Frontiers

Multiple sulfur isotopes and the evolution of the atmosphere

James Farquhar *, Boswell A. Wing

Earth System Science Interdisciplinary Center and Department of Geology, University of Maryland, College Park, MD 20742, USA

Abstract

Interest in multiple sulfur isotope analyses has been fueled by recent reports of mass-independent sulfur isotope signatures in the geologic record. A non-zero multiple isotopic signature of sulfur ($\Delta^{33}S$ and $\Delta^{36}S$) is produced primarily through photochemical reactions, and it is an almost perfect tracer of the source of sulfur. Once the signature is passed on to a given sulfur reservoir, it will be preserved unless there is addition of sulfur with a different $\Delta^{33}S$ or $\Delta^{36}S$. In the geological record, this signature has been used to study the evolution of the Earth's atmosphere and to trace movement of sulfur through geological systems early in Earth's history. Recently, small but significant mass-independent signatures have been reported for some younger samples, raising the possibility of additional applications of multiple isotope studies. The purpose of this review is to introduce and discuss the implications of multiple isotope studies and to focus attention on these anomalous, but not uncommon isotopic signatures.
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Our present understanding of Earth's surface environment from the Archean to the present day has been influenced greatly by a half century of studies on sulfur isotope geochemistry. To date, most studies have focused only on the two most abundant isotopes of sulfur, ^{32}S and ^{34}S. There are historical and analytical reasons for this, but the dominant motivation behind it has been theoretical. At thermodynamic equilibrium, the distribution of sulfur isotopes among sulfur-bearing compounds is governed strictly by the rel-

ative mass differences of each isotope [1]. This leads to sulfur isotope variations that can be described by $\delta^{33}S \sim 1/2 \times \delta^{34}S$ and $\delta^{36}S \sim 2 \times \delta^{34}S$ [2,3]. These mass-dependent relationships can be shown to hold for many non-equilibrium processes as well [4–6]. Deviation from the mass-dependent trends for fractionation processes composed of a sequence of individual kinetic and equilibrium steps (e.g. bacterial sulfate reduction) was simply not expected in the geologic record and the multiple sulfur isotope analyses needed to test this expectation were rarely performed. However, sulfur isotopic compositions that deviate significantly from mass-dependent expectations have been measured recently in some of Earth's oldest rocks [7–12], in volcanic horizons in ice cores [13], and in modern sulfate aerosols [14,15]. These anomalous or mass-independent compositions are char-

* Corresponding author.

E-mail addresses: jfarquha@essic.umd.edu (J. Farquhar),
wing@essic.umd.edu (B.A. Wing).

BOX 1:

Mass-dependent and mass-independent sulfur isotope fractionations

⇒ The application of multiple sulfur isotope analyses in geochemistry began when Hulston and Thode published two papers [2, 3] that described the principles of mass-dependent sulfur isotope fractionations and introduced the three isotope plot. Sulfur has four stable isotopes and ratios of these isotopes are reported relative to the international reference standard V-CDT. The abundances of ^{32}S, ^{33}S, ^{34}S, and ^{36}S of V-CDT have been determined to be 0.9503957, 0.0074865, 0.0419719, and 0.0001459, respectively [44].

⇒ Following current convention [3-6, 45, 46] mass-dependent fractionation is defined by the following equation:

$$(1) \qquad ^{3X}\lambda = \ln(1+\delta^{3X}S/1000)/\ln(1+\delta^{34}S/1000),$$

$$(2) \qquad ^{3X}\theta = \ln(^{3X}\alpha)/\ln(^{34}\alpha),$$

where λ refers to fractionation relationships between measured quantities (i.e. fractionation arrays), θ refers to relationships due to the fractionation process itself (i.e. fractionation factors), and the 3x superscript refers to ^{33}S and ^{36}S.

The terrestrial mass fractionation array shown in Figure 2 was regressed using equation 1 for $^{33}\lambda = 0.515$. The terrestrial mass fractionation array represents an average of all mass-dependent fractionation processes that occur on Earth [2, 3]. Fractionation relationships for individual mass dependent processes can deviate from 0.515 by a few percent at most [3-6, 46]. Fractionation relationships for equilibrium isotopic exchange tend to exhibit $^{33}\theta$ values near 0.515 (Figure 3) while fractionation relationships for kinetic processes generally follow values of $^{33}\theta$ closer to 0.5 [4-6].

⇒ Mass-independent fractionations are produced by isotopic fractionation processes that do not obey commonly accepted mass fractionation laws (e.g., $\delta^{33}S \sim \frac{1}{2} \delta^{34}S$, and $\delta^{36}S \sim 2 \delta^{34}S$) discussed above. These processes produce isotopic compositions with nonzero $\Delta^{33}S$ and $\Delta^{36}S$, and have been attributed to nucleosynthetic processes and in some cases chemical processes [19, 47, 48]. A number of experimental and theoretical studies have focused on the causes of chemically-produced mass-independent fractionation effects [21, 22, 37-40, 49], but our understanding of these processes is incomplete.

⇒ Analytical techniques for the high-precision measurement of isotopic ratios can allow for discrimination among different fractionation relationships in the third decimal place of a λ value [5, 46], which has obscured the difference between mass-dependent and mass-independent fractionation at small values of $\Delta^{33}S$ and $\Delta^{36}S$. We note that the definitions of $\Delta^{33}S$ and $\Delta^{36}S$ used in this paper specifically refer to the terrestrial distribution of sulfur isotopes and that $\Delta^{33}S$ ($\Delta^{36}S$) values within ± 0.2 ‰ (± 0.4 ‰) of zero can arise through the normal operation of mass-dependent fractionation processes.
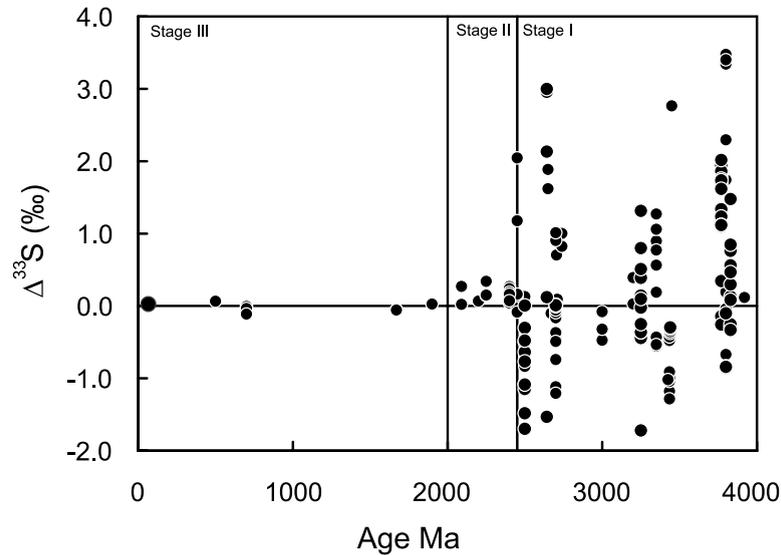
Box 1. Information from [2–6,19,21,22,37–40,44–49]

Fig. 1. Plot of $\Delta^{33}S$ vs. age after [7–9]. The record divides Earth's history into three stages: Stage I extends from before 3.8 Ga to 2.45 Ga and is characterized by $\Delta^{33}S$ of variable sign and magnitude; Stage II extends from 2.45 to 2 Ga and displays more subdued $\Delta^{33}S$ variability; and Stage III extends from 2 Ga until present and is characterized by $\Delta^{33}S$ variability much less than $\pm 0.2‰$. The large filled circle represents hundreds of analyses of samples younger than 2.0 Ga. Stage III is defined on the basis of these measurements, not on the representative samples shown in the figure. The change from Stage I to Stage II is attributed to a change in the Earth's atmospheric chemistry. Photolysis reactions involving SO_2 and SO in Earth's early atmosphere, coupled with an efficient transfer of the signature to the Earth's surface, produced the Stage I record. The smaller Stage II record may reflect the onset of oxidative weathering or it may reflect stabilization of atmospheric oxygen to intermediate levels (10^{-5}–10^{-2} PAL).

acterized by non-zero $\Delta^{33}S$ ($=\delta^{33}S-1000((1+\delta^{34}S/1000)^{0.515}-1)$) and $\Delta^{36}S$ ($=\delta^{36}S-1000((1+\delta^{34}S/1000)^{1.91}-1)$). The observations in the ancient rock record are providing new insights into the environmental conditions on early Earth, and observations in the recent record promise to yield new insights into atmospheric chemistry and transport. These insights are built upon the foundation provided by theoretical and experimental research on mass-dependent and mass-independent fractionation processes, as described in Box 1. In the following, we will describe the observations, working hypotheses, unanswered questions, and future opportunities provided by multiple sulfur isotope studies.

2. The geologic record of $\Delta^{33}S$

The geologic record of $\Delta^{33}S$ is unique in the field of geochemistry and carries implications for

a diverse range of processes that extend from atmospheric chemistry to crustal recycling on early Earth. The signature is thought to have a single, atmospheric source and is essentially confined to rocks older than ~2.0 Ga. Fig. 1 illustrates the geologic record of $\Delta^{33}S$ through time. This record divides Earth history into three stages that reflect fundamental changes in both Earth's atmosphere and its sulfur cycle through time. Stage I extends from the oldest terrestrial samples to 2.45 Ga and is characterized by $\Delta^{33}S$ with a range extending to values greater than $\pm 1‰$. Stage II extends from 2.45 Ga to approximately 2 Ga, and has a smaller range of $\Delta^{33}S$ variability (-0.1 to $+0.5‰$). Stage III extends from approximately 2 Ga until present and is characterized by an even smaller range of $\Delta^{33}S$ variability (-0.1 to $+0.2‰$).

First-order interpretation of the terrestrial $\Delta^{33}S$ record hinges on the identification of chemical reactions that can produce the mass-independent signature. We discuss experimental evidence for
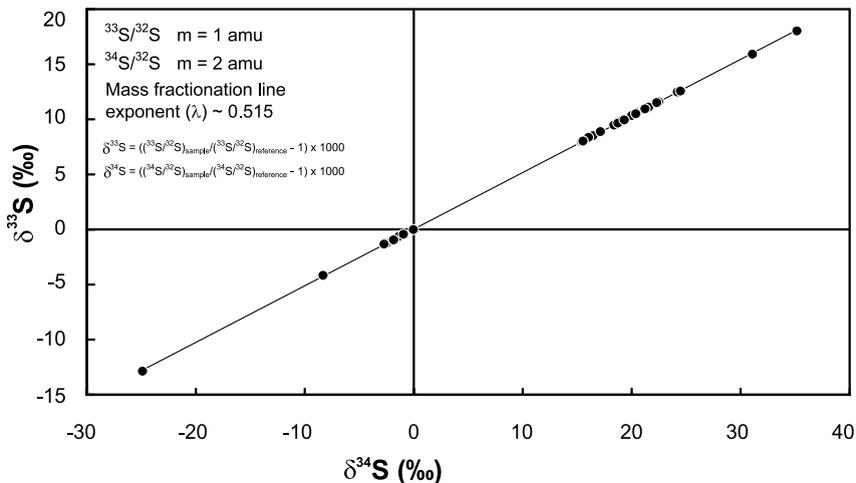
Fig. 2. Plot of $\delta^{33}S$ vs. $\delta^{34}S$ for terrestrial sulfide and sulfate younger than 2.0 Ga [7–9,26,50]. The array defines a tightly constrained curve with $^{33}\lambda = 0.515$. This terrestrial mass fractionation line does not reflect a single fractionation process but represents the average effects of the various mass-dependent fractionation processes that have operated over Earth's history. The slope of the array reflects the mass differences among ^{32}S, ^{33}S, and ^{34}S and arises because the drive for mass-dependent fractionation is approximately half as strong for $\delta^{33}S$ variations as it is for $\delta^{34}S$ variations.

the photochemical origin of the signature and address the implications of this origin for atmospheric evolution. Characterization of the atmospheric conditions that allow the proposed reactions to occur and their products to be transferred to the geologic record places further constraints on the surface environment and sulfur cycling on early Earth. We examine the implications of the $\Delta^{33}S$ record in this context as well.

3. Stage I (before ∼ 2.45 Ga)

The large $\Delta^{33}S$ in Stage I is inversely correlated with $\Delta^{36}S$ [7,16]. This correlation is not significantly affected by mass-dependent fractionation processes, and, therefore, is characteristic of the mass-independent reactions that produced the signature in the geologic record. Photolysis reactions involving SO_2 (and SO) have been studied in closed photocells using ultraviolet radiation with wavelengths of 193 nm, 248 nm, and a continuous spectrum > 220 nm [17,18]. These reactions have been shown to produce large mass-independent isotopic effects (Fig. 4). Other photochemical reactions have also been shown to produce mass-independent fractionation effects (e.g. photolysis

of H_2S, CS_2, S_2F_{10}) [17–22]. Presently, the only reactions that produce large mass-independent fractionations with a relationship between $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ similar to that produced by the Stage I sulfur isotope fractionations are associated with SO_2–SO photolysis by deep ultraviolet radiation. Other reactions that are known to produce mass-independent fractionations are either unlikely to play a significant role in the chemistry of the Earth's early atmosphere (e.g. photolysis of CS_2 and S_2F_{10}) [17–22] or do not provide a good match to the sulfur isotope fractionations observed in the rock record of Stage I (e.g. photolysis of H_2S or > 220 nm photolysis of SO_2) [17–22].

Stage I $\Delta^{33}S$ appears to vary systematically with $\delta^{34}S$ (Fig. 5), but it is less certain that this relationship is characteristic of the primary mass-independent chemistry because secondary mass-dependent fractionation processes could alter $\delta^{34}S$. Ongoing studies of geologic samples have documented different relationships between $\Delta^{33}S$ and $\delta^{34}S$ than those shown here [11,12], which suggests that $\Delta^{33}S$ and $\delta^{34}S$ covariation records secondary mass-dependent fractionation and mixing processes as well as primary mass-independent chemistry. Although we take deep UV SO_2–SO
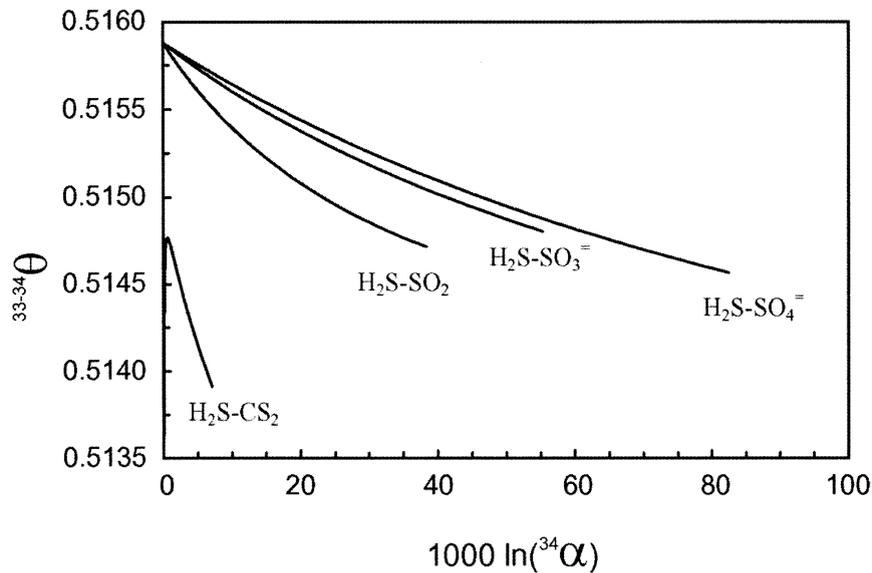
Fig. 3. Plot of $^{33}\theta$ versus $1000\ln(^{34}\alpha)$ calculated for equilibrium isotope exchange reactions between CS_2, SO_2, SO_3^{2-}, SO_4^{2-} and H_2S. These values have been calculated using the theory [1,51] and vibrational spectra [51–55]. The values of $^{33}\theta$ for equilibrium sulfur isotope exchange fall in a narrow range that is similar to the high-temperature limit calculated using methods presented in prior studies [3–5]. At high temperature, $1000\ln(^{34}\alpha)$ approaches 0 and $^{33}\theta$ approaches 0.5159 for all curves. These calculations illustrate the range of $^{33}\theta$ that is expected for equilibrium exchange reactions. Note there is a discontinuity in $^{33}\theta$ for the H_2S–CS_2 pair at $1000\ln(^{34}\alpha)=0$. This effect has recently been noted by Deines [56] as a way to produce anomalous $\Delta^{33}S$ and $\Delta^{36}S$ by mass-dependent processes. The magnitudes of these fractionation effects are small (<100 per Meg), but may be measurable if they are amplified by a process such as Rayleigh distillation.

photolysis as our working model for the source of the Stage I mass-independent fractionation, these reactions have been studied only to a limited extent and a more refined candidate is likely to emerge with more experimental and theoretical research.

SO_2 and SO photolysis driven by deep ultraviolet radiation imposes strict constraints on the ultraviolet transparency of the primitive atmosphere. Ozone and, to a lesser extent, oxygen are the principal atmospheric constituents that absorb the ultraviolet radiation at wavelengths less than ~ 300 nm. Evidence for the SO_2–SO photolysis reactions implies that the atmosphere was transparent at these ultraviolet wavelengths and that the ozone ultraviolet shield was not present. It can also be used to place upper limits on the carbon dioxide content of the atmosphere because at high levels ($\approx 1/2$ bar for CO_2) the Rayleigh scattering tail of CO_2 would have blocked the ultraviolet radiation required for the reactions [17]. The presence of sufficient ultravio-

let radiation for the photolysis reactions is also inconsistent with hypotheses that call on high altitude methane-induced organic haze (e.g. [23]).

If deep UV SO_2–SO photolysis is the source for mass-independent fractionation of sulfur isotopes, the likely agents for transferring the anomalous signature to Earth's surface were elemental S and H_2SO_4 [17]. Pavlov and Kasting [24,25] recognized that effective transfer of both reduced and oxidized sulfur species to Earth's surface places limits on the oxidative capacity of the atmosphere during Stage I. They used a one-dimensional model of Archean atmospheric chemistry to estimate the distribution of the sulfur isotopic signature between atmospheric sulfur species and then to determine the relative proportions of these species that would be transferred to the Earth's surface. By applying this approach to hypothetical Archean atmospheres, they were able to argue that the transfer of the SO–SO_2 photolysis signature from the atmosphere to the surface occurred only when oxygen levels were $\ll 10^{-5}$ PAL

(present atmospheric level) because oxidized sulfur species with negative $\Delta^{33}S$ (sulfate aerosols and SO_2) and neutral-to-reduced sulfur species with positive $\Delta^{33}S$ (S_8 aerosols, H_2S, HS) exit the atmosphere in sub-equal proportions only at these low oxygen levels.

Estimates of early Earth's $\Delta^{33}S$ budget are preliminary but point to unique characteristics of the Archean sulfur cycle. The average $\Delta^{33}S$ difference between sulfate and sulfide in Archean samples is approximately 1–2‰ [12,17,26]. When evaluated in the context of the experimental results on SO_2–SO photolysis ($\Delta^{33}S$ of elemental sulfur ≈ 65‰ and sulfate ≈ -17‰), these data are consistent with at least 1–2% of sedimentary sulfur being derived from the atmosphere. If sulfur exiting the atmosphere were chemically or isotopically homogenized, the fractional amount of sedimen-
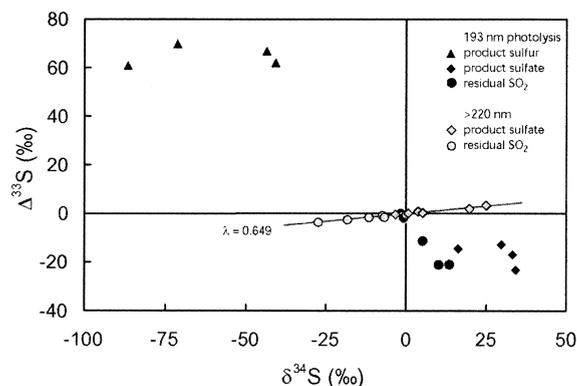
Fig. 5. Plot of $\Delta^{33}S$ vs. $\delta^{34}S$ for Archean Stage I samples (triangles) and data for samples younger than 2 Ga (diamonds) [7–9,26,50]. Field of data delimited by barite and sulfide of hydrothermal origin is also illustrated on this plot (note that data from other types of samples also plot in these fields). The similar aspect ratio of these data to results of SO_2 photolysis experiments as illustrated by arrows designating the sense of the arrays generated in the experiments and also the similar negative $\Delta^{33}S$ signature of sulfate both in experiments with 193 nm radiation (not >220 nm radiation) and in the Archean data has led to the suggestion that SO_2 (or SO) photolysis contributed to the signature observed in the Archean record.

Fig. 4. Plot of $\Delta^{33}S$ vs. $\delta^{34}S$ for closed cell photolysis of SO_2 at 193 nm (black-filled symbols) and at >220 nm (gray-filled symbols). Data for product elemental sulfur are plotted as triangles. Data for product sulfate are plotted as diamonds. Residual sulfur dioxide data are plotted as circles. The large magnitude mass-independent isotopic fractionation generated in these experiments for elemental sulfur and complementary depletions of ^{33}S (and enrichments of ^{36}S) for sulfate and residual sulfide of the 193 nm experiments make this the preferred candidate to explain the mass-independent sulfur isotope fractionations in the Archean. SO was an intermediate product of the photochemistry that occurred during the experiments, and, therefore, photolysis of SO (in addition to SO_2) is also included as a candidate for the observed isotopic fractionation effects. Fractionation effects associated with photolysis at >220 nm are also considered because these wavelengths would have been available for chemistry in a low-oxygen atmosphere.
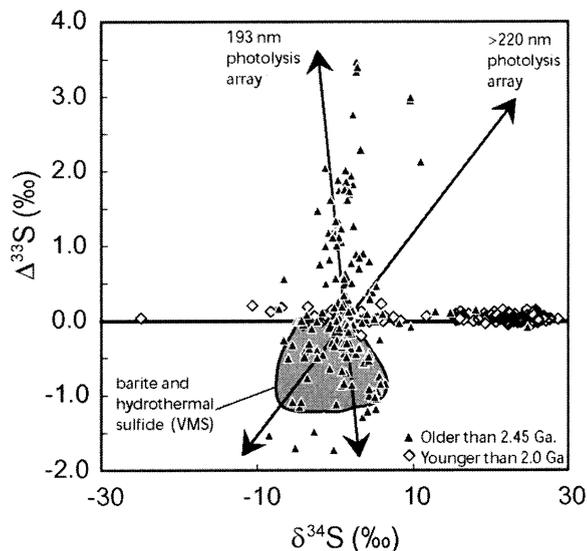
tary sulfur of atmospheric origin would be higher. Material balance of sulfur cycled through the Archean atmosphere also requires that the average of all mass-independently fractionated sulfur equals the isotopic composition of juvenile sulfur ($\Delta^{33}S \approx 0$‰) [26]. To date, most sulfides yield $\Delta^{33}S$ values that are ≥ 0‰ and average to a small but positive value (0.5 ± 0.2‰ [26]). This indicates a missing reservoir of sulfur with negative $\Delta^{33}S$. Known reservoirs with negative $\Delta^{33}S$ include barite and sulfides of hydrothermal origin. Archean oceanic sulfate and hydrothermally altered oceanic crust likely had negative $\Delta^{33}S$ as well. Whether these were sufficiently negative or massive to close the $\Delta^{33}S$ imbalance is an open question.

Fig. 6 presents a schematic illustration of the Earth's early sulfur cycle and the nature of sulfur
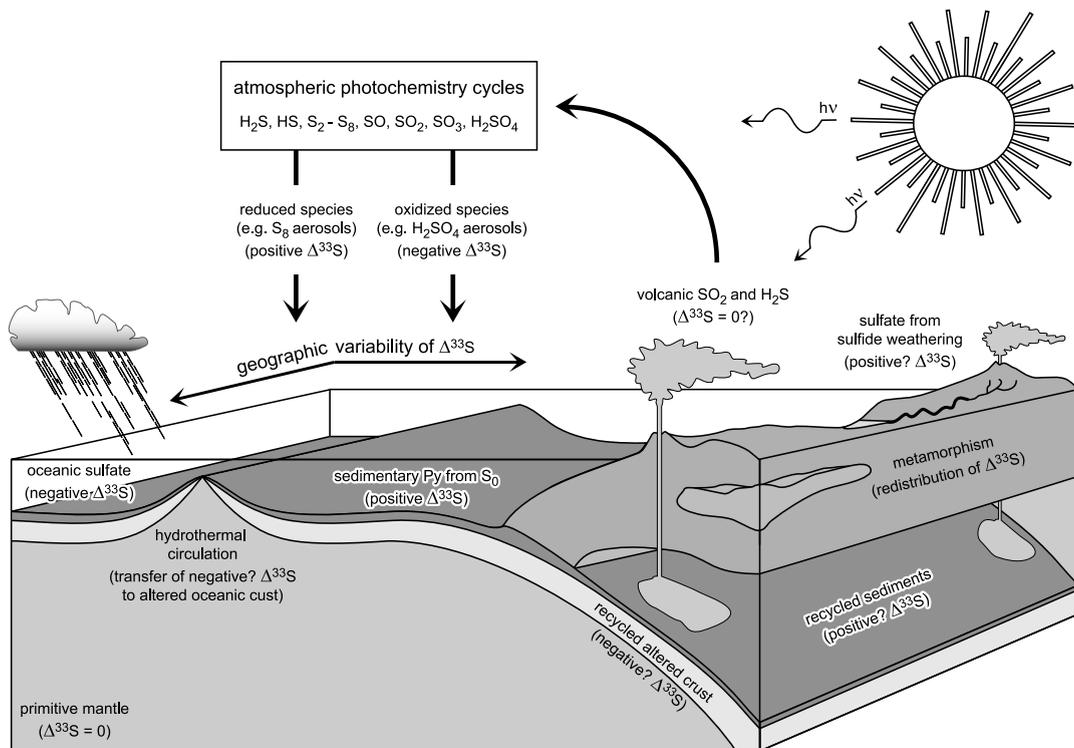
Fig. 6. Diagram of the Earth's early sulfur cycle (Stage I) as indicated by the sulfur isotope data. The sulfur cycle can be thought of as starting in the atmospheric subcycle when atmospheric sulfur dioxide of volcanogenic origin is photodissociated by deep ultraviolet radiation. Atmospheric chemistry distributes this signature among sulfur species and is transferred to the surface subcycle through at least two channels. Elemental sulfur with positive $\Delta^{33}S$ is reduced to sulfide, possibly by sulfur-reducing bacteria or by reaction of FeS with S, and is preserved as sedimentary sulfides. Atmospheric sulfate with negative $\Delta^{33}S$ is soluble and eventually deposited to the oceans. Vigorous oxidative weathering of sulfides with positive $\Delta^{33}S$ to produce sulfate with positive $\Delta^{33}S$ is thought to be largely suppressed because the signature has not been homogenized in the Stage I record. Metasedimentary rocks and rocks with hydrothermal sulfides also carry an anomalous $\Delta^{33}S$ signature and reflect the transfer and redistribution that accompany their formation. Anomalous positive $\Delta^{33}S$ in sulfide inclusions in diamond indicate that recycling of sedimentary sulfur to the mantle has occurred and may also indicate that hydrothermal sulfides deposited in the oceanic crust with complementary (negative) $\Delta^{33}S$ may also have been recycled. Geographic variations for $\Delta^{33}S$ are likely to be present in the record and will provide new insights into the nature of Archean surface environments.

transfer between the different reservoirs. Sulfur dioxide and hydrogen sulfide gases were introduced to the atmosphere by ancient volcanic eruptions and quiescent degassing. After this, the sulfur-bearing gases reacted in the early atmosphere as a result of photochemistry driven by deep ultraviolet light to produce a mass-independent signature in aerosols and gases. Preservation of this signature requires that it was transferred to the Earth's surface by at least two different channels. One channel transferred sulfur with negative $\Delta^{33}S$ predominantly as sulfate; the other transferred sulfur with positive $\Delta^{33}S$ as elemental sulfur and possibly other reduced sulfur species. Sulfur with positive $\Delta^{33}S$ was incorporated in ancient sedimentary rocks as sulfides and sulfur with negative $\Delta^{33}S$ resided in the oceanic sulfate reservoir. A negative $\Delta^{33}S$ signature was also transferred to some sulfides by hydrothermal or bacterial reduction of oceanic sulfate [12]. Analyses of sulfide inclusions in diamonds from the Orapa kimberlite pipe indicate that some sedimentary sulfide was recycled into the Earth's mantle [26] and documents active sulfur cycling among the atmosphere, ocean, sediments, and mantle in the Archean.

4. Stage II ($\sim$2.45 to $\sim$2.0 Ga)

Stage II lasted several hundred million years, extending from 2450 Ma until approximately 2090 Ma. This time interval contains major variations in established biogeochemical records (e.g. $\delta^{13}C$ [27])as well as geological evidence for some of Earth's earliest low-latitude glaciations [28,29]. As a result, many singular changes in the geochemical evolution of Earth's surface environment have been proposed for this time, such as the 'great oxidation event' [30,31], the first rise of oceanic sulfate concentrations above a few hundred μM [32–34], and the beginning of the end of a CH_4+CO_2 dominated greenhouse [35,36]. The significance of the multiple sulfur isotope record of Stage II and its links to these changes remain to be explored, but two hypotheses have been advanced to account for the smaller $\Delta^{33}S$ variations for Stage II.

One hypothesis attributes the $\Delta^{33}S$ record of Stage II to the onset of oxidative weathering of a large reservoir of continental sulfide with anomalous positive $\Delta^{33}S$. This reservoir would have formed during the first two billion years of Earth history (Stage I). According to this interpretation, the oxygen content of the atmosphere must have increased dramatically at $\sim$2450 Ma, from Stage I levels ($<10^{-5}$ PAL) to levels greater than 10^{-2} PAL. This change would shut down the photochemistry required to produce the signature and would close the exit channels required to transfer the signature to the rock record. Elevated oxygen levels, in turn, imply that the sink provided by reduced volcanic and metamorphic gases was overwhelmed at this time, and sulfide weathering could begin to take up oxygen and stabilize the atmosphere's oxidative capacity. A prediction of this hypothesis is that the sulfate produced by weathering would retain the mass-independent composition of the sulfides being weathered. We estimate the $\Delta^{33}S$ of average Archean sedimentary reduced sulfur to be $0.5\pm0.2‰$ and the $\Delta^{33}S$ of juvenile sulfur to be $\approx0‰$ [26]. The oceanic sulfate produced by oxidative weathering of sedimentary and juvenile sulfide, therefore, would have a $\Delta^{33}S$ between 0 and 0.5‰, consistent with observations from Paleoproterozoic samples (Fig. 1).

A second hypothesis attributes the Stage II $\Delta^{33}S$ record to an atmosphere with levels of oxygen that were intermediate between the very low levels of Stage I and the near-modern levels of Stage III. According to this hypothesis, oxygen and ozone levels would be sufficiently low to allow passage of the deep ultraviolet radiation required for photolysis of SO_2 and SO, but not low enough for the efficient transfer of anomalous $\Delta^{33}S$ to the rock record. Representative calculations suggest that UV fluxes in atmospheres with 10^{-5}–10^{-2} PAL O_2 would be high enough to allow the photolysis to occur [17]. Incomplete homogenization mass-independent signature through atmospheric reactions or isotopic exchange might generate the smaller range of $\Delta^{33}S$ observed in the Stage II record. This hypothesis requires either a precarious balance of oxygen sources relative to reduced volcanic sinks, or another oxygen sink that had the capacity to stabilize oxygen to levels intermediate between those sustained by volcanic and metamorphic emissions (Stage I) or oxidative weathering (Stage III).

5. Stage III (since $\sim$2.0 Ga)

The $\Delta^{33}S$ record of Stage III is characterized by near-zero $\Delta^{33}S$. Variations of $\Delta^{33}S$ are generally much smaller than $\pm0.2‰$ and can usually be attributed to slight changes in the way that sulfur isotope are fractionated by different mass-dependent processes (cf. Figs. 2 and 3). A dominantly mass-dependent multiple sulfur isotope record over the last 2 billion years is strong confirmation that oxygen levels were high enough to close the UV window required to drive the photolysis of SO_2 and SO in the troposphere ($>10^{-2}$ PAL [17]). This interpretation is consistent with a broad variety of other geological evidence [31].

Recent reports indicate, however, that the Stage III record may contain very small contributions from mass-independent chemical reactions. It is known that UV fluxes in today's stratosphere are sufficient to drive mass-independent sulfur photochemistry [17]. Evidence that mass-independent chemistry has continued to occur in the Earth's atmosphere includes small but significant

mass-independent signatures for atmospheric sulfate aerosols and for horizons in ice cores containing the products of stratosphere-piercing plinian volcanic eruptions [13–15]. Both the full characterization of these signatures and the examination of their causes and implications are the subjects of current research.

6. Unanswered questions and future applications

As the protocols to measure precise and accurate $\Delta^{33}S$ and $\Delta^{36}S$ values are improved, we will be able to apply multiple sulfur isotope analyses to a number of questions related to the chemistry of Earth's evolving surface environments. The findings up to this point have raised a number of unresolved issues that include:

- The mechanism of mass-independent fractionation of sulfur isotopes: Work by Marcus and colleagues [37–40] on the anomalous fractionation of oxygen isotopes during the formation of ozone provides a perspective for evaluating and predicting anomalous and mass-independent isotope effects. This theoretical framework has yet to be applied to describe mass-independent fractionation in the sulfur isotope system. It is worth noting that recent theoretical advances concerning the ozone isotope effect came after more than 20 years of experimental characterization. The most urgent need in the present case is for an experimental campaign aimed at elucidating the chemical conditions that are necessary for mass-independent fractionation of sulfur isotopes to occur.

- Implications of the Archean sulfur isotope record: Interpretations of the Stage I sulfur isotope record in terms of SO_2–SO photolysis have provided new insights into atmospheric conditions and the sulfur cycle during the Archean. It is unknown whether other mass-independent chemical reactions may also have contributed to this record. It is also unresolved whether the fraction of sulfur contained in the barite and hydrothermal sulfides is sufficient to close the $\Delta^{33}S$ balance, or whether recycling of hydrothermally altered crust to the mantle early in Earth history is required by the data. Fur-

ther studies should focus on investigating temporal and spatial isotopic variability across Archean sedimentary basins (see [12] for an excellent example of this approach), on analyses of different types of sulfur compounds (e.g. carbonate-associated sulfate, organic sulfur), and on analyses of $\Delta^{36}S$ in addition to $\Delta^{33}S$.

- Earth's surface environment at the beginning of the Proterozoic: A damped, but measurable $\Delta^{33}S$ signature from ~ 2.45 to ~ 2.0 Ga samples implies that atmospheric oxygen levels increased at the start of Stage II. It is unknown whether this signature is principally the signature of the first cycle of oxidative weathering or limited transfer of an anomalous $\Delta^{33}S$ signature to the Earth's surface by an atmosphere stabilized to intermediate oxygen levels (10^{-5}–10^{-2} PAL). A focus on this critical interval is necessary because of its importance for understanding the interaction between Earth's climatic and geochemical evolution (e.g. the causes of Paleoproterozoic glaciations and the possibility of oscillations in atmospheric oxygen levels [41]).

- Muliple sulfur isotope variability on the post-2.0 Ga Earth: Although the very limited $\Delta^{33}S$ variations imply that oxygen levels have remained relatively high since ~ 2.0 Ga, the record of Stage III deserves further examination with high-precision multiple sulfur isotope analyses. Much of the current research on this subject has yet to appear in the peer-reviewed literature, but preliminary results [13–15] emphasize anthropogenic influences on atmospheric sulfur chemistry as well as perturbations caused by extreme geological events like large volcanic eruptions or asteroid impacts. The significance of these observations is unclear. A need exists to incorporate the production and transfer of mass-independent fractionation in the sulfur isotope system into current models of atmospheric chemistry and transport (cf. [42] for a comparable treatment of the ozone isotope effect.)

- Multiple isotope fingerprints of specific metabolic pathways: Model calculations and preliminary experiments suggest that different microbial sulfur metabolisms will produce diagnostic values of $^{33}\lambda$ and $^{36}\lambda$ (Fig. 7) [43]. If this
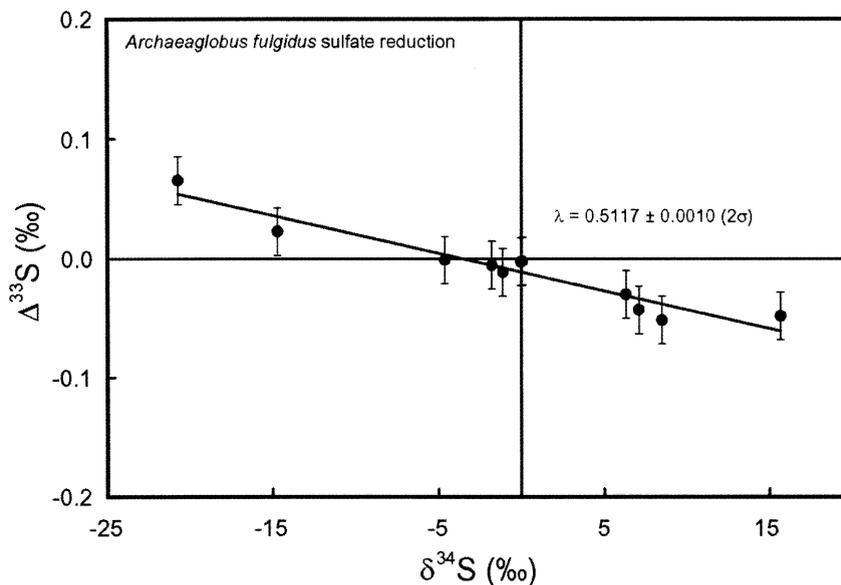
Fig. 7. Plot of $\Delta^{33}S$ vs. $\delta^{34}S$ for sulfate reduction experiments with *Archaeglobus fulgidus* [43]. Error bars are 2σ estimates. The mass-dependent samples that define the terrestrial fractionation line would plot as a horizontal array corresponding to a $^{33}\lambda = 0.515$. The observed $^{33}\lambda$ for the experimental data is 0.5117 ± 0.0010 (2σ). Note that we use variations in $\Delta^{33}S$ to quantify small differences between two mass-dependent fractionation processes, not to imply the operation of mass-independent isotopic fractionation during sulfate reduction.

holds, multiple sulfur isotope analyses will have great application in studies that seek to map out cellular-level metabolic pathways, identify the presence or absence of specific metabolisms in modern natural environments, or to pinpoint when a particular sulfur metabolism shows up in the geological record. The ability to uniquely identify metabolic signatures in the multiple isotopic compositions of extraterrestrial sulfur compounds will have application in astrobiology as well. Before the potential of high-precision multiple sulfur isotope analyses can be exploited, they must be combined with laboratory studies to isolate specific metabolic signatures and with field studies to validate their application.

We have reviewed the recent progress and promise of multiple sulfur isotope research. The application of multiple sulfur isotopes in geochemistry is providing a new perspective on a number of geological problems and is the subject of active research. To date, most research has focused on the implications of anomalous $\Delta^{33}S$ in the ancient rock record. Here we have de-scribed the terrestrial multiple sulfur isotope record in terms of three stages and explored some of the implications of this record for the evolution of Earth's atmosphere. High-precision multiple sulfur isotope measurements have application outside the Archean, however, with new developments to be expected in fields ranging from microbiology to atmospheric dynamics. The geochemical advantages of studying multiple sulfur isotopes went largely unrecognized for nearly 40 years because isotopic analyses were usually limited to the ^{34}S–^{32}S pair. We hope that this review will bring multiple sulfur isotope research to the attention of the wider geochemical community so that future analytical advances and new applications of the rich variety of isotopic effects in this system will proceed in concert.

References

[1] H.C. Urey, The thermodynamic properties of isotopic substances, J. Chem. Soc. (1947) 562–581.

[2] J.R. Hulston, H.G. Thode, Variations in ^{33}S, ^{34}S and ^{36}S contents of meteorites and their relation to chemical and nuclear effects, J. Geophys. Res. 70 (1965) 3475–3484.

[3] J.R. Hulston, H.G. Thode, Cosmic-ray-produced ^{36}S and ^{33}S in metallic phase of iron meteorites, J. Geophys. Res. 70 (1965) 4435–4442.

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

[5] E.D. Young, A. Galy, H. Nagahara, Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, Geochim. Cosmochim. Acta 66 (2002) 1095–1104.

[6] W.G. Mook, Environmental Isotopes in the Hydrological Cycle: Principles and Applications, Vol. I: Introduction - Theory, Methods, Review, 1 (2000).

[7] J. Farquhar, H.M. Bao, M. Thiemens, Atmospheric influence of Earth's earliest sulfur cycle, Science 289 (2000) 756–758.

[8] G.X. Hu, D. Rumble III, P. Wang, Geochim. Cosmochim. Acta, in press (2003).

[9] S.J. Mojzsis, C.D. Coath, J.P. Greenwood, K.D. McKeegan, T.M. Harrison, Mass-independent isotope effects in Archean (2.5-3.8 Ga) sedimentary sulfides determined by ion microprobe multicollection, Geochim. Cosmochim. Acta 67 (2003) 1635–1658.

[10] B. Runnegar, C.D. Coath, J.R. Lyons, K.D. McKeegan, Mass-independent and mass-dependent sulfur processing throughout the Archean, Geochim. Cosmochim. Acta 66 (2002) A655–A655.

[11] A. Bekker, H.D. Holland, D. Rumble, W. Yang, P.L. Wang, L.L. Coetzee, MIF of S, oolitic ironstones, redox sensitive elements in shales, and the rise of atmospheric oxygen, Geochim. Cosmochim. Acta 66 (2002) A64.

[12] S. Ono, J.L. Eigenbrode, A. Pavlov, P. Kharecha, D. Rumble III, J.F. Kasting, K.H. Freeman, New insights into the Archean sulfur cycle from mass-independent sulfur isotope records, Earth Planet. Sci. Lett. 213 (2003) 10.1016/S0012-821X(03)00295-4.

[13] J. Savarino, J. Cole-Dai, S. Bekky, A. Romero, T. Jackson, M.H. Thiemens, Sulfur oxidation chemistry preserved in South Pole snow and ice: The origin of sulfur and oxygen mass-independent fractionations generated in plinian eruptions, EOS Trans. AGU 83 (2002) B61D–11.

[14] A. Romero, M.H. Thiemens, Mass-independent sulfur isotopic compositions in sulfate aerosols: implications for atmospheric chemistry and sulfate deposition, EOS Trans. AGU 81 (2000) A51B–07.

[15] A. Romero, M.H. Thiemens, Mass-independent sulfur isotopic compositions in sulfate aerosols and surface sulfates derived from atmospheric deposition: possible sources of the mi anomaly and implications for atmospheric chemistry, EOS Trans. AGU 83 (2002) B71A–0731.

[16] J. Farquhar, H.M. Bao, M.H. Thiemens, G.X. Hu, D. Rumble, Questions regarding Precambrian sulfur isotope fractionation - Response, Science 292 (2001) U6–U7.

[17] J. Farquhar, J. Savarino, S. Airieau, M.H. Thiemens, Observation of wavelength-sensitive mass-independent sulfur isotope effects during SO_2 photolysis: Implications for the early atmosphere, J. Geophys. Res. 106 (2001) 32829–32839.

[18] J. Farquhar, J. Savarino, M.H. Thiemens, T.L. Jackson, Evidence of atmospheric sulphur in the martian regolith from sulphur isotopes in meteorites, Nature 404,

[19] M.H. Thiemens, J.E. HeidenreichIII, The mass-independent fractionation of oxygen: A novel isotope effect and its possible cosmochemical implications, Science 219 (1983) 1073–1075.

[20] S.K. Bains-Sahota, M.H. Thiemens, A mass-independent sulfur isotope effect in the nonthermal formation of S_2F_{10}, J. Chem. Phys. 90 (1989) 6099–6109.

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

[22] J.J. Colman, X.P. Xu, M.H. Thiemens, W.C. Trogler, Photopolymerization and mass-independent sulfur isotope fractionations in carbon disulfide, Science 273 (1996) 774–776.

[23] C. Sagan, C. Chyba, The early faint sun paradox: Organic shielding of ultraviolet-labile greenhouse gases, Science 276 (1997) 1217–1221.

[24] A.A. Pavlov, J.F. Kasting, Mass-independent fractionation of sulfur isotopes in archean sediments: strong evidence for an anoxic Archean atmosphere, Astrobiology 2 (2002) 27–41.

[25] J.F. Kasting, Earth history - The rise of atmospheric oxygen, Science 293 (2001) 819–820.

[26] J. Farquhar, B.A. Wing, K.D. McKeegan, J.W. Harris, P. Cartigny, M.H. Thiemens, Mass-independent sulfur of inclusions in diamond and sulfur recycling on early Earth, Science 298 (2002) 2369–2372.

[27] J.A. Karhu, H.D. Holland, Carbon isotopes and the rise of atmospheric oxygen, Geology 24 (1996) 867–870.

[28] D.A. Evans, N.J. Beukes, J.L. Kirschvink, Low-latitude glaciation in the Palaeoproterozoic era, Nature 386 (1997) 262–266.

[29] A. Bekker, A.J. Kaufman, J.A. Karhu, N.J. Beukes, Q.D. Swart, L.L. Coetzee, K.A. Eriksson, Chemostratigraphy

of the paleoproterozoic Duitschland Formation, South Africa: Implications for coupled climate change and carbon cycling, Am. J. Sci. 301 (2001) 261–285.

[30] R. Rye, H.D. Holland, Geology and geochemistry of paleosols developed on the Hekpoort basalt, Pretoria Group, South Africa, Am. J. Sci. 300 (2000) 85–141.

[31] R. Rye, H.D. Holland, Paleosols and the evolution of atmospheric oxygen: A critical review, Am. J. Sci. 298 (1998) 621–672.

[32] K.S. Habicht, M. Gade, B. Thamdrup, P. Berg, D.E. Canfield, Calibration of sulfate levels in the Archean Ocean, Science 298 (2002) 2372–2374.

[33] D.E. Canfield, Biogeochemistry of sulfur isotopes, Rev. Mineral. Geochem. 43 (2001) 607–636.

[34] D.E. Canfield, K.S. Habicht, B. Thamdrup, The Archean sulfur cycle and the early history of atmospheric oxygen, Science 288 (2000) 658–661.

[35] A. Pavlov, M.T. Hurtgen, J.F. Kasting, M.A. Arthur, Methane-rich Proterozoic atmosphere?, Geology 31 (2003) 87–90.

[36] A.A. Pavlov, J.F. Kasting, J.L. Eigenbrode, K.H. Freeman, Organic haze in Earth's early atmosphere: Source of low-^{13}C Late Archean kerogens?, Geology 29 (2001) 1003–1006.

[37] B.C. Hathorn, R.A. Marcus, An intramolecular theory of the mass-independent isotope effect for ozone. I, J. Chem. Phys. 111 (1999) 4087–4100.

[38] Y.Q. Gao, R.A. Marcus, On the theory of the strange and unconventional isotopic effects in ozone formation, J. Chem. Phys. 116 (2002) 137–154.

[39] Y.Q. Gao, R.A. Marcus, Strange and unconventional isotope effects in ozone formation, Science 293 (2001) 259–263.

[40] B.C. Hathorn, R.A. Marcus, An intramolecular theory of the mass-independent isotope effect for ozone. II. Numerical implementation at low pressures using a loose transition state, J. Chem. Phys. 113 (2000) 9497–9509.

[41] B.A. Wing, E. Brabson, J. Farquhar, A.J. Kaufman, D. Rumble, A. Bekker, Δ^{33}S, δ^{34}S and δ^{13}C constraints on the Paleoproterozoic atmosphere during the earliest Huronian glaciation, Geochim. Cosmochim. Acta 66 (2002) 840–840.

[42] J.R. Lyons, Transfer of mass-independent fractionation in ozone to other oxygen-containing radicals in the atmosphere, Geophys. Res. Lett. 28 (2001) A3231–A3234.

[43] J. Farquhar, D.T. Johnston, B.A. Wing, K.S. Habicht, D.E. Canfield, S.A. Airieau, M.H. Thiemens, Multiple sulfur isotopic interpretations of biosynthetic pathways: Implications for biological signatures in the sulfur isotope record, Geobiology 1 (2003) in press.

[44] T. Ding, S. Valkiers, H. Kipphardt, P. De Bievre, P.D.P. Taylor, R. Gonfiantini, R. Krouse, Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur, Geochim. Cosmochim. Acta 65 (2001) 2433–2437.

[45] A. Angert, S. Rachmilevitch, E. Barkan, B. Luz, Effects of photorespiration, the cytochrome pathway, and the alternative pathway on the triple isotopic composition of atmospheric O_2, Glob. Biogeochem. Cycles 17 (2003) 10.1029/2002GB001933.

[46] M.F. Miller, Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance, Geochim. Cosmochim. Acta 66 (2002) 1881–1889.

[47] D.D. Clayton, S. Ramadurai, On presolar meteoritic sulphides, Nature 265 (1977) 427–428.

[48] R.N. Clayton, L. Grossman, T.K. Mayeda, A component of primitive nuclear composition in carbonaceous meteorites, Science 182 (1973) 485–488.

[49] N.J. Turro, Influence of nuclear spin on chemical reactions: Magnetic field and magnetic isotope effects (A Review), Proc. Natl. Acad. Sci. 80 (1983) 609–621.

[50] D. Heymann, T.E. Yancey, W.S. Wolbach, M.H. Thiemens, E.A. Johnson, D. Roach, S. Moecker, Geochemical markers of the Cretaceous-Tertiary boundary event at Brazos River, Texas, USA, Geochim. Cosmochim. Acta 62 (1998) 173–181.

[51] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Wiley, New York, 1962, 632 pp.

[52] P. Richet, Y. Bottinga, M. Javoy, Review of hydrogen, carbon, nitrogen, oxygen, sulfur, and chlorine stable isotope fractionation among gaseous molecules, Ann. Rev. Earth Planet. Sci. 5 (1977) 65–110.

[53] H.C. Urey, C.A. Bradley, The vibrations of pentatonic tetrahedral molecules, Phys. Rev. 38 (1931) 1969–1978.

[54] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds part A: Theory and Applications in Inorganic Chemistry, Van Nostrand, Reinhold, New York, 1997, 387 pp.

[55] L. Peter, B. Meyer, Preparation and raman-spectra of thallium(I) disulfite and thallium (I) sulfite, Inorg. Chem. 24 (1985) 3071–3073.

[56] P. Deines, A note on intra-elemental isotope effects and the interpretation of non-mass-dependent isotope variations, Chem. Geol. 199 (2003) 172–182.

James Farquhar obtained his B.S. Degree from Washington and Lee University in 1987, M.S. degree from the University of Chicago in 1990, and his Ph.D. degree from the University of Alberta in 1995. He was a postdoctoral fellow at the Geophysical Laboratory, Carnegie Institution of Washington from 1995 to 1997, and at the University of California San Diego, 1997–2000. He has been an Assistant Professor in the Department of Geology and the Earth System Science Interdisciplinary Center at the University of Maryland College Park since 2000. He was awarded the F.W. Clarke medal of the Geochemical Society in 2000.

Boz Wing obtained his BA from Harvard University in 1996 and his MA from Johns Hopkins University in 1998. He has been a research assistant in the Department of Geology and the Earth System Science Interdisciplinary Center at the University of Maryland since 2001.