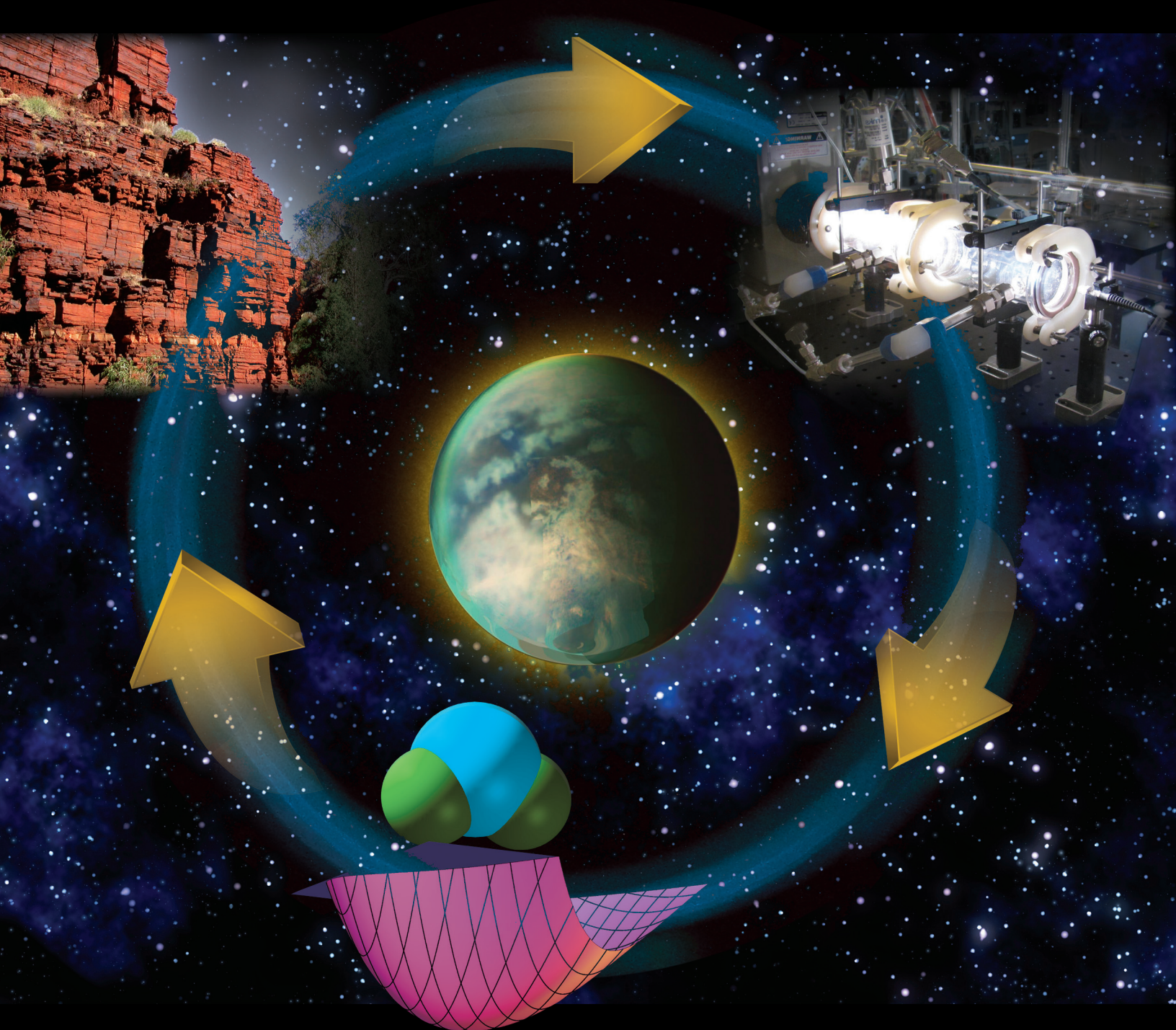SUMMARY REPORT FROM WORKSHOP ON

"Mass-Independent Fractionation of Sulfur Isotopes: Carriers and Sources"

Authors: Shawn D. Domagal-Goldman, Bill Poirier, Boswell Wing

This document is the summary of a workshop held in the summer of 2011 to explore future directions in research on mass-independent fractionation of sulfur isotopes.

The cover image represents the interdisciplinary discussions fostered at the workshop. These discussions brought together physical chemists (represented by the SO_2 potential energy surface), field geologists (represented by the rock outcrop), and laboratory chemists and geochemists (represented by the SO_2 photolysis chamber). The future research directions described in this document will produce a path towards a better understanding of the early Earth's atmosphere and biota, which may have had organic hazes similar to modern Titan (center image).

Plot of SO_2 potential energy surface by Bill Poirier. Photo of an Archean outcrop from Australia, deposited at a time that the mass-independent fractionation signal was prominent, by Professor Simon Poulton, Newcastle University. Photo of SO_2 photolysis chamber by Professor Shuhei Ono, Massachusetts Institute of Technology. Picture of Titan from NASA.

Cover illustration and report design by Alissa Taylor, www.actdesign.us.

SUMMARY REPORT FROM WORKSHOP ON

"Mass-Independent Fractionation of Sulfur Isotopes: Carriers and Sources"

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BACKGROUND OF THE S-MIF WORKSHOP

INTRODUCTION TO MASS-INDEPENDENT FRACTIONATION OF SULFUR ISOTOPES (S-MIF)

Just over a decade ago, a team of geochemists made an astounding discovery, altering a long-standing debate about the history of the planet. While measuring the chemical composition of ancient rock, Dr. James Farquhar and his colleagues at the University of California, San Diego (UCSD) found surprisingly large quantities of certain sulfur isotopes that almost certainly must have been produced or preserved in an oxygen-free atmosphere. Even more remarkably, the trends they uncovered exist only in rock samples dating prior to 2.4 billion years ago, suggesting that the atmosphere underwent a profound change at that precise time. The finding confirmed for many the long-held theory suggested by previous rock analyses that, during this era, oxygen arose from being a trace gas to a substantial component of the Earth's atmosphere—a great event that caused permanent changes in both the atmosphere itself and the biosphere, eventually enabling the emergence of complex life.

For researchers, the discovery provided a direct link between atmospheric composition and signals in the rock record and a new metric for the investigation of early Earth. Sulfur isotopes in rock have long been a tool used to analyze the chemistry of the ancient environment. However, all isotopic measurements to that point had exhibited a predictable trend: the isotope ratios changed consistently and always in proportion to one another, and deviations from these linear relationships were miniscule. Dr. Farquhar's serendipitous discovery presented isotopic ratios that diverged significantly from all previous measurements, a deviation referred to as "Sulfur Mass-Independent Fractionation" (S-MIF). Since then, S-MIF has provided geologists with a powerful new analytical approach. The geological/geochemical community now recognizes that not only are the proportions of sulfur isotopes meaningful, but additionally, that deviations from

the expected isotopic trends are also capable of providing important information about the history of the planet.

Currently, wide-ranging investigations are utilizing S-MIF to uncover new details about the Earth's early atmosphere. One critical avenue of research aims to improve the timing of geological events surrounding the rise of oxygen—for instance, the disappearance of methane and the onset of global glaciation. Other investigations are utilizing the size of the S-MIF signal, which fluctuated over time prior to the rise of oxygen, to examine the relationship between the anoxic state of the planet and the microbial life that existed at that time.

> THE DIRECT RELATIONSHIP BETWEEN THE S-MIF SIGNAL AND THE ATMOSPHERE HAS YET TO BE UNDERSTOOD AT A MOLECULAR LEVEL. WITHOUT THIS THEORETICAL FOUNDATION, MANY QUESTIONS PERSIST.

However, the direct relationship between the S-MIF signal and the atmosphere has yet to be understood at a molecular level. Without this theoretical foundation, many questions persist. What caused S-MIF to appear in the early rock record? What precise relationship does the record have to the atmosphere? Scientists have proposed various theories about the generation of the S-MIF signal and about the processes that caused it to fluctuate in oxygen-free environments. A few even remain skeptical about conclusions drawn from the S-MIF signature, and maintain that the S-MIF signal occurs independently of atmospheric composition. In order to evaluate these theories and substantiate arguments about the influence of atmospheric oxygen, the field still requires a better understanding of the chemistry of S-MIF. The future of research in this area depends upon

pinpointing the chemical and photophysical processes responsible for: 1) the creation of the S-MIF signature; 2) the process by which the S-MIF signal was transferred to ancient rock; and 3) the preservation of the signal in the rock record.

To facilitate the next stage of research, NASA's Exobiology Program, NSF's Chemistry Special Projects program, and NSF's Geobiology and Low-Temperature Geochemistry program established a three-day workshop in the summer of 2011. The goal of the gathering in Alexandria, VA, was to generate ideas from a variety of experts about how the critical questions in S-MIF chemistry may be addressed. Participants had backgrounds in the following fields: astrobiology, isotope analysis, geobiology, atmospheric modeling, geochemistry, chemical dynamics, and experimental and computational chemistry.

This document is a summary of the workshop entitled "Mass-Independent Fractionation of Sulfur Isotopes: Carriers and Sources," including a list produced by participants of research topics with high potential to advance the field. The document also stands as an invitation to the wider scientific community to consider applying tools and approaches that might be novel to S-MIF studies and capable of furthering this area.

THE MOTIVATION FOR THE S-MIF WORKSHOP

NASA's Exobiology Program has long recognized the opportunity presented by S-MIF to study the planet. Among the program's goals are to "understand how life on Earth and its planetary environment have co-evolved through geological time." S-MIF provides an unprecedented glimpse of early Earth and of the interrelationship between the planet and the microbes that inhabited it. Further, it provides astrobiologists with a data-based relic of an anoxic biosphere, and is thus capable of broadening the detectable traces of life on other planets. Thus, the program has continually funded research regarding early Earth, and in the last ten years has supported research that has significantly expanded knowledge about the S-MIF record.

However, in the summer of 2010, members of NASA's Exobiology Program recognized that

further progress in the study of S-MIF would require expertise from new disciplines and perspectives. It was determined that a workshop would be the best way to bring international experts together to review the status of the field, discuss current barriers impeding progress, and strategize new avenues of research. In particular, it was proposed that a dialogue-based meeting centered around group discussions would be the best way to foster new collaborations.

IN THE SUMMER OF 2010, MEMBERS OF NASA'S EXOBIOLOGY PROGRAM RECOGNIZED THAT FURTHER PROGRESS IN THE STUDY OF S-MIF WOULD REQUIRE EXPERTISE FROM NEW DISCIPLINES AND PERSPECTIVES.

Members of the Exobiology Program began by identifying the areas of expertise in which investigators had already been studying S-MIF signals and their implications. Among the current researchers were geochemists observing isotopic fractionation in the laboratory, atmospheric scientists creating computational models of signals that occur in the rock record, geologists measuring those signals, and biologists utilizing the S-MIF signal to make inferences about Earth's history.

There was broad recognition that the field severely lacks a molecular level understanding of fundamental chemical reactions related to S-MIF production and preservation. Even though several theories exist regarding S-MIF generation, including photolysis reactions, reactions with isotopic symmetry, and heterogeneous reactions on surface interfaces, none of the theories have been adequately substantiated. The physical chemistry community has the expertise required for a detailed molecular-level understanding of such phenomena. However, there was also acknowledgement that physical chemists might not be aware of S-MIF-related investigations or of how their community might be able to advance the field. The vision for the workshop was to create

an extended opportunity to introduce experts in physical chemistry to S-MIF research and to discuss and brainstorm how contributions on a molecular-level may lead to new insights. The long-term goal is to incorporate the lens of molecular science in S-MIF research and to engage and actively involve physical chemists in future studies.

SELECTION OF WORKSHOP PARTICIPANTS

NASA's Exobiology Program looked to two scientists to co-chair the workshop: geochemist Dr. Boswell Wing (McGill University), who studies S-MIF; and physical chemist Dr. William Poirier (Texas Tech University), whose expertise is in quantum dynamics of chemical reactions, though not specifically related to S-MIF. The co-chairs were funded by NSF's Chemistry Special Projects program and the Geobiology and Low-Temperature Geochemistry program to provide support for a post-workshop publication and to assist with outreach to the physical chemistry community.

After the proposal was awarded, an organizing committee was formed consisting of the co-chairs and two members of NASA's Astrobiology Program (Dr. Shawn Domagal-Goldman and Dr. Michael New), with input from NSF's Chemical Theory, Models and Computational Methods Program (Dr. Evelyn Goldfield). The first task for the organizing committee was to draft a list of potential participants to be invited to the fully-funded workshop. The final invitation list included individuals with a variety of backgrounds needed to broaden S-MIF research: geochemistry, atmospheric modeling, and physical chemistry, including subdisciplines within those areas. Invitees were chosen based on the relevance of their backgrounds and publications to the workshop's mission; in particular, those whose areas of expertise overlapped with more than one workshop objective were given preference. Consideration was given to represent a diversity of institutions, genders, ages, and geographic regions. A number of graduate student and postdoctoral researchers from similar disciplines were also invited.

THE VISION FOR THE WORKSHOP WAS TO CREATE AN EXTENDED OPPORTUNITY TO INTRODUCE EXPERTS IN PHYSICAL CHEMISTRY TO S-MIF RESEARCH AND TO DISCUSS AND BRAINSTORM HOW CONTRIBUTIONS ON A MOLECULAR-LEVEL MAY LEAD TO NEW INSIGHTS.

THE LONG-TERM GOAL IS TO INCORPORATE THE LENS OF MOLECULAR SCIENCE IN S-MIF RESEARCH AND TO ENGAGE AND ACTIVELY INVOLVE PHYSICAL CHEMISTS IN FUTURE STUDIES.

Responses from researchers began appearing immediately, with many expressions of enthusiasm about the concept of broadening the field. Workshop organizers were particularly pleased by the interest in the topic expressed by the physical chemistry community. The final list of 33 participants, along with their area of expertise, is provided in an appendix to this document.

STATED OBJECTIVES OF THE WORKSHOP

The objectives of the workshop were to:

1. Review state-of-knowledge regarding S-MIF in the rock record.

2. Review experiments and calculations that have been published on S-MIF sources.

3. Review state-of-art in pertinent reaction dynamics experiments, measurements, theories, and calculations.

4. Identify and outline future research that may be capable of resolving questions about the sources and carriers of S-MIF.

WORKSHOP PROCEEDINGS

OVERVIEW TALKS: A DETAILED INTRODUCTION TO S-MIF RESEARCH AND ANALOGOUS STUDIES

The workshop commenced with an introduction to the goals of the S-MIF workshop, delivered by the workshop organizers. Three overview talks followed: an introduction to the geological S-MIF research by Dr. James Farquhar; a description of chemical physics reaction dynamics tools as they have been applied to oxygen MIF (O-MIF) and could be applied to S-MIF, by Dr. Dmitri Babikov; and an overview of previous interdisciplinary collaborations in S-MIF and O-MIF research by Dr. Gerardo Dominguez and Dr. Mark Thiemens. These presentations are now available online at: http://is.gd/s_mif.

Sulfur Isotopes in the Rock Record (Dr. James Farquhar)

The first overview talk provided an introduction to S-MIF tools, terminology, and notation. It also described the history and current state of geological S-MIF research.

S-MIF is inherently different from mass-dependent fractionation (MDF), which is the premier tool for quantifying sulfur flow through modern and ancient environments (see Box 1). With the use of MDF, it is possible to "fingerprint" sulfur sources and understand whether the sulfur isotope signatures are due

> S-MIF IS INHERENTLY DIFFERENT FROM MASS-DEPENDENT FRACTIONATION (MDF), WHICH IS THE PREMIER TOOL FOR QUANTIFYING SULFUR FLOW THROUGH MODERN AND ANCIENT ENVIRONMENTS (SEE BOX 1).

to biological or non-biological processes. The primary source of MDF's diagnostic power is that it provides a straightforward framework for describing the fractionation relationships among sulfur isotope ratios. In contrast, S-MIF reveals significant isotopic *deviations* from the predicted proportions that define MDF. The standard MDF pattern is defined by relative differences in ^{33}S-^{32}S ratios that are approximately one half the size of relative differences in ^{34}S-^{32}S ratios (see Figure 1) and by relative differences in ^{36}S-^{32}S ratios that

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BOX 1. SIMPLE DERIVATION OF MASS-DEPENDENT FRACTIONATION:

Let a and b label specific sulfur isotopes, ^aS and ^bS, with a = {32,33,34,36}, b = {32,33,34,36}, and $a \neq b$. Consider the hypothetical isotopic substitution reaction, $^aSA + {}^bSB \leftrightarrows {}^bSA + {}^aSB$. The equilibrium constant is given by:

$$K^{ab}_{eq} = \exp(-\Delta E_{ab}/kT) = \frac{[^bSA]_{eq}[^aSB]_{eq}}{[^aSA]_{eq}[^bSB]_{eq}},$$

where $\Delta E_{ab} = E(^bSA) + E(^aSB) - E(^aSA) - E(^bSB)$ is the energy (or free energy) difference between reactant and product species. Using, e.g., zero-point-energy arguments, it is easy to show that $\Delta E_{ab} \propto (1/\sqrt{m_a} - 1/\sqrt{m_b})$. Now ^{32}S is the lightest and most prevalent isotope, and will thus be taken as the reference, i.e. henceforth, a=32. Introducing a third isotope c, and exploiting the fact that the S isotope mass differences are small, one can derive the approximate relation, $\Delta E_{ab} / \Delta E_{ac} \approx (1/m_a - 1/m_b)/(1/m_a - 1/m_c) = \lambda_{eq}$. Evaluating the logarithm of both sides of the first equation above, for both K^{ab}_{eq} and K^{ac}_{eq}, and setting a=32, yields:

$$\ln\left(\frac{[^bSA]_{eq}[^{32}SB]_{eq}}{[^{32}SA]_{eq}[^bSB]_{eq}}\right) = \ln\left(\frac{[^cSA]_{eq}[^{32}SB]_{eq}}{[^{32}SA]_{eq}[^cSB]_{eq}}\right)\left(\frac{1/m_{32} - 1/m_b}{1/m_{32} - 1/m_c}\right).$$

BOX 2. DEFINITION OF "DELTA" VALUES:

Let a and b label specific sulfur isotopes, with a=32 the reference isotope as described in the previous box. The standard abundances for the four isotopes b = {32,33,34,36}, as defined by the Vienna-Cañon Diablo Troilite scale, are taken to be {0.9503957, 0.0074865, 0.0419719, 0.0001459}. These abundances define the standard isotope ratios (^br) of the rare isotopes relative to the reference isotope. In a given sample containing the compound SA, the isotope fractionation enhancement for ^bS taken with respect to the reference isotope a=32 and the standard ratios, can be defined as follows:

$$\delta^bS = \left[\left(\frac{[^bSA]}{[^{32}SA]} - {}^br\right)\Big/ {}^br\right].$$

The δ values are typically expressed as relative parts per thousand variations (‰ notation), which requires multiplying the above expression by 1000. Capital Delta (Δ) values are used to identify S-MIF, and therefore the definition requires a second reference isotope, taken to be ^{34}S. The definition is:

$$\Delta^bS = \delta^bS - \left[\left(1 + \delta^{34}S\right)^{{}^b\lambda_{eq}} - 1\right],$$

where ${}^b\lambda_{eq} = (1/m_{32} - 1/m_b) / (1/m_{32} - 1/m_{34})$. Note that ${}^b\lambda_{eq}$ is equal to λ_{eq} from the previous box, with the identification of the appropriate reference isotopes, a=32 and c=34; thus for example, ${}^{33}\lambda_{eq} \approx 0.515$. Also, the arbitrary standard (V-CDT) can be taken as the $[SB]_{eq}$ of the previous box. As with δ values, Δ values are typically expressed as relative parts per thousand variations (‰ notation), which requires multiplying the above expression by 1000.

While the S-MDF relation given at the end of the previous box implies $\Delta^bS_{eq} = 0$, small variations in ${}^b\lambda$ are associated with different S-MDF processes (or different standards), which can cause slight deviations from $\Delta^bS = 0$. Conversely, large-magnitude values of Δ^bS imply S-MIF. Precise thresholds between S-MIF and S-MDF are not defined when dealing with small-magnitude Δ^bS values, but a rough laboratory rule-of-thumb for $\Delta^{33}S$ values is that magnitudes greater than 0.5 ‰ (parts per thousand) signal the presence of S-MIF. We note that different definitions for Δ values have been used in the literature.

are approximately twice the size of relative differences in ^{34}S-^{32}S ratios. S-MIF produces anomalous increases or decreases of ^{33}S-^{32}S and ^{36}S-^{32}S ratios, relative to those expected from the accompanying ^{34}S-^{32}S ratios. These anomalies are quantified by $\Delta^{33}S$ or $\Delta^{36}S$ values (see Box 2).

Although the precise source of the S-MIF signal preserved in the rock record remains a mystery, some intriguing clues suggest a possible origin. As mass independent fractionation is a characteristic feature of many atmospheric compounds, and S-MIF has been produced in the laboratory in photochemistry experiments, it is conceivable that the S-MIF originated in the atmospheric environment. Studying S-MIF preserved in rock opens up the tantalizing possibility of assaying the composition of Earth's early atmospheres.

In the geologic record of S-MIF, four fundamental observations pose conundrums. To fully exploit the forensic capabilities of S-MIF, and to determine its origin, these characteristics must be explained. First, S-MIF is present in the ancient rock record, up until the point at which it definitively disappears, 2.4 billion years ago (Figure 2). Second, the magnitude of the S-MIF signal in the geologic record fluctuates. Third, anomalous enrichments in ^{33}S are consistently coupled with anomalous depletions in ^{36}S, and vice versa (Figure 3). Fourth, anomalous enrichments in ^{33}S are often, but not always, coupled with ^{34}S enrichments (Figure 4).

One conceptual model for these first-order features suggests that the presence of S-MIF is directly linked to the state of the ancient atmosphere. Photochemical experiments in the laboratory have produced S-MIF in reduced (e.g., elemental sulfur) and oxidized sulfur compounds (e.g., sulfate aerosols) by using short-wavelength ultraviolet light to dissociate sulfur dioxide gas

(SO$_2$). In order for a similar process to occur on early Earth, ultraviolet light of sufficient intensity must have pervaded the atmosphere, making it likely that an ozone shield was not present at the time. Since ozone levels are directly dependent upon the presence of oxygen (O$_2$), the absence of O$_3$ suggests the absence of widespread O$_2$. In this model, the sudden disappearance of S-MIF at 2.4 billion years ago suggests the rise of atmospheric oxygen. Significantly, this interpretation is consistent with other geologic studies to date that suggest an increase in Earth's oxidation state at this time.

However, even if the atmospheric model is valid, the specific mechanisms that produced S-MIF, and led to the signature isotopic deviations in the geologic record (Figures 3 and 4), remain unknown. Ongoing studies addressing these questions include: the refinement of the S-MIF timeline at progressively higher resolutions; the development of hypotheses for fluctuations

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in the magnitude of S-MIF prior to 2.4 billion years ago; the investigation of "missing" components of the geological S-MIF record; and new experimental work that could give direction to potential mechanisms for S-MIF production. These studies, and those that evolve from them, will open new doors towards understanding

FIGURE 1 – MULTIPLE SULFUR ISOTOPE MEASUREMENTS FROM ROCKS YOUNGER THAN 2.0 BILLION YEARS OLD
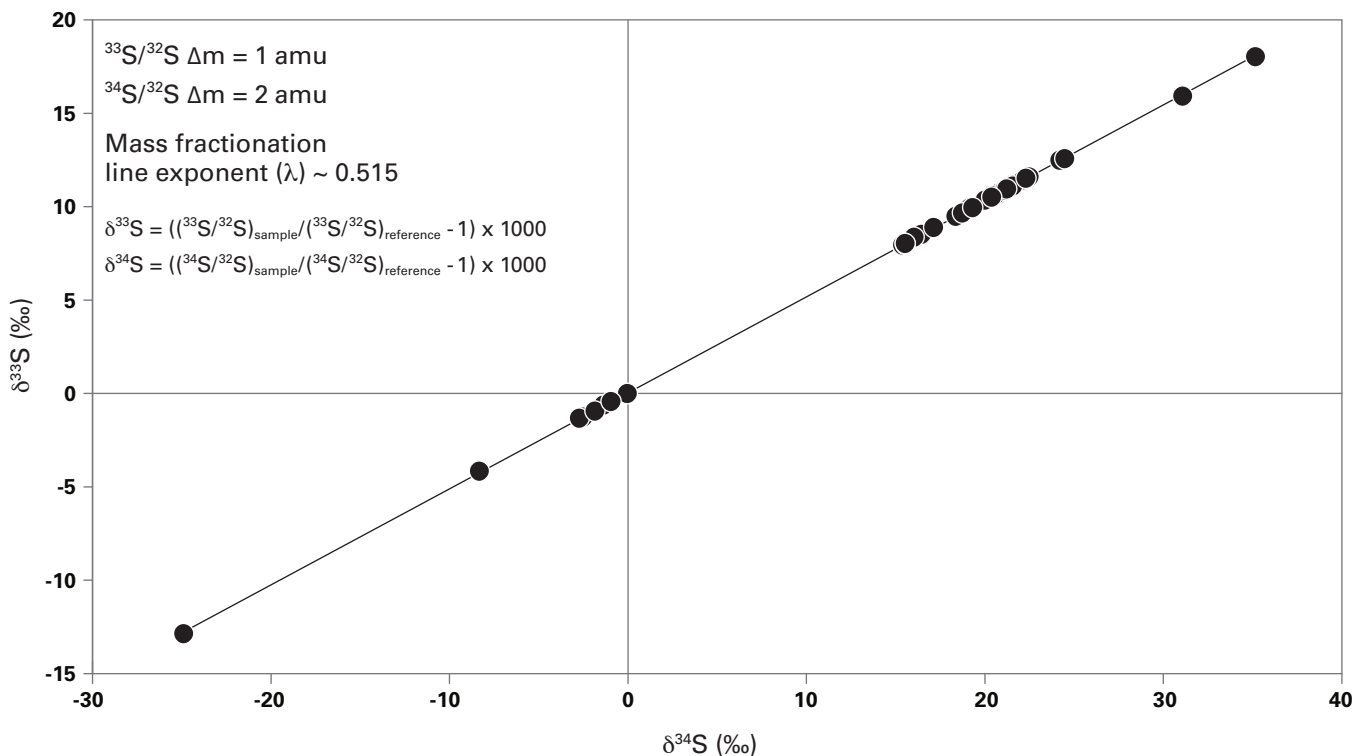
These data define the mass-dependent fractionation (MDF) line, which has a slope (λ) of 0.515. The MDF pattern results from the fact that ^{33}S is 1 atomic mass unit (amu) greater than ^{32}S, and ^{34}S is 2 amu greater than ^{32}S, therefore the relative differences in ^{33}S-^{32}S ratios will be approximately half the size of the relative differences in ^{34}S-^{32}S ratios. See Box 2 for a discussion of δ notation and of the expected value for λ. Plot from Farquhar and Wing (2003).

FIGURE 2 – VARIATION IN THE GEOLOGIC RECORD OF S-MIF THROUGH TIME
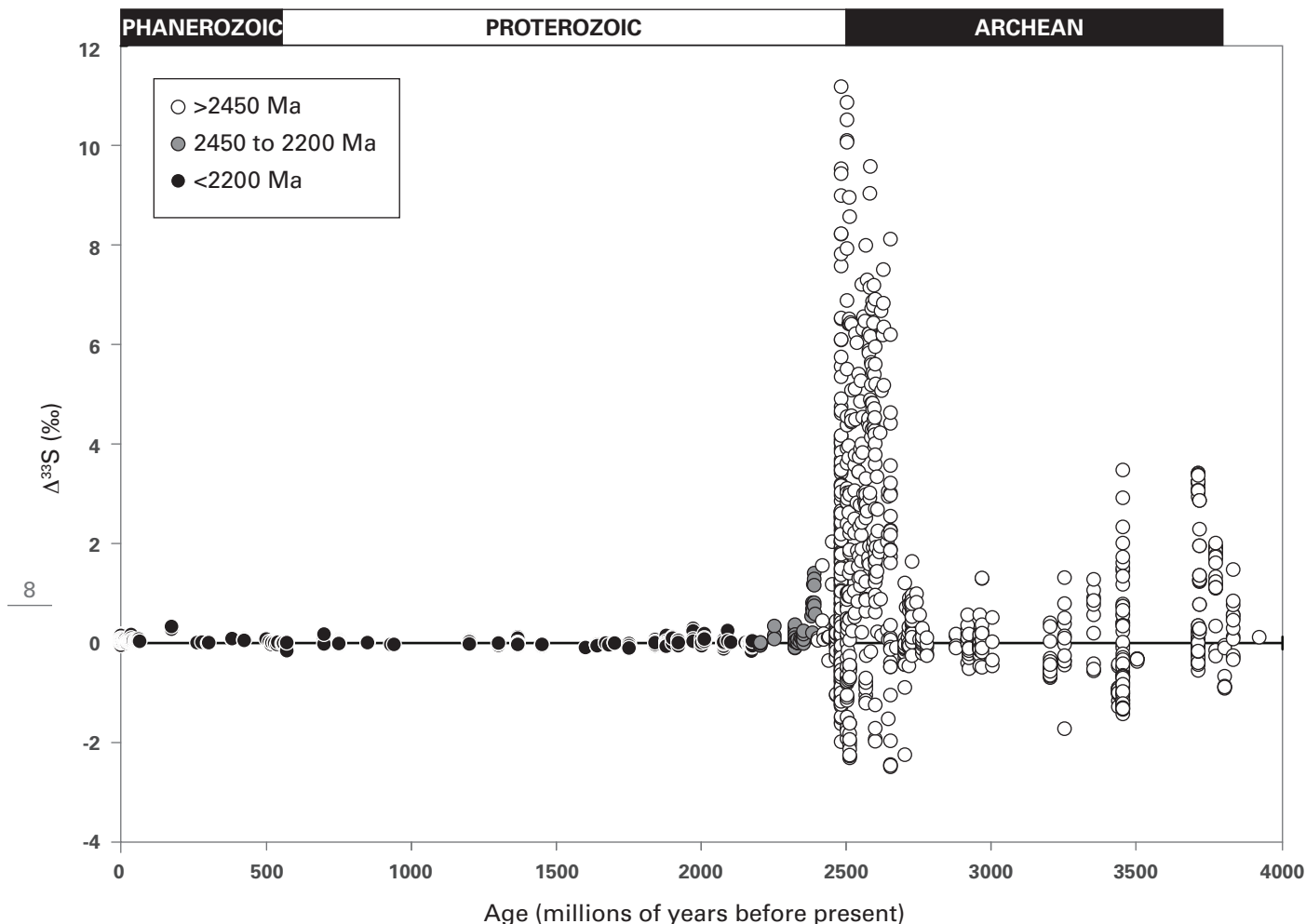
White circles indicate samples older than 2450 Ma, gray circles indicate samples younger than 2450 Ma but older than 2200 Ma, and black circles indicate samples younger than 2200 Ma. Geologic Eons are indicated at the top of the figure. The first-order feature in the record is an abrupt and apparently permanent disappearance of S-MIF around the boundary between the Archean and Proterozoic Eons. Second-order features in the record include the asymmetry in the record throughout much of the Archean Eon, the contraction in the magnitude of $\Delta^{33}S$ values in the middle of the Archean Eon, and the expansion in the magnitude of $\Delta^{33}S$ values at the end of the Archean Eon. Compilation after (Johnston, 2011).

the surface environment of early Earth, the rise of oxygen and its effect on life, and similar atmospheric and geologic conditions that may exist on other planets.

Chemical Physics Tools: Quantum Reaction Dynamics and O-MIF (Dr. Dmitri Babikov)

Because S is only one row removed from O on the periodic table, fundamental similarities are likely to exist between S-MIF and oxygen MIF (O-MIF). In order to understand the underlying

mechanisms of S-MIF, and how the mechanisms may be elucidated, it is helpful to consider previous research strategies used to understand O-MIF. The study of O-MIF has been an extremely active area of research, especially because of its relation to ozone (O_3) depletion in Earth's modern atmosphere.

The second overview talk demonstrated the essential relevance of the tools and techniques of chemical physics, particularly quantum dynamics, for understanding O-MIF. Quantum dynamics is the
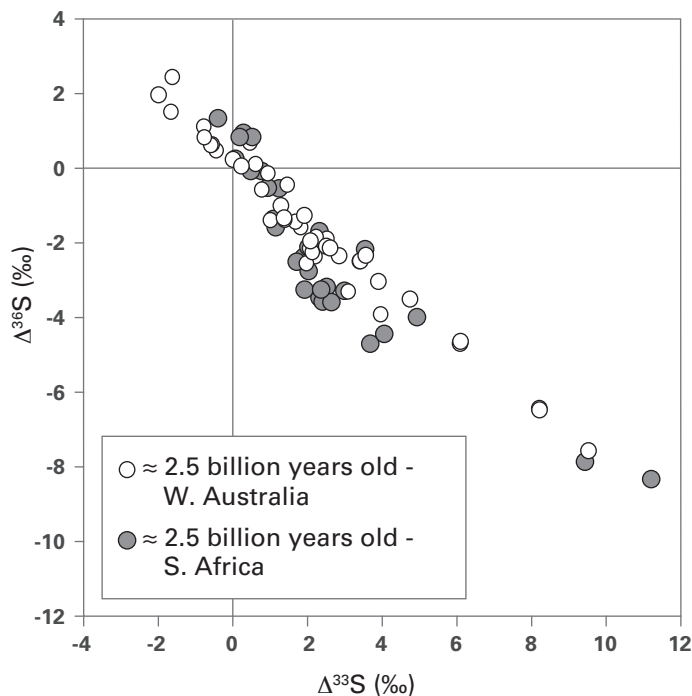
FIGURE 3 – TIGHT CORRELATION BETWEEN $\Delta^{36}S$ VALUES AND $\Delta^{33}S$ VALUES FROM ≈2500 MILLION-YEAR-OLD ROCKS.

This correlation is shared by many samples throughout the Archean, and the slope of ≈-1 reflects a consistent origin for S-MIF during this time (Farquhar et al., 2000). These correlations are strikingly different than those identified in samples from the middle of the Archean Eon, pointing to the possibility of multiple mechanisms for S-MIF generation (Farquhar et al., 2007). Data from (Kaufman et al., 2007; Ono et al., 2009)

FIGURE 4 – VARIATION IN THE GEOLOGIC RECORD OF S-MIF AND S-MDF THROUGH TIME
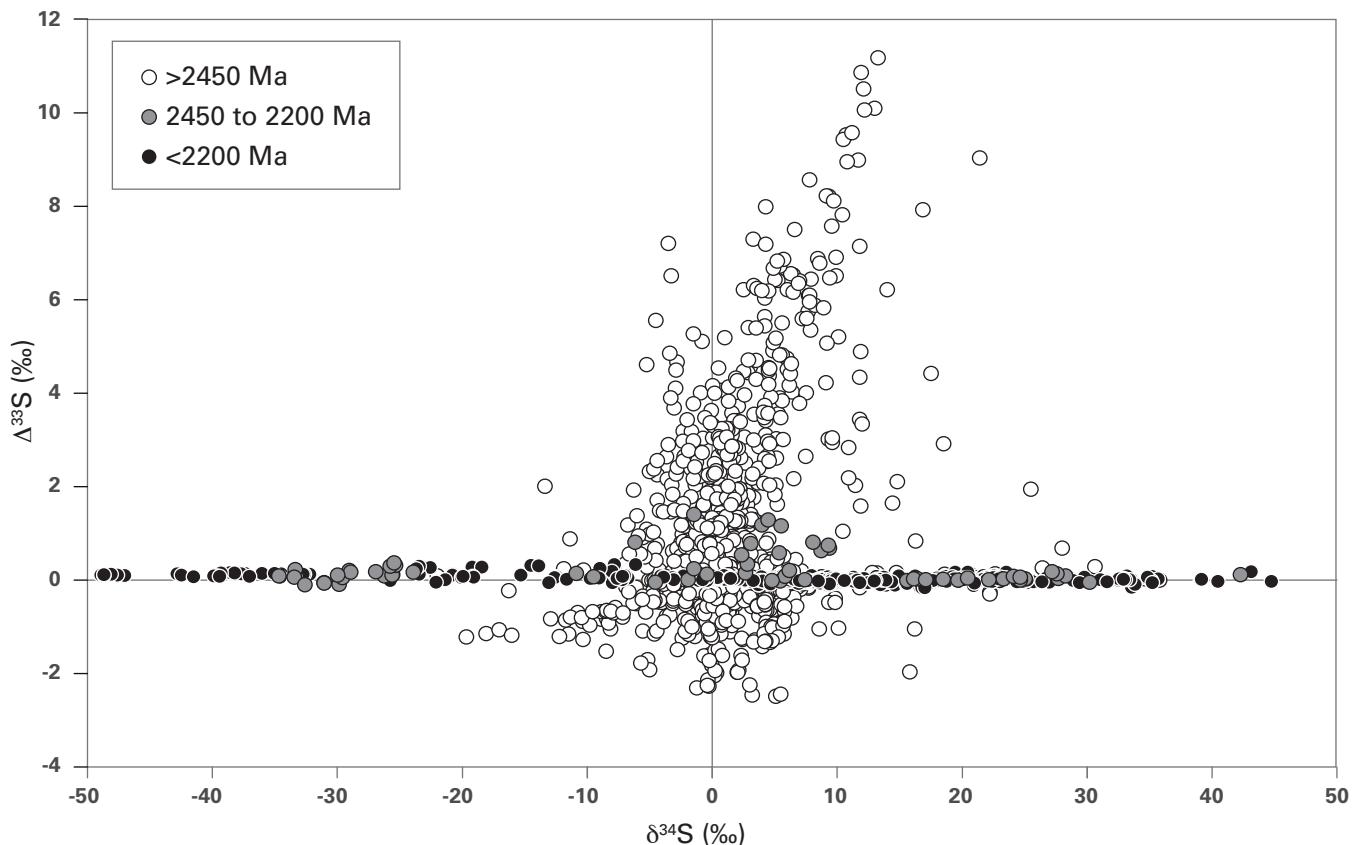
White circles indicate samples older than 2450 Ma, gray circles indicate samples younger than 2450 Ma but older than 2200 Ma, and black circles indicate samples younger than 2200 Ma. The disappearance of S-MIF is accompanied by an increased spread of $\delta^{34}S$ values, indicating the transition to complete biological control of the S isotope record. The broad positive correlation between $\Delta^{33}S$ values and $\delta^{34}S$ values in samples older than 2450 Ma is known as the 'Archean Array' (Ono et al., 2003). While this feature is less well-preserved than the $\Delta^{36}S$-$\Delta^{33}S$ correlation shown in Figure 3, it is critically important as it may reflect how the S-MIF process fractionates all isotope pairs. Compilation after (Johnston, 2011).

highly accurate, detailed study of few or individual molecules, incorporating the Schrödinger equation of motion. At the molecular scale, Newton's equations of motion (used in classical simulations) are only approximate; thus, to attain an accurate understanding of molecular dynamical processes, quantum dynamics may be required.

The marked presence of O-MIF in O_3 formation and dissociation is well known, but the underlying sources remain only partially understood. It is known that the isotopes of the individual oxygen atoms play an important role in determining how quickly ozone can form or fall apart. In particular, the experimental studies of ozone formation rates have shown several key features that require explanation:

1. Formation rate: Oxygen atoms exist in three different isotopic forms: ^{16}O, ^{17}O, and ^{18}O. The individual oxygen isotopes in a given ozone molecule give rise to various combinations (isotopologues). Varying the isotopologue can have a substantial effect on the formation rate, in some cases altering the rate by as much as 50%.

2. Effect of ground state energy: A strong linear correlation exists between the ozone formation rate, and the ΔZPE (zero point energy) of each isotopologue. (Here, ΔZPE is the difference between ground state energies of reactant and product O_2 molecules) (Figure 5).

3. Symmetry effects: When the terminal O atoms in the bent ozone molecule are identical isotopes, the ozone formation rates deviate significantly from the linear ΔZPE correlation otherwise observed in 2.

Conventional MDF explanations do not adequately explain the experimental observations relating formation rates to isotopologues. To understand these features, a plethora of detailed theoretical studies have ensued—primarily statistical density of states analyses, and classical trajectory simulations. But such treatments have not definitively resolved a cause. An important lesson learned from this work—which has spanned two decades and is still ongoing—is that an accurate quantum dynamical treatment is required to explain the observed O-MIF features properly.

Indeed, quantum dynamical treatments have been satisfactorily able to explain how various

AN IMPORTANT LESSON LEARNED FROM THIS WORK—WHICH HAS SPANNED TWO DECADES AND IS STILL ONGOING—IS THAT AN ACCURATE QUANTUM DYNAMICAL TREATMENT IS REQUIRED TO EXPLAIN THE OBSERVED O-MIF FEATURES PROPERLY.

isotopologues affect the observed formation rate of ozone and the substantial presence of O-MIF. To do this, quantum dynamical treatments directly address such phenomena as zero point energy (ZPE) effects, for instance. The ZPE is a quantum mechanical energy shift. In a classical treatment, there is no ZPE, and thus no predicted energy difference between reactant and product O_2 molecules, regardless of isotopologue. A quantum treatment automatically incorporates the ZPE shift, offering a more refined description of reactant and product energies. Specifically the difference in the shifts gives rise to a difference in energy, the ΔZPE. The ΔZPE, in turn, alters the reaction rate. ZPE is isotope-dependent and therefore ΔZPE has been considered as a source of O-MIF. A recent study applied a theoretical quantum dynamical treatment to the isotopologue-dependent rates of ozone formation. The study found that the ΔZPE for different O isotopes should lead to pronounced differences in the formation rates. Moreover, the theoretical rate differences do not adhere to the usual mass-dependent pattern, but rather, exhibit pronounced O-MIF. These predictions confirmed the experimental observations of ozone formation and shed important insight into the sources of O-MIF.

Quantum dynamics can also explain another source of O-MIF. Experimental studies have shown a significant difference in the formation rates of ozone, depending on whether the two terminal O atoms in the bent ozone molecule are the same isotope or not. For instance, an ozone molecule with terminal atoms ^{17}O-^{17}O has an
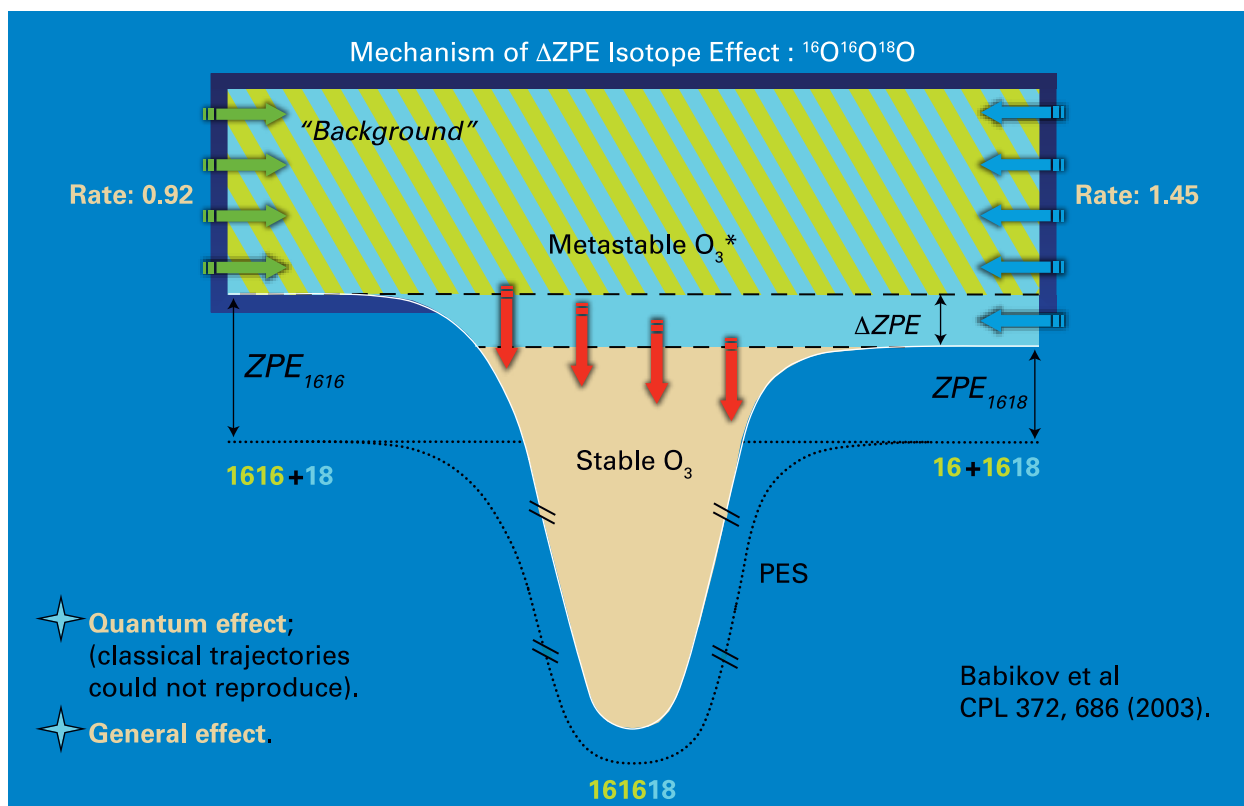
ozone formation rate that is two percent greater than ^{16}O-^{16}O. Deviating significantly from mass-dependent trends, the ozone molecule with terminal atoms ^{16}O-^{17}O has a formation rate 23 percent greater than ^{16}O-^{16}O. Quantum dynamics is able to corroborate this deviation from mass-dependence by utilizing the nuclear spin-symmetry restriction. This quantum effect is a dramatic reduction in the number of available states that a molecule can occupy. It occurs whenever the isotopic species are identical, but does not occur when they are different. As a result, ^{16}O-^{16}O and ^{17}O-^{17}O are, quantum mechanically speaking, much more similar to each other than either is to ^{16}O-^{17}O. Thus, the non-identical particle isotopologue could have an ozone formation rate that deviates substantially from that for identical particles. This theoretical contribution confirms the experimental observations. It predicts one manifestation of O-MIF in ozone and provides additional insight to the overall causes of O-MIF.

The O_3 molecule is similar to S_3 and SO_2, both of which are regarded as important atmospheric sources or carriers of S-MIF. Therefore, the chemical physics tools that have successfully provided a mechanistic understanding of O-MIF in the ozone context are likely to be essential for understanding and predicting S-MIF in S_3 and SO_2. These tools may be useful, not only for

THE CHEMICAL PHYSICS TOOLS THAT HAVE SUCCESSFULLY PROVIDED A MECHANISTIC UNDERSTANDING OF O-MIF IN THE OZONE CONTEXT ARE LIKELY TO BE ESSENTIAL FOR UNDERSTANDING AND PREDICTING S-MIF IN S_3 AND SO_2.

FIGURE 5 – SCHEMATIC OF ZPE DIFFERENCES (ΔZPE) BETWEEN ISOTOPICALLY DISTINCT DISSOCIATION PATHWAYS FOR $^{16}O^{16}O^{18}O$ OZONE

Mechanism of ΔZPE Isotope Effect : $^{16}O^{16}O^{18}O$

"Background"

Rate: 0.92

Rate: 1.45

Metastable O_3*

ΔZPE

ZPE_{1616}

ZPE_{1618}

Stable O_3

1616+18

16+1618

PES

Quantum effect; (classical trajectories could not reproduce).

General effect.

Babikov et al CPL 372, 686 (2003).

161618

Though comparatively small in magnitude, the different ΔZPE values for the different isotopologues of ozone can lead to dramatic differences in formation/dissociation rates, and thus, to an important source of O-MIF. Plot from Babikov et al (2003).

understanding expected sources of S-MIF such as ΔZPE and nuclear spin-symmetry, but for other quantum S-MIF sources that may also exist.

Interdisciplinary Collaboration on O-MIF (Dr. Gerardo Dominguez and Dr. Mark Thiemens)

The third talk presented an overview of the historical interplay between the geochemistry, cosmochemistry, and physical chemistry communities, in understanding the mechanisms underlying O-MIF. The scientific history of O-MIF studies shows how the analysis of natural samples, the design of laboratory experiments, and the production of new theoretical models established an interconnected body of knowledge and forged a solution to the O-MIF "problem." O-MIF studies provide a roadmap for the route S-MIF investigations could take.

Studies of O-MIF began 30 years ago. The initial identification of O-MIF was made by cosmochemists who measured the oxygen isotope composition of high-temperature silicate minerals from meteorite samples that dated to the earliest epochs of the solar system. These high-temperature silicate minerals were deficient in the rare isotope of oxygen (^{17}O) relative to the levels expected from mass-dependent fractionation of oxygen isotopes. [As with S-MIF, the mass-dependent isotope fractionation provides a framework for quantifying and understanding O-MIF.] Since no O-MIF producing processes endogenous to the early solar system were known at the time, an external physical process was proposed as the production mechanism. The theory was that the isotopic anomalies resulted from a nearby supernova that injected pure ^{16}O into the early solar system. At the time, nobody had conceived of a chemical process that could cause O-MIF.

However, when isotope geochemist Dr. Mark Thiemens produced O-MIF in experiments on gas-phase ozone formation, it became clear that an endogenous *chemical* mechanism for producing the meteoritical O-MIF signal was plausible.

That finding opened the door for a string of further experimental studies, documenting a wide range of O-MIF effects and attracting the interest of theoretical physical chemists. Several conceptual explanations were proposed for the origin of the O-MIF effect, but the field took off after laboratory chemists performed a series of critical experiments on formation rates of individual ozone isotopologues. The studies provided sufficient experimental data for theoreticians to develop a quantitative chemical theory for the origin of O-MIF. In turn, their approach, which incorporated a minimum of free parameters, validated O-MIF as an approachable target for computational chemists to focus their skill set on studying the specific microscopic mechanisms behind O-MIF. This trajectory, from serendipitous discovery in natural samples to a quantum-level understanding of the origin of O-MIF, provided an experimentally and theoretically validated isotopic system that coupled microscopic processes to effects at solar-system scales.

Thirty years after these investigations began, contributions from various disciplines have provided a detailed understanding of the source of the O-MIF effect in ozone. The studies have also provided a firm foundation to expand the field with scientific studies ranging from atmospheric pollution to early solar nebular processes. Applications of O-MIF to environmental and cosmochemical studies continue to stimulate increasingly sophisticated laboratory experiments and chemical computations. For instance, the study of O-MIF in early solar nebular materials has revived a range of fascinating discussions about O-MIF origins prior to the existence of ozone in our solar system. In particular, questions about the role of isotopic self-shielding of CO have led to new experiments investigating the photodissociation of CO at high energies. In addition, investigators of O-MIF have developed new theories about how heterogenous reactions

THE O-MIF STUDIES REVEAL THE
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at low temperatures may have caused O-MIF on dust surfaces in nebular clouds.

Three decades of O-MIF studies present a model system of multidisciplinary contributions. Individual findings advanced the field in a step-wise fashion as each discipline played a role. However, the contributions occurred largely independently. The O-MIF studies reveal the necessity of multiple fields to tackle such a topic as S-MIF, but also suggest that concerted interdisciplinary investigations between laboratory physical chemists, computational chemists, cosmochemists, and geochemists may speed the process of discovery.

Lightning Talks: Cutting-Edge Tools for the Study of S-MIF

After the three overview talks, there was a series of short presentations on state-of-the-art tools and research directions related to S-MIF sources, presented by various workshop participants. These presentations were on the following topics:

• Massively parallel quantum dynamics codes (Dr. Bill Poirier)

Newly available codes enable highly accurate quantum dynamical calculations to be performed on massively parallel supercomputers. Such calculations for SO_2 could verify or refute the self-shielding hypotheses; calculations for other molecules could also contribute to a quantum dynamical understanding of S-MIF.

• Nonadiabatic effects in simple chemical reaction systems (Dr. Millard Alexander)

Nonadiabatic effects in quantum dynamics must be considered whenever photodissociation processes occur. Because photodissociation of SO_2 is likely the important source of S-MIF in the atmosphere, nonadiabatic theoretical approaches are necessary to advance the field.

• Sunlight-initiated chemistry of sulfur compounds (Dr. Veronica Vaida)

Studying photodissociation (photolysis) may lead to insights about potential sources of S-MIF in the atmosphere. Even though much research has been conducted on purely gas-phase reactions, further experimentation may help elucidate the relationship between photodissociation, aerosol particles, and water-mediated reactions at the aerosol-gas or surface-gas interfaces.

• SO_2 photodissociation (Dr. Hua Guo)

After photon absorption, the SO_2 molecule undergoes time-dependent dynamics leading to dissociation. Quantum dynamical studies of the second step have been performed, but could be repeated with greater accuracy, to address this potential atmospheric source of S-MIF.

• Key conclusions from experimental and theoretical studies of isotopic fractionation in photolysis (Dr. Matt Johnson)

Photolysis experiments simulate the photodissociation of SO_2 in the atmosphere and look for signs of S-MIF in the reaction products. Understanding the source of the experimental S-MIF requires a precise theoretical understanding of the molecular mechanisms, as well as careful experiments that use isotopically labelled samples.

• High resolution spectroscopy and dynamics (Dr. Trevor Sears)

Highly accurate and time-resolved experimental techniques are employed to study individual molecular collision events. In the S-MIF context, these could be used to monitor individual quantum states of transient species such as SO.

- High-resolution spectroscopy of SO₂ isotopologues and the self-shielding effect (Dr. James Lyons)

  High-precision spectroscopy of the various SO_2 isotopologues can help test one potential source of S-MIF in the atmosphere: the "self-shielding effect." High resolution spectroscopy will provide essential information for computational models of this mechanism, which addresses S-MIF implications of $^{32}SO_2$ predominance in the atmosphere.

- Non-intuitive "backwards-magnitude" S-MIF predictions from photochemical models (Dr. Mark Claire)

  Photochemical simulations of the early Earth's atmosphere provide an opportunity to test various hypotheses on S-MIF creation. One model has produced a compelling, non-intuitive result, including a backwards relationship between the sign (+ or -) of the predicted S-MIF and the signal found in the rock record. Future theoretical studies may resolve this paradox by exploring the transference of S-MIF from the atmosphere to rock.

- Transfer of atmospherically-derived S-MIF to the rock record (Dr. Itay Halevy)

  Sulfur cycling in the marine environment distorts the original atmospheric S-MIF signature, providing the crucial link between the geological record of S-MIF and atmospheric source reactions. Microbial biogeochemistry, fluid-mineral aqueous chemistry, and sedimentology may all contribute to this research direction.

- Absorption-induced fractionation of sulfur isotopes (Dr. Hiroshi Ohmoto)

  Although many lines of evidence point toward an atmospheric origin for S-MIF, experimental and theoretical studies have shown that anomalous signatures in ^{33}S can be associated with absorptive processes. Absorption-induced fractionation of sulfur isotopes offers an alternative hypothesis for the geological S-MIF record, and provides an arena in which physical and computational chemists can play an immediate role.

- S-MIF in Paleoproterozoic metasedimentary rocks (Dr. Seth Young)

  All published measurements indicate that the geological S-MIF record is essentially binary, with sulfur isotope anomalies disappearing for good at ≈2.4 billion years ago. Investigation of S-MIF in rocks younger than 2.4 billion years old is an emerging and important area of study to which geology and geochemistry can directly contribute.

A compilation of these lightning talks is also available online at: http://is.gd/s_mif.

ONCE PROVIDED WITH THE BACKGROUND KNOWLEDGE FROM THE MORNING PRESENTATIONS, THE FULL GROUP OF WORKSHOP PARTICIPANTS WAS THEN DIVIDED INTO FOUR SEPARATE PANELS, FOR INDEPENDENT DISCUSSION OF THE S-MIF PROBLEM.

BREAKOUT PANEL I: DEFINING AND ADDRESSING GAPS IN S-MIF KNOWLEDGE

Once provided with the background knowledge from the morning presentations described above, the full group of workshop participants was then divided into four separate panels, for independent discussion of the S-MIF problem. Each panel was composed of a mix of physical chemists and geochemists/modelers, under an assigned panel leader from these different communities. Executive secretaries from the graduate student pool were tasked with maintaining a record of the discussion. Each panel was provided with the same set of three broad questions to address, corresponding to the three primary objectives of the workshop:

1. Which features from the geological record of S-MIF need explaining?

2. What are some potential mechanisms for producing S-MIF?

3. How can the physical chemistry community contribute to understanding S-MIF?

During this first breakout session, taking place during the afternoon of the first day of the workshop, the four individual panels were tasked with identifying specific topics, research activities, and additional specific questions, pertinent to each of the three broad questions listed above. The independent responses were then presented to the full group by a designated member from each of the four panels, and then collated (and in some cases clarified) by the workshop organizers.

BREAKOUT PANEL II: ESTABLISHING PRIORITIES FOR THE FUTURE OF S-MIF RESEARCH

Day two of the workshop began with the task of prioritizing the suggestions for future research, based on the previous day's discussions. To this end, the participants divided into four new working panels, in order to prompt new conversations and cross-pollinate a wide range of perspectives.

Each of the second set of panels was asked to prioritize the full set of collated responses, using the following three criteria:

1. How quickly and easily can the proposed activity be accomplished?

2. How important is the proposed activity in advancing the understanding of S-MIF in the rock record?

3. What are the intellectual risks involved in embarking on the proposed activity? For example, is the work controversial or are similar projects already underway?

After the panel discussions, the workshop re-convened as a full group to summarize and discuss each group's conclusions. The comprehensive set of recommendations was collated by the workshop organizers to present in this document.

1. WHICH FEATURES FROM THE GEOLOGICAL RECORD OF S-MIF REQUIRE EXPLANATION?

2. WHAT ARE SOME CHEMICAL AND PHOTOPHYSICAL MECHANISMS THAT MAY CAUSE S-MIF?

3. HOW CAN THE PHYSICAL CHEMISTRY COMMUNITY CONTRIBUTE TO UNDERSTANDING S-MIF?

CONCLUDING ACTIVITIES

The workshop concluded with a series of logistical presentations. Dr. Mary Voytek, Senior Scientist for Astrobiology at NASA, explained the sources of funding at NASA that have supported research on S-MIF in the past. The workshop formally ended with an explanation of the synthesis process that would lead to the creation of the present document, which was further developed in a smaller, post-workshop meeting of conference organizers, panel leaders, and executive secretaries. The final discussion also covered likely avenues for future interdisciplinary meetings regarding S-MIF research.

After the workshop, the organizers met to create an initial draft of this document. An opportunity for revision was then provided to the panel leaders and overview talk presenters. The document then was sent to all participants for comments, questions, critique, and clarification prior to publication.

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WORKSHOP SUMMARY RECOMMENDATIONS

The ultimate recommendations of the workshop are intended to suggest further research efforts into the origins and carriers of S-MIF. The panel discussions were conducted completely independently, each group made up of scientists whose fields do not traditionally overlap. There was vigorous discussion about the vocabulary specific to the respective fields, about important background information that represents foundational knowledge in each field, and about how best to communicate the specific expertise in each field to non-specialists. However, the recommendations that arose from each panel were remarkably similar, indicating agreement about the avenues of S-MIF research most likely to be productive. Specific recommendations were organized to answer three broad questions:

1. *Which features from the geological record of S-MIF require explanation?*

2. *What are some chemical and photophysical mechanisms that may cause S-MIF?*

3. *How can the physical chemistry community contribute to understanding S-MIF?*

1. WHICH FEATURES FROM THE GEOLOGICAL RECORD OF S-MIF NEED EXPLAINING?

Our understanding of the geologic record of S-MIF will benefit from two lines of investigation: (1) the systematic patterns of isotopic fractionation; and (2) the preservation of the S-MIF signal. In large part the first research focus reflects the actual source mechanisms producing S-MIF, while the second reveals the complex realities of interpreting a temporally and spatially limited rock record. The most prominent feature in the Δ^{33}S record is the dramatic decrease in the spread of Δ^{33}S values at ≈2.4 billion years ago (Figure 2). Beyond this first-order feature, there are three major systematic patterns of Earth's early S-MIF record that require explanation.

The first pattern is non-random variation in the temporal record of ^{33}S isotope anomalies

(Figure 2). This variability in the record can be divided into three regions: a period of very large-magnitude Δ^{33}S values in the late Archean (2.5 to 2.7 billion years ago), a period of very small magnitude Δ^{33}S values in the middle Archean (2.7 to 3.2 billion years ago), and a period of mid-magnitude Δ^{33}S values in the early Archean (>3.2 billion years ago).

OUR UNDERSTANDING OF THE GEOLOGIC RECORD OF S-MIF WILL BENEFIT FROM TWO LINES OF INVESTIGATION: (1) THE SYSTEMATIC PATTERNS OF ISOTOPIC FRACTIONATION; AND (2) THE PRESERVATION OF THE S-MIF SIGNAL.

The second pattern is a correlation between Δ^{33}S values and Δ^{36}S values (both of which quantify the deviation from S-MDF). The correlation is consistently negative; samples that are anomalously enriched in ^{33}S are anomalously depleted in ^{36}S and vice versa (Figure 3). The correlation has a shallower slope, and larger overall magnitude, than the extremely tight Δ^{33}S-Δ^{36}S correlations associated with the small Δ^{33}S and Δ^{36}S values observed in mass dependent fractionations. As a result, it is interpreted to reflect the isotopic consequences of the S-MIF source mechanism. (Original work identified a slope of ~ -1 for this correlation, with subsequent work documenting how the magnitude of the slope evolves throughout the Archean Eon.)

The third pattern is a correlation between Δ^{33}S values and the amount of fractionation recorded by ^{34}S-^{32}S ratios (δ^{34}S values; Figure 4). This correlation is less ubiquitous than the Δ^{33}S-Δ^{36}S correlation, likely because mass-dependent sulfur cycling after the initial formation of the Δ^{33}S - δ^{34}S correlation can alter δ^{34}S values. Mass-dependent sulfur isotope fractionation should lead to variability in δ^{33}S and δ^{34}S values, but

since $\delta^{33}S$ values will co-vary by about one-half the magnitude of the $\delta^{34}S$ values, the original $\Delta^{33}S$ values associated with correlation will be largely unaffected. The $\Delta^{33}S$ - $\delta^{34}S$ correlation is also interpreted to represent the overall S-MIF source reaction.

While the $\Delta^{33}S$-$\Delta^{36}S$-$\delta^{34}S$ correlations is a broadly consistent characteristic of the Archean S-MIF record, their precise details are not fixed. For example, a broad time interval (2.8 to 3.2 billion years ago) during the middle of the Archean Eon appears to be characterized by $\Delta^{33}S$-$\Delta^{36}S$ correlations with highly variable slopes. Likewise, the most prominent $\Delta^{33}S$-$\delta^{34}S$ correlations appear to be restricted to a time interval at the end of the Archean (2.5 to 2.7 billion years ago). It is not clear, however, whether this apparent variability represents changes in the source of S-MIF production, or whether it is an artifact of sampling biases. The geological (specifically, the mineralogical) context of sulfur isotope measurements is critical for understanding the origin of this variability.

Past work has focused on looking at iron sulfide minerals (typically pyrite) in fine-grained rocks that are rich in organic carbon and that were deposited in marine sedimentary basins. While these rocks are natural targets for S-MIF studies as they are typically rich in sulfur and often represent mineral precipitation in direct communication with the surface environment, a wider variety of rock types and sulfur hosts clearly needs to be examined in a systematic framework. These investigations can be guided by such questions as: "What are the geologic controls on the magnitude, sign, and frequency distribution of S-MIF in specific geologic environments?"

To date, the current S-MIF record is largely based on observations made at a single scale, from closely related samples. Most S-MIF measurements have been made on bulk powders, each made from a sample of 10-100 grams of rock ($\approx$3 to 30 cm^3), collected predominantly from Archean sedimentary sequences in Western Australia and Southern Africa. At the time of deposition, the Western Australia and Southern Africa sequences were possibly part of the same contiguous basin and were subsequently separated through plate tectonics. There are

CURRENTLY, THE LINK BETWEEN THE ENVIRONMENTS IN WHICH S-MIF IS PRODUCED AND PRESERVED IS ONLY BROADLY FLESHED OUT. SPECIFIC QUANTITATIVE PREDICTIONS ARE NEEDED TO DESCRIBE HOW THE S-MIF SIGNAL MIGHT CHANGE IN VARIOUS GEOLOGICAL ENVIRONMENTS UNDER DIFFERING PRODUCTION MECHANISMS.

two complementary approaches for evaluating the robustness of the current S-MIF record: 1) a broader examination of S-MIF variations on the microscale in samples from these well-studied localities, and 2) expanded development of new S-MIF records from understudied Archean field areas. Combined, these approaches should enable an evaluation of the global nature of S-MIF as well as a determination of the timing of its fluctuations. These questions are important, as their answers will constrain the geographic distribution and characteristic timescales of S-MIF source mechanisms.

Currently, the link between the environments in which S-MIF is produced and preserved is only broadly fleshed out; quantitative predictions have been made with only simple low-dimensional models of the Archean sulfur cycle. Specific quantitative predictions are needed to describe how the S-MIF signal might change in various geological environments under differing production mechanisms. These predictions would form a natural counterpart to the suite of field investigations highlighted above, and would illuminate the chemistry, physics, and biology that transferred the S-MIF signature to the rock record.

While the Archean S-MIF record has attracted much attention because of the apparent global nature of the signal, S-MIF has been identified in rare sulfur reservoirs on modern Earth. These include the smallest size fraction of high-altitude sulfate aerosols as well as sulfate-rich layers in polar ice and snow. Both of these reservoirs contain stratospheric sulfate aerosols. The presence of S-MIF in stratospheric sulfate points toward an underexploited source of knowledge

FIGURE 6 – CORRELATION DIAGRAM
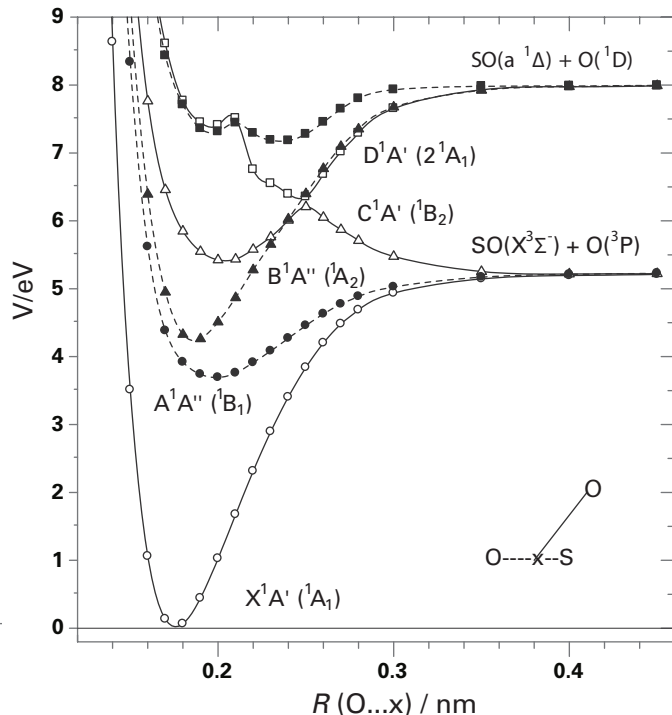OF SO$_2$ WITH SO+O

Figure 6 – Correlation diagram of SO$_2$ (left) with SO+O (right), showing multiple potential energy surfaces (each associated with a different electronic state), as a function of SO-O separation distance, R. The SO bond length is fixed at 148 pm, which is the equilibrium value for the ground electronic state of SO, i.e. the $X\,^3\Sigma^-$ electronic state. Plot from Takue and Nanbu (2010).

about the fundamental chemical production of S-MIF. Although the isotopic systematics of S-MIF in the stratospheric sulfate reservoir are not exactly the same as those in the Archean geological S-MIF record, sulfur chemistry in the modern stratosphere is significantly better understood than sulfur chemistry in the Archean atmosphere. Stratospheric sulfate, therefore, has the potential to act as a well-defined 'model' system for the generation and preservation of S-MIF. Field studies that aim to further characterize this system, along with photochemical models that enable sulfur isotopes to be tracked through the stratosphere, are clear priorities for solving the S-MIF problem. In addition, the expansive base of knowledge of stratospheric sulfur chemistry could be used to inform strategic targets for computational chemical studies of S-MIF.

2. WHAT ARE SOME POTENTIAL CHEMICAL AND PHOTOPHYSICAL MECHANISMS THAT CAUSE S-MIF?

One of the most challenging hurdles of S-MIF research is identifying and exploring specific mechanisms that could cause the signal observed in the rock record. In fact, there was consensus at the workshop that a mechanistic understanding is essential in order for S-MIF research to progress. At the workshop, participants highlighted a number of mechanisms that are particularly likely as sources of S-MIF. Foremost among potential sources are photo-initiated processes—particularly SO$_2$ dissociation—and other gas-phase sulfur reactions such as S + S$_2$ → S$_3$. Other mechanisms identified as potentially informative are heterogeneous reactions at mineral, liquid, or aerosol surfaces. Finally, it was deemed important to find an explanation for S-MIF observed during thermochemical sulfate reduction.

The most commonly proposed explanations for S-MIF involve the photodissociation (photolysis) of SO$_2$. There is ample theoretical and experimental evidence to suggest that the photodissociation reaction, SO$_2$ + $h\nu$ → SO + O, is not direct, but occurs via a multi-step predissociation mechanism. UV photon absorption first excites the molecule from the ground electronic state ($X\,^1A_1$) to a specific excited electronic state ($C\,^1B_2$). Once excited, the molecule occupies a potential well, i.e., an energy valley in the excited state potential energy surface (PES). The well is adjacent to a potential energy barrier to dissociation. (There is also an avoided crossing in the vicinity, see Figure 6). Because of the presence of the barrier, the excited SO$_2$ molecule is a metastable activated complex (denoted SO$_2^*$) that must eventually dissociate into fragments, unless some other process intervenes. Experimentally, the activated complex lifetime (i.e., the time before dissociation) has been found to range over very broad time scales, from ≈1 ps to 45 ns. The lifetime variability suggests that many different dissociation mechanisms might be involved (e.g., barrier tunneling, Feshbach resonances, internal conversion, and/or other mechanisms). S-MIF could potentially be created during any of these steps in the overall SO$_2$ photodissociation process.

SO$_2$ photodissociation could also lead to a "self-shielding" effect, which would create S-MIF near the surface of the Earth. As light passes through Earth's atmosphere, photodissociation of the various SO$_2$ isotopologues is brought about by photons of distinct wavelengths. It is theoretically possible that accumulation of SO$_2$ in the Archean atmosphere could have absorbed all of the photons of the wavelengths necessary to dissociate the ^{32}SO$_2$ isotopologue. This phenomenon, known as "optical thickness," would have prevented the photons from reaching the Earth's surface. Thus, ^{32}SO$_2$ would have remained intact in the lower atmosphere.

> ONE OF THE MOST CHALLENGING HURDLES OF S-MIF RESEARCH IS IDENTIFYING AND EXPLORING SPECIFIC MECHANISMS THAT COULD CAUSE THE SIGNAL OBSERVED IN THE ROCK RECORD. IN FACT, THERE WAS CONSENSUS AT THE WORKSHOP THAT A MECHANISTIC UNDERSTANDING IS ESSENTIAL IN ORDER FOR S-MIF RESEARCH TO PROGRESS.

Meanwhile, because the other isotopologues (^{33}SO$_2$, ^{34}SO$_2$, and ^{36}SO$_2$) are much less abundant, and because the Archean atmosphere did not contain ozone, which absorbs photons that dissociate all the isotopologues, it is also possible that the atmosphere was *not* optically thick for the photons that dissociate the non-^{32}S isotopologues. Consequently, only these isotopologues would have been photodissociated near the surface of the Earth, leading to substantial S-MIF type deviations in the rock record.

From a physical chemistry perspective, the explanation for self shielding resides in the quantum mechanics of the SO$_2$ molecule. Specifically, the rovibronic energy levels (discrete quantum levels of the SO$_2$ PES) depend on the identity of the particular S isotope in the molecule. Thus, each SO$_2$ isotopologue absorbs photons of a unique specific set of wavelengths, including those photons that

lead to photodissociation via a predissociation mechanism. The viability of the self-shielding hypothesis depends on a detailed elucidation of rovibronic levels, which have not yet been established with sufficient precision.

Another potential source of S-MIF might arise from couplings among the SO$_2$ electronic ground state ($X\,^1A_1$) and excited states (including $C\,^1B_2$), and the interplay with dissociation products [likely SO($X\,^3\Sigma^-$) and O(^{3}P)]. Inelastic excitation through collision may lead to S-MIF, as could "downstream chemistry" including bimolecular exchange and three-body recombination reactions exhibiting isotope effects of various kinds [e.g., zero point energy (ZPE), tunneling, nuclear spin symmetry restrictions, vibrational mode degeneracy breaking, electronically excited states and isotope-dependent nonadiabatic coupling, magnetic isotope effects, isotope exchange reactions]. Similar mechanisms may be important in producing S-MIF in reactions involving other S-bearing compounds (SO, SO$_3$, H$_2$SO$_4$, CS$_2$, OCS, CH$_3$SSCH$_3$, CH$_3$SCH$_3$, CH$_3$SH, and H$_2$S).

Another potential source for S-MIF is suggested by the substantial O-MIF present during gas-phase reactions in the modern Earth's atmosphere. In the three-body ozone formation reaction O + O$_2 \rightarrow$ O$_3^* \rightarrow$ O$_3$, isotopic substitution of one of the terminal O atoms in O$_3$ destroys the symmetry of the molecule, which breaks the degeneracy (multiple quantum states with the same energy) and creates additional vibrational energy levels. The presence of additional energy levels in the O$_3^*$ activated complex implies that collisional de-excitation (i.e. collision with a third body that carries away excess energy) is more likely. As a result of the increased frequency of de-excitation collisions, the overall O$_3$ formation rate is enhanced. In addition, the asymmetric molecule exhibits slightly asymmetric reactant and product arrangements, with different ZPEs, introducing a slight endo- or exo-thermicity to the overall exchange reaction. Similar effects may occur with S during S-chain forming reactions, in particular S + S$_2 \rightarrow$ S$_3$. Further, nuclear spin symmetry-induced S-MIF may occur in reactions of short-lived species formed as a result of photodissociation of SO$_2$, such as O-S-S-O.

One final potential source of S-MIF is heterogeneous reactions. These are reactions that occur at interfaces between various phases: liquid, solid, and air. For example, reactions between gas-phase molecules and liquid aerosols in the atmosphere could cause S-MIF. Other potential S-MIF producing heterogeneous reactions occur during absorption/ desorption to mineral surfaces. Isotopic fractionation during sorption is one explanation of experimental work suggesting that thermochemical sulfate reduction leads to S-MIF.

Given the wide variety of potential reaction pathways for the creation and promulgation of S-MIF, the workshop participants strongly recommended that additional meetings be held to help focus the directions of future research. Some specific suggestions that have already emerged are provided in the next subsection.

3. HOW CAN THE PHYSICAL CHEMISTRY COMMUNITY CONTRIBUTE TO UNDERSTANDING S-MIF?

The strongest sentiment to come out of the S-MIF workshop was that cooperation between the physical chemistry and geochemistry/ atmospheric modeling communities will likely lead to significant progress on the S-MIF problem. This suggestion was echoed independently by all of the breakout panels. It was felt by many of the participants that both experimental and theoretical/ computational researchers could make significant contributions, and that these efforts should be conducted in close interplay with each other.

Progress in this field will require a highly detailed and accurate understanding of the underlying mechanisms involved in S-MIF. It was generally felt that the existing state-of-the-art methodologies, currently used in experimental and computational physical chemistry, will suffice for exploration of potential S-MIF sources, especially for three- and four-atom systems. There are, however, some areas in which new methodological development will likely be required. For example, new experimental techniques may be required for the accurate measurement of isotopologue ratios for reactive intermediate species such as SO (and resultant products).

All of the breakout panels emphasized the need to identify the role of photodissociation of SO_2 (and possibly SO) in the generation of S-MIF. The first goal in any mechanistic understanding will be an accurate and isotope-specific computational and/or experimental determination of the SO_2 UV absorption spectrum. Such an approach will be required, regardless of whether S-MIF arises during the initial predissociation phase, or as a consequence of some self-shielding mechanism or "downstream" chemical reaction.

THE STRONGEST SENTIMENT TO COME OUT OF THE S-MIF WORKSHOP WAS THAT COOPERATION BETWEEN THE PHYSICAL CHEMISTRY AND GEOCHEMISTRY ATMOSPHERIC MODELING COMMUNITIES WILL LIKELY LEAD TO SIGNIFICANT PROGRESS ON THE S-MIF PROBLEM.

Determining the SO_2 UV absorption spectrum will require a highly accurate calculation of the potential energy surfaces for the $X\,^1A_1$ and $C\,^1B_2$ electronic states, the corresponding rovibrational energy levels and wavefunctions, and the transition dipole surfaces. The ideal computational accuracy is to within a tenth of a wavenumber. Such accuracy is attainable with cutting edge quantum dynamics calculations, but poses a significant challenge for current electronic structure calculations. However, even achieving wavenumber accuracy will refine the UV photoabsorption calculation to the extent that S-MIF aspects can be much better understood. On the experimental side, preliminary electric discharge experiments have been performed in which SO_2 was dissociated. The remaining reactants and products were analyzed for their isotopic composition. Although S-MIF was not observed, it could theoretically exist. It was suggested by some of the workshop participants that these experiments be revisited in a more systematic fashion.

Subsequent to UV photoabsorption, the photoexcited SO_2^* ($C\,^1B_2$) activated complex

species undergoes dissociation to form the products, SO + O. The dissociation dynamics must also be considered in mechanistic detail. The $C\,{}^1B_2$ electronic state correlates asymptotically to dissociation products SO($X\,{}^3\Sigma^-$) and O(^{3}P) in their ground electronic states (Figure 6). Thus the single-surface dissociation pathway is generally regarded to dominate in the overall photodissociation dynamics. Although rates for radiationless transitions from $C\,{}^1B_2$ are generally regarded to be too small to compete dynamically, there is an avoided crossing with the $D\,{}^1A_1$ electronic state, in the vicinity of the $C\,{}^1B_2$ transition state barrier to dissociation. In addition, there are various triplet states nearby. The extent to which these other mechanisms play a significant dynamical role, vis-à-vis isotopic substitution, may require accurate first-principles investigations. Likewise, the S + O_2 dissociation channel is energetically accessible. Accurate calculations may be necessary to confirm the widely-held hypothesis that the competing S + O_2 pathway is also not significant. Finally, photoexcited SO_2 may in principle dissociate via a collision-induced dissociation (CID) mechanism, perhaps even to electronically excited products. The extent to which forward CID (or the reverse, three-body formation) enhances (or inhibits) overall dissociation may depend on the details of the Archean atmospheric temperature, pressure, and composition, and should be investigated. In particular, workshop participants noted the need to establish likely concentrations for SO_2 and other compounds in the Archean atmosphere.

After the photodissociation of SO_2, many "downstream" chemical and photophysical processes may occur that may introduce or propagate S-MIF. A clear identification of the most likely relevant pathways and elementary reaction steps remains essential. The dissociated fragments of SO_2 are radicals that may be energetically excited, and are therefore highly chemically reactive. They may also absorb additional photons. It has been proposed that UV photodissociation of SO into elemental O and S is a potential source of S-MIF, and so this process also should be investigated in mechanistic detail. However, as a competing mechanism, SO (which is highly reactive) may undergo a

chemical reaction prior to the absorption of additional photons, even under low atmospheric pressures. Standard theoretical and experimental physical chemistry techniques could be useful in ascertaining qualitative and semiquantitative rates for each downstream elementary reaction step. The moderate level of accuracy achieved with these techniques should be sufficient to identify specific, dynamically dominant mechanistic pathways, and to assess which pathways may introduce or propagate S-MIF.

A qualitative understanding of reaction rates may suffice for the purpose of identifying the most important elementary reaction steps. However, a quantitative (highly accurate) determination of the rate constants for the most important individual elementary reaction steps will be required in order to elucidate S-MIF. Existing experimental techniques that could be useful include:

- high resolution UV photon absorption spectroscopy for the "pure" SO_2 isotopologues
- molecular beam methods to measure reactive and dissociative cross sections
- techniques that can resolve individual rotational states and correlated velocities for small free radicals

The spectroscopic techniques might include Fourier transform spectrometry, and cavity enhanced methods. State-specific techniques should encompass excitation of individual rotational states and time-resolution of collisional events for transient species.

In addition to SO_2, SO, and O, other compounds that should be regarded as likely products or reaction intermediates resulting from the initial SO_2 photodissociation might include:

- S_n, H, H_2, SH, H_2S, OH, H_2O, SO, and HSO
- carbon-bearing compounds such as CO, CO_2, and CH_n

Examples of elementary bimolecular collision reactions that might be pertinent to the overall dynamics include:

• SO+O, SO+S, SO+SO, SO_2+O, S+S_2, S_2+S_2, SO+H, S+SH, S+OH, O+SH

These particular reactions, among others, would also likely be tractable using current experimental and computational physical chemistry techniques.

Elementary rate data for some of the downstream reactions already exist in communal resources such as the JPL or IUPAC kinetics database and are routinely used in atmospheric modeling studies. However, exhaustive and highly accurate data for many of the reactions do not exist, and so the reaction rate constants in photochemical models are often the "best guesses" based on chemical intuition. It will therefore first be necessary to identify critical kinetic data that is still lacking, and then to update and extend rate constant data for the key relevant reactions.

In addition to SO_2-initiated reactions, other chemical sources or mediators of S-MIF might exist. An example is H_2S-initiated chemistry (although this compound per se has not been directly identified with S-MIF signals observed to date). In fact, a wide range of gas-phase atmospheric chemistry might potentially impact the S-MIF phenomenon. At present, accurate quantum dynamical experiments and calculations often can be reliably performed for triatomic and tetra-atomic reactions, even for electronically excited reactants. However, such investigations require a substantial investment of effort for each individual reaction, and so investigating numerous reactions is not feasible. For this reason, the input of geochemists and atmospheric modelers is absolutely crucial to provide a *priori* hypotheses about the reactions likely to be most relevant.

Workshop participants also felt that sensitivity analyses of the various atmospheric models will be important. In a sensitivity study, the input quantities in the model are varied independently over a broad range of values, as other quantities are held fixed. The varying quantities consist of the individual elementary reaction rate constants, as well as temperature, pressure, and initial concentrations of chemical species. The sensitivity of the overall kinetics, and also of isotopic

substitution, with respect to these variations, then provides important information about which elementary reactions require the most accurate quantum dynamical elucidation.

IT WILL FIRST BE NECESSARY TO IDENTIFY CRITICAL KINETIC DATA THAT IS STILL LACKING, AND THEN TO UPDATE AND EXTEND RATE CONSTANT DATA FOR THE KEY RELEVANT REACTIONS.

Another important consideration is the transfer of the S-MIF signal from the atmosphere to the Earth's surface, via rainout, and subsequent preservation in the rock record. Sulfur, in its elemental form, transfers easily through rainout and therefore is worthy of investigation. Thus, gas phase reactions involving atomic S and its allotropes, e.g. S-chain-forming reactions such as S+S_n→S_{n+1}, are identified for special consideration. More accurate rate constants, and a better quantum dynamical knowledge of these reactions, are required for understanding S-MIF ramifications. A direct (single-step) three-body formation mechanism is possible for these reactions and may be a fruitful area of research. However, the dominant three-body mechanism is likely to be a two-step process. In the two-step process, two reactants first collide to form the activated complex, S_{n+1}^*, which is later stabilized into S_{n+1} via subsequent inelastic collision with the third body. Both the single-step and the two-step three-body formation processes described above might in principle exhibit substantial S-MIF effects.

In the atmosphere, allotropic forms of sulfur up to S_8 are common, any or all of which may be relevant for S-MIF creation and/or preservation. Total concentrations of sulfur compounds in the Archean atmosphere are likely to have been small, suggesting that only negligible quantities of the larger allotropes would have been formed from the S-chain-forming reactions. However, such reactions may have taken place in local

pockets of high S concentration—in the vicinity of volcanic vents, for example—which would render S-chain-forming mechanisms more feasible.

In order to study sulfur allotropes, previous work with ozone (O_3) may be informative. As in ozone studies, sulfur allotropes up to S_3 are likely amenable to accurate quantum dynamical elucidation, using current physical chemistry methodologies. The triatomic species has two distinct potential energy surface (PES) minima, of which the lower energy minimum corresponds to an equilateral triangle geometry, and the higher energy minimum to a bent geometry. The two minima are mutually energetically accessible to each other because the PES exhibits a low energy transition state barrier. The low transition state barrier renders facile isotopic rearrangement that could have important S-MIF ramifications—e.g., related to the different ZPEs of the dissociated S_2+S isotopologues.

However, S studies will be "new" and challenging in various ways. For example, the low-lying triangular geometry of S_3 does not exist in ozone, which therefore does not exhibit facile rearrangement. Thus, quantum dynamical studies for S_3 will have no ozone benchmarks for comparison. On the experimental side, an additional important difference is that sulfur is much "messier" to work with than oxygen. On the computational side, the consideration of $S_{n>3}$ presents serious challenges for accurate quantum dynamics calculations. The quantum dynamics challenges arise from the scaling of computational effort, which increases exponentially with number of atoms. Important new advances in massive parallelization and in the application of the multiconfiguration time-dependent Hartree (MCTDH) approach to rovibrational state problems, may render such calculations feasible in time. New classical trajectory simulation methodologies that incorporate approximate ZPEs may also be useful in this context, at least for modeling ZPE-based S-MIF effects. (The ZPE effects are known to be relevant for O-MIF in ozone.)

Even though S-MIF may originate via gas phase processes in the atmosphere, it is also possibly generated—and certainly mediated—in the subsequent liquid, solid, and heterogeneous

chemistry that is encountered prior to its incorporation in the rock record. These condensed phase processes should be investigated. However, using current physical chemistry techniques, condensed phase studies are not possible to the same level of accuracy as can be achieved for the gas phase. Aerosol chemistry,

EVEN THOUGH S-MIF MAY ORIGINATE VIA GAS PHASE PROCESSES IN THE ATMOSPHERE, IT IS ALSO POSSIBLY GENERATED—AND CERTAINLY MEDIATED—IN THE SUBSEQUENT LIQUID, SOLID, AND HETEROGENEOUS CHEMISTRY THAT IS ENCOUNTERED PRIOR TO ITS INCORPORATION IN THE ROCK RECORD. THESE CONDENSED PHASE PROCESSES SHOULD BE INVESTIGATED.

associated with the major sulfur rainout channels, may play a significant role in S-MIF transfer. Even small water clusters may mediate thermal and photochemical reactions involving sulfur species, in a manner that could significantly be altered by each particular isotopologue. Such mediation occurs chiefly through van der Waals interactions. Fairly accurate electronic structure and quantum dynamics calculations with one, two, or three water molecules may be feasible. In addition, specific dynamics methodologies exist to address light-initiated sulfur reactions as mediated by water clusters.

Techniques other than quantum dynamics are needed to address S-MIF in the full-fledged condensed phases. In aqueous solution, solvent caging of sulfur-bearing reactants could in principle lead to a magnetic isotope effect involving a [33]S species. This is the only sulfur isotope with non-zero nuclear spin, and also the only fermionic isotope. The existence of [33]S could lead to nuclear spin-symmetry restrictions with substantial S-MIF implications. A complex mechanism such as caging, or some other

ALTHOUGH CONDENSED PHASE INVESTIGATIONS WILL CERTAINLY BE MORE CHALLENGING THAN GAS PHASE APPLICATIONS, PHYSICAL CHEMISTRY TECHNIQUES MAY WELL BE ABLE TO SHED SOME LIGHT INTO THESE PROCESSES AS WELL.

theoretical trapping mechanism, would likely need to be invoked in order to extend the reaction time scale sufficiently for this phenomenon to occur. Moreover, even though substantial ^{33}S -MIF has been observed in the ancient rock record, so has ^{36}S-MIF, which does not arise from this magnetic isotope effect. These findings do not appear to support magnetic isotope effects as the dominant source of S-MIF in the ancient rock record.

S-MIF might also arise during chemical interactions with solid phases in the sediment itself. The proposed diagenetic mechanism posits adsorption/ desorption of sulfur compounds onto decomposed organic materials (for example, amino acids) as a potential source of S-MIF. Although condensed phase investigations will certainly be more challenging than gas phase applications, physical chemistry techniques may well be able to shed some light into these processes as well.

Finally, fractionation of other isotopic species, such as oxygen, may accompany S-MIF. In SO_2 for example, the isotopic identity of the two O atoms leads to a substantial nuclear spin-symmetry restriction isotope effect. This effect manifests in the set of physically allowed rovibrational states, as well as PES nonadiabatic coupling contributions. As the abundance of ^{16}O in the atmosphere is 99.8%, the effect of co-fractionation on overall S-MIF may be limited, although it may play an auxiliary role in the downstream reactions. Even though oxygen cofractionation likely represents a secondary contributor to S-MIF, it may well be worth investigating using physical chemistry approaches (especially quantum dynamics), as it ultimately may provide additional insight about the more dominant sources of S-MIF.

FINAL SUMMARY OF RECOMMENDATIONS

At the end of the workshop, the conference leaders convened to summarize the most important recommendations for advancing the understanding of S-MIF. They agreed that the most important aspect will be increased interaction between the physical chemistry and geochemistry/atmospheric modeling communities. Further, such collaborations stand as a potential strategy to address other isotope-related grand challenges in geochemistry and astrobiology. To this end, four specific recommendations were put forward:

1. Existing physical chemistry literature that might be relevant for S-MIF should be synthesized. (Some detailed and accurate spectroscopic studies, for instance, of the SO molecule, may already exist.)

2. Further interdisciplinary meetings, similar to the S-MIF Workshop, should be supported. (Various possible options were suggested, e.g., Gordon-style conference, national ACS session, NASA astrobiology meeting, virtual/telecon workshop, etc.).

3. "Primer" materials should be distributed across the relevant scientific communities to facilitate understanding of the problems that need solving and the tools that are available. (In addition to this document, other materials should be made available, including all other S-MIF workshop materials, the NASA Astrobiology Primer, and background literature.)

4. Workshop participants, and others from relevant scientific communities, should be encouraged to engage in joint funding ventures. (Grants might be pursued through NASA, NSF, etc. Information about funding opportunities should be shared across scientific disciplines, and announced through email reminders of relevant solicitations and upcoming deadlines.)

In addition, the following specific scientific activities were identified as high priority. This list reflects the combined perspective of potential impact on the S-MIF problem and high likelihood of success for the effort involved.

1. Theoretical modeling of closed photocell SO_2 dissociation reactions.

2. Sensitivity studies of model atmospheres to identify the key formation and exchange reactions that might cause or mediate S-MIF, after initial photodissociation of SO_2.

3. Accurate calculations (10^{-1} cm^{-1} or better) of potential energy surfaces, transition dipole surfaces, and rovibrational states for the $X\,^1A_1$ and $C\,^1B_2$ electronic states of SO_2 (and similarly for SO).

4. Subsequent accurate calculations of the UV photon absorption cross sections for SO_2 (and SO), and of the resultant photodissociation dynamics.

5. Quantum dynamical calculations of S-MIF in S_3 formation that are analogous to those that exist for O_3 formation.

6. Accurate experimental and theoretical measurements of elementary rate constants, particularly for the key S-MIF formation and exchange reactions identified in the sensitivity studies.

APPENDICES

A1. ACKNOWLEDGEMENTS

A2. WORKSHOP PARTICIPANTS

The final list of workshop participants is provided below. In addition, program officers from NASA and the NSF were in attendance for some of the events.

Millard Alexander (University of Maryland College Park)
Dmitri Babikov (Marquette University)
Bridget Bergquist (University of Toronto)
Kristie Boering (University of California Berkeley)
Mark Claire (University of Washington)
Sebastian Danielache (Tokyo Institute of Technology)
Shawn Domagal-Goldman (NASA Headquarters)
Gerardo Dominguez (University of California San Diego)
James Farquhar (University of Maryland College Park)
James Green (Texas Tech University)
Hua Guo (University of New Mexico)
Weifu Guo (Woods Hole Oceanographic Institute)
Itay Halevy (California Institute of Technology)
Brian Harms (University of Maryland College Park)
Juske Horita (Texas Tech University)
Matt Johnson (University of Copenhagen)

James Lyons (University of California Los Angeles)
Amy Mullin (University of Maryland College Park)
Shinkoh Nanbu (Sophia University)
Harry Oduro (University of Maryland College Park)
Hiroshi Ohmoto (Penn State University)
Shuhei Ono (Massachusetts Institute of Technology)
Bill Poirier (Texas Tech University)
Johan Schmidt (University of Copenhagen)
Trevor Sears (Brookhaven National Laboratories)
Yuichiro Ueno (Tokyo Institute of Technology)
Veronica Vaida (University of Colorado Boulder)
Yumiko Watanabe (Penn State University)
Andrew Whitehill (Massachusetts Institute of Technology)
Boswell Wing (McGill University)
Seth Young (Indiana University)
Aubrey Zerkle (Newcastle University)

A3. WORKSHOP AGENDA

The following is the scheduled agenda for the meeting. While the meeting did not follow this schedule to the minute, it does accurately convey the order of events and the rough amounts of time spent on each activity.

Prior to Meeting - Preparation/Homework

The goal of this workshop is to bring two communities together: geochemists that have been studying S-MIF, and theoretical/experimental chemists that can shed new light on this topic. Thus, we will send a few review articles to familiarize the chemical physics community with the S-MIF problem, and the geochemistry community with reaction dynamics mechanisms and tools. Reading these documents in advance will assist our conversations at the workshop.

Sunday Evening - Meet-and-greet dinner

6:00-9:00   We will have heavy appetizers and non-alcoholic drinks, along with a cash bar. Not mandatory, but a good way to start getting to know each other and to kick off the meeting.

Monday Morning - Overview talks

8:30-9:30   Overview of the geological S-MIF problem: James Farquhar
9:30-9:45   Break
9:45-10:45   Overview of chemical physics reaction dynamics tools: Dmitri Babikov
10:45-11:00   Break
11:00-12:00   Interdisciplinary collaboration on O-MIF: Gerardo Dominguez & Mark Theimens

Monday Afternoon - Discussions, Part I

12:00-1:00   "Working lunch" in panels, used to introduce each other
1:00-2:00   "Lightning round" talks covering material not conveyed in overview talks
2:00-2:15   Charge by conference organizers on goal for afternoon discussion
2:15-2:30   Break
2:30-4:30   Panel discussions to identify and discuss the current challenges faced by S-MIF research, and the tools that could be used to address these issues
4:30-5:00   Report back from individual panels to entire workshop

Monday Evening - Group dinner

Not mandatory. Opportunity to discuss the day's events, facilitate cross-panel communication, and start planning for day two

Tuesday Morning - Discussions, Part II

9:00-9:30   Wrap up, summarize, and clarify Monday activities, and discussion of areas that still need to be resolved or discussed in more detail
9:30-11:30   Panel discussion of agreed-upon topics/questions, and of specific research that could lead to progress in S-MIF
11:30-12:30   Report back from panels to entire workshop, review of specific areas of research that could improve our understanding and applications of S-MIF

Tuesday Afternoon - Report Planning

12:30-2:30   Working lunch for co-chairs, panel chairs, and exec secs to plan/outline report

A4. GLOSSARY OF PHYSICAL CHEMISTRY TERMS[1]

activated complex: *Internally excited form of a molecule with sufficient energy for dissociation. In quantum dynamics, activated complex states are usually associated with resonances, i.e., bound-like but metastable quantum states with finite lifetimes. All activated complexes will eventually and spontaneously dissociate into fragments, unless something else occurs first. **Note:** this term is sometimes (improperly) used to refer to transition state barriers.*

allotropes: *Different molecular structures for which all constituent atoms belong to the same element. Different isotopes of a given element may belong to the same allotrope, however.*

classical trajectory simulation: *Approximate mathematical description of the dynamical evolution of a molecular system, for which the positions and momenta of the atomic nuclei are presumed to change over time in accord with the classical Newton's laws of motion, as applied to a given potential energy surface.*

collision-induced dissociation (CID): *Dissociation of a molecule into two (or more) fragments, brought about via inelastic collision with another, "third" body. Some of the relative translational energy of the initial colliding partners is converted into internal energy of the molecule, which is increased to the extent that dissociation becomes energetically accessible.*

electronic state or electronic structure: *Arrangement of electrons within an atom, molecule, or system of molecules, as allowed by the laws of quantum mechanics for fixed energies. Electronic states occur at discrete energies, whose values vary from one molecular geometry to another. This variation gives rise to the potential energy surfaces.*

elementary chemical reaction: *A chemical reaction that occurs in a single mechanistic step—typically collision of reactant molecules, but also dissociation (of an activated complex), photon emission/absorption (an elementary photophysical process), etc. Also refers to any single step of a composite or complex reaction involving multiple steps.*

internal conversion: *a form of radiationless transition in which electronic energy is converted into internal energy, without inducing a change in the spin character of the electronic state.*

internal energy: *Molecular energy in a form that is "internal" to the molecule, i.e. associated with vibrational (and sometimes rotational or rovibrational) motion rather than translation.*

molecular geometry: *The relative positions of the atomic nuclei as situated in three-dimensional physical space, for a molecule or system of molecules, often described by a set of bond lengths and bond angles. The molecular geometry is unaffected by overall spatial translations and rotations. A change in molecular geometry is therefore associated with vibrational motion, and (for a system of molecules) with relative translation and rotation.*

nonadiabatic or electronic transition: *Transition between two different electronic states of a molecular system, induced by electromagnetic (photon emission/absorption) or other interactions (radiationless transitions).*

photodissociation or photolysis: *Dissociation of a molecule into two or more fragments, brought about via absorption of an ultraviolet, visible, or infrared photon(s), generally inducing an electronic (or rovibronic) transition.*

photophysical process: *Production of an excited quantum state of a molecular entity by the absorption of ultraviolet, visible, or infrared radiation, and subsequent events which lead from one to another quantum state through electronic transitions without chemical change.*

potential energy surface: *Geometric surface on which the potential energy of a set of atomic nuclei in a molecular system is plotted as a function of the coordinates representing the molecular geometries of the system. A given potential energy surface corresponds to a given electronic state, generally varying adiabatically from one molecular geometry to another.*

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[1] Many of the chemistry terms in this glossary used the "IUPAC Gold Book" as a guide for their definitions.

predissociation: *The first step in a composite molecular dissociation mechanism involving two or more steps. In the predissociation step, an activated complex is formed, i.e. the internal energy of the molecule is increased to the point where dissociation is energetically possible, but has not yet occurred.*

quantum dynamics: *Accounting for the intermolecular and intramolecular motions and quantum states of molecules that occur in the elementary steps of chemical and photophysical change (e.g., molecular collisions, photon emission/absorption, activated complex dissociation, etc.) In particular, the motions of atomic nuclei are treated accurately, using the laws of quantum rather than classical mechanics.*

radiationless transition: *Nonadiabatic transition between two electronic states of a system without photon emission or absorption, induced by nonadiabatic coupling interactions.*

rovibrational states: *Refers to the combined vibration-rotation quantum states of a molecule, for which variable excitations in both the rotational and vibrational motions are simultaneously considered, but for which the electronic state is always the same.*

(ro)vibronic transition: *Electronic transition for which the (ro)vibrational states of the molecule also change.*

three-body formation (recombination): *The reverse of collision-induced dissociation. Two fragments merge into a single molecule, with excess internal energy carried off by a third body, in the form of increased relative translational kinetic energy.*

transition state barrier: *Saddle point in a chemical reaction potential energy surface, lying at an intermediate molecular geometry along the pathway from reactants to products, where the potential exhibits its maximal value. The most important single geometry for determining the rate constant for an elementary chemical reaction, although an accurate quantum dynamical characterization also requires all geometries along the entire reaction pathway and nearby.*

tunneling: *Inherently quantum phenomenon in which a chemical reaction can occur even when the total energy is below the transition state barrier value. In this case, the reactants are said to "tunnel" through the barrier to form products. Requires a quantum dynamical treatment, i.e. tunneling does not occur at all in classical trajectory simulations.*

A5. WORKSHOP READINGS AND DOCUMENTS

The following readings were assigned to workshop participants to read before their arrival at the meeting. The purpose of these readings was to introduce geochemists to computational chemistry tools, and to introduce chemists to the geochemistry of the S-MIF problem. We believe this remains a good list of introductory texts.

Computational Chemistry Background Readings

K. Mauersberger et al., "Assessment of the ozone isotope effect," vol. 50, Advances In Atomic, Molecular, and Optical Physics (Academic Press, 2005), 1-54.

SC Althorpe and DC Clary, "Quantum scattering calculations on chemical reactions," *Annual Review of Physical Chemistry* 54 (2003): 493-529.

R. Schinke, S.Yu. Grebenshchikov, and H. Zhu, "The photodissociation of NO_2 in the second absorption band: Ab initio and quantum dynamics calculations," *Chemical Physics* 346, no. 1-3 (May 4, 2008): 99-114.

Hiroki Nakamura, "Theoretical Studies of Chemical Dynamics: Overview of Some Fundamental Mechanisms," *Annual Review of Physical Chemistry* 48 (October 1997): 299-328.

L. Takue and S. Nanbu, "Theoretical studies of absorption cross sections for the $C\,^1B_2$ - $X\,^1A_1$ system of sulfur dioxide and isotope effects," *J. Chem. Phys.* 132 (2010): 024301.

D. Babikov et al., "Quantum origin of an anomalous isotope effect in ozone formation," *Chemical Physics Letters*, 372 (2003): 686-691.

Geochemistry Background Readings

Sebastian O. Danielache et al., "High-precision spectroscopy of ^{32}S, ^{33}S, and ^{34}S sulfur dioxide: Ultraviolet absorption cross sections and isotope effects," *J. Geophys. Res.* 113, no. 17 (2008): D17314.

James Farquhar, Huiming Bao, and Mark Thiemens, "Atmospheric influence of Earth's earliest sulfur cycle", *Science* 289, no. 5480 (2000): 756-758.

James Farquhar and Boswell A Wing, "Multiple sulfur isotopes and the evolution of the atmosphere," *Earth and Planetary Science Letters* 213, no. 1-2 (August 1, 2003): 1-13.

James Farquhar et al., "Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry," *Nature* 449, no. 7163 (2007) 706.

Itay Halevy, David T. Johnston, and Daniel P. Schrag, "Explaining the Structure of the Archean Mass-Independent Sulfur Isotope Record," *Science* 329, no. 5988 (July 9, 2010): 204 -207.

David T. Johnston, "Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle," *Earth-Science Reviews* 106, no. 1-2, (2011) 161-183.

A. Jay Kaufman et al., "Late Archean biospheric oxygenation and atmospheric evolution," *Science* 317, no. 5846 (2007) 1900-1903.

James R. Lyons, "Mass-independent fractionation of sulfur isotopes by isotope-selective photodissociation of SO_2," *Geophys. Res. Lett.* 34, no. 22 (November 27, 2007): L22811.

Shuhei Ono et al., "New insights into Archean sulfur cycle from mass-independent sulfur isotope records from the Hamersley Basin, Australia," *Earth and Planetary Science Letters* 213, no. 1-2 (August 1, 2003): 15-30.

Shuhei Ono et al., "Lithofacies control on multiple-sulfur isotope records and Neoarchean sulfur cycles," *Precambrian Research* 169, no. 1-4, (2009) 58-67.