.; Nyquist, L. E.; Shih, C. Y.; Wiesmann, H.; Reese, Y. The Age of the Carbonates in Martian Meteorite ALH84001. *Science* **1999**, *286* (*5437*), 90–94.

(35) Gale, N. H.; Arden, J. W.; Hutchison, R. The chronology of the Nakhla achondritic meteorite. *Earth Planet. Sci. Lett.* **1975**, *26*, 195–206.

(36) Papanastassiou, D. A.; Wasserburg, G. J. Evidence for Late Formation and Young Metamorphism in the Achondrite Nakhla. *Geophysi. Res. Lett.* **1974**, *1*, 23–26.

(37) Podosek, F. A. Thermal history of the nakhlites by the (super 40) Ar–(super 39) Ar method. *Earth Planet. Sci. Lett.* **1973**, *19*, 135–144.

(38) Shih, C. Y.; Nyquist, L. E.; Reese, Y.; Wiesmann, H. The Chronology of the Nakhlite, Lafayette: Rb–Sr and Sm–Nd Isotopic Ages. *Abstracts of papers submitted to the twenty-ninth lunar and planetary science conference*; Lunar Planetary Institute: Houston, TX, 1998; Vol. 29, p 1145.

(39) Swindle, T. D.; Grier, J. A.; Li, B.; Olson, E.; Lindstrom, D. J.; Treiman, A. H. K–Ar ages of Lafayette weathering products; evidence for near-surface liquid water on Mars in the last few hundred million years. *Abstracts of papers submitted to the twenty-eighth Lunar and planetary science conference*; Lunar Planetary Institute: Houston, TX, 1997; Vol. 28, Part 3, pp 1403–1404.

(40) Wadhwa, M.; Lugmair, G. W. The controversy of young vs. old age of formation of carbonates in Allan Hills 84001. *Conference on early Mars*: *geologic and hydrologic evolution, physical and chemical environments, and the implications for life*; Lunar and Planetary Institute, Houston, TX, 1997; pp 79–81.

(41) Bridges, J. C.; Grady, M. M. A halite–siderite–anhydrite–chlarapatite assemblage in Nakhla: Mineralogical evidence for evaporites on Mars. *Meteorit. Planet. Sci.* **1999**, *34*, 407–415.

(42) Romanek, C. S.; Grady, M. M.; Wright, I. P.; Mittlefehldt, D. W.; Socki, R. A.; Pillinger, C. T.; Gibson, E. K. Record of Fluid-Rock Interactions on Mars from the Meteorite ALH84001. *Nature* **1994**, *372*, 655–657.

(43) Gooding, J. L. Soil Mineralogy and Chemistry on Mars—Possible Clues from Salts and Clays in SNC Meteorites. *Icarus* **1992**, *99*, 28–41.

(44) Treiman, A. H.; Barrett, R. A.; Gooding, J. L. Preterrestrial Aqueous Alteration of the Lafayette (Snc) Meteorite. *Meteoritics* **1993**, *28*, 86–97.

(45) Wood, C. A.; Ashwal, L. D. SNC meteorites; igneous rocks from Mars? Section 2, Planets, asteroids and satellites. In *Abstracts of papers submitted to the twelfth lunar and planetary science conference*; Lunar Planetary Institute: Houston, TX, 1981; pp 1359–1375.

(46) McSween, H. Y., Jr. SNC Meteorites; are they Martian rocks? *Geology* **1984**, *12*, 3–6.

(47) Bogard, D. D.; Johnson, P. Martian gases in an Antarctic meteorite? *Science* **1983**, *221*, 651–654.

(48) Wiens, R. C.; Becker, R. H.; Pepin, R. O. The case for a Martian origin of the shergottites; II, Trapped and indigenous gas components in EETA 79001 glass. *Earth Planet. Sci. Lett.* **1986**, *77*, 149–158.

(49) Romanek, C. S.; Perry, E. C.; Treiman, A. H.; Socki, R. A.; Jones, J. H.; Gibson, E. K., Jr. Oxygen isotopic record of silicate alteration in the Shergotty-Nakhla-Chassigny meteorite Lafayette. *Meteorit. Planet. Sci.* **1998**, *33*, 775–784.

(50) Farquhar, J.; Thiemens, M. H. Oxygen cycle of the Martian atmosphere–regolith system: $\Delta^{17}O$ of secondary phases in Nakhla and Lafayette. *J. Geophys. Res.-Planets* **2000**, *105*, 11991–11997.

(51) Farquhar, J.; Thiemens, M. H.; Jackson, T., Atmosphere–surface interactions on Mars: $\Delta^{17}O$ measurements of carbonate from ALH 84001. *Science* **1998**, *280*, 1580–1582.

(52) Karlsson, H. R.; Clayton, R. N.; Gibson, E. K.; Mayeda, T. K. Water in Snc Meteorites—Evidence For a Martian Hydrosphere. *Science* **1992**, *255*, 1409–1411.

(53) Matsuhisa, Y.; Goldsmith, J. R.; Clayton, R. N. Mechanisms of hydrothermal crystallization of quartz at 250 degrees C and 15 kilobars, *Geochim. Cosmochim. Acta* **1978**, *42*, 173–182.

(54) Wen, J.; Thiemens, M. H. Multi-Isotope Study of the O((1)D)+Co2 Exchange and Stratospheric Consequences. *J. Geophys. Res.-Atmospheres* **1993**, *98*, 12801–12808.

(55) Johnston, J. C.; Rockmann, T.; Brenninkmeijer, C. A. M. CO2/sub +/O(/sup 1/D) isotopic exchange: laboratory and modeling studies. *J. Geophys. Res.* **2000**, *105*, 15213–15229.

(56) Thiemens, M. H.; Jackson, T. L.; Brenninkmeijer, C. A. M. Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric $CO_2$, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere. *Geophys. Res. Lett.* **1995**, *22*, 255–257.

(57) Benner, S. A.; Devine, K. G.; Matveeva, L. N.; Powell, D. H. The missing organic molecules on Mars. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 2425–2430.

(58) Farquhar, J.; Savarino, J.; Jackson, T. L.; Thiemens, M. H. Evidence of atmospheric sulphur in the Martian regolith from sulphur isotopes in meteorites. *Nature* **2000**, *404*, 50–52.

(59) Zmolek, P.; Xu, X. P.; Jackson, T.; Thiemens, M. H.; Trogler, W. C. Large mass independent sulfur isotope fractionations during the photopolymerization of $(CS_2)$-$^{12}C$ and $(CS_2)$-$^{13}C$. *J. Phys. Chem.* **1999**, *103*, 2477–2480.

(60) Fisk, M. R.; Giovannoni, S. J. Sources of nutrients and energy for a deep biosphere on Mars. *J. Geophys. Res.-Planets* **1999**, *104*, 11805–11815.

AR960224F