CAREER:
Earth System Science Perspective on the Sulfur Cycle

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Funded by: National Science Foundation, 2004

Directorate: GEO (Geosciences)
Division(s): EAR (Earth Sciences)
Programs: Petrology and Geochemistry

Project Summary

This proposal requests funds to support an integrated education and research plan that will lay the foundation for the PI's academic and scientific career. The education component is planned to facilitate the PI's role as an undergraduate and graduate educator and advisor. It consists of two goals:

(1) Integration of research and education by formalizing an ongoing program in which the PI works with graduate students and postdoctoral researchers who mentor undergraduate students. This program will encourage discussions and discovery-based learning for all involved.

(2) Development of a new pair of courses focused on *Revolutions of the Earth System* that will be directed toward freshman and sophomore level undergraduates in the University of Maryland general core and, in alternate years, for the University of Maryland Honors program. This course will be an essential part of a new interdisciplinary Earth System Science curriculum at the University of Maryland.

The research shares a common analytical and phenomenological approach to study Earth's sulfur cycle that is rooted in the information provided by multiple sulfur isotope analyses. Three targets well-suited to the scope of this grant have emerged from the recent work of the PI and his research group.

(1) *Assessing mass-dependent isotopic fractionations in the geologic record:* Task 1 will be among the first field applications of the idea that mass-dependent fractionations can be used to provide insight into geologic process and may provide a new test for a recent hypothesis of Canfield and others that an evolutionary development in bacteria caused a fundamental change in the way that sulfur isotopes were fractionated.

(2) *Assessing mass-independent isotopic fractionations of sulfides in diamond:* Research task 2 extends the unexpected findings of Farquhar et al (2002) that mass-independent isotopic fractionations are observed in sulfide inclusions in diamonds from the Orapa Kimberlite. The present working hypothesis is that this observation reflects early recycling of sedimentary sulfur to the diamond source area. The proposed work will carry implications for our understanding of material transfer involving Earth's early mantle and crust.

(3) *Assessing* $\Delta^{33}S$ *of carbonate associated sulfate*: Research task 3 addresses a fundamental unknown in the present effort to understand the significance of nonzero $\Delta^{33}S$ in Archean crustal rocks – the nature of the marine sulfate record. The proposed work will also assess whether the marine sulfate reservoir is sufficient to close the Archean sulfur mass balance. This will provide information that can be used for more realistic reconstructions of the Archean sulfur cycle.

The PI has experience with the techniques used to analyze the multiple sulfur isotope system and has recently completed construction of a state-of-the-art laboratory that will be used for this research.

Intellectual merit and broader impacts include contributions to the PI's development as an educator and scientist, education and mentoring of undergraduate and graduate students, involvement of female graduate, undergraduate, high school, and postdoctoral researchers, support of ongoing outreach efforts of the PI, and impacts to science through acquisition, interpretation and publication of fundamental new data that will shed light on several key unanswered questions about the Earth's sulfur cycle.

I. Results from prior NSF support

NSF Postdoctoral Fellowship EAR 9704676 (9/1/97-8/31/99 $70,000): The following publications resulted from support by NSF Earth Sciences Post-doctoral fellowship to Farquhar, 1997-1999. (Some publication dates extended beyond the formal period of funding by the grant, but all were conducted with this support.)

J Farquhar, M Thiemens, T L Jackson (1998) *Science* 280, 1580-1582.

J Farquhar, E Hauri, J Wang (1999) *Earth and Planetary Science Letters,* 171, 607-621.

J Farquhar, J Savarino, T L Jackson, and M H Thiemens (2000) *Nature, 404, 50-52.*

J Farquhar, T L Jackson, and M H Thiemens (2000) *Geochim Cosmochim Acta, 64, 1819-1825.*

J Farquhar and M H Thiemens (2000) *Journal of Geophysical Research 105, 11,991-11,997.*

H Bao, M Thiemens, **J Farquhar**, D A Campbel, K Heine, and D B Loope (2000) *Nature 406, 176-178.*

J Farquhar, H Bao, M Thiemens (2000) *Science, 289, 756-758.*

J Farquhar, H Bao, M H Thiemens, G Hu, and D Rumble (2001) (Response) *Science* 292(5524), U6-U7.

M H Thiemens, J Savarino, H Bao, **J Farquhar** (2001) *Accounts of Chemical Research, 34 (8): 645-652.*

J Farquhar, J Savarino, S Airieau, M H Thiemens (2001) *Journal of Geophysical Research-Planets,12, 32829-32839.*

E Widom and **J Farquhar** (2003) *Chemical Geology* 193, 237-255.

G K Benedix, L A Leshin, **J Farquhar**, T Jackson, and M H Thiemens (2003)*Geochimica et Cosmochimica Acta* 67 (8): 1577-1588.

D RM Pattison, T Chacko, **J Farquhar**, and C RM McFarlane (2003) *Journal of Petrology* 44 (5): 867-900.

NSF Grant EAR 0003419 Multiple isotope insights into the Earth's early sulfur cycle (5/1/01-4/31/04 $217,968) As Farquhar's primary operating grant, NSF EAR 0003419 has supported research by a number of students[1]. The following three publications (plus 11 invited talks and 13 contributed talks) resulted from this grant. Two manuscripts describing scientific results supported by this grant are presently being prepared by Wing and Brabson. This proposal would begin with the end of this research support.

J Farquhar , B A Wing, K D McKeegan, J W Harris, P Cartigny, and M H Thiemens (2002) *Science* **298**(5602), 2369-2372.

J Farquhar BA Wing (2003) *Earth and Planetary Science Letters* 213 101016/S0012-821X(03)00296-6.

J Farquhar, D T Johnston, and B A Wing, K S Habicht and D E Canfield, S Airieau and M H Thiemens (2003) *Geobiology 1, 27-36.*

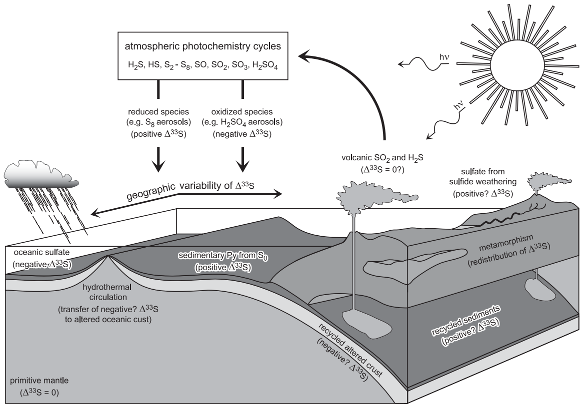

Figure 1. Research conducted as part of NSF EAR 0003419 focused on Earth's early sulfur cycle. The geochemical record of this cycle has been found to preserve signatures of a variety of geological processes that involve atmospheric, oceanic, biological, sedimentary, metamorphic, crustal, and mantle reservoirs. From Farquhar and Wing (2003).

NSF EAR 0004130 Acquisition of a Gas source mass spectrometer (1/1/01-2/28/03 $178,254): This grant was used to acquire two gas source mass spectrometers (Finnigan MAT 253, Finnigan delta plus) for Farquhar's research. The instruments have been installed, and are being used for research in the stable isotope laboratory at the University of Maryland.

NSF EAR 0132377 Acquisition of a UV laser system (1/03/02-1/02/04, $61,600): This grant was used to acquire an excimer laser (Lambda Physik

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[1] Four undergraduate students (Brabson, O'Driscoll, Schwartz, and Baker), four graduate students (Cooney (Nee Young), Johnston, Mann, and Burcar), and a faculty research associate (Wing)

Compex 110) and beam delivery system (New Wave DUV) for isotopic analysis of solid samples. These instruments are presently being installed in the stable isotope laboratory at the University of Maryland.

II. Objectives and Significance:

The PI of this proposal is an assistant professor in his third year at the Department of Geology and the Earth System Science Interdisciplinary Center at the University of Maryland. The plan presented here will help the PI build a firm foundation integrating research and education with the long-term goal of contributing to science and society through work done by the PI and his collaborators. Emphasis is placed on providing an environment where each member of the PI's group can meet their goals and potential. This proposal consists of two parts, an education plan and a research plan. The education plan integrates graduate and undergraduate research and teaching through two goals. The first part focuses on non-lecture based learning experiences. This plan formalizes a program that is already underway and involves graduate students and postdoctoral researchers as mentors for undergraduate students. The second part of the education plan focuses on developing two new interdisciplinary courses to be taught alternate years as a core course with discussion sections to the wider student community and as an honors course in the University of Maryland Honors Program (www.honors.umd.edu). This new pair of courses will involve freshman and sophomore level undergraduates in a new and interdisciplinary Earth System Science class that will focus on long-term changes of the Earth System.

The research plan targets three areas of investigation that share an analytical approach - the application of measurements of the four stable isotopes of sulfur to focus on issues associated with our understanding of the biogeochemical processes that have influenced Earth's sulfur cycle. The focus of this research is consistent with the educational goals in that the research projects touch on issues that are addressed in courses taught by the PI. The first research task focuses on high precision and accuracy measurements of sulfur isotopes to test a hypothesis that different biosynthetic processes (e.g., sulfate reduction and sulfur disproportionation) have left recognizable and distinct mass-dependent sulfur isotope fractionations in the geologic record (cf., Farquhar et al. 2003). The second task focuses on microscale measurements of sulfur isotopes of sulfide inclusions from diamonds to assess the nature and extent of isotope heterogeneity in their mantle source areas (cf., Farquhar et al., 2002). The third task focuses on the measurement of sulfur isotopes in the trace sulfate that is present in carbonates as a proxy of the multiple sulfur isotopic composition of Archean and Proterozoic seawater (cf., Farquhar and Wing, 2003).

The University of Maryland, Department of Geology, and ESSIC have strongly supported the PI by establishing a state of the art laboratory facility through generous infrastructure support and cost share commitments for prior acquisition of equipment. Continued departmental support in the form of a commitment for a teaching assistant as part of a proposed undergraduate curriculum in Earth System Science is included as a match for this proposal (see letter from Brown and Busalacchi). Additional departmental support to invite scientists form local institutions (e.g., Carnegie Institution of Washington, Smithsonian Institiion, NASA Goddard, Johns Hopkins University, NOAA, USGS) to participate in and contribute their perspectives to the PI's courses is also available.

III. Relationship of education and research activities to current state of knowledge in the field:

The University of Maryland, the College of Computer Mathematical and Physical Sciences, the Department of Geology, and the Earth System Science Interdisciplinary Center, have recognized the important role that research plays in undergraduate education and have established courses to encourage this such as GEOL 393/394 (Technical Writing for Geoscientists/Research Problems in Geology). The PI is has been able to contribute to this undergraduate educational objective because he has an active laboratory with talented and motivated group of graduate students who have been gaining experience working with and mentoring undergraduate students.

The first education task (the establishment of a graduate-undergraduate mentoring program) builds upon interactions that have developed on a case-by-case basis in the past two years. It benefits undergraduate students by providing hands-on learning experiences, graduate students by giving them responsibility for training and education. These interactions encourage responsible research through regular discussions about experimental design, the reasons for using a particular analytical approach, and even the underlying context and rationale for the project as a whole. This program supports a non-classroom mode of learning that provides practice with development and communication of ideas and is of value whether they continue in research, academic, or other pursuits.

The proposed course and curriculum development will contribute to efforts to establish an undergraduate concentration in Earth System Science at the University of Maryland. The proposed course development will focus on disseminating cutting-edge Earth System Science to both majors and nonmajors at the University of Maryland, which is consistent with NSF goals (1997, 2000, 2001).

As a member of ESSIC, the PI has experience with interdisciplinary courses. For instance, the PI's paleoclimatology course (GEOL 437) was recently modified and added to the Meteorology graduate curriculum (METO 685), and the upcoming *topics in Biogeochemistry* seminars (GEOL 489F/GEOL789F) will focus on studies that are relevant to Meteorology, Chemistry, and Engineering students at the University of Maryland[2].

The research plan will add fundamental new data and interpretations to a subfield of stable isotope geochemistry that is only a few years old. The application of multiple isotope studies to the terrestrial rock record has been boosted by recent observations of mass-independently fractionated oxygen and sulfur in the records of rock and ice (Bao et al., 2000a; Bao et al., 2000b; Bao et al., 2000c; Bekker et al., 2002; Farquhar et al., 2000; Farquhar et al., 2002; Hu and Rumble, 2003; Mojzsis et al., 2003; Ono et al., 2003a; Romero and Thiemens, 2002; Runnegar et al., 2002; Savarino et al., 2002). A focus of this proposal develops from the recent observation of large $\Delta^{33}S$ anomalies in the early part of Earth's sulfur isotope record (e.g., Figure 2). The research outlined in this proposal adds to this because it is designed to use what we know about sulfur isotope effects to study basic questions in Earth science.

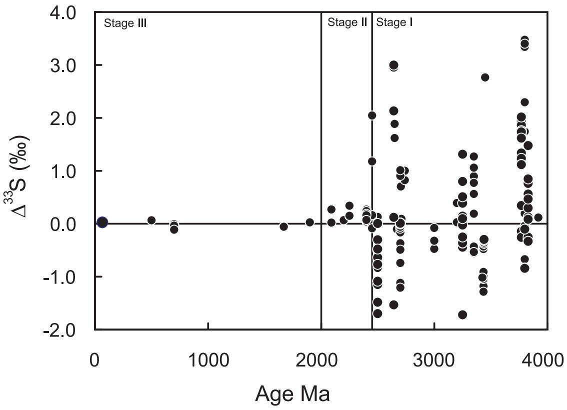

Figure 2. Plot of $\Delta^{33}S$ versus sample age (after Farquhar and Wing, 2003). $\Delta^{33}S$ is one of the measures of mass-independent sulfur isotope signatures. The symbol on the left gives the range of $\Delta^{33}S$ for more than 100 analyses of phanerozoic-age samples. Note the change in magnitude of $\Delta^{33}S$ as a function of age. This change is attributed to a change in atmospheric chemistry.

The first task will focus on a new application of multiple isotope analyses to address a recent hypothesis by Canfield and coworkers that a change in oceanic oxidation state and a related change in the relative importance of bacterial sulfate reduction and bacterial sulfur disproportionation left its signature on the sulfur isotope record. Recent work by the PI and members of his group (Johnston and Wing) in a collaboration with Canfield and others (Farquhar et al., 2003) indicates that the multiple isotope signature of disproportionators and sulfate reducers can be accounted for by biosynthetic models and are distinct from one another.

The second research task will focus on a new application of multiple sulfur isotopes to study transfer of sulfur between the surface reservoirs (crust, sediment) and the mantle. The PI and coworkers recently identified the signature of nonzero $\Delta^{33}S$ for sulfide inclusions in diamond from one kimberlite pipe (Orapa) in Botswana (Farquhar et al., 2002). It is not known how widespread this signature is, or if there are alternate interpretations of the observa-

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[2] The PI's Ph D training is as a geologist, but he also worked as a research chemist in the atmospheric chemistry group of Mark Thiemens in the Department of Chemistry and Biochemistry at UCSD for four years, and this added to the present experience with ESSIC, puts the PI in a good position to add a cross disciplinary, but geological perspective to the ESSIC curriculum.

tions. This work will address these issues and will carry implications for our understanding of crust-mantle transfer in the Archean.

The third task will combine a time-tested approach for studying $\delta^{34}S$ of marine sulfate (carbonate-associated sulfate) with $\Delta^{33}S$ and $\Delta^{36}S$ analyses to examine the Archean marine sulfate record. Examination of the sulfur multiple isotope data collected for Archean samples points to a missing (or not yet identified) sulfur reservoir in the Archean (Farquhar and Wing, 2003). This work will address issues associated with the distribution, composition, sources, and mass balance of sulfur in the Archean oceans. It has been hypothesized that the marine sulfur reservoir may be sufficient to close the sulfur balance, but this is unknown.

Preliminary work for all three of these tasks has been completed. The first two tasks will continue as collaborations between the PI, Johnston, and Wing. The third task will form the basis for the graduate research of John Jamieson who is an incoming graduate student for 2003-2004. The number of analyses and the effort that is planned for addressing each of these tasks is well suited to the five-year timeline of the NSF CAREER program. These tasks will be described in more detail below.

IV. Background: Present research group and laboratory infrastructure

The PI presently has a large and active research group with interests that cover a range of scientific topics and involves members of underrepresented groups in geoscience (six women have been directly involved in research with the group)[3]. Current members of the group include[4]:

Ning Bao, a high school student at Montgomery Blair High School joined us in June 2003 and is interested in conducting an empirical but conceptually straightforward study of gas-phase isotope effects as part of his science research at Montgomery Blair High School.

Elizabeth Brabson, a first year Ph.D. student and formerly an undergraduate with the group, worked on sulfur isotope effects associated with the Huronian glaciations. She presently has an interest in the factors that control El Nino and is coadvised by the PI and Ragu Murtugudde of ESSIC. Liz presented the results of her undergraduate senior thesis at the Geological Society of America Conference in 2002 and will coauthor a paper with Boswell Wing on these results.

Katherine Cooney (Nee Young), a third year Ph.D. student, has interests in developing ways to track the contributions of atmospheric chemistry to nitrate in the Cheaspeake Bay by using oxygen, sulfur, and nitrogen isotopes for nitrate and sulfate. Katherine has recently established the chemical procedures that are required for the collection, extraction, and oxygen isotopic analysis of nitrate in rainwater in our lab. Katherine's research is supported by a Maryland Water Resources Research Council Grant that she wrote (Farquhar PI). Debra Baker, an undergraduate Physical Sciences major, works as an intern with Katherine and is an example of mentoring that is already underway in the PI's laboratory.

John Jamieson is an incoming M.S. student from the University of Alberta who has interests in sulfur isotope geochemistry that are closely related to research task 3 in this proposal.

David Johnston is a second year Ph.D. student who has interests in developing ways to study sulfur isotope fractionations produced by different biosynthetic processes. David is working with Don Canfield and Kirsten Habicht (University of Southern Denmark) this summer (2003) to culture a variety of Bacteria and Archaea that metabolize sulfur compounds. He has devised a framework for evaluating these fractionations and is focusing his research on documenting them in culture experiments. His work is supported by the Carnegie Institute of Washington NASA Astrobiology Grant (Farquhar Co-I). David's work provides the foundation for research task 1 that is described in more detail below.

Jacqueline Mann, a Ph.D. student in Geology (Karen Prestegaard: advisor), and Bradley Burcar a M.S. student in Meteorology (Michael Fahnestock

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[3] One high school student (Zhao), two undergraduate students (Baker, Brabson), three graduate students (Cooney (Nee Young), Mann, and Brabson who is a former undergraduate), and two post-doctoral researchers (Huff, Carmody).

[4] Where relevant, the source of support for these lab members stipends and research is listed. The present proposal ***does not*** request support that duplicates this support, but will be used to support an incoming student from the University of Alberta (John Jamieson) and possibly another student in the later part of the project.

and Jim Carton: advisors), are collaborating for summer 2003 with the group by contributing to an effort to analyze the multiple sulfur isotope composition of carbonate-associated sulfate in Archean and Paleoproterozoic samples (related to scientific task 3 of this proposal). Both have strong backgrounds in analytical chemistry.

Mark Tyra is a second year M.S. student who is studying secondary minerals in primitive meteorites to ascertain whether they are produced by extraterrestrial or terrestrial processes. He uses oxygen and carbon isotopes (including radiocarbon) and is working to gain insight not only into the alteration process but also into the geochemical/cosmochemical implications of his observations. Mark is supported by a NASA cosmochemistry grant (Farquhar PI).

Jacob Schwartz is an undergraduate Education/Geology double major who has worked with us for the past year as a lab assistant. Jacob will be designing his own project as part of the undergraduate Geology independent research requirements this fall (GEOL 393-394 - senior thesis).

Boswell Wing is a Faculty Research Associate in Geology and ESSIC who has a broad array of interests in experimental and theoretical aspects of the physical chemistry of mass-independent isotope effects and also their manifestation in the geological record. Boswell has also worked on a variety of related topics that include applications of multiple sulfur isotopes to Archean and Paleoproterozoic geologic record and has been directly involved in a recent study that documented nonzero Δ^{33}S for sulfide inclusions in diamond and forms the basis for research task 2 of this proposal (See Figure 3). Boswell has a very important role as mentor for several students[5] and colleague to the PI. Boswell is supported by a NASA exobiology proposal that he wrote (Farquhar PI).

As a group, we occupy two 500 square foot laboratories in a newly renovated geochemistry wing of the Chemistry building. The stable isotope preparation laboratory houses several extraction manifolds, a gas cabinet, dry box, freeze dryer, wet chemical facilities, freezer, and UV lamps/monochrometers for experiments. We share the instrumentation laboratory with Dr. A.J. Kaufman and his students. This laboratory houses Jay Kaufman's two Micromass Isoprime mass spectrometers, and our Finnigan Delta plus and Finnigan MAT 253 mass spectrometers. We have been extremely fortunate to share a laboratory with someone like Jay who is interested in mutually beneficial collaborative arrangements. Because of close interactions with Jay, we are able to work with a large array of isotope systems (D/H, δ^{13}C ,δ^{15}N ,δ^{17}O, δ^{18}O, δ^{33}S δ^{34}S, and δ^{36}S). We also have built three on-line extraction manifolds for pyrolysis of nitrate, laser fluorination of oxides, silicates, and laser fluorination of sulfides. We have two 25 Watt Synrad CO_2 lasers and a 30 Watt Lambda Physik Excimer laser with a New-Wave beam delivery system.

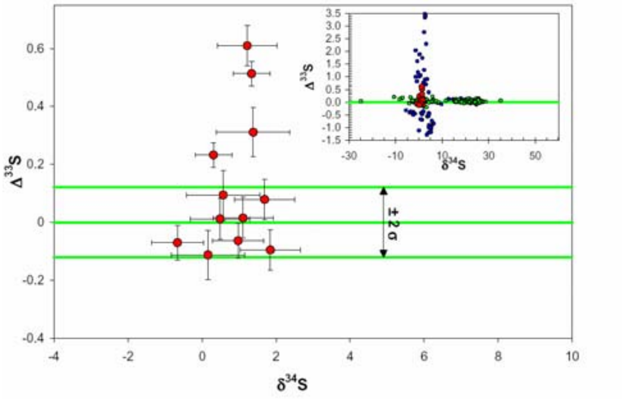

Figure 3. Plot of Δ^{33}S vs δ^{34}S for sulfide inclusions from diamonds from the Orapa Kimberlite pipe reported in Farquhar et al., (2002). Inset is same data plotted on expanded plot with Archean sedimentarty sulfides and sulfate (blue) and post Archean sedimentary sulfide and sulfate (green).

V. Plan of work:

The research and education components of this proposal are designed to have goals that are reasonable over the course of the five-year timeline of this program. The education tasks have grown from the PI's interactions with graduate students and undergraduate students in the laboratory and classroom. Most of the research tasks have grown from a series of discoveries made in the past few years. Although the educational and research tasks are in many ways integrated, the most straightforward way to describe them is individually.

Education task 1: Mentoring program

Mentoring activities in the PI's laboratory are ongoing and are well-established at a number of levels.

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[5] Boswell has acted as mentor to Liz Brabson, Jacob Schwartz, and Ning Bao.

As in other labs that the PI is familiar with, postdoctoral researchers and graduate students have taken roles as mentors. They have worked with other graduate students, undergraduates, and high school students. The interactions have facilitated the science and learning that is done in the laboratory, improved the efficiency of the researchers by providing a sense of responsibility and teamwork, and provided ready access to others who have direct knowledge of the research projects.

The first education task is one that will formalize a graduate-undergraduate mentoring program that has developed in the PI's laboratory. This program is very well suited to the research style and research interactions that have developed in the research group. Graduate students who work in the lab concentrate mostly on their research projects, but the undergraduate students have taken one of three main roles. Some have worked in the laboratory on projects related to their senior thesis requirements. A few students have worked as laboratory assistants and have contributed to the laboratory by becoming proficient with specific analytical tasks, and a few have worked closely with graduate students.

In cases where undergraduates have worked closely with graduate students, the graduate students have provided hands-on training for the undergraduates and have had interest in maintaining the quality of this training because the quality of the work has a direct impact on their research. This benefits graduate students because it helps them develop skills to work with others and to train others to work with them. The benefits also include practice explaining and discussing the significance of the work, and as a result the research questions become better defined and the targets are adjusted to reflect this refined perspective. This program also promises interactions that will result in greater productivity and more thorough science. It will encourage and formalize a program that has developed from the natural progression of research in a laboratory group setting.

Recruiting and Management: Up to this point, most undergraduates who have worked in the laboratory have approached me about work possibilities[6]. The program described here will require suitable candidates and to meet this goal, we will implement a formal program of advertising to students in appropriate fields of study. We have projects that overlap with several other departments and units (Chemistry, Meteorology, Biology, Astronomy, ESSIC, Geology) and we will conduct formal searches with interviews and ask for short letters of reference. This process is designed to give the graduate student mentors the chance to select the most suitable candidate. We will always actively encourage members of underrepresented groups to apply.

Not every graduate student will be suitable as an undergraduate mentor and care will be taken only to select those who have reached the stage where it is an effective option. As a preparation for the process The PI will ask graduate students to read and discuss with the PI literature on mentoring. As a starting point we will use "Advisor, Teacher, Role Model Friend, on being a mentor to students in science and engineering", National Academy of Sciences, National Academy of Engineering, Institute for Medicine (1997).

Evaluation and Reporting: We presently hold weekly laboratory meetings, and the PI asks students and others working in the lab direct questions about its normal operations and about specific questions or concerns they may have about lab safety and efficiency. We generally deal with concerns as they arise, and only in rare cases have we had to work on issues for more than a week or two. In addition to the weekly laboratory meetings, the PI will institute a monthly meeting for active and prospective graduate student mentors to assign and discuss mentoring literature and to hear their reports.

In addition, the PI will solicit a short written progress report (evaluation of positives and suggestions for changes) from both the graduate and undergraduate students. To maintain consistency with the University's yearly teaching schedule, the PI will ask for these at the same time that I hand out course evaluations at the end of each term. The Geology Department and the University also have established procedures for reporting problems, and participants in the mentoring program will be informed at the onset regarding where to go with problems they do not think are appropriate to dis-

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[6] The one exception was Leland O'Driscoll who responded to an e-mail request I sent to colleagues asking about students who might want to visit for summer research.

cuss with the PI. A summary of the written evaluations as well as an assessment by the PI will be provided with the NSF reports.

Education Task 2: Contributions to a new curriculum in Earth System Science.

One of the most important roles of the PI in ESSIC and Geology at the University of Maryland is his role as a teacher of undergraduate core courses. The union of Geology and ESSIC is truly synergistic. It benefits the PI's geological perspective by broadening its focus and strengthening its interdisciplinary nature to include atmospheric and oceanic science perspectives, and it benefits the PI's Earth System perspective because it reinforces the important context of time. This combination also provides a unique opportunity for the PI to contribute to the core curriculum for first and second year University of Maryland undergraduate students through the development of a new pair of related courses, a course for the Maryland Honors program and a general core course modeled after the same theme that will be taught in alternate years. The focus of the course will be the relationship between the Earth's climate and changes in the Earth system through geologic time (*Revolutions of the Earth System)*. It will have a distinctly interdisciplinary focus that brings a variety of Earth system science approaches[7] to bear on this topic.

The PI has taught an upper level undergraduate course on paleoclimate (GEOL 437) that was recently modified as a graduate-level Meteorology course (METO 685), and a seminar course on atmospheric and environmental evolution early in Earth's history (GEOL 489F/789F). A developing goal of the PI is to refocus some of the information that is present in these upper level courses in order to make it accessible to first and second year undergraduate students. The PI believes that knowledge of this and related Earth System Science subjects will be of high value and interest for students at the University of Maryland.

The undergraduate student population at Maryland numbers approximately 25,000 and the quality of the students has steadily improved over the past ten years. The students that graduate in the next few decades will benefit from a background that includes an Earth System Science perspective (Ireton et al., 1997; Lawton, 2001). The Earth System Science Interdisciplinary Center is a relatively young entity at the University of Maryland, and its members are currently involved in devising a consistent set of course offerings. In the foreseeable future, all courses in Earth System Science will retain the designations of the departments that offer them (GEOL, GEOG, & METO), but the way that these courses tie together is viewed as an important consideration. Earth System Science related undergraduate course offerings include thirteen courses[8], but only three of these are at or below 200 level or listed as satisfying the university core requirements. The courses proposed here are aimed at the students who will take core requirements. A benefit of this course will be that a broader cross-section of students will be familiar with the Earth system and its changes through geologic time. A goal will be to pique students' interest in other Geoscience-related courses and draw some to Geoscience-related studies.

Honors course: The Honors program at the University of Maryland is a highly selective program of approximately 2000 of the most talented incoming students. The program aims to provide an exciting array of smaller enrollment courses of approximately 20 students that are aimed at meeting the University's distribution requirements while also fostering an environment that encourages these talented students to think in new and creative ways and to engage in dialogues and discussions about subjects of interest. The interdisciplinary nature of the proposed course is well suited to this program. The PI has met with the Associate director of the Honors program (Dr. Jim Airozo) and discussed the suitability of the proposed course, the general nature of Honors courses, and the processes involved in their implementation. This type of course and its students are well suited to the implementation of non-lecture based teaching strategies. Once devel-

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[7] The Earth system approach incorporates and studies interactions between a large variety of Earth Science system components (e.g., atmospheric, biological, chemical, geological, oceanic, radiative, and physical).

[8] METO123/GEOG123/GEOL123 Global Change, GEOG 140 Coastal Environments, METO 200/201 Weather and Climate/Lab, GEOG 345 Climatology, GEOG 361 Introduction to Human dimensions of global Change, GEOG 372 Remote Sensing, GEOL 375 General Oceanography, METO 400 The atmosphere, METO 401 Global Environment, METO 434 Air Pollution, GEOL 437 Global Climate Change: Past and Present, GEOG 446 Applied Climatology

oped, these methods will be migrated to the core course component of this education task.

Core Course: The proposed Core course that will be the complement of the Honors course will be a non-laboratory lecture course with discussion sections to facilitate active learning. The initial enrollment target will be approximately 60 students, but if the demand is greater, and the resources are available, a larger enrollment will be considered. The PI has been encouraged by the quality of the students and the interest expressed by students in his GEOL 100 Physical Geology course and looks forward to teaching similar students in the proposed Core course. As a companion to the Honors course, this core offering will disseminate science to a wider group of students and have an impact on a larger cross section of the University of Maryland student body. Both courses are consistent with a move to provide high quality science education to today's undergraduates (Greeenspan, 2000).

Evaluation and Reporting: Evaluation of both courses will be undertaken using standard University and Departmental practices each time the courses are taught (e.g., student evaluations, and evaluations by colleagues). An assessment of these as well as an assessment by the PI will be provided to the NSF with the NSF reports.

Research Tasks:

The research tasks that are outlined below are intertwined with the educational mission. The research will form part of the foundation for graduate-undergraduate mentoring as well as provide fundamental findings that relate to the ESS courses.

The tasks have grown out of projects that have been done by members of this group, and in two of the three cases, will form logical extensions for work that is presently underway. The first task has grown from research undertaken with graduate student, David Johnston (Farquhar et al., 2003). Johnston is investigating mass-dependent isotopic fractionations in biological systems. The second task has grown from a collaborative project between the PI and Boswell Wing that was published in 2002 (Farquhar et al., 2002). This work will continue as a collaborative project with Wing. The third task developed from a finding reported by the PI in 2000 (Farquhar et al., 2000a). This work will form the basis for work to be done by incoming graduate student John Jamieson. Both Johnston and Wing have support, so the request for graduate student stipends are directed to the support of Jamieson. All three tasks have begun and address questions raised during the course of our prior work.

Background: Many if not most isotopic fractionations are rooted in the mass differences between the different isotopes. Molecules with different isotopes have different partition functions (Urey, 1947; Urey and Grief, 1934; Bigeleisen and Mayer, 1947). Because modern mass spectrometry has resulted in analytical improvements (e.g., peak tail corrections, signal stability, and better electronics), it has become possible to resolve distinct types of mass-dependent fractionations.

For sulfur, which has four stable isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S), the isotope ratios are measured relative to ^{32}S, and the isotopic compositions given by the delta notation (δ^{33}S, δ^{34}S, and δ^{36}S) vary as a function of the 1,2, and 4 amu mass differences between the isotopes. As a rule of thumb, variations of δ^{33}S are approximately half the magnitude of variations of δ^{34}S and one quarter the magnitude of variations of δ^{36}S (Hulston and Thode, 1965). These mass–dependent isotopic fractionations are not strictly $\delta^{33}S = 0.5\ \delta^{34}S = 0.25\ \delta^{36}S$ because they depend on the form of the mass fractionation law. Different mass-fractionation laws (e.g., equilibrium, kinetic, gravitational) generally yield relationships that vary from 0.50 (or 0.25) by a few percent or less (Hulston and Thode, 1965; Matsuhisa et al., 1978; Young et al., 2002)(Figure 4).

Variations in the relationships between δ^{33}S, δ^{34}S, and δ^{36}S also occur because of properties inherent to the delta notation. Although mixing lines form as straight-line arrays on plots of δ^{33}S versus δ^{34}S, or δ^{34}S versus δ^{36}S, many isotopic fractionation processes do not produce straight line arrays on these plots. This has been recognized (Miller 2002; Angert et al., 2003) and introduces additional considerations when interpreting δ^{33}S, δ^{34}S, and δ^{36}S measurements. Standard convention uses two factors (θ and λ) that describe mass-dependent fractionations:

$$(1) \qquad {}^{3X}\theta = \ln({}^{3X}\alpha)/\ln({}^{34}\alpha),$$

$$(2) \qquad {}^{3X}\lambda = \frac{\ln\left[\dfrac{1+\delta^{3x}S_1/1000}{1+\delta^{3x}S_2/1000}\right]}{\ln\left[\dfrac{1+\delta^{34}S_1/1000}{1+\delta^{34}S_2/1000}\right]}$$

where θ refers to relationships resulting from the fractionation process itself (i.e. fractionation factors), λ refers to fractionation relationships between measured quantities (i.e. fractionation arrays), and the 3x superscript refers to ^{33}S and ^{36}S. In this context, θ describes the variations in the mass fractionation laws. λ incorporates variations in fractionation laws, but also incorporates the additional considerations that are introduced because of properties inherent to the δ-notation (see Angert et al., 2003; Farquhar et al., 2003). Figure 4 illustrates the variability of $^{33}\theta$ that occurs for different isotopic exchange reactions as a function of temperature and magnitude of isotopic fractionations 1000 ln (α).

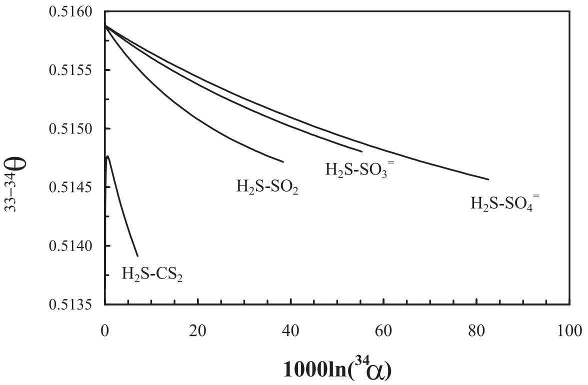


Figure 4. Plot of $^{33}\theta$ vs 1000 ln (α) for mass-dependent equilibrium isotopic exchange between CS_2, H_2S, SO_2, $SO_3^=$, and $SO_4^=$. These values have been calculated using (Herzberg, 1962; Urey, 1947) and vibrational spectra from (Herzberg, 1962; Nakamoto, 1997; Peter and Meyer, 1985; Richet et al., 1977; Urey and Bradley, 1931). The values of $^{33}\theta$ for equilibrium sulfur isotope exchange vary, but defined a narrow range that is similar to the high temperature limit calculated using methods presented in prior studies. Note there is a discontinuity in $^{33}\theta$ for the H_2S-CS_2 pair at 1000ln($^{34}\alpha$) = 0. It results from a cross-over point difference between 1000ln($^{34}\alpha_{H2S\text{-}CS2}$) and 1000ln($^{33}\alpha_{H2S\text{-}CS2}$).

Figure 5 illustrates the way that distillation associated with bacterial sulfate reduction produces variations of λ and forms the theoretical context for part of research task 1.

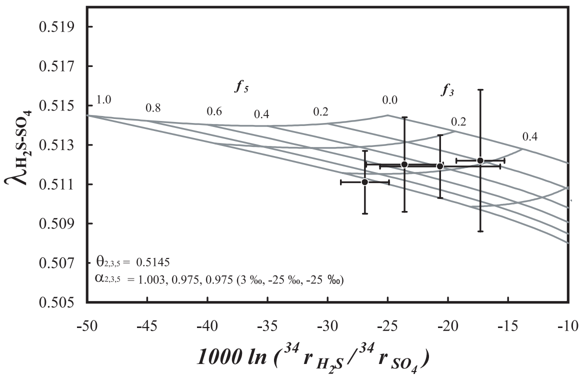
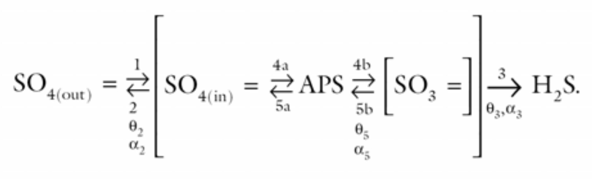


Figure 5. Plot of $\lambda_{H_2S\text{-}SO_4}$ versus 1000ln($^{34}r_{H_2S}/^{34}r_{SO_4\,(out)}$) $^{3x}r = {}^{3x}S/^{32}S$. for the biosynthetic network proposed by Rees (1973). Values for θ_1, θ_2, and θ_3 are set at 0.5145. The contours are for different values of branching ratios (f_3 and f_5) in the Rees (1973) network. Also plotted are data from sulfate reduction experiments with *Archaeglobus fulgidus* (Habicht et al., 2002). Error bars are estimates of 2σ uncertainties. (From Farquhar et al., 2003) . The Rees (1973 network described by this diagram is:



$$SO_{4(out)}^{=} \underset{\substack{2\\ \theta_2\\ \alpha_2}}{\overset{1}{\rightleftarrows}} \left[SO_{4(in)}^{=} \underset{5a}{\overset{4a}{\rightleftarrows}} APS \underset{\substack{5b\\ \theta_5\\ \alpha_5}}{\overset{4b}{\rightleftarrows}} \left[SO_3^{=} \right] \right] \xrightarrow[\theta_3,\alpha_3]{3} H_2S.$$

Research Task 1: Assessing mass-dependent isotopic fractionations in the geologic record:

Research task 1 focuses on measurement of mass-dependent sulfur isotope fractionation arrays to a high level of precision as a means of gaining insight into geologic processes. The overarching goal of task 1 is to explore the feasibility of using $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ to identify specific mass-dependent processes. This approach will be used to test a recent hypothesis by Canfield and coworkers (Canfield, 1998; Canfield and Teske, 1996) that at ~1 Ga, a change in ocean oxidation state allowed sulfur disproportionating bacteria to replace sulfate reducing bacteria as the cause of the largest $\delta^{34}S$ fractionations in the sulfur cycle.

Research task 1 will explore the possibility of using variations in λ (a measured quantity) as a means of gaining insight into a specific geologic question. To accomplish this we need to (1) be able to make the measurements with sufficient accuracy and precision to resolve difference in λ, (2) have a theoretical context that allows us to relate variations in λ to process, and (3) identify a geologic question that has the potential to be addressed by high-precision determinations of λ.

Measuring λ: As a general rule, our ability to determine λ depends both on the precision and accuracy of our measurements and on the magnitude (spread) of geological fractionations - $\lambda \sim (\delta^{33}S_a - \delta^{33}S_b)/(\delta^{34}S_a - \delta^{34}S_b)$, where *a* and *b* are the different phases between which the fractionation is measured. The most straightforward way to assess the level to which one can determine λ is in the context of our ability to measure $\Delta^{33}S$. Consider the approximation $\Delta^{33}S \sim \delta^{33}S - 0.515\ \delta^{34}S$ and the case of resolving a λ that is different from 0.515 (e.g., $\lambda_2 = 0.512$). For a $\delta^{34}S$ fractionation of 30 ‰, the measured $\Delta^{33}S$ will be ~ 0.09 ‰ [=(0.515-0.512)*30 ‰]. This effect is small, but measurable with present techniques and instrumentation.

While these measurements are not routine, ongoing projects to study biological fractionation effects in experiments both at Maryland (David Johnston PhD) and at Carnegie (Pei-Ling Wang) involve determination of λ in the fourth decimal place. We have recently completed a laboratory for making high-precision sulfur isotope measurements. We have a state-of-the-art, four collector Finnigan MAT 253 mass spectrometer that is dedicated to sulfur isotope measurements that we have modified by optimizing the resistors. Our ability to measure $\Delta^{33}S$ (≤ 0.01‰) is better than the PI was able to attain with the MAT 252 at UCSD and the MAT 251 at the Geophysical Laboratory. In Figure 6 we present the results of tests to assess the level of uncertainty that we can attain with our mass spectrometer. These tests indicate that we can improve upon the previously obtained level of uncertainty.

Theoretical Context: In a recent paper, we have evaluated λ in the context of both disproportionation and dissimlatory sulfate reduction (Farquhar et al., 2003). Our theoretical treatment of existing models for disproportionation and dissimilatory sulfate reduction suggests that fractionations produced by these different processes follow different fractionation laws and will have different values for λ. There is not sufficient space to reproduce the mathematical treatment of these effects so the reviewer is referred to the appendix of Farquhar et al. (2003). Figure 5 (previous page) illustrates the effect of the dissimilatory sulfate network proposed by Rees (1973) on λ for the case when all θs are = 0.5145. Note that λ is different from 0.5145 for most fractionations. The λ for disproportionation networks can be shown to be a weighted average of the θs associated with the fractionations (or 0.5145). The measured value for λ of sulfate reduction is 0.5117 +/- 0.009 (2σ) (Farquhar et al., 2003) which is resolvable from 0.5145. This is a simple consequence of the nature of the role of distillation in the sulfate reduction pathways and not in the disproportionation pathways. Ongoing laboratory studies by David Johnston and Pei-Ling Wang (funded through the NASA Astrobiology Institute) are investigating this hypothesis further.

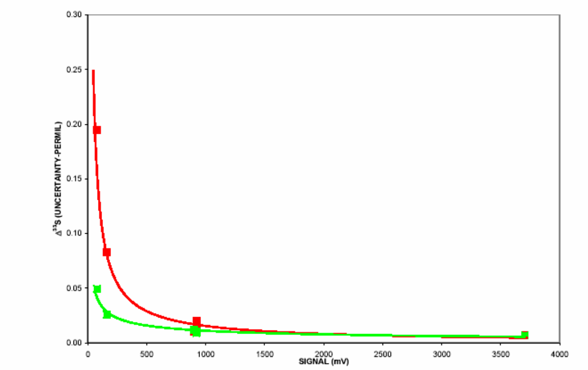


Figure 6. This graph illustrates the uncertainties for $\Delta^{33}S$ as a function of signal intensity that is measured with the Finnigan MAT 253 at UMCP with the configuration delivered from the factory (red data) and with modifications that the PI made to the instrument after delivery (green data). Error bars are presented for averages of seven analyses with each configuration. The factory configurations met specifications.

Geologic Target Question: A hypothesis proposed by Canfield and coworkers (Canfield, 1998; Canfield and Teske, 1996) is the focus for task 1. Canfield and coworkers have argued that the range of $\delta^{34}S$ fractionations is larger for rocks younger than 1 Ga than it is for rocks older than 1 Ga (Canfield, 1998; Canfield and Teske, 1996; Canfield and Thamdrup, 1994; Thamdrup et al., 1993). They argue that this change reflects a change in the imprint of sulfur metabolisms at ~1 Ga. They argue that before 1 Ga the main metabolism was dissimilatory sulfate reduction and that maximum fractionation effects were < 40‰. They argue that changes in ocean chemistry and oxidation state allowed disproportionationators to leave their signature, a larger range of $\delta^{34}S$ fractionations of up more than 60 ‰. This hypothesis is not universally accepted.

Collaboration with Don Canfield, Jay Kaufman, Andrew Knoll, and Yanan Shen gives us access to a wide array of Mesoproterozoic and Neoproterozoic sample suites that can be used to test this hypothesis using $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$. We presently have plans to start with samples from the Roper Group that have been the subject of a recent study by Shen and others (Shen et al., 2002, 2003). Many of the samples have been previously analyzed for $\delta^{34}S$, and a goal of this work will be to identify whether additional information can be obtained through additional analyses of $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$. We will treat each sample set independently by focusing on collecting thorough $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ datasets for each suite to determine λ and to evaluate this λ in the context of biological and physical processes. *Once this has been done, we will evaluate the data in the context of other sample suites and the larger question of whether multiple sulfur isotope measurements and determinations of λ can be used to evaluate the Canfield disproportionation hypothesis.* The relevance of this particular application is framed in terms of the timing of evolutionary events, the oxidation of the oceans, and the evolution of Earth's sulfur cycle. This work will be among the first attempts to apply measurements of small variations of mass-dependent sulfur isotope fractionations to a geological question.

Research Task 2: Assessing mass-independent isotopic fractionations of sulfides in diamond:

We recently reported the observation of sulfide mineral inclusions with nonzero $\Delta^{33}S$ in diamonds from the Orapa Kimberlite pipe (Farquhar et al., 2002)[9]. This observation was interpreted as a signature of recycled sedimentary sulfide of Archean age in the diamond source area.

This proposal includes a more thorough investigation of diamond sulfide inclusions from diamonds of a wider range of ages and source affinities than were investigated in the first study. A goal of this research will be to assess the extent of nonzero $\Delta^{33}S$ in the diamond source areas and also the validity of the hypothesis that they represent the signature of a recycled sedimentary sulfide component of Archean age. This research has the potential to provide important constraints on the transfer of sulfur between surface reservoirs (atmosphere, ocean, sediments, and crust) and mantle reservoirs early in Earth history. *The presence of nonzero $\Delta^{33}S$ in the diamond source areas presents us with a new way to examine mass transfer to Earth's early mantle.* This task will involve continued close collaboration with Jeff Harris, Kevin McKeegan, and Pierre Cartigny (see appended letters).

Context: We published a paper three years ago that described observations of sulfide and sulfate with nonzero $\Delta^{33}S$ from Archean and Paleoproterozoic sedimentary and metasedimentary rocks (Farquhar et al., 2000). Since that time, a number of studies have confirmed these observations (Bekker et al., 2002; Hu and Rumble, 2003; Mojzsis et al., 2003; Ono et al., 2003a; Ono et al., 2003b; Runnegar et al., 2002) and have made significant contributions to our understanding of their meaning (Bekker et al., 2002; Hu and Rumble, 2003; Kasting, 2001; Mojzsis et al., 2003; Ono et al., 2003a; Ono et al., 2003b; Pavlov and Kasting, 2002; Runnegar et al., 2002). It is generally, although not universally[10], thought that the presence of large magnitude nonzero $\Delta^{33}S$ in the Archean rock record is a signature of sulfur chemistry in an atmosphere with very low oxygen concentrations (Farquhar et al., 2001; Kasting, 2001; Ono et al., 2003a; Pavlov and Kasting, 2002). It has been hypothesized that the sulfide reservoir has a positive $\Delta^{33}S$ signature, and that the sulfate reservoir has a negative $\Delta^{33}S$ signature (Farquhar et al., 2000; Farquhar et al., 2001; Ono et

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[9] Subsequent to submission of our study for publication, we sent the inclusions mounts to Pierre Cartigny and Marc Chaussidon. They repeated and confirmed our measurements using their Cameca IMS 1270. Uncertainties for isotopic measurements of $\Delta^{33}S$ using the UCLA IMS 1270 are ~0.1 ‰, which is sufficient for the proposed work.

[10] An alternative hypothesis has been proposed by Deines (2003) who suggests that these signatures can be produced by amplification of isotope effects near isotopic fractionation crossovers. The effects arise because the temperature conditions at which $\delta^{34}S$ fractionations go to zero are not the same as those at which $\delta^{33}S$ and $\delta^{36}S$ fractionations go to zero. Determination of $\Delta^{33}S \sim \delta^{33}S - 0.515\ \delta^{34}S$ and $\Delta^{36}S \sim \delta^{36}S - 1.90\ \delta^{34}S$ at this point where $\delta^{34}S = 0$ yields small nonzero $\Delta^{33}S$ and $\Delta^{36}S$. The basic hypothesis is sound, but carries with it a number of testable implications for temperature, mass balance, and relationships between $\Delta^{33}S$ and $\Delta^{36}S$. These and other processes will be considered in the data interpretation associated with the proposed work.

al., 2003a; Pavlov and Kasting, 2002). The observation of different (negative and positive) $\Delta^{33}S$ signatures for Archean sulfide and sulfate suggests that the two reservoirs are to some extent decoupled.

The sulfur isotope signature of sulfide inclusions in Orapa diamonds overlies the field defined by Archean sedimentary sulfides (Figure 1, page 5) and a common origin has been suggested. We have interpreted this to indicate that the sulfide inclusions in Orapa diamonds contain at least some sulfur that was once in the sedimentary sulfide reservoir.

Research task 2 of this proposal will involve making sulfur isotope measurements of diamond sulfide inclusions from a variety of Kimberlites. We will examine sulfide inclusions from both E (eclogite) and P (peridotite) parageneses. We will examine inclusions from different localities and that are thought to sample different age source areas (e.g., (Pearson, 1999; Pearson et al., 1993; Richardson et al., 1990; Richardson and Harris, 1997; Richardson et al., 1993; Shirey et al., 2001; Shirey et al., 2002). Our evaluation of the data will be undertaken in the context of prior work with sulfide inclusions from diamond ($\delta^{34}S$ studies (Chaussidon et al., 1987; Eldridge et al., 1991; Eldridge et al., 1995; Rudnick et al., 1993), trace and major element studies (Bulanova et al., 1996; Joswig et al., 1999; Law et al., 1998; Schrauder et al., 1996; Spetsius and Griffin, 1997; Stachel and Harris, 1997; Wang et al., 2000; Zhang et al., 2000); (Deines and Harris, 1995; Harris, 1968a; Harris, 1968b). Because of prior arrangements, the PI will not analyze the carbon and nitrogen compositions of these diamonds, but these measurements will be made as part of other collaborations, and the composite datasets will be available to the scientific community (see reference letters from Cartigny and Harris).

The PI has requested funds to support two analytical sessions per year of three days each using the UCLA IMS 1270 SIMS facility. The UCLA SIMS facility can be run 24 hours/day and two investigators will travel to UCLA to engage in a series of consecutive 12-hour shifts for this project. Sample mounts of diamond sulfide inclusions and secondary standards will be prepared using standard procedures and analyzed using accepted analytical protocols (Farquhar et al., 2002; Greenwood et al., 1999; Mojzsis et al., 2003).

The three goals of research task 2 include addressing (1) the issue of geographic extent and age distribution of the nonzero $\Delta^{33}S$ signature in diamond sulfide inclusions, (2) whether the sign of the signature is only positive, or whether populations exist with negative $\Delta^{33}S$, and (3) the validity of the hypothesis that the signature reflects a recycled sedimentary sulfide component of Archean age.

Research Task 3: Assessing $\Delta^{33}S$ of carbonate-associated sulfate:

A number of recent studies have focused attention on the significance of the observed nonzero $\Delta^{33}S$ in rocks of Archean and Paleoproterozoic age (Bekker et al., 2002; Farquhar et al., 2000; Hu and Rumble, 2003; Ono et al., 2003a; Ono et al., 2003b; Runnegar et al., 2002). These studies have raised a number of significant new insights into the sulfur cycle and early environments of Early Earth. For instance, it has been shown by SIMS analyses that $\Delta^{33}S$ can vary on the scale of a single thin section and that information about sulfate reduction, and extent of equilibration can be obtained from microscale analysis (Mojzsis et al., 2003). It has also been shown that individual drill cores carry dramatic down-core isotope variations, not just for $\Delta^{33}S$, but also correlated with $\delta^{34}S$ that can be interpreted in the context of atmospheric processes and biological activity (Ono et al., 2003). It has been demonstrated that the $\Delta^{33}S$ signature of sedimentary rocks persists through metamorphism and can be used as a tracer for fluids (Wing et al., 2002) and also to make arguments about the nature of the protolith (Mojzsis et al., 2003). All of these studies point to an active, and vital research community with common interests in applying this tool to study of the earth's early environments.

For research task 3, we propose to combine multiple isotope techniques with a time-tested method for determining the $\delta^{34}S$ of marine sulfate that relies on extracting carbonate-associated sulfate (e.g., (Burdett et al., 1989; Hurtgen et al., 2002). The goal of task 3 will be to study the record of sulfate $\delta^{34}S$ and $\Delta^{33}S$ through the Archean and Paleoproterozoic. Alan J. Kaufman, Bruce Simonson, Yuichiro Ueno, and Shige Maruyama have generously provided samples for this study and expressed an interest in further collaboration (see letters of support).

The choice of carbonate-associated sulfate as a target for task 3 was made on the basis of the perceived value of this information to the wider geological community and in the context provided by the Archean sulfur cycle. Information about the isotopic composition of Archean sulfate reservoirs can be inferred from other types of analyses (e.g., barite, hydrothermal sulfide deposits, and some pyrite thought to be of biological origin), but the information provided by these analyses is incomplete. This work will provide a new type of constraint on the sign of marine sulfate.

Box 1: CAS analyses The analysis of carbonate-associated sulfate for Paleoproterozoic and Archean samples is not a trivial exercise. The samples are limited in quantity and the sulfate concentrations in these samples are lower than those observed in Phanerozoic samples. Another issue that must be considered is the degree of recrystallization that the samples have been subject to. The PI is not a carbonate petrologist, but his collaborators (Kaufman, Simonson, Ueno) can provide this guidance. The low concentrations of sulfate have led us to modify the extraction techniques. After careful selection, the samples are powdered and treated according to accepted protocols (Millipore water and sodium hypochlorite rinses, followed by acidification in weak acid, and then filtering) (Burdett et al., 1989; Hurtgen et al., 2003), the acidic solution is reduced in volume by evaporation under flowing nitrogen at 80 ºC and then chemically reduced to H_2S using 'Thode' solution (a mixture of hypophosphorous, hydriodic, and hydrochloric acids), The H_2S is converted to Ag_2S by bubbling it through $AgNO_3$ solution. Preliminary results indicate that it is possible to work with Archean samples that have low sulfate concentrations.

Research Questions: While there has been considerable effort invested in building an understanding of $\Delta^{33}S$ variations in the Archean, the subject is very broad and data sets are incomplete. A number of issues need to be addressed more thoroughly. These include:

It has been hypothesized that $\Delta^{33}S$ of Archean marine sulfate is negative. This hypothesis has been formulated on the basis of three observations that are consistent with this interpretation: (1) negative $\Delta^{33}S$ for barite from the Pilbara block of Australia and the Barberton Greenstone belt of Africa, (2) sulfides of hydrothermal origin and also those inferred to be the product of biological sulfate reduction have negative $\Delta^{33}S$ (Farquhar et al., 2000; Ono et al., 2003; Mojzsis et al., 2003), and (3) laboratory photochemical experiments that produce the largest $\Delta^{33}S$ signatures also produce sulfate with negative $\Delta^{33}S$[11]. The proposed analyses will provide a test for this working hypothesis.

- *There does not appear to be sufficient data with negative $\Delta^{33}S$ to close the ^{33}S mass balance* (e.g., averages undertaken by resampling the dataset yield nonzero values (Farquhar et al., 2002)). It is possible that continued collection of isotopic data for sulfides will result in a solution to this issue, but it is also possible that we have missed a part of the sulfur cycle with our present sample selection strategy and that at least part of the resolution to this may be preserved by carbonate-associated sulfate. The additional information about the sulfur isotope composition of carbonate-associated sulfate should also help us to provide better constraints on the isotopic composition of the sulfate reservoir, and with better constraints, we will be able to undertake more realistic reconstructions of the Archean sulfur cycle.
- *It is unknown whether the sulfate concentrations and isotopic compositions in the Archean oceans varied with depth.* Wing et al. (2002) have argued that differences in the $\Delta^{33}S$ signature of hydrothermal sulfide minerals formed in deep water ($\Delta^{33}S \sim 0$) and shallow water ($\Delta^{33}S < 0$) suggests that the oceans may have been stratified both in the isotopic composition of sulfate and also the concentration of sulfate. It is uncertain whether analyses of carbonate-associated sulfate from deep and shallow water carbonates from the Wittenoon and Carawine will yield insight into this issue because much of the deeper water carbonates may have been formed in shallow water and mechanically transported to the deep water. Nevertheless, sulfur isotope analyses of these carbonates that can be evaluated in the context of their depositional setting and insight into this issue may be obtained.
- *It is not known whether the $\delta^{34}S$ and $\Delta^{33}S$ of marine sulfate varied with time in the Archean.* It is possible that the $\Delta^{33}S$ of the oceans changed sign from negative to positive immediately after the at-

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[11] Note that some photolysis experiments at longer wavelengths produced smaller magnitude, but positive $\Delta^{33}S$.

mospheric oxygen content rose to levels high enough to permit oxidation reactions of exposed but negative $\Delta^{33}S$ continental sulfide minerals. The record of this may be preserved in the record of carbonate-associated sulfate.

Reporting of research results:

The results of the research for research tasks 1,2, and 3 will be published and presented at conferences as have prior results. A full reporting of these results and student work will also be included with progress reports to the NSF.

VI. Intellectual merit and broader impacts:

Summary of prior educational and research accomplishments

The PI currently advises three male and two female graduate students. The laboratory currently supports Jacob Schwartz, who is an undergraduate student working to obtain his degree to be a high-school science teacher, and Debra Baker, who is an undergraduate Physical Sciences major who plans to attend graduate school in atmospheric sciences. In the past 12 months, Farquhar has employed Leland O'Driscoll, an undergraduate student from Humboldt State University, to work on a summer project, and has mentored two high school students from Montgomery Blair High School[12]. The PI has also worked with Boswell Wing, Amy Huff, and Rebecca Carmody, who, themselves, have undertaken research and mentoring roles.

The PI leads an upper level *topics in biogeochemical cycles seminar*. The seminar is taught as a reading and discussion course by identifying an overarching topic of interest and by having the students meet weekly to present written and oral reports on articles from the scientific literature to the rest of the class. At the end of the term each student has a collection of papers and reports that they and others have written, a better command of the topic, and valuable experience in critical thinking. The discussions focus on a broad range of topics but include devising ways to test the hypotheses, understanding the reasons why alternative hypotheses may not have been chosen, identifying the underlying assumptions, and gaining a deeper appreciation of the reasoning and hypotheses that are presented. Visits by a scientist whose work they have studied allow students a window into research as practiced by one scientist and into the discussion that is so integral to scientific progress[13]. It is also unique because the background work places them at a level where they can interact with the scientist at a higher level. This policy is relevant to the stated goals of geoscience education as outlined in NSF document 97-171 because it brings cutting-edge research into the education mainstream. The PI has also included with the supplementary documentation, written comments from course evaluations taught by the PI.

The PIs prior research accomplishments include: (1) devising an inverse approach to oxygen isotope thermometry that provided a means of seeing through the veil of retrograde exchange and applying isotopic thermometry to ultra high temperature rocks (part of the PI's Ph.D. research), (2) using oxygen and sulfur isotopes of carbonate and sulfate minerals to gain insight into the nature of atmosphere-surface interactions and oxidation pathways on the SNC parent body (Mars); (3) observing and interpreting a change in the multiple sulfur isotopic composition of crustal sulfides and sulfates of Archean and Proterozoic age in the context of a change in the sulfur cycle and evolution of Earth's atmosphere; (4) identifying similar sulfur isotope signatures for sulfide inclusions in diamonds from the Orapa kimberlite pipe that carry implications for the transfer of sulfur between crust and mantle early in Earth's history (with Wing); (5) providing a theoretical context and isotopic measurements consistent with this context for a change in mass-

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[12] NSF document 01-53 argues for the importance of diversity in Geoscience and that multi-year research experiences and mentoring are a critical part of undergraduate level activities, and that recruitment should extend to other related departments (physics, chemistry, biology, mathematics, engineering, and geography). In the past two years, the PIs lab has involved seven male and six female researchers with education levels high-school to post Ph.D. and expertise in Geology, Earth Systems Processes, Chemistry, Meteorology, Physical Sciences, and education.

[13] Layman (1996) describes a five step modified learning cycle that in includes (1) engaging the learner, (2) exploring the concept, (3) explaining the concept and defining the terms, (4) elaborating on the concept, and (5) evaluating the (student's) understanding of the concept. The approach used in the seminar class places the students in the role of the initiator, explorer, explainer, elaborator, and evaluator. Interactions with the visiting scientist reinforce the prior reading, discussion, and learning.

dependent isotopic fractionations associated with different sulfur metabolisms to test hypotheses about changing roles for bacteria with different sulfur metabolisms in the sulfur cycle (with Johnston and Wing).

Although funds to support outreach are not requested as a part of this proposal, the PI has made a strong commitment to outreach efforts associated with the Carnegie Institution of Washington's NASA NAI that involves contributing to a proposed exhibit at the NMNH, K-12 teacher training, and to contributing to a joint project with "Time for Kids" - a Time magazine publication. Although these efforts are not being undertaken with NSF funds they are included because they reflect a commitment to outreach efforts that extend naturally across disciplines. Work associated with the research proposed here will be included as the PI contributes to these efforts.

Statement about relation of this research to the PI's career goals

The education plan outlined in this proposal focuses on ways to integrate the PI's role as a researcher and an educator of undergraduate students, graduate students, and postdoctoral fellows.

- Education task 1 (graduate-undergraduate mentoring program) will facilitate this by providing hands-on experience for graduate researchers to work with and advise undergraduates.
- Education task 2 (Developing lower level and honors courses in paleoclimatology for the Earth System Science Curriculum) has been one of the PIs long-term goals since arriving at the University of Maryland. This proposal takes a significant step toward making that goal into a reality.

The research goals that are outlined in this proposal focus on the type of fundamental questions in Geoscience that the PI will work to address throughout his career. The specific tasks were chosen because of the nature of the questions that they ask.

- *Assessing mass-dependent isotopic fractionations in the geologic recodr:* Research task 1 will be among the first applications of the idea that mass-dependent fractionations may provide insight into geologic process and may provide a new test for a recent hypothesis of Canfield and others that an evolutionary development in Bacteria caused a fundamental change in the way that sulfur isotopes were fractionated.
- *Assessing mass-independent isotopic fractionations of sulfides in diamond:* Research task 2 extends the unexpected findings of Farquhar et al (2002) that mass-independent isotopic fractionations are observed in sulfide inclusions in diamonds from the Orapa Kimberlite. The present working hypothesis is that this observation reflects early recycling of sedimentary sulfur to the diamond source area. The proposed work will carry implications for our understanding of material transfer involving Earth's early mantle and crust.
- *Assessing $\Delta^{33}S$ of carbonate-associated sulfate*: Research task 3 addresses a fundamental unknown in the present effort to understand the significance of nonzero Δ^{33}S in Archean crustal rocks – the nature of the marine sulfate record. The proposed work will also assess whether the marine sulfate reservoir is sufficient to close the Archean sulfur mass balance. This will provide information that can be used for more realistic reconstructions of the Archean sulfur cycle.

The PI's goals include making an impact on science and education with contributions of solid research findings that are useful for others in the discipline. The PI aims to provide an opportunity for undergraduate, graduate, and postdoctoral researchers who work with the PI to make a similar impact[14].

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[14] The philosophy of the PI has been to allow the graduate students to formulate research projects that are consistent with their own career goals as a result.

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