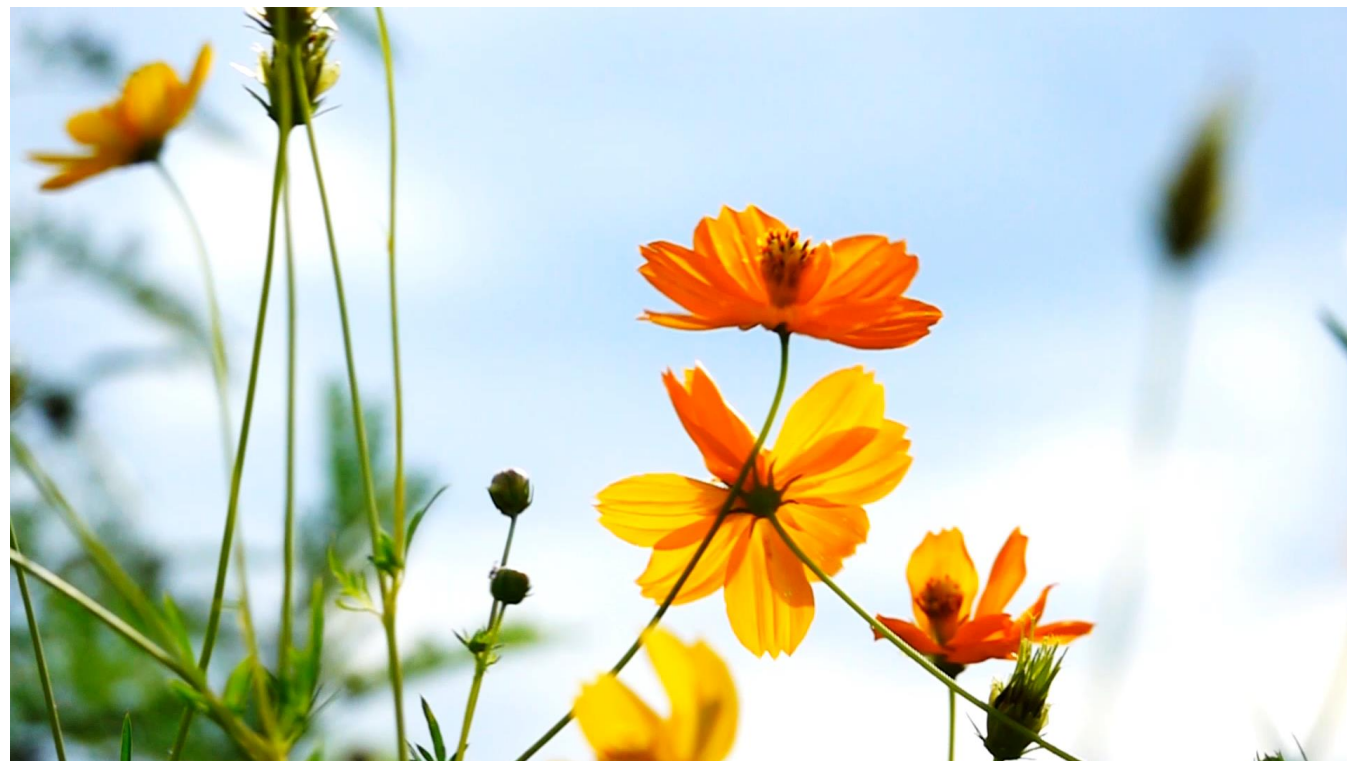


肆硫同位素： 发现及应用

鲍惠铭 (bao@lsu.edu)

LSU/南京大学



Aug. 12, 2020 Zoom 西北大学

有机食品

高温超导

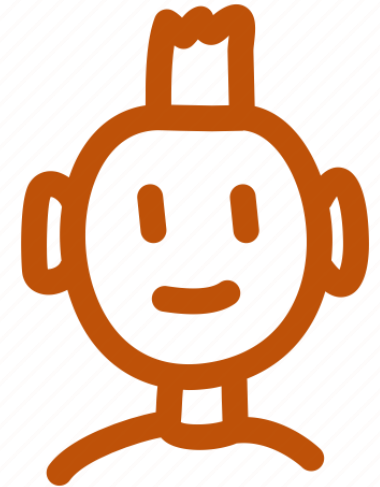
低温地球化学

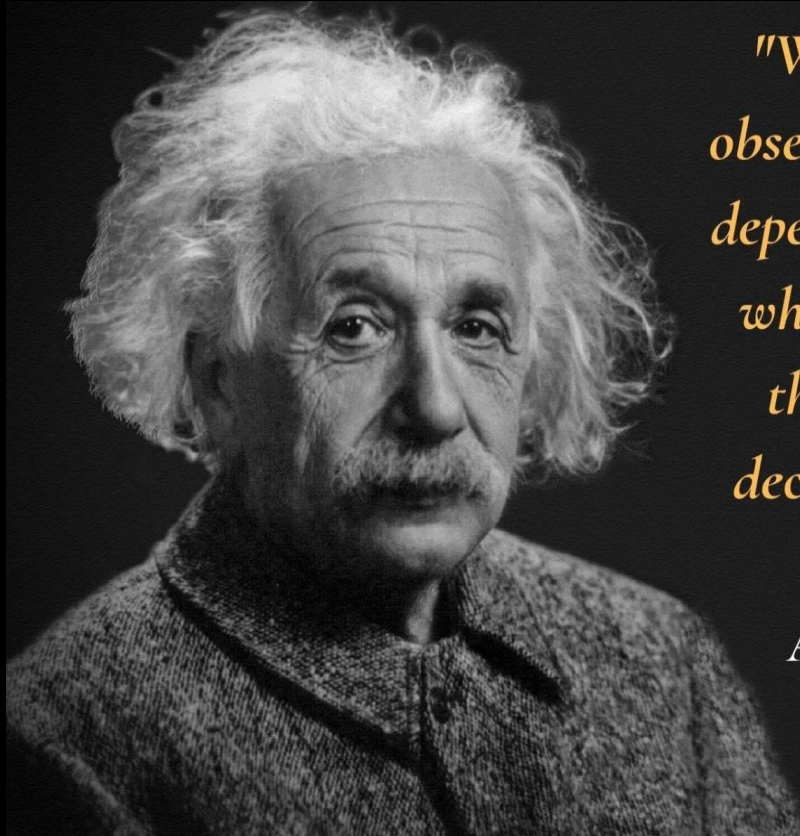
Heavy-element isotope effect

非传统同位素

非传统 + time = 传统

I will pause frequently during the lecture.
When I pause, you raise you hand to ask or answer questions.



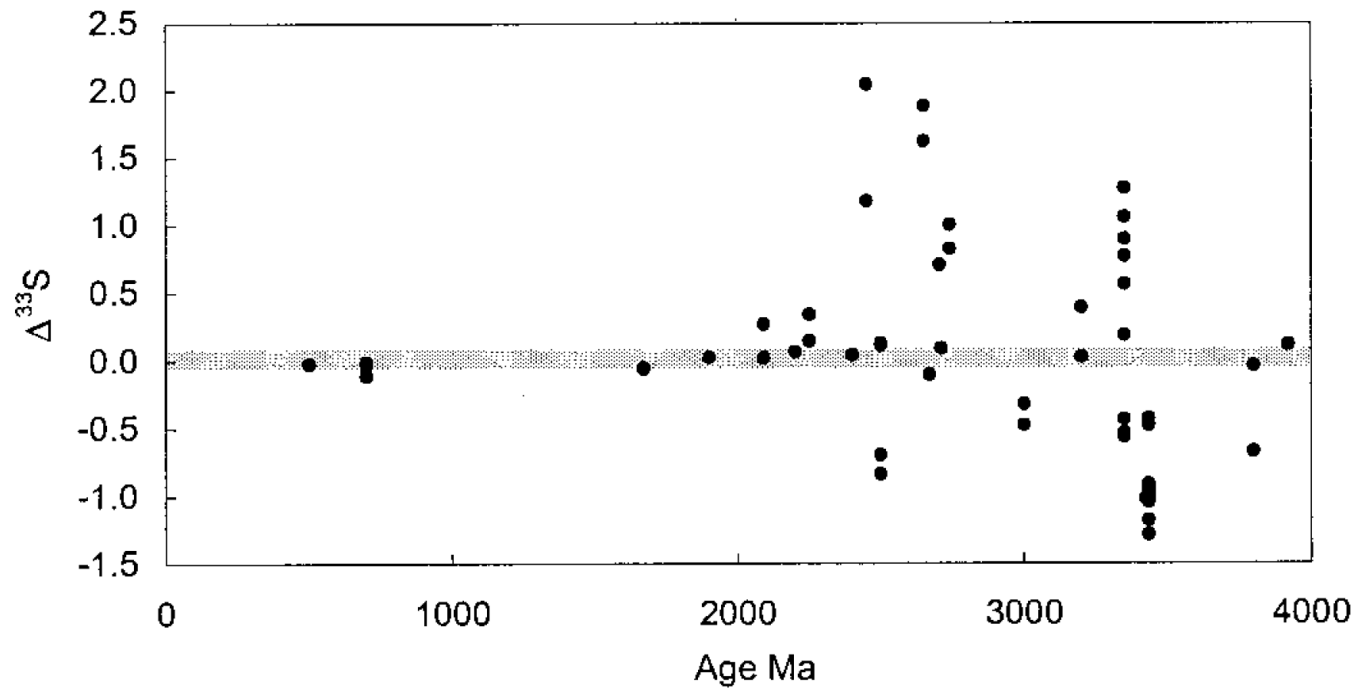


*"Whether you can
observe a thing or not
depends on the theory
which you use. It is
the theory which
decides what can be
observed."*

Albert Einstein

coachingleaders.co.uk





cycle dominated by oxidative weathering of continental sulfide and sulfate. The 0 represents the mean and 1 SD of data collected to date from younger sulfide samples that include mantle xenoliths, marine barite, desert gypsum, evaporite, deposits, ash deposits, and building surface deposits. Age data for these samples

Fig. 2
older 1
 $\Delta^{33}\text{S}$ a
mass-i
inating
hyperf
 $\Delta^{33}\text{S}$ b
plot at
sent 1
0.3‰



December 1999

James Farquhar

www.sciencemag.org SCIENCE VOL 289 4 AUGUST 2000

Farquhar et al, 2000

Google citation ~1500
by Aug. 12, 2020

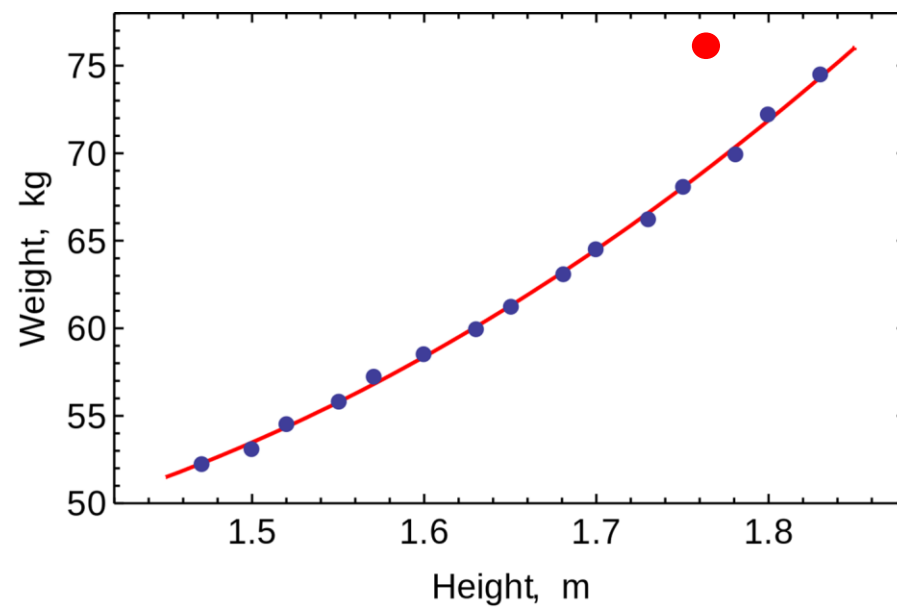
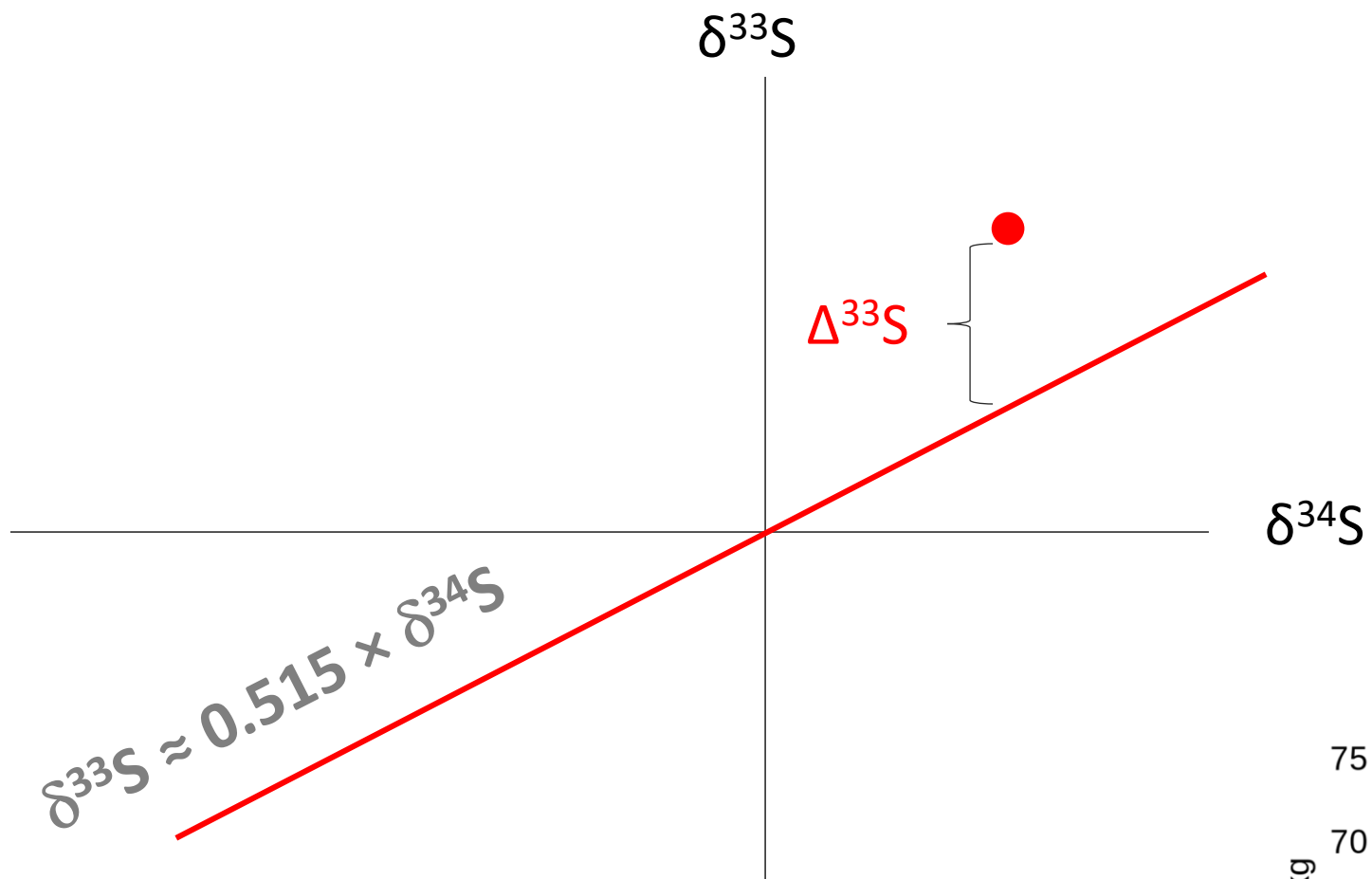
For mass-dependent processes:

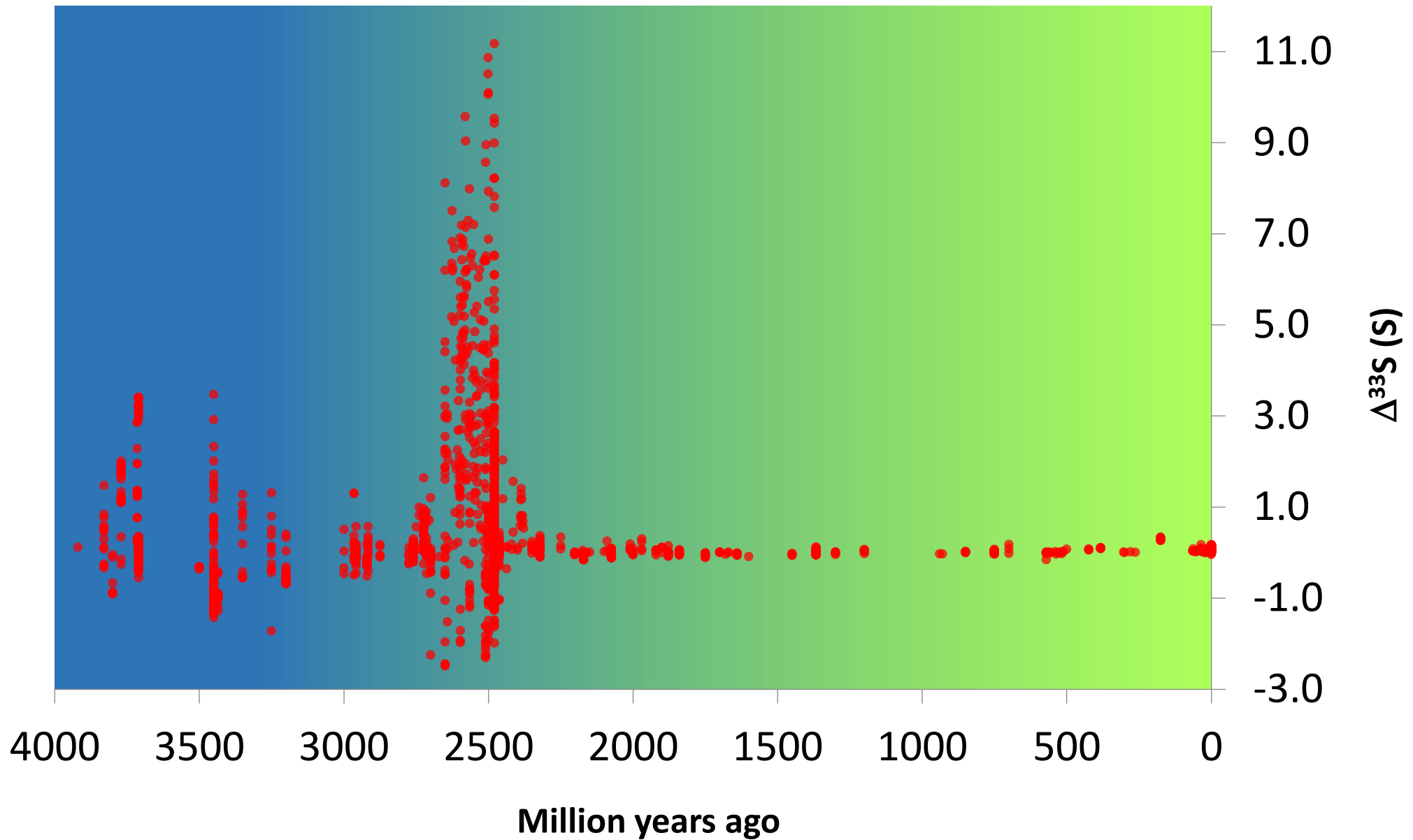
- ^{32}S : 95.02%
- ^{33}S : 0.75%
- ^{34}S : 4.21%
- ^{36}S : 0.02%

$$\delta^{33}\text{S} \approx 0.515 \times \delta^{34}\text{S}$$

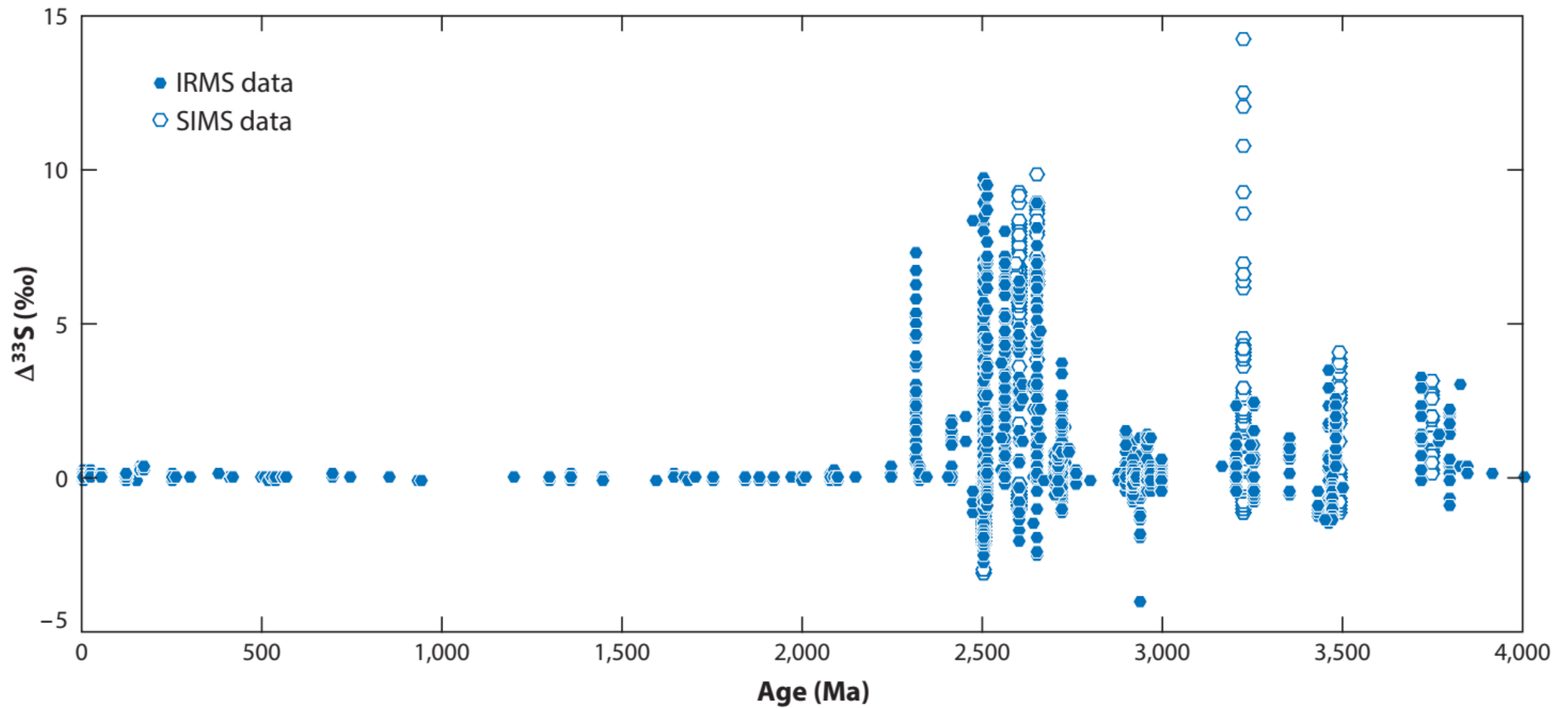
$$\delta^{36}\text{S} \approx 1.90 \times \delta^{34}\text{S}$$

$$\Delta^{33}\text{S} \equiv \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$$





Johnston 2011



Ono, 2017

Figure 1

Compilation of $\Delta^{33}\text{S}$ values against age of samples (see Johnston 2011 for data sources and additional references in **Figure 3**). Filled symbols are data measured by isotope ratio mass spectrometer (IRMS) via SF_6 . Open symbols are data measured by secondary ion mass spectrometer (SIMS).

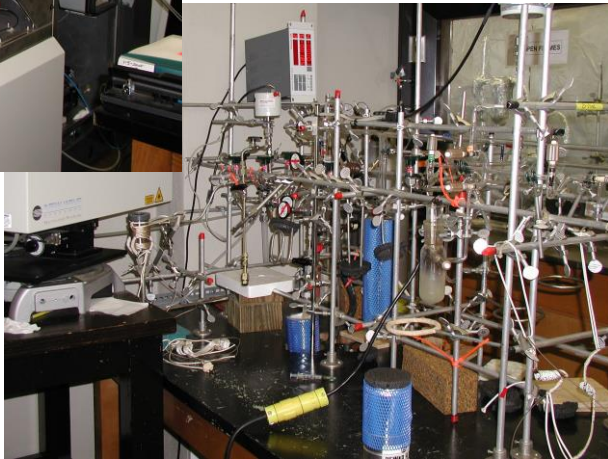
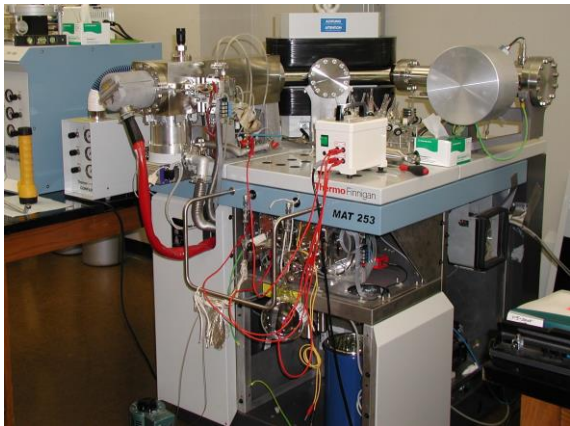
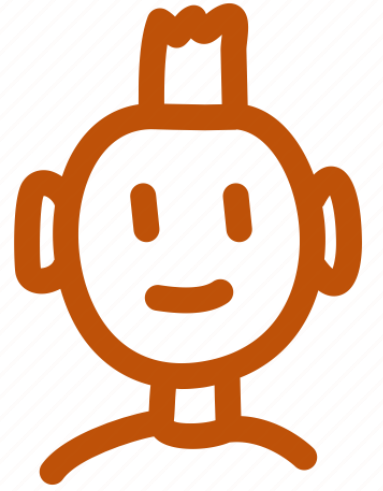
In-lecture question 1:

IRMS vs. SIMS?

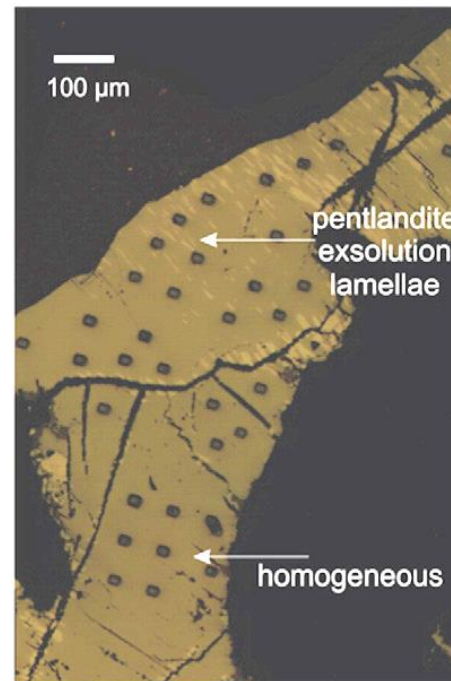
SF₆; <0.01 ‰

2SD for $\Delta^{33}\text{S}$

S ions; 0.1‰



LSU Bao Lab

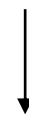


LaFlamme et al., 2016

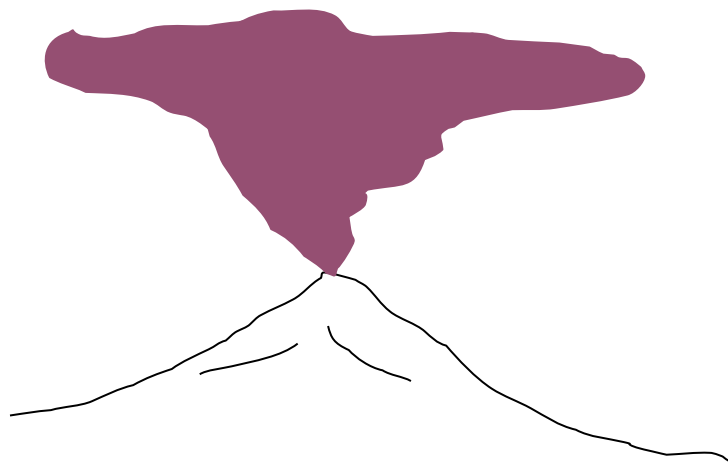




No O₂, no O₃ shield (>2.3 Ga)



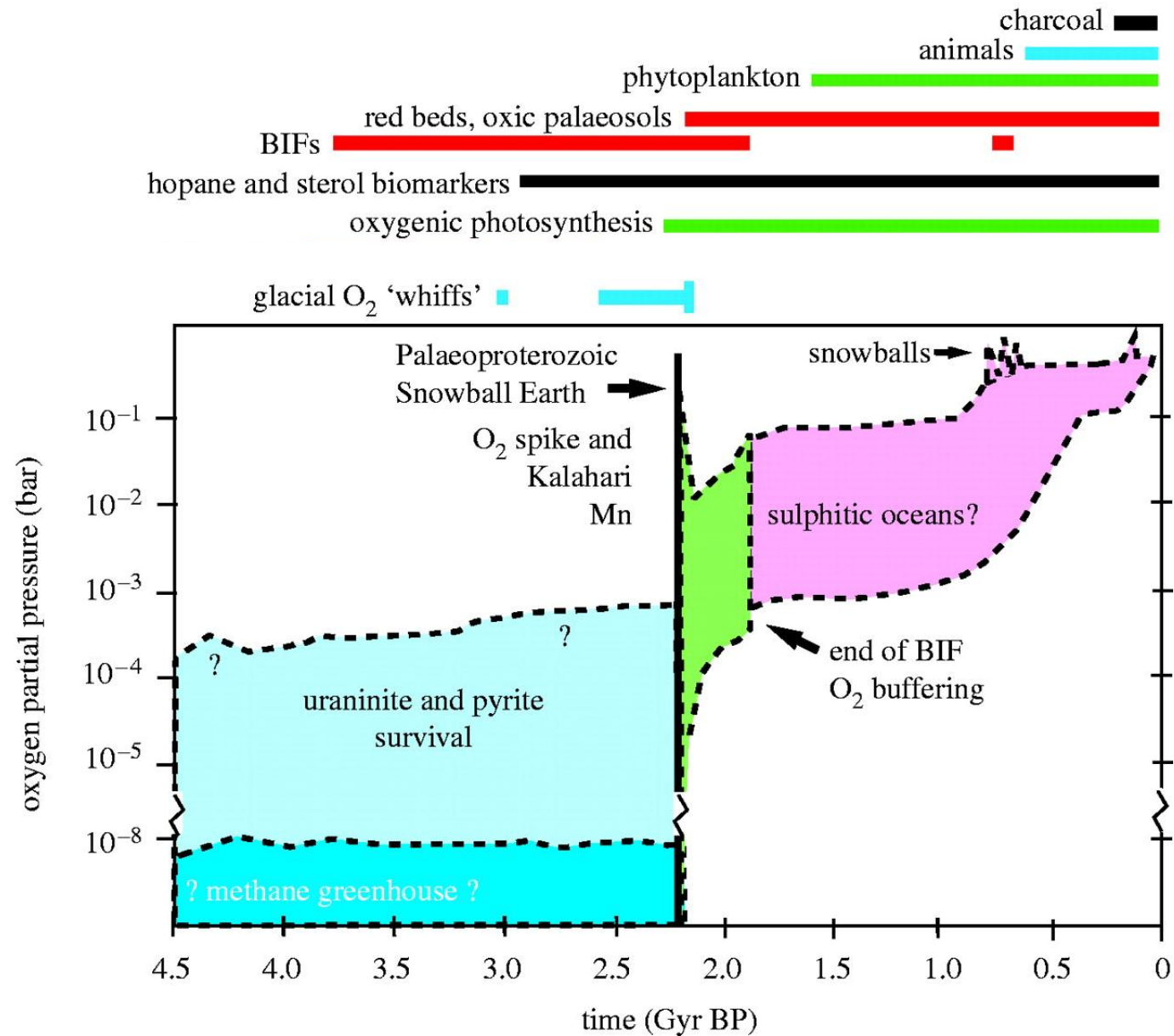
Wet & dry deposition



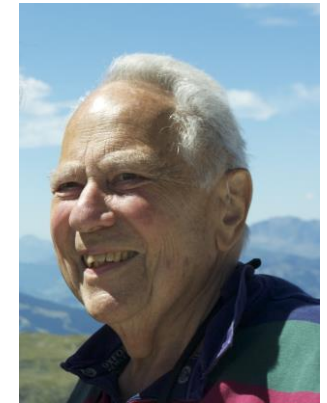
**S-33
anomaly**



Hiroshi Ohmoto



<http://rstb.royalsocietypublishing.org/content/363/1504/2755>

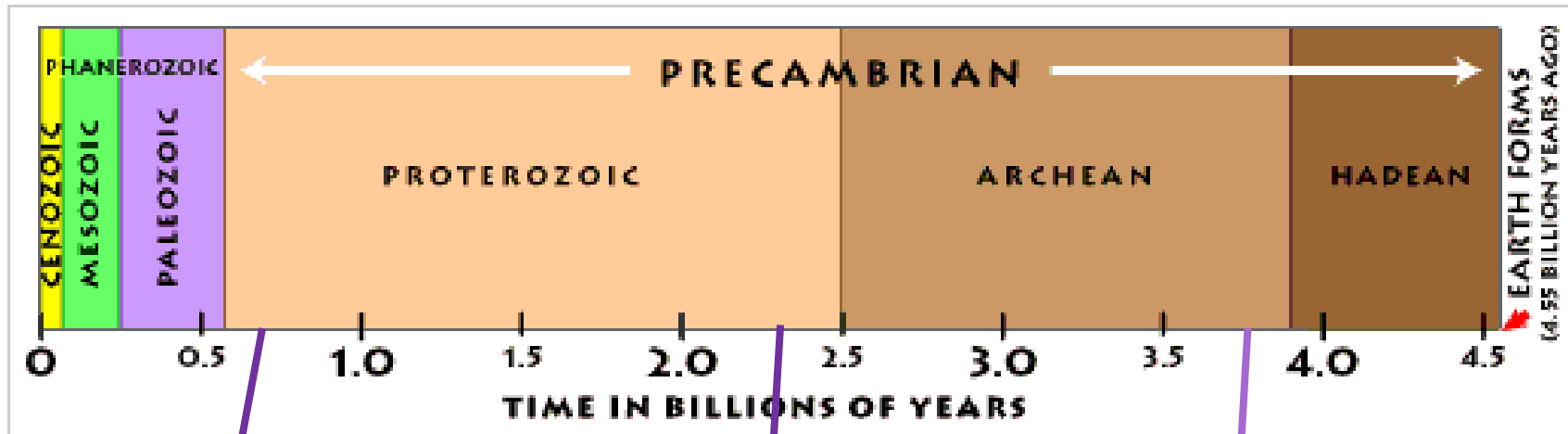


Dick Holland

Generation vs. preservation



<http://geomaps.wr.usgs.gov/parks/gtime/gtime2.html>



~2.3-2.5

The Great Oxidation
Event

**A sudden pO_2 increase
($>10^{-5}$ PAL)**

In-lecture question 2:

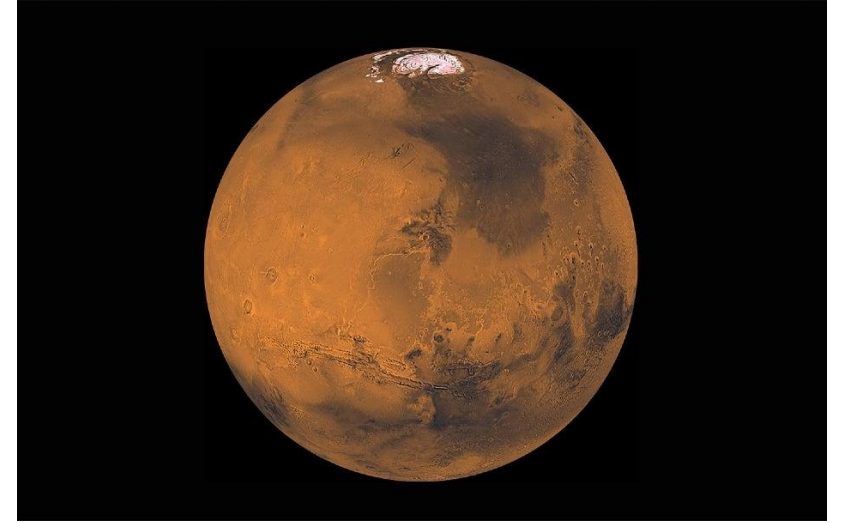
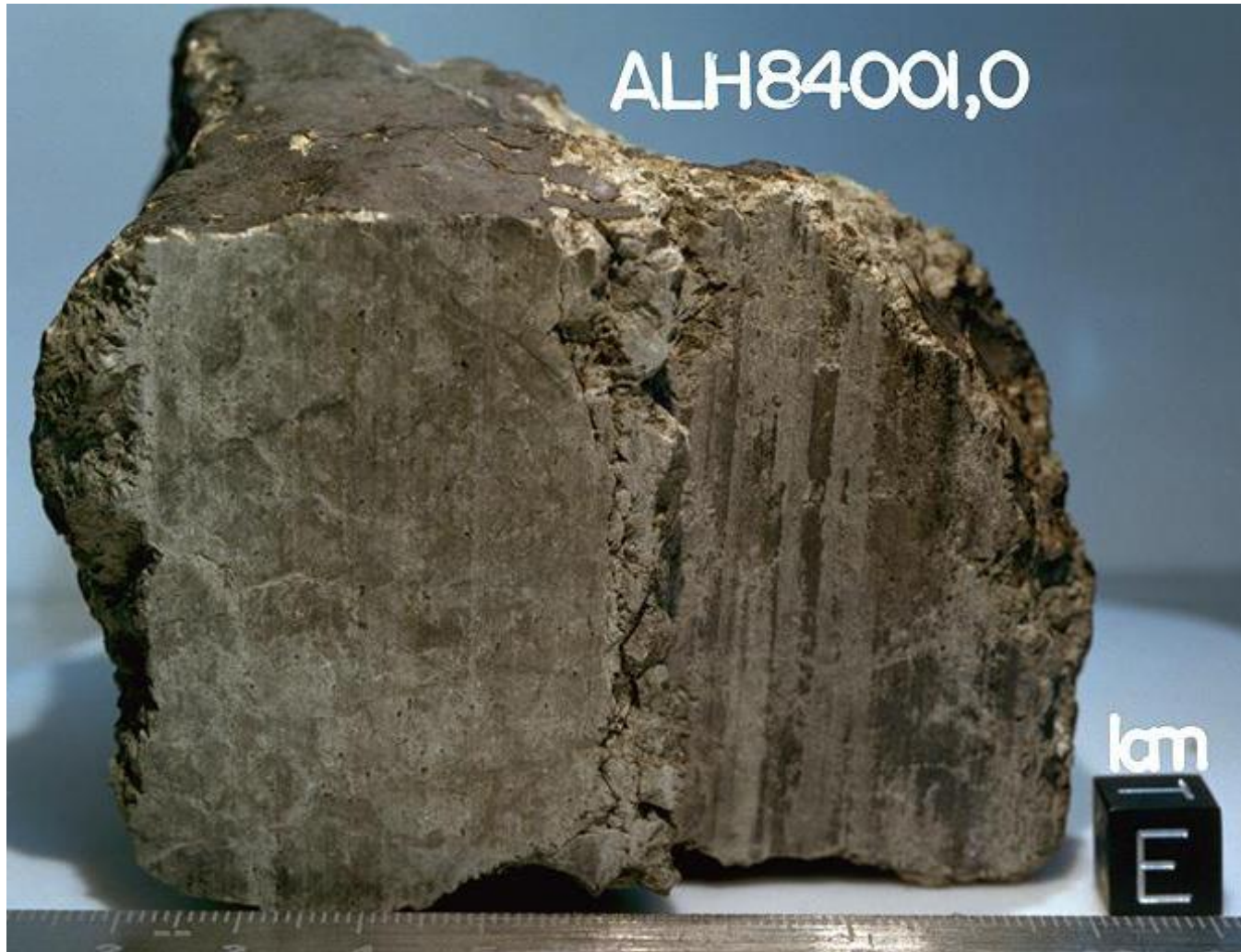
What's original reason for the division of Archean and Proterozoic Eons?



The end of **Archean Eon** was never clearly defined by an event. Oxygenation, appearance of red beds, or modern-style plate tectonics have been mentioned.

发现 How was it discovered

当年， JF在做太阳系及陨石的问题。



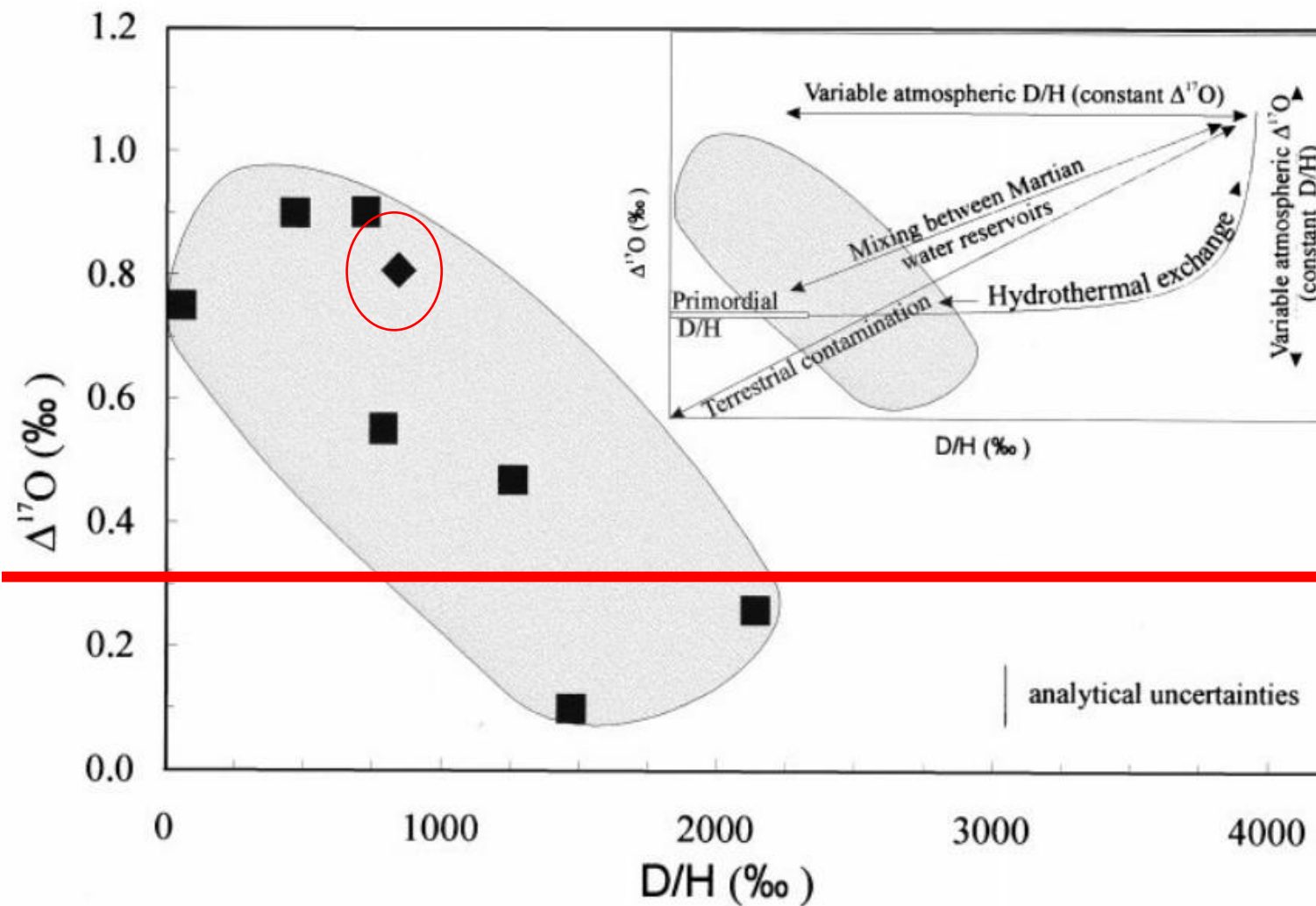
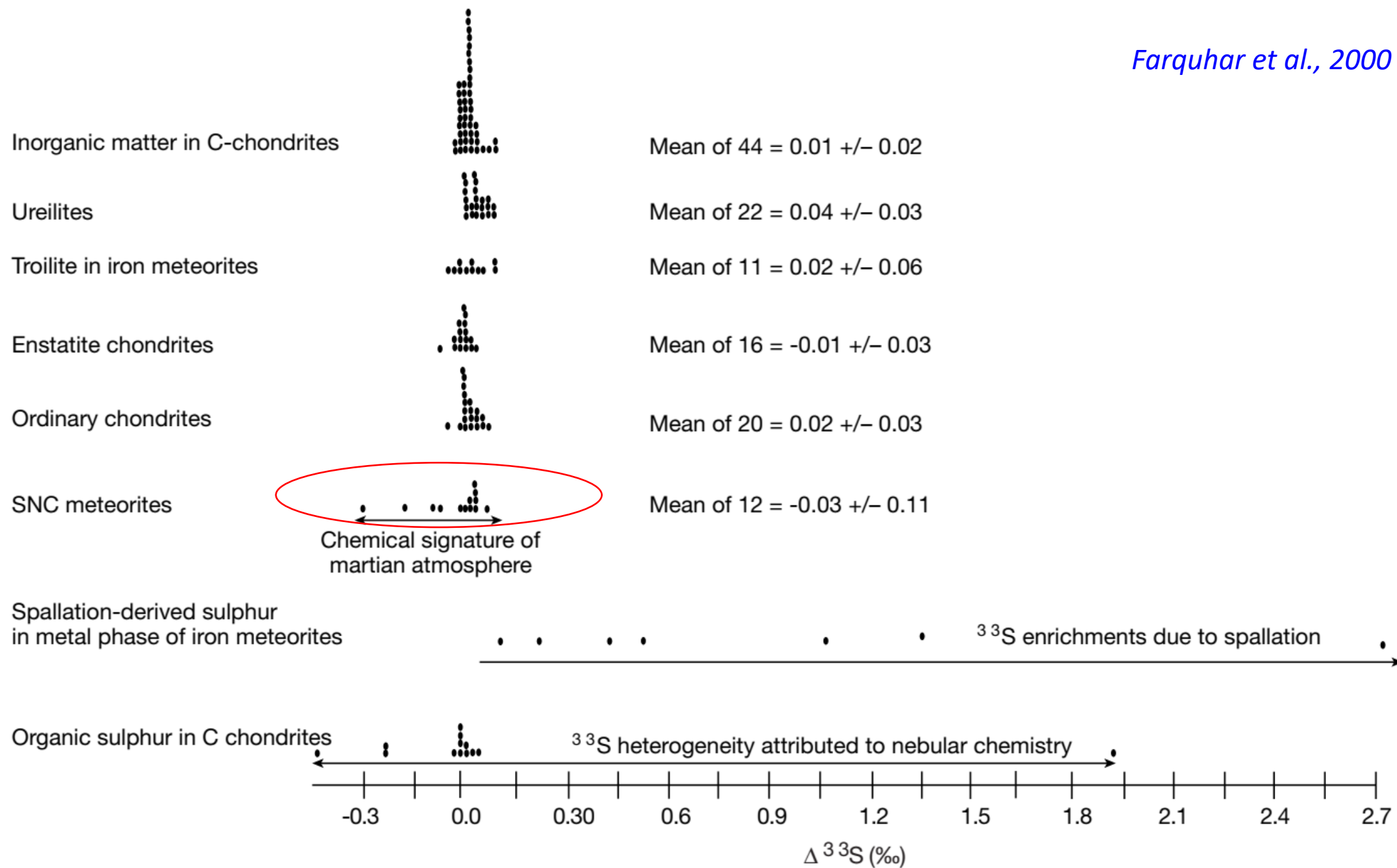


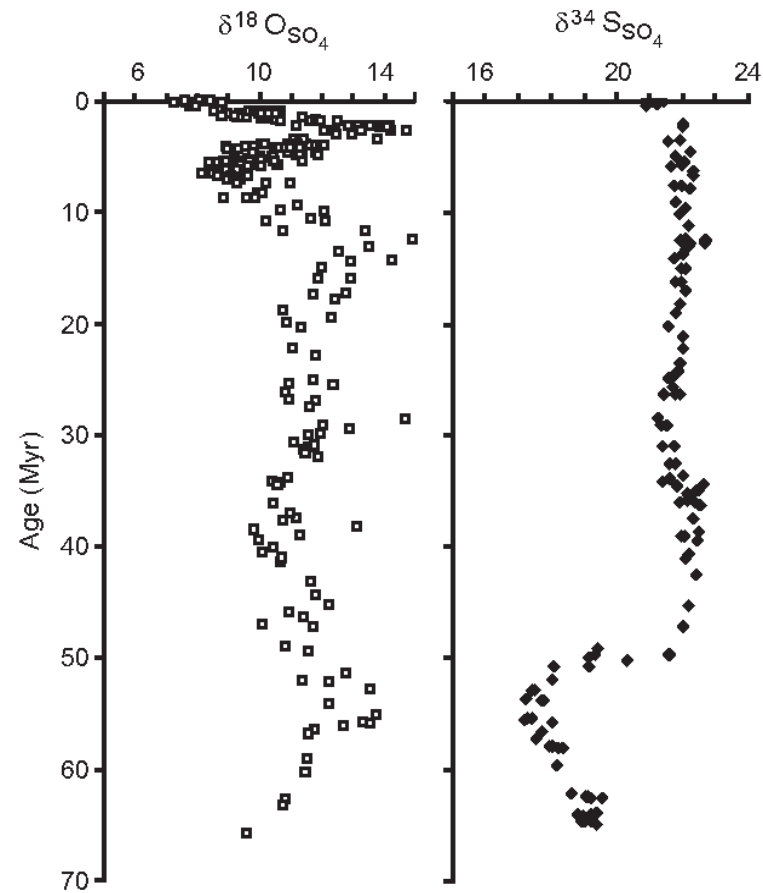
Fig. 1. Plot of maximum values of D/H versus $\Delta^{17}\text{O}$ for martian meteorite H_2O (■) extracted by pyrolysis (14, 27) and carbonate (◆) $\Delta^{17}\text{O}$ data versus pyrolysis D/H data from (14). Note that D/H and $\Delta^{17}\text{O}$ were collected in different sets of experiments. The H_2O and the carbonate data form a negatively sloped array. Assuming the martian atmosphere has elevated D/H and $\Delta^{17}\text{O}$, positively sloped arrays would be predicted by simple mixing with terrestrial waters (terrestrial contamination arrays), hydrothermal exchange, or mixing of juvenile and evolved martian reservoirs. Variable atmospheric D/H ratios would produce horizontal arrays, and variable atmospheric $\Delta^{17}\text{O}$ would produce vertical arrays. The primordial D/H field is from (13).

Farquhar et al., 1998

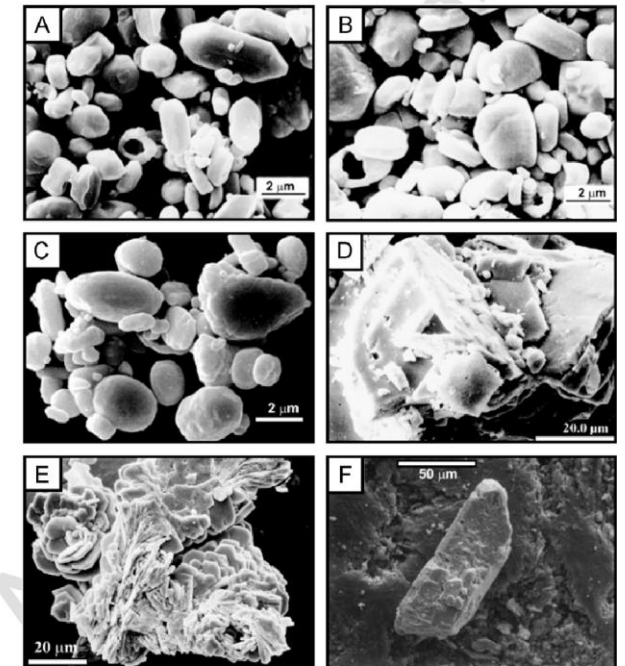


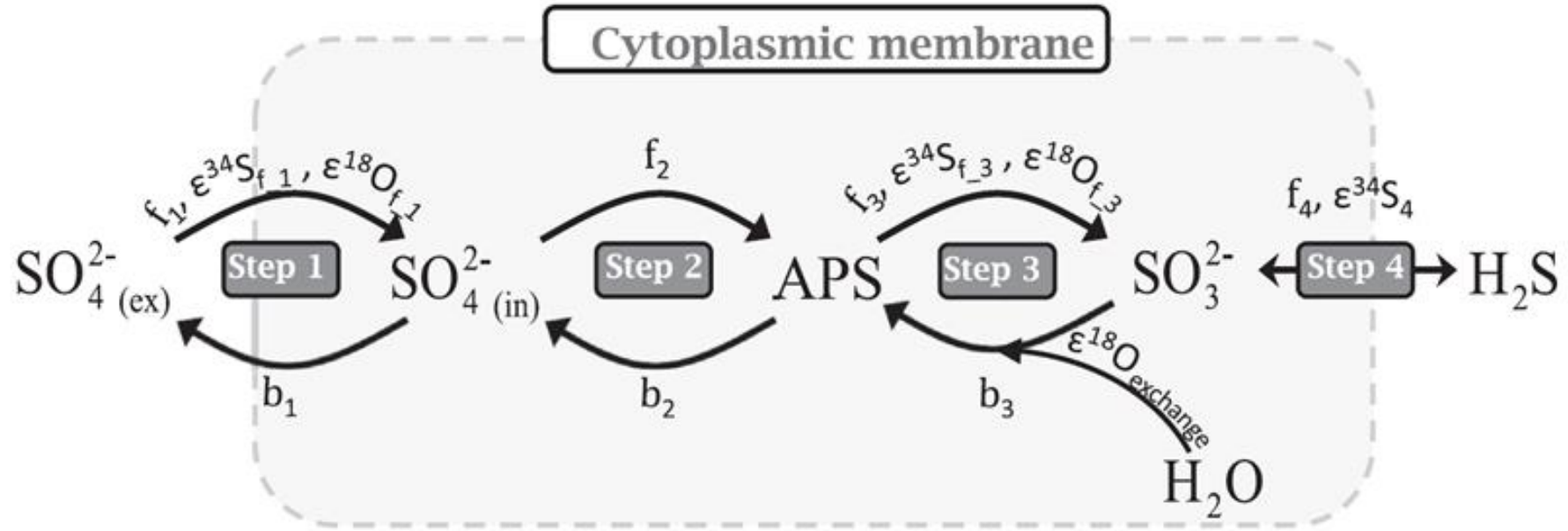


Adina Paytan
University of California, Santa Cruz



Miriam Kastner
Scripps Institution of Oceanography, UC San Diego



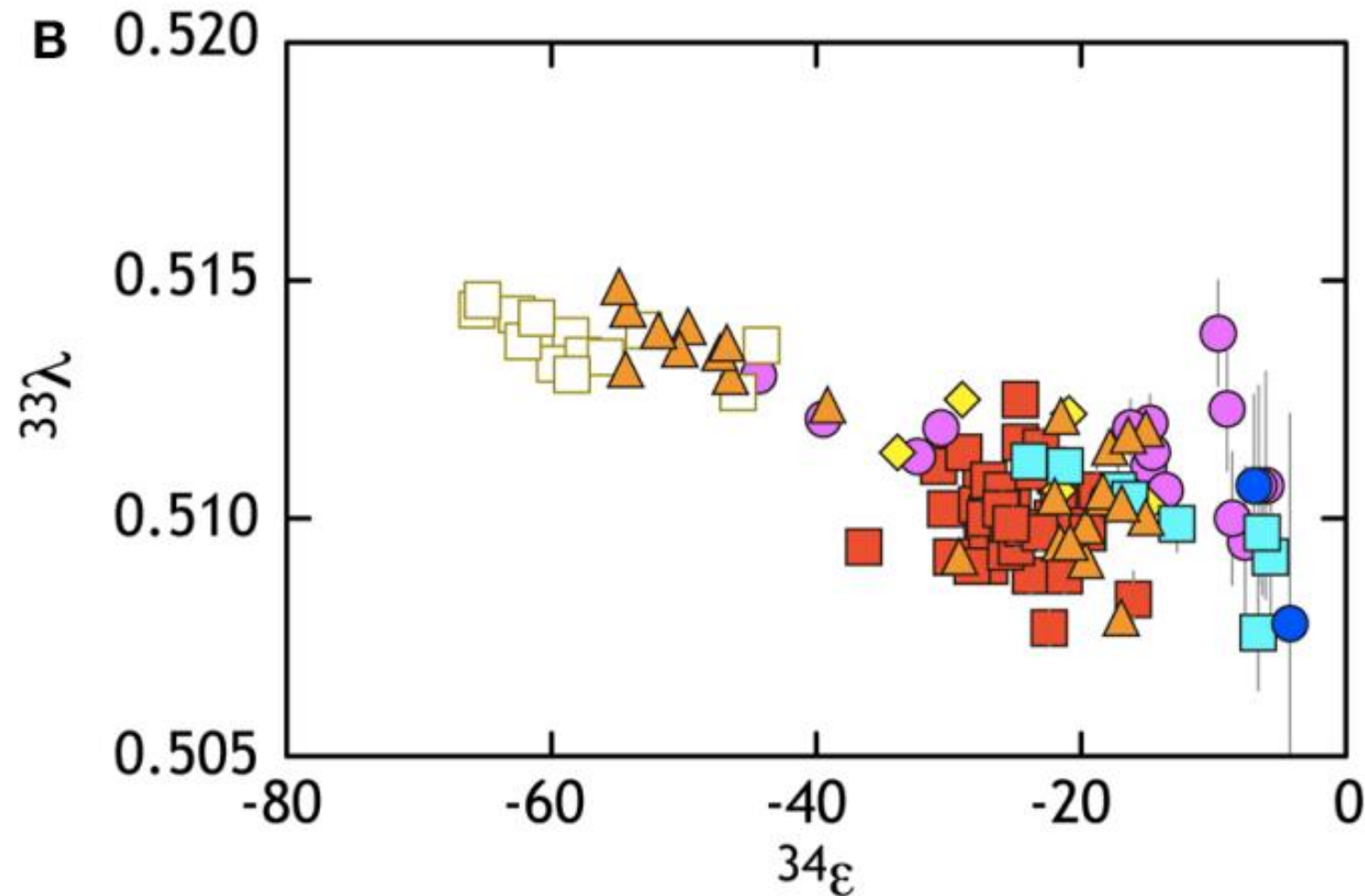


Antler et al., 2013

$$^{33}\theta \equiv \frac{\ln^{34}\alpha}{\ln^{33}\alpha}$$

Apparent $^{33}\theta$ value may change due to different kinetics/dynamics of SO_4 reduction.

~0.508 to 0.5145 for pure cultures

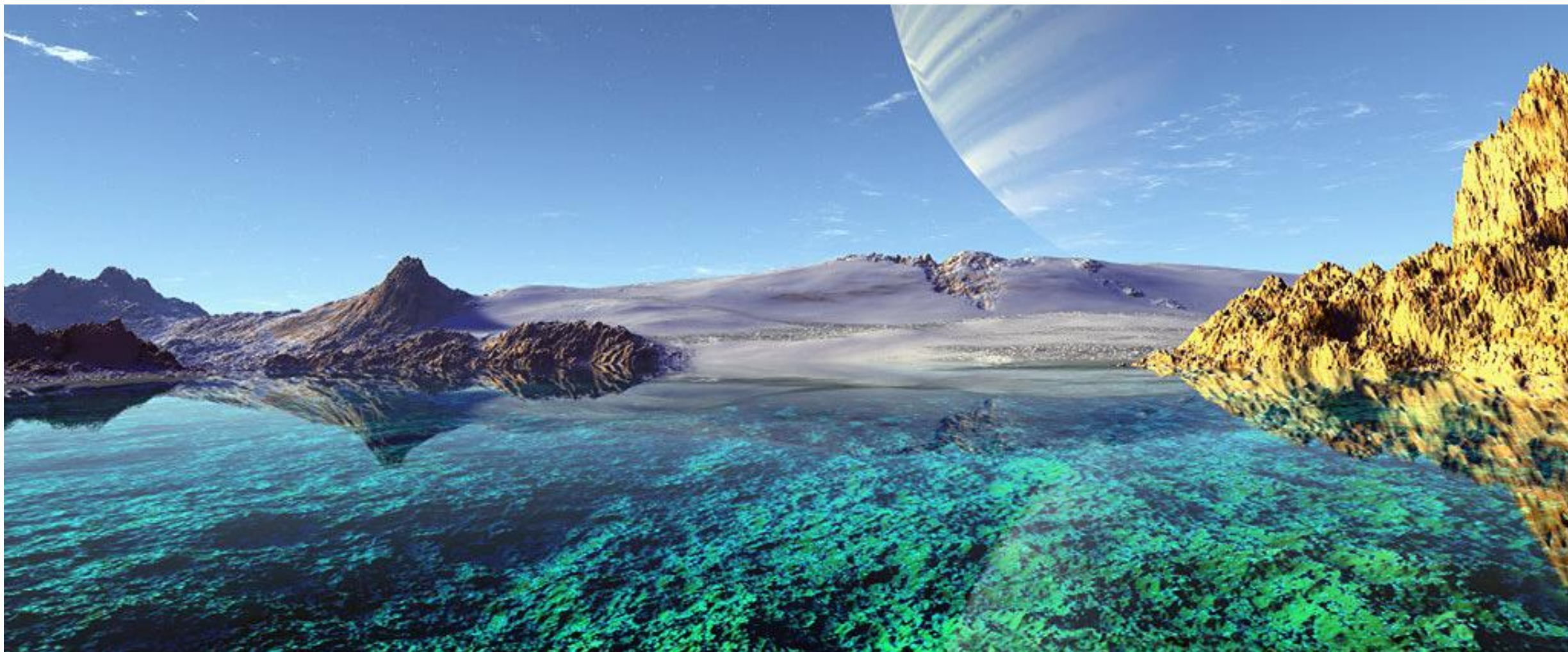


◆ Johnston *et al.*, 2005 ■ Johnston *et al.*, 2007 □ Sim *et al.*, 2011a
● Sim *et al.*, 2011b ■ Bradley *et al.*, 2013 ▲ Leavitt *et al.*, 2013

Levitte et al 2014

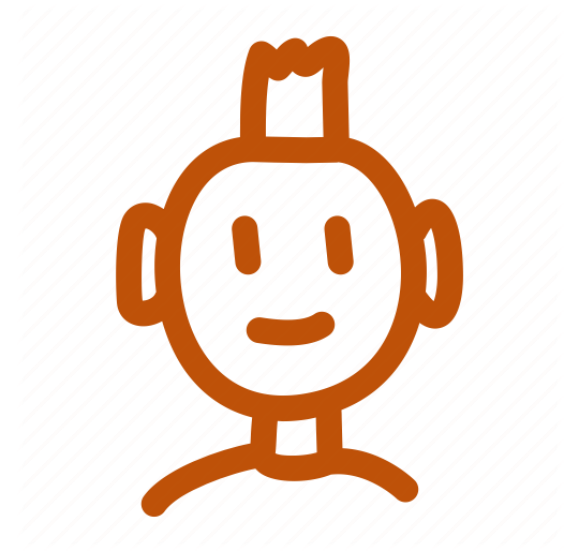
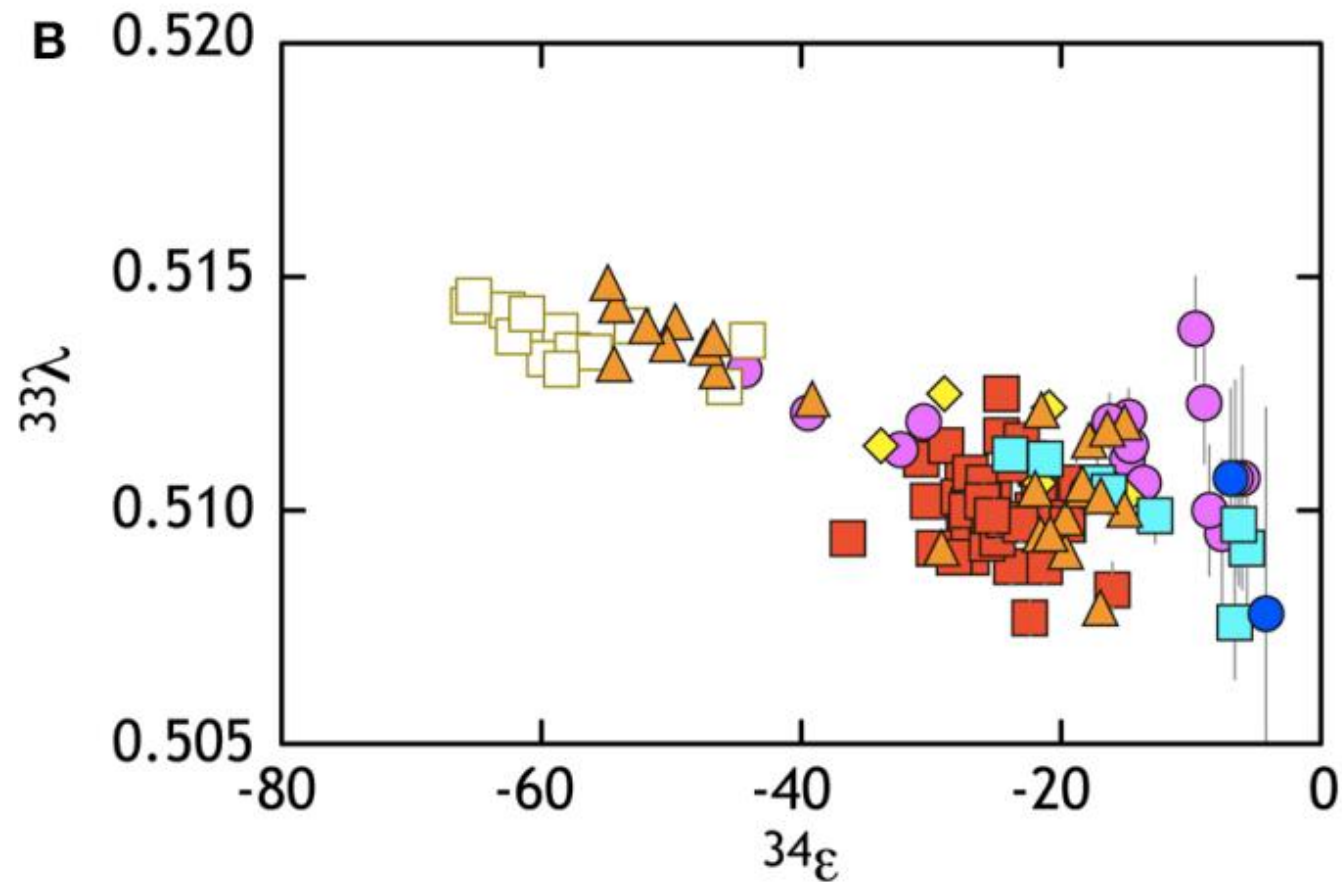
但，深海的细小重晶石没有肆硫同位素的异常。

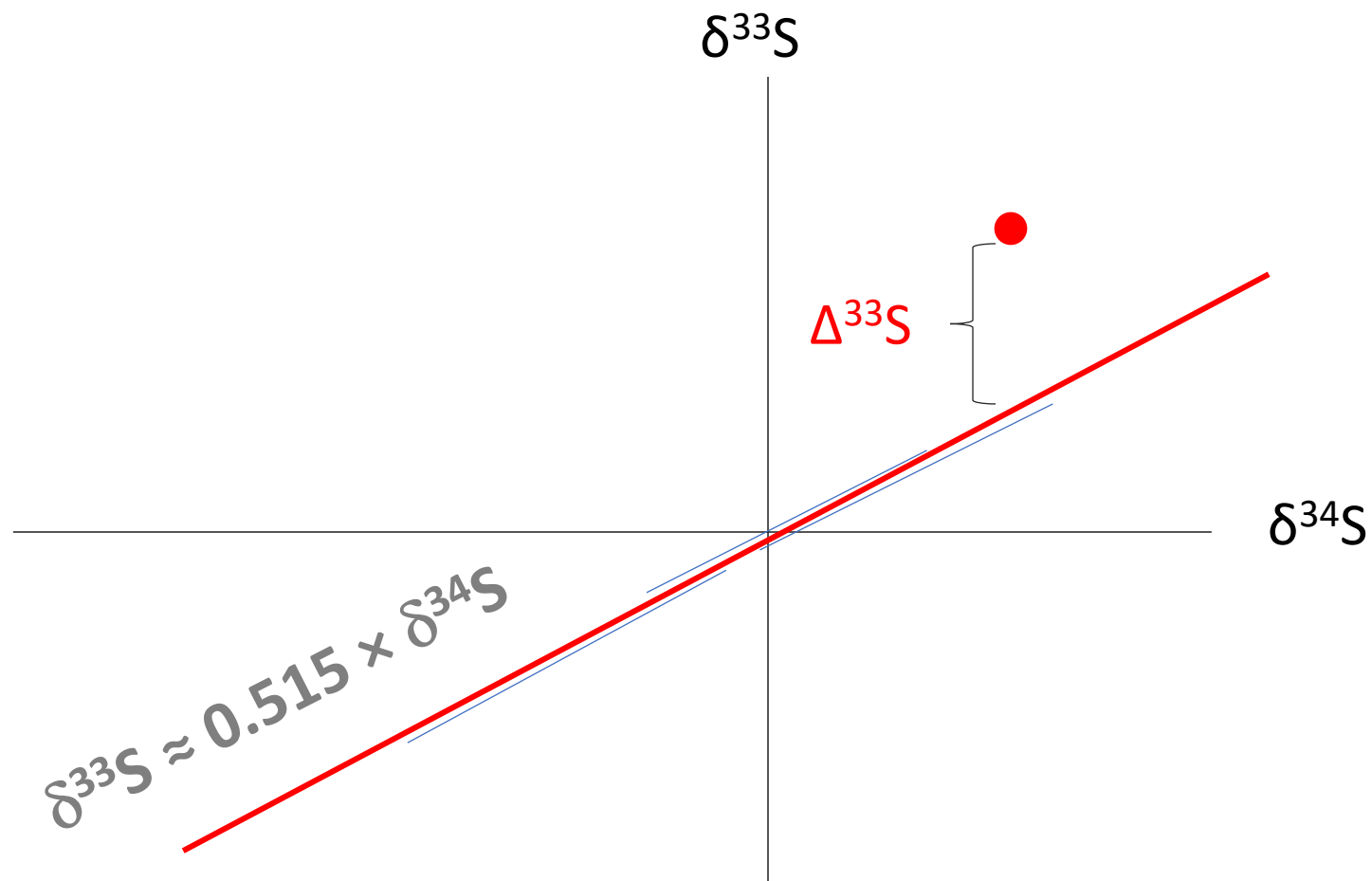
What about Archean microbes?

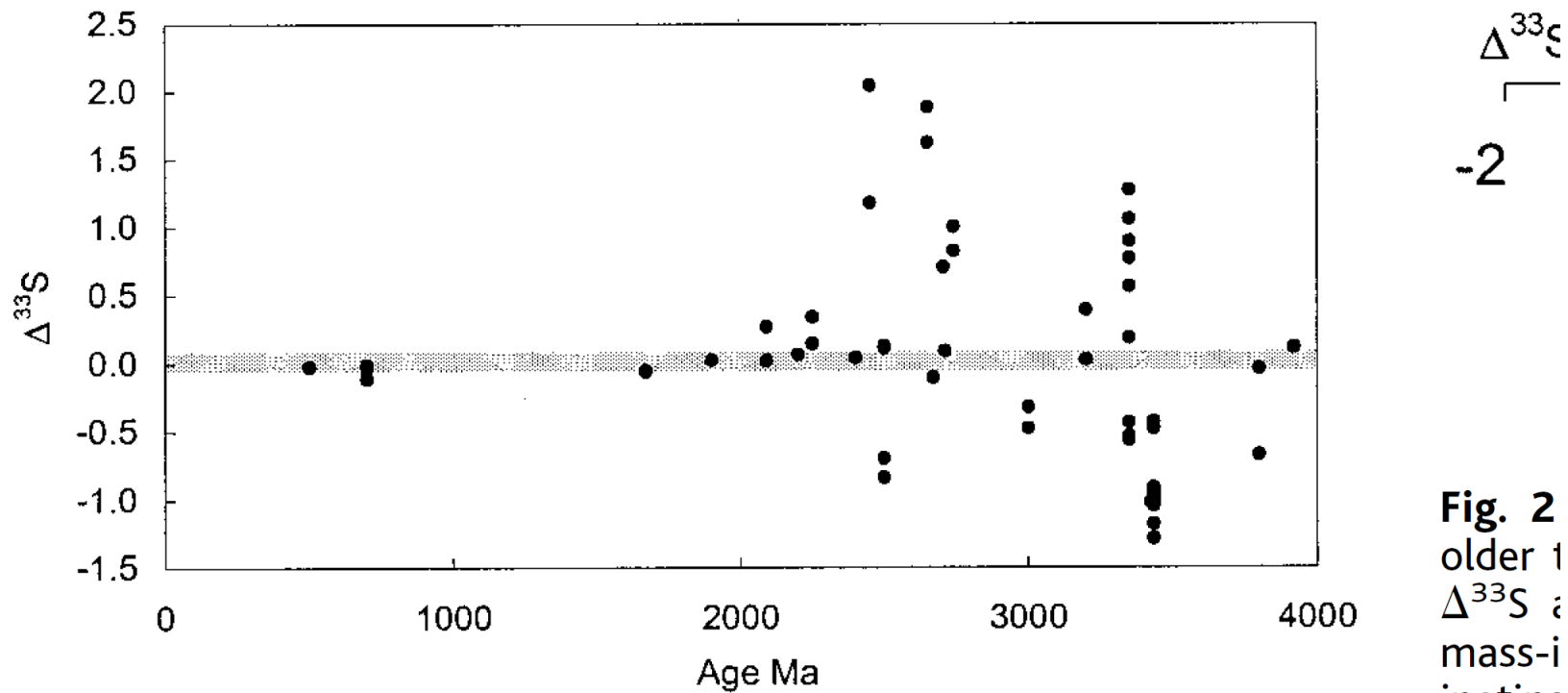


In-lecture question 3:

Where should Archean pyrite be plotted on this diagram?







cycle dominated by oxidative weathering of continental sulfide and sulfate. The shaded band represents the mean and 1 SD of data collected to date from younger sulfide samples that include mantle xenoliths, marine barite, desert gypsum, evaporite, ash deposits, and building surface deposits. Age data for these samples

Fig. 2
older than 2000 Ma
 $\Delta^{33}\text{S}$ &
mass-inde-
pendent
hyperfractionation
 $\Delta^{33}\text{S}$ > 0.3‰
plot at
least 1
0.3‰

应用

Mass-Independent Sulfur of Inclusions in Diamond and Sulfur Recycling on Early Earth

J. Farquhar,¹ B. A. Wing,¹ K. D. McKeegan,² J. W. Harris,³
P. Cartigny,⁴ M. H. Thiemens⁵

2002, Sci.

Populations of sulfide inclusions in diamonds from the Orapa kimberlite pipe in the Kaapvaal-Zimbabwe craton, Botswana, preserve mass-independent sulfur isotope fractionations. The data indicate that material was transferred from the atmosphere to the mantle in the Archean. The data also imply that sulfur is not well mixed in the diamond source regions, allowing for reconstruction of the Archean sulfur cycle and possibly offering insight into the nature of mantle convection through time.

An understanding of the nature of the source materials for diamonds would provide important insights into large-scale geophysical pro-

cesses in Botswana. We also discuss the implications of $\Delta^{33}\text{S}$ as an almost perfect tracer of the exchange between Earth's geochemical res-

Sulfur isotopes in diamonds reveal differences in continent construction

Karen V. Smit^{1*}, Steven B. Shirey², Erik H. Hauri^{2†}, Richard A. Stern³

Neoproterozoic West African diamonds contain sulfide inclusions with mass-independently fractionated (MIF) sulfur isotopes that trace Archean surficial signatures into the mantle. Two episodes of subduction are recorded in these West African sulfide inclusions: thickening of the continental lithosphere through horizontal processes around 3 billion years ago and reworking and diamond growth around 650 million years ago. We find that the sulfur isotope record in worldwide diamond inclusions is consistent with changes in tectonic processes that formed the continental lithosphere in the Archean. Slave craton diamonds that formed 3.5 billion years ago do not contain any MIF sulfur. Younger diamonds from the Kaapvaal, Zimbabwe, and West African cratons do contain MIF sulfur, which suggests craton construction by advective thickening of mantle lithosphere through conventional subduction-style horizontal tectonics.

Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust

Rita A. Cabral¹, Matthew G. Jackson¹, Estelle F. Rose-Koga², Kenneth T. Koga², Martin J. Whitehouse^{3,4}, Michael A. Antonelli⁵, James Farquhar⁵, James M. D. Day⁶ & Erik H. Hauri⁷

Basaltic lavas erupted at some oceanic intraplate hotspot volcanoes are thought to sample ancient subducted crustal materials^{1,2}. However, the residence time of these subducted materials in the mantle is uncertain and model-dependent³, and compelling evidence for their return to the surface in regions of mantle upwelling beneath hotspots is lacking. Here we report anomalous sulphur isotope signatures indicating mass-independent fractionation (MIF) in olivine-hosted sulphides from 20-million-year-old ocean island basalts from Mangaia, Cook Islands (Polynesia), which have been suggested to sample recycled oceanic crust^{3,4}. Terrestrial MIF sulphur isotope signatures (in which the amount of fractionation does not scale in proportion with the difference in the masses of the isotopes) were generated exclusively through atmospheric photo-

processes to generate the HIMU mantle beneath Mangaia have been suggested^{12,13}. Here we report MIF S-isotope compositions in Mangaia lavas that require the presence of recycled, ancient (>2.45 Gyr old) surface material in the HIMU mantle source for Mangaia lavas.

Fresh basaltic glass for S-isotope measurement is not available from Mangaia, where subaerial lavas are ~20 million years old¹⁴ and have suffered from extensive weathering in a tropical climate. However, magmatic olivine phenocrysts encapsulate primary magmatic sulphides and isolate them from surface weathering processes. Olivine phenocrysts were separated from three basaltic lavas collected from Mangaia. The largest inclusions were exposed for S-isotope analysis by secondary ion mass spectrometry (SIMS). Whereas sulphides <10 µm in diameter are relatively common, the largest sulphides, which permit



Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume

Hélène Delavault^{a,1,2}, Catherine Chauvel^a, Emilie Thomassot^b, Colin W. Devey^c, and Baptiste Dazas^a

^aISTerre, Université Grenoble Alpes, CNRS, 38000 Grenoble, France; ^bCentre de Recherches Pétrographiques et Géochimiques, Université de Lorraine, CNRS, 54501 Vandœuvre-Les-Nancy, France; and ^cGeomar Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany

Edited by Richard W. Carlson, Carnegie Institution for Science, Washington, DC, and approved September 20, 2016 (received for review June 1, 2016)

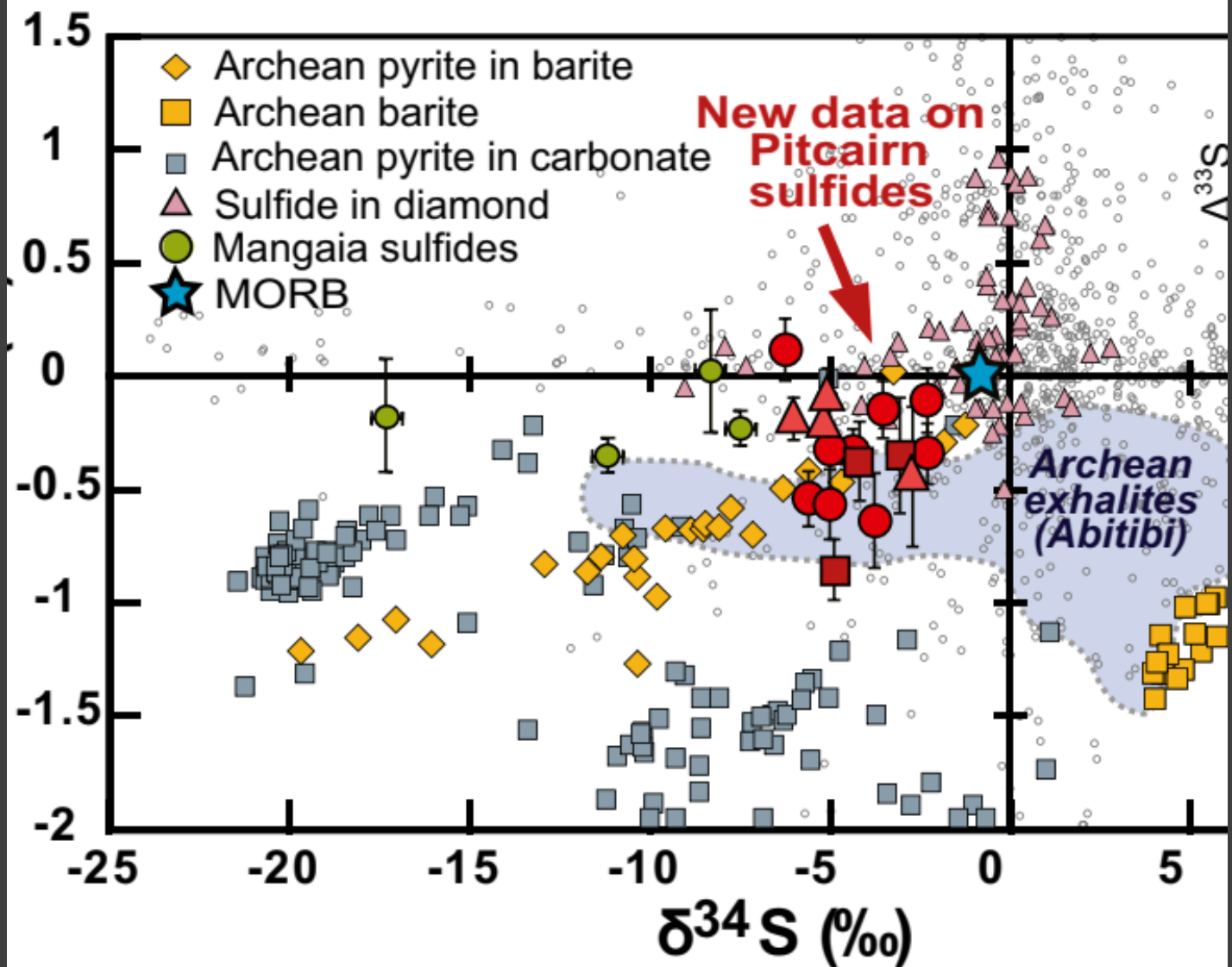
The isotopic diversity of oceanic island basalts (OIB) is usually attributed to the influence, in their sources, of ancient material recycled into the mantle, although the nature, age, and quantities of this material remain controversial. The unradiogenic Pb isotope signature of the enriched mantle I (EM I) source of basalts from, for example, Pitcairn or Walvis Ridge has been variously attributed to recycled pelagic sediments, lower continental crust, or recycled subcontinental lithosphere. Our study helps resolve this debate by showing that Pitcairn lavas contain sulfides whose sulfur isotopic compositions are affected by mass-independent fractionation ($\delta^{34}\text{S}$ down to $\Delta^{33}\text{S} = -0.8$), something which is thought to have occurred on Earth only before 2.45 Ga, constraining the youngest possible age of the EM I source component. With this independent age constraint and a Monte Carlo refinement modeling of lead isotopes, we place the likely Pitcairn source age at 2.5 Ga to 2.6 Ga. The Pb, Sr,

but all remain model-dependent, as the problem is unresolved. Independent constraints on either the age or the nature of the component are therefore required to choose the best model.

Here we revisit the possible origin of the EM I source component by presenting in situ sulfur isotopic analyses of Pitcairn lavas. These data, combined with modeling of new high-precision Pb and Sr, Nd, and Hf isotopes allows us to constrain the material involved in their source.

Results and Discussion

The sulfur isotopic data measured on sulfide inclusions, plagioclases, and matrix material at Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Nancy are shown in Fig. 2. The data are plotted in Fig. 2. The data are plotted in Fig. 2.



Atmospheric record in the Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone Belt (Nunavik, Quebec)

Emilie Thomassot^{a,b,c,1}, Jonathan O'Neil^d, Don Francis^b, Pierre Cartigny^e, and Boswell A. Wing^{b,c}

^aCentre de Recherches Pétrographiques et Géochimiques, Université de Lorraine, 54501 Vandœuvre-Lès-Nancy, France; ^bDepartment of Earth and Planetary Sciences and ^cGEOTOP, McGill University, Montreal, QC H3A 0E8, Canada; ^dDepartment of Earth Sciences, University of Ottawa, Ottawa, ON K1N 6N5, Canada; and ^eLaboratoire de Géochimie des Isotopes Stables, Institut de Physique du Globe de Paris, UMR 7154 CNRS, Université Paris Denis-Diderot, Sorbonne Paris Cite, 75005 Paris, France

Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved December 7, 2014 (received for review October 15, 2014)

Mass-independent fractionation of sulfur isotopes (S-MIF) results from photochemical reactions involving short-wavelength UV light. The presence of these anomalies in Archean sediments [(4–2.5 billion years ago, (Ga)) implies that the early atmosphere was free of the appropriate UV absorbers, of which ozone is the most important in the modern atmosphere. Consequently, S-MIF is considered some of the strongest evidence for the lack of free atmospheric oxygen before 2.4 Ga. Although temporal variations in the S-MIF record are thought to depend on changes in the abundances of gas and aerosol species, our limited understanding of photochemical mechanisms complicates interpretation of the S-MIF record in terms of atmospheric composition. Multiple sulfur isotope compositions ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$) of the >3.8 billion-year-old Nuvvuagittuq Greenstone Belt (Ungava peninsula) have been investigated to track the early origins of S-MIF. Anomalous S-isotope compositions ($\Delta^{33}\text{S}$ up to +2.2‰) confirm a sedimentary origin of sulfide-bearing banded iron and silica-

wide intervals in time and are shared among a variety of rock-forming environments.

High-resolution measurements on Neoarchean samples (2.5–2.8 Ga) (13, 14) have provided evidence for temporal variation of the multiple S-isotopic signal reflecting changes in the relative proportions of atmospheric gases of volcanogenic and biogenic origin. The S-isotopic signal then appears as a robust metric of atmospheric composition that reflects both the photolytic reactions involving S-bearing phases and their transfer to the sediments. The present study focuses on the origins and extent of this atmospheric memory in the sedimentary record. To probe the sensitivity of early Archean photochemical processes to major surface perturbations, including emergence of dominant biogenic elemental cycling, intense volcanic activity, bombardment of Earth's surface by bolides, and evolution of the solar flux, we



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Letters

Multiple sulfur isotope evidence for surface-derived sulfur in the Bushveld Complex

Sarah C. Penniston-Dorland^{a,*}, Edmond A. Mathez^b, Boswell A. Wing^{c,d}, James Farquhar^e, Judith A. Kinnaird^f^a Department of Geology, University of Maryland, College Park, MD 20742, USA^b Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY 10024, USA^c Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada H3A 2A7^d GEOTOP-UQAM-McGill, University of Quebec, Montreal, Quebec, Canada H3C 3P8^e Department of Geology and ESSIC, University of Maryland, College Park, MD 20742, USA^f Department of Geological Sciences, University of the Witwatersrand, Private Bag 3, Johannesburg, Wits 2050, South Africa

ARTICLE INFO

Article history:
Received 9 February 2012

ABSTRACT

The Rustenberg Layered Suite of the Bushveld Complex originated in the mantle, but is characterized by unusually radiogenic strontium, neodymium, lead, and cerium initial isotope ratios and more elevated $\delta^{18}\text{O}$

2.06 Ga

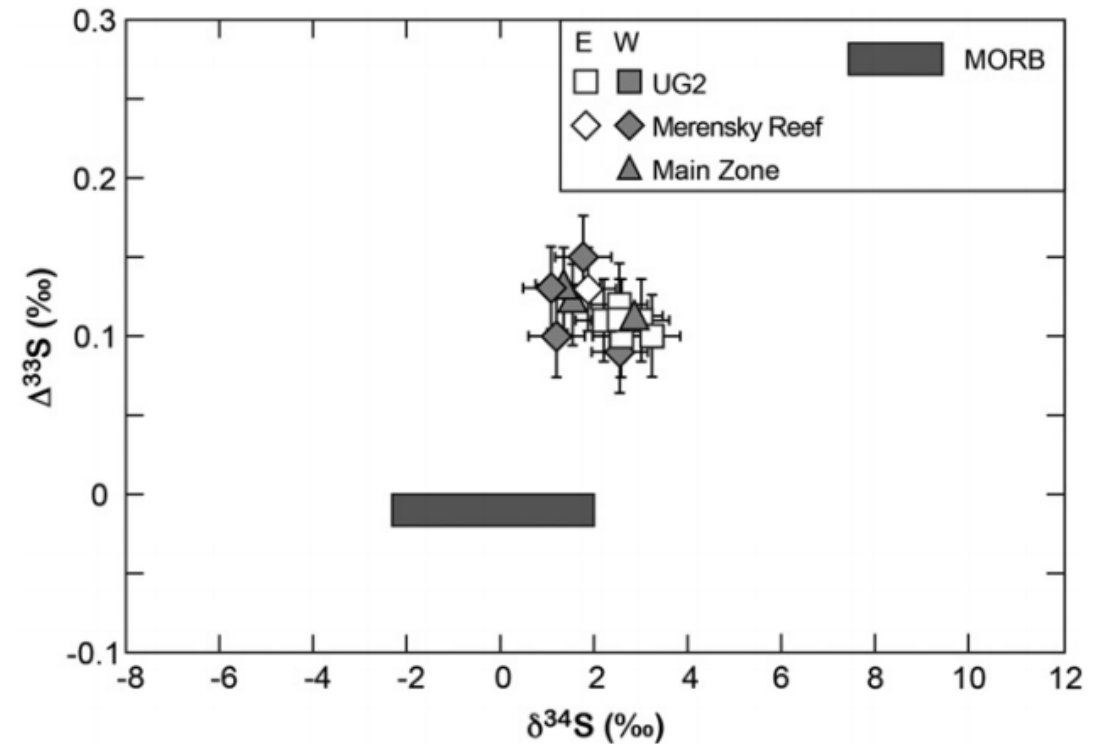


Fig. 2. Sulfur isotope composition of samples. Ranges of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ for mid-ocean ridge basalt (MORB) are plotted for reference (Sakai et al., 1984; Peters et al., 2010). E and W indicate samples from the Eastern and Western limbs of the Bushveld. Error bars are 2σ uncertainty.

Multiple Sulfur Isotope Constraints on Sources and Formation Processes of Sulfate in Beijing PM_{2.5} Aerosol

Xiaokun Han,^{†,‡} Qingjun Guo,^{*,†,‡,§} Harald Strauss,[§] Congqiang Liu,^{||} Jian Hu,^{||} Zhaobing Guo,[⊥] Rongfei Wei,[†] Marc Peters,[†] Liyan Tian,[†] and Jing Kong[†]


[†]Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, 11A Datun Road, Chaoyang, Beijing 100101, China

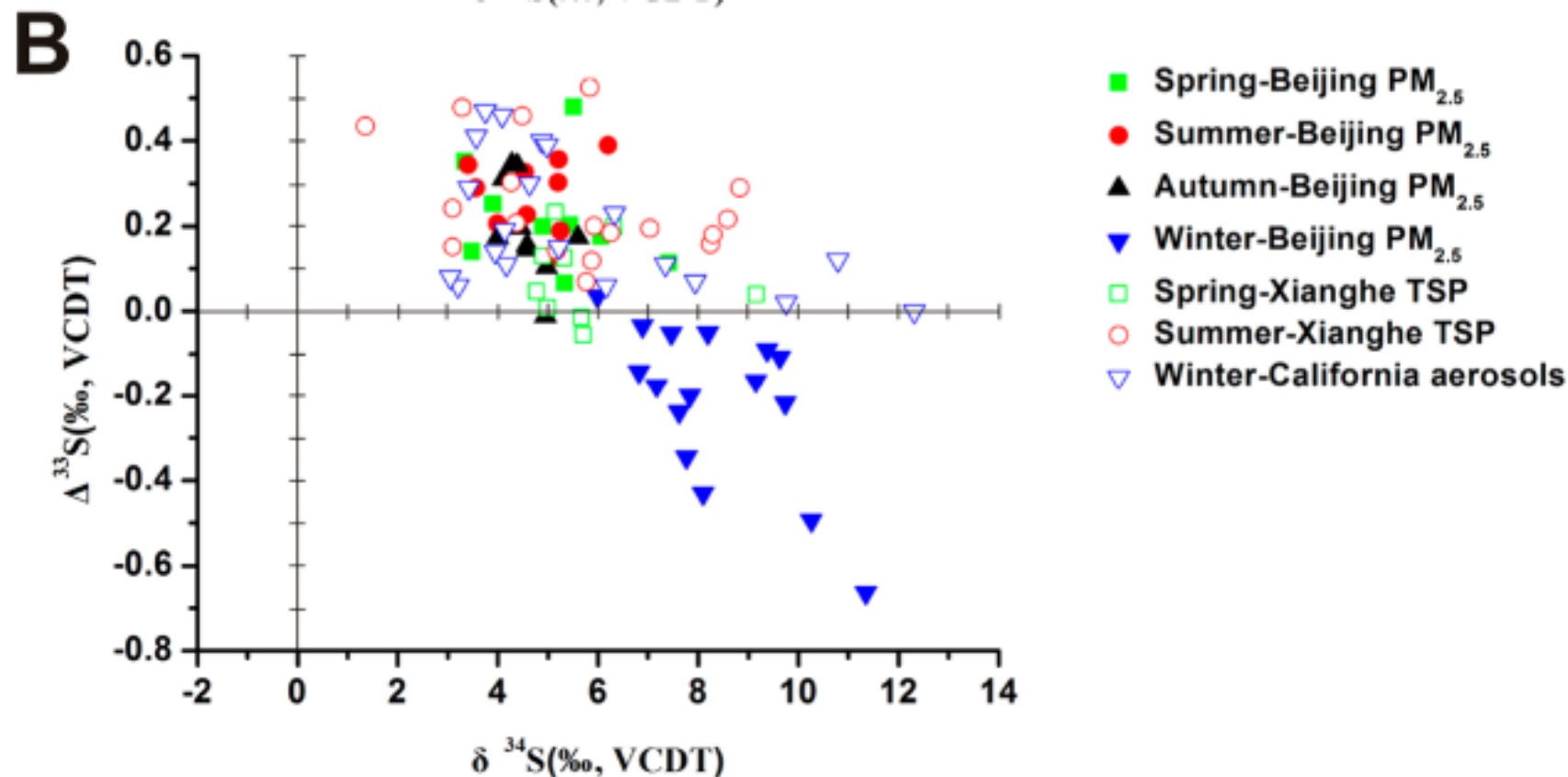
^{*}College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049, China

[§]Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 24, 48149 Münster, Germany

^{||}State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

[⊥]School of Environmental Science and Engineering, Nanjing Unive China

 Supporting Information



Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres

Mang Lin^{a,1,2}, Xiaolin Zhang^b, Menghan Li^b, Yilun Xu^b, Zhisheng Zhang^c, Jun Tao^c, Binbin Su^d, Lanzhong Liu^d, Yanan Shen^{b,1}, and Mark H. Thiemens^{a,1}

^aDepartment of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093; ^bSchool of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China; ^cSouth China Institute of Environmental Sciences, Ministry of Environmental Protection of China, Guangzhou 510655, China; and ^dNational Atmospheric Background Monitoring Station in Wuyi Mountain of Fujian Province, Wuyishan 354300, China

Edited by Thure E. Cerling, University of Utah, Salt Lake City, UT, and approved July 2, 2018 (received for review February 27, 2018)

The signature of mass-independent fractionation of quadruple sulfur stable isotopes (S-MIF) in Archean rocks, ice cores, and Martian meteorites provides a unique probe of the oxygen and sulfur cycles in the terrestrial and Martian paleoatmospheres. Its mechanistic origin, however, contains some uncertainties. Even for the modern atmosphere, the primary mechanism responsible for the S-MIF observed in nearly all tropospheric sulfates has not been identified. Here we present high-sensitivity measurements of a fifth sulfur isotope, stratospherically produced radiosulfur, along with all four stable sulfur isotopes in the same sulfate aerosols and a suite of chemical species to define sources and mechanisms on a field

be
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Atmospheric sulfur isotopic anomalies recorded at Mt. Everest across the Anthropocene

Mang Lin^{a,b,1,2}, Shichang Kang^{c,d,e}, Robina Shaheen^a, Chaoliu Li^{d,f}, Shih-Chieh Hsu^{b,3}, and Mark H. Thiemens^{a,1}

^aDepartment of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093; ^bResearch Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan; ^cState Key Laboratory of Cryospheric Sciences, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, 730000 Lanzhou, China; ^dCenter for Excellence in Tibetan Plateau Earth Sciences, Chinese Academy of Sciences, 100101 Beijing, China; ^eUniversity of Chinese Academy of Sciences, 100049 Beijing, China; and ^fKey Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, 100101 Beijing, China

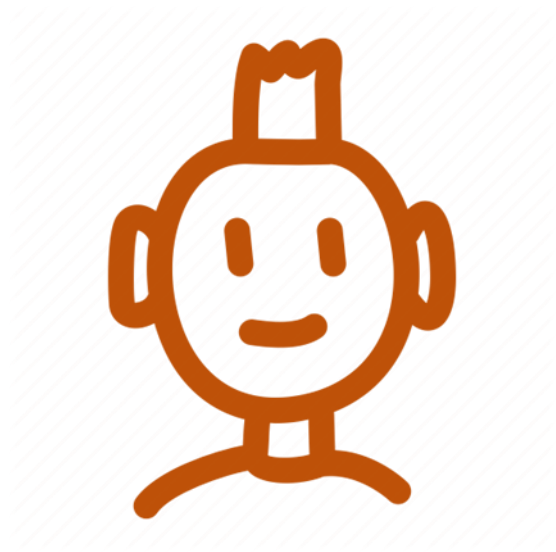
Edited by Barbara J. Finlayson-Pitts, University of California, Irvine, CA, and approved May 17, 2018 (received for review February 2, 2018)

Increased anthropogenic-induced aerosol concentrations over the Himalayas and Tibetan Plateau have affected regional climate, accelerated snow/glacier melting, and influenced water supply and quality in Asia. Although sulfate is a predominant chemical component in aerosols and the hydrosphere, the contributions from different sources remain contentious. Here, we report

the aerosol budget and evaluate its influences on climate and hydrological systems.

The sulfur isotopic anomaly (or mass-independent fractionation [MIF]) is quantified by nonzero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, where $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1,000 \times [(1 + \delta^{34}\text{S}/1,000)^{0.515} - 1]$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1,000 \times [(1 + \delta^{34}\text{S}/1,000)^{1.9} - 1]$ (*Materials and*

Check for updates



“You see what you want to see”

1989

JOURNAL GEOLOGICAL SOCIETY OF INDIA
Vol. 34, Nov. 1989, pp. 461–466

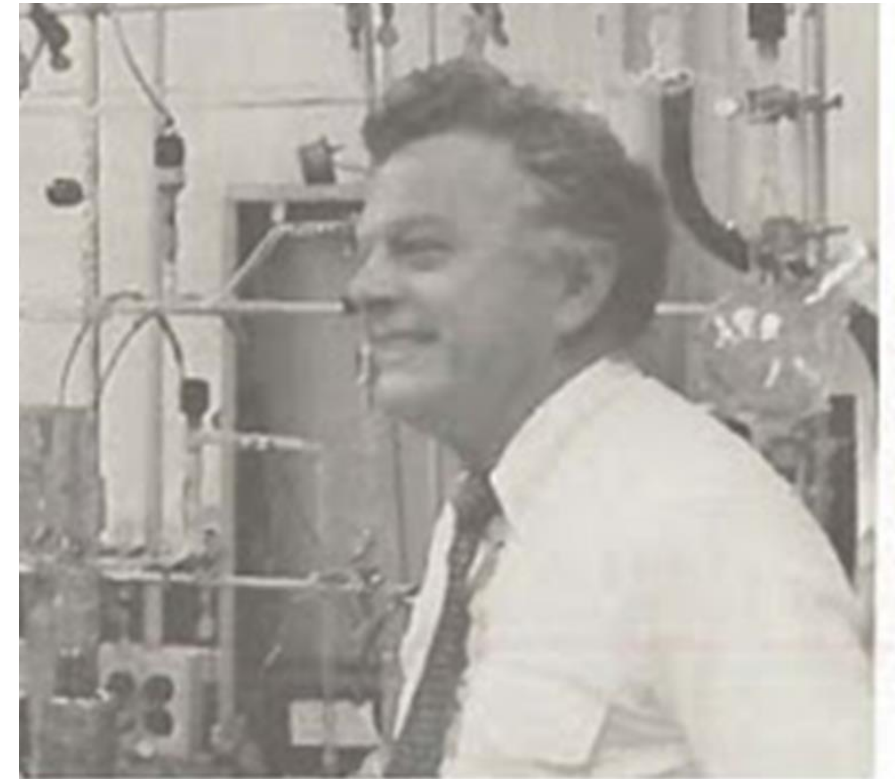
The Isotopic Composition of Bedded Barites from the Archean of Southern India

THOMAS C. HOERING

Geophysical Laboratory, Carnegie Institute, Washington DC.

INTRODUCTION

The stable isotopes of sulfur in ancient sedimentary rocks record unique features of early life on earth. For example, in rocks older than 2.8×10^9 years,





RESULTS AND DISCUSSION

The values obtained for the sulfur isotope ratios in the barite and coexisting pyrite are as follows:

	BARITE	PYRITE
$\delta^{33}\text{S}$	$+1.73 \pm 0.17$	-3.20 ± 0.16
$\delta^{34}\text{S}$	$+4.26 \pm 0.21$	-5.55 ± 0.20
$\delta^{36}\text{S}$	$+10.24 \pm 1.20$	-10.25 ± 1.50

The results on the barite were obtained by analyzing six portions of silver sulfide that had been prepared by the graphite reduction of a single sample of the starting mineral. The pyrite results are from a composite sample of randomly chosen grains that were then reduced by chromous chloride. Six separate analyses of the resulting silver sulfide were made. The errors shown are one standard deviation and are typical of the reproducibility of the method at its present state of development.

Because all four isotopes of sulfur were measured, the mass dependence of the fractionation can be calculated. The relationships between $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$ observed by Rees and Thode (1978) for several terrestrial and extra-terrestrial samples are as follows:

$$\Delta^{33}\text{S} \equiv \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$$

In-lecture question 4:

*Please calculate
Hoering's $\Delta^{33}\text{S}$ value.*

	BARITE	PYRITE
$\delta^{33}\text{S}$	$+1.73 \pm 0.17$	-3.20 ± 0.16
$\delta^{34}\text{S}$	$+4.26 \pm 0.21$	-5.55 ± 0.20
$\delta^{36}\text{S}$	$+10.24 \pm 1.20$	-10.25 ± 1.50

“The value of the mass dependence observed for the Archean samples of this study do not differ significantly from those of Rees and Thode (1978) [predicted by mass dependency]”

fractionation can be calculated. The relationships between $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$ observed by Rees and Thode (1978) for several terrestrial and extra-terrestrial samples are as follows:

$$\delta^{33}\text{S}/\delta^{34}\text{S} = 0.51$$

$$\delta^{36}\text{S}/\delta^{34}\text{S} = 1.91$$

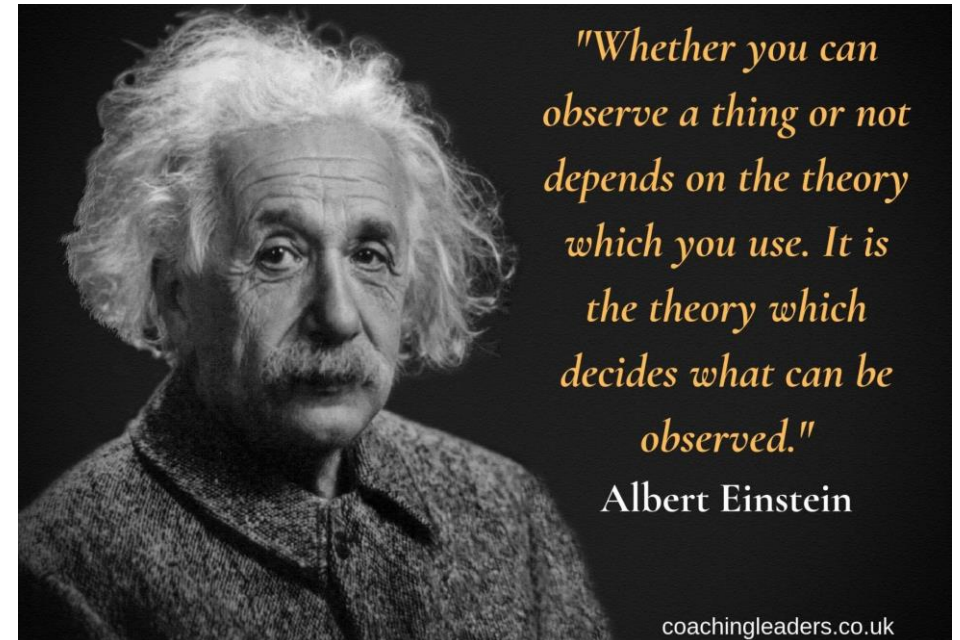
These same relationships have been observed in other research at this laboratory.

The values of the mass dependence observed for the Archean samples of this study do not differ significantly from those of Rees and Thode (1978).

$$\Delta^{33}\text{S} \equiv \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$$

$$\Delta^{33}\text{S}_{\text{barite}} = 1.73 - 0.515 \times 4.26 = -0.46\text{‰}$$

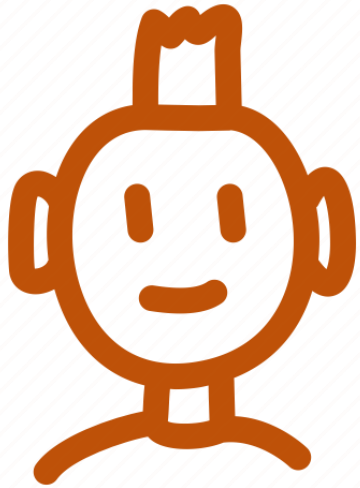
$$\Delta^{33}\text{S}_{\text{pyrite}} = -3.20 - 0.515 \times (-5.55) = 0.34\text{‰}$$



“优秀的人看见别人的优点”

“See the good in people and you'll be happier”

“Good people bring out the good in people”



Name one of the best
love quotes of all time.



15-min break

Isotopic links between atmospheric chemistry and the deep sulphur cycle on Mars

Heather B. Franz^{1,2}, Sang-Tae Kim³, James Farquhar², James M. D. Day⁴, Rita C. Economos⁵, Kevin D. McKeegan⁵, Axel K. Schmitt⁵, Anthony J. Irving⁶, Joost Hoek² & James Dottin III²

The geochemistry of Martian meteorites provides a wealth of information about the solid planet and the surface and atmospheric processes that occurred on Mars. The degree to which Martian magmas may have assimilated crustal material, thus altering the geochemical signatures acquired from their mantle sources, is unclear¹. This issue fea-

in this study provide insight into processes of assimilation of sulphur into magma during transport (observed in shergottites), processes of assimilation of sulphur salts or sulphur-bearing fluids at the time the flows were emplaced (observed in nakhlites), and in some cases processes that introduce MIF sulphur signatures through secondary alteration pr

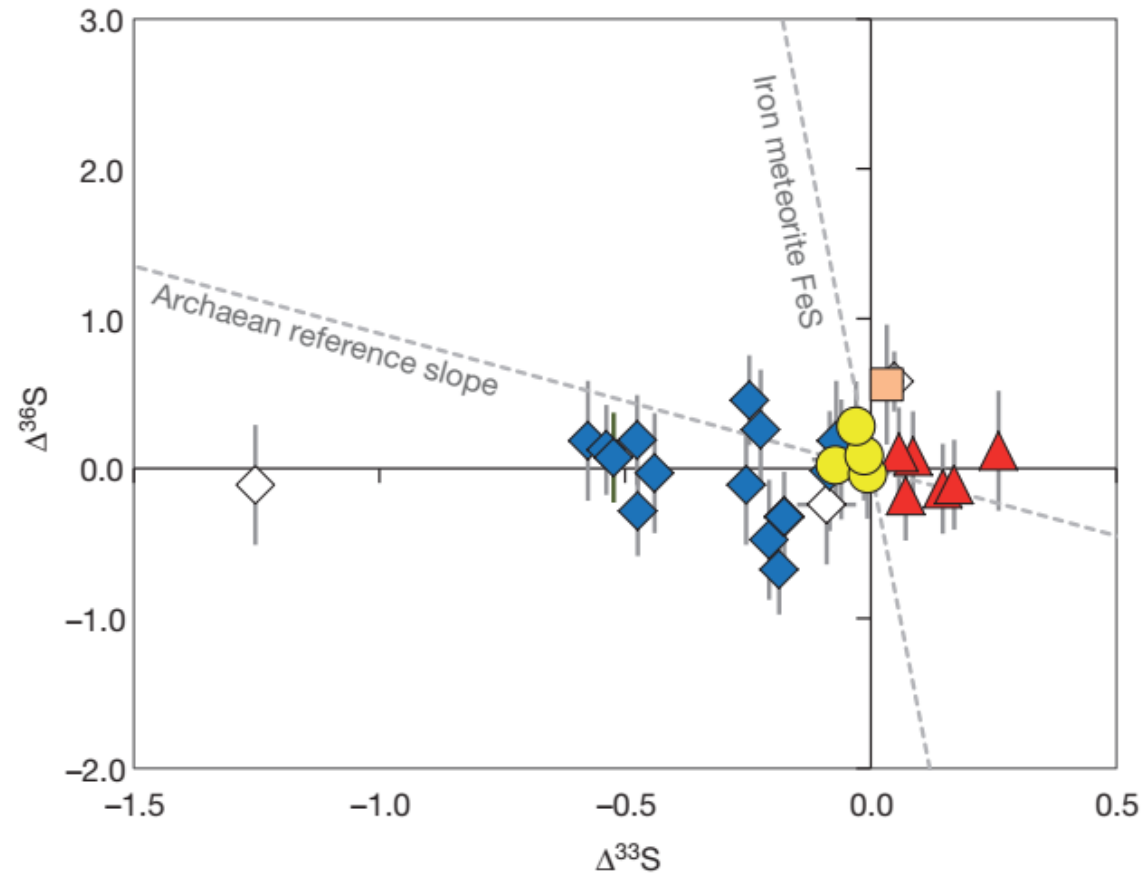
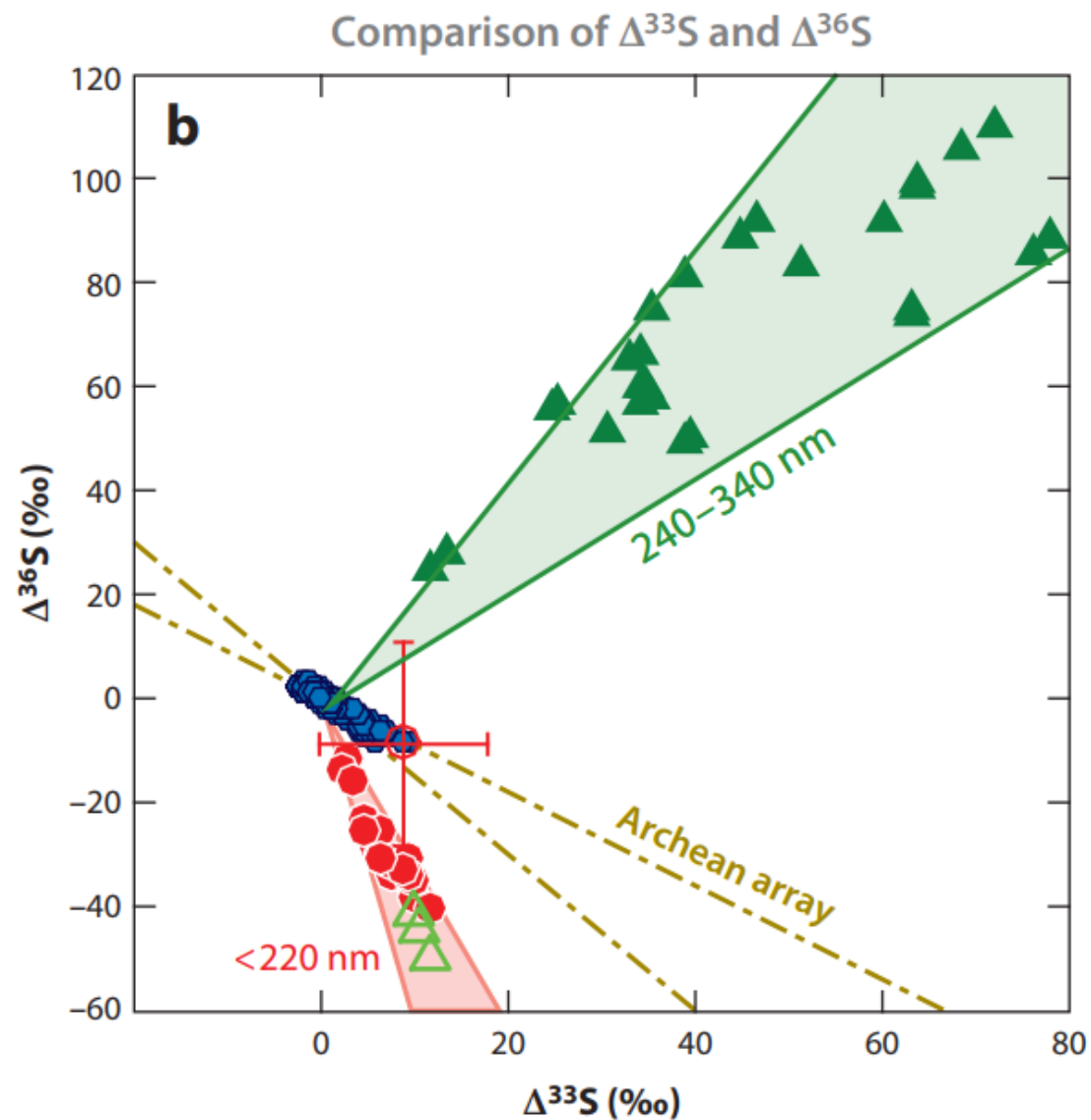
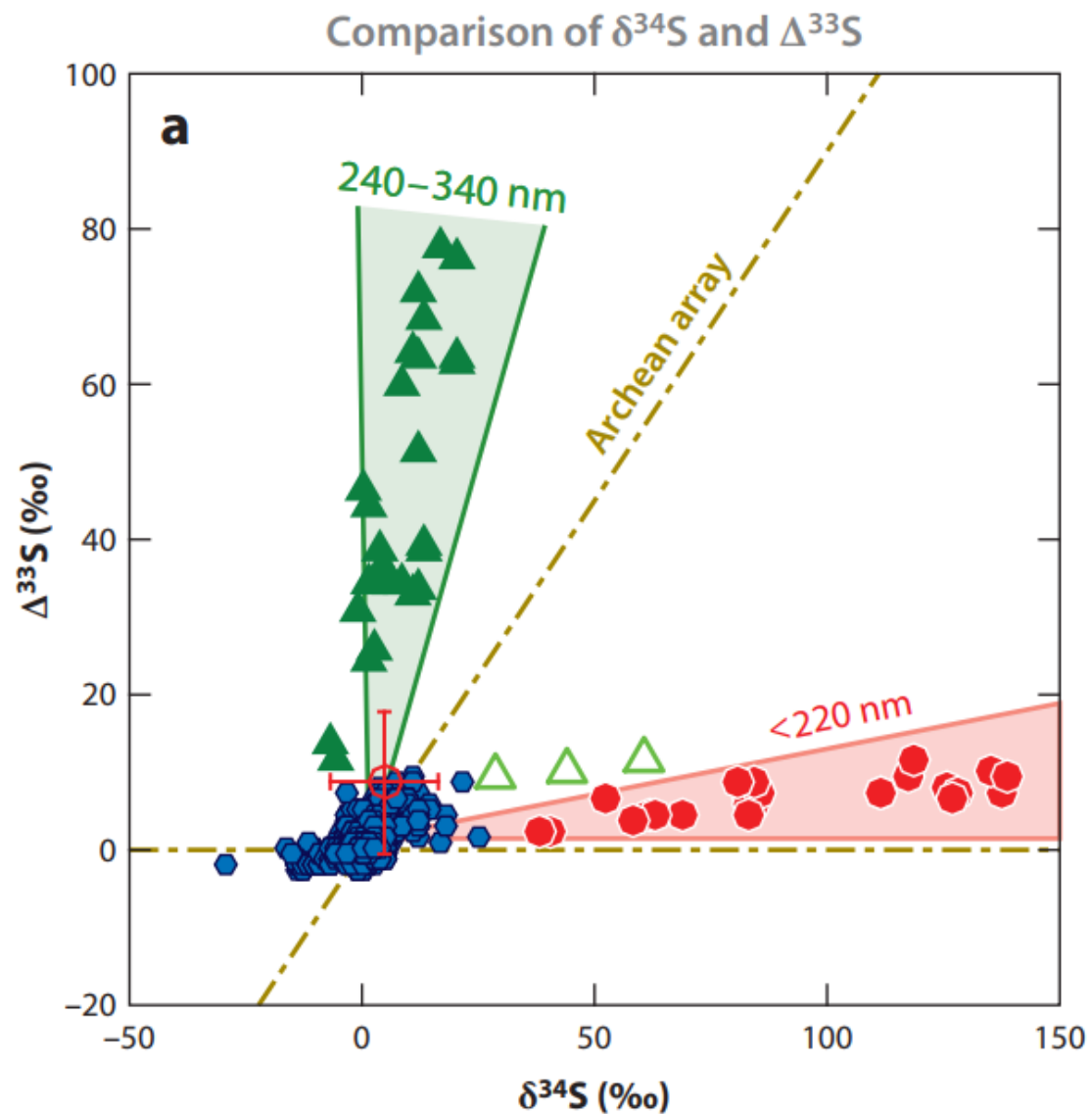
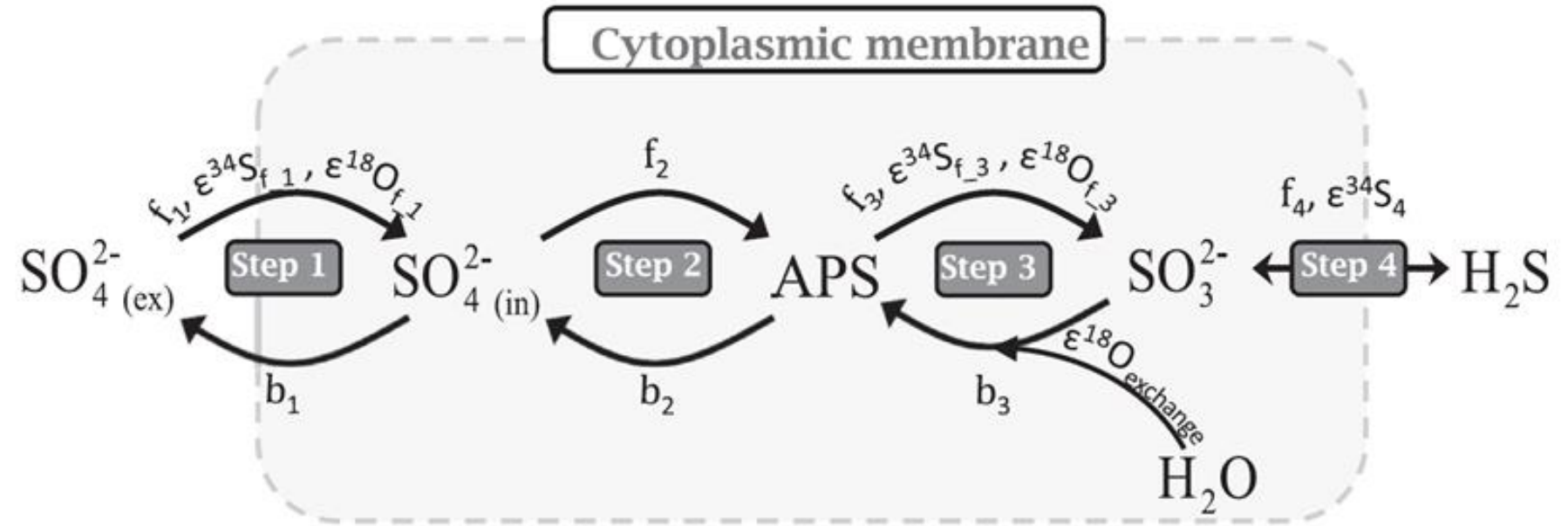


Figure 4 | Covariation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in different groups of Martian meteorites. Diamonds, nakhilites; circles, ALH 84001; triangles, shergottites; square, Chassigny. Martian meteorite data from other studies are included^{5,6} (open symbols). Dashed lines depict arrays formed by Archaean terrestrial samples and iron meteorite FeS for comparison. (See Extended Data Fig. 2 for details.) Error bars, 2 s.d.



--- Archean reference array ($\Delta^{33}\text{S} = 0.9 \delta^{34}\text{S}$ and $\Delta^{36}\text{S} = -0.9$ or $-1.5\Delta^{33}\text{S}$)

Back to the starting point.



Antler et al., 2013

$$^{33}\theta \equiv \frac{\ln^{34}\alpha}{\ln^{33}\alpha}$$

Diagnostic or apparent $^{33}\theta$ value may change due to different kinetics/dynamics of sulfate reduction.

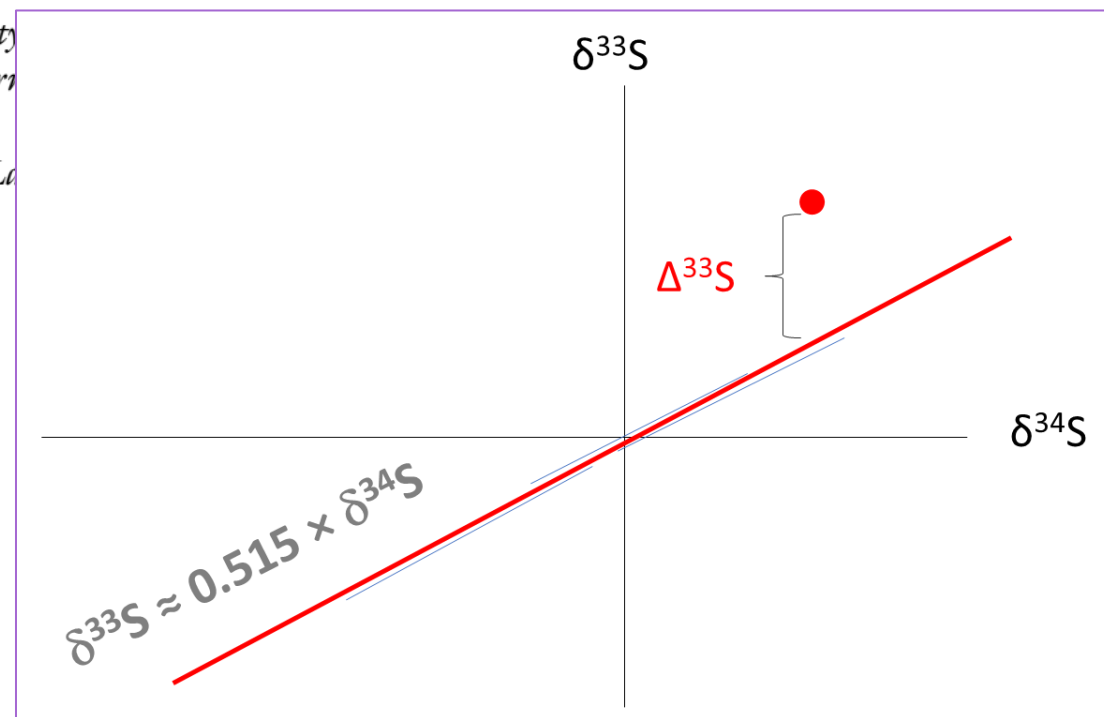
Multiple sulphur isotopic interpretations of biosynthetic pathways: implications for biological signatures in the sulphur isotope record

JAMES FARQUHAR,¹ DAVID T. JOHNSTON,¹ BOSWELL A. WING,¹ KIRSTEN S. HABICHT,²
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Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record

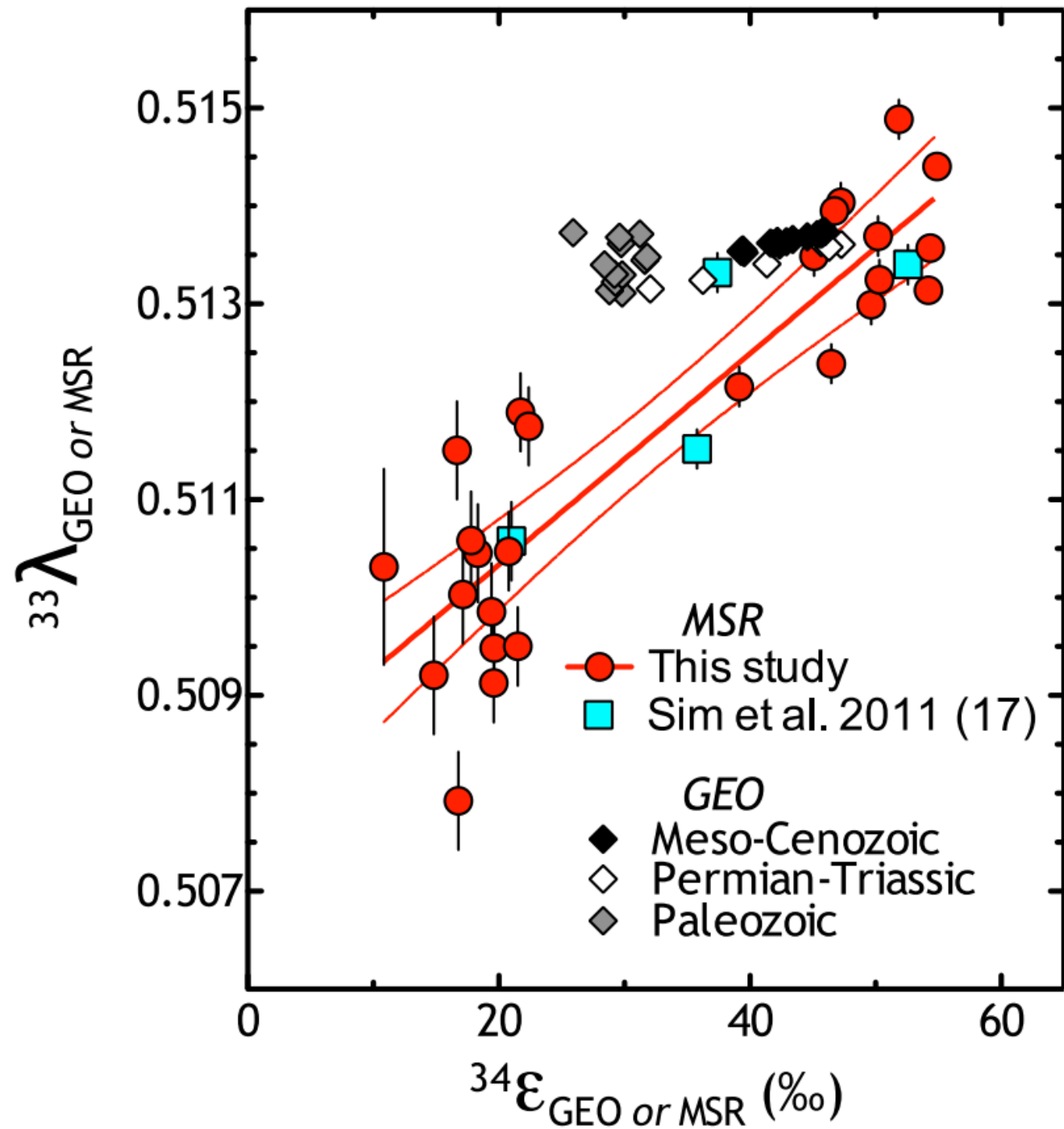
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Edited by Mark H. Thiemens, University of California San Diego, La Jolla, CA, and approved May 8, 2013 (received for review October 30, 2012)

Phanerozoic levels of atmospheric oxygen relate to the burial histories of organic carbon and pyrite sulfur. The sulfur cycle remains poorly constrained, however, leading to concomitant uncertainties in O₂ budgets. Here we present experiments linking the magnitude of fractionations of the multiple sulfur isotopes to the rate of microbial sulfate reduction. The data demonstrate that such fractionations are controlled by the availability of electron donor (organic matter), rather than by the concentration of electron acceptor (sulfate), an environmental constraint that varies among sedimentary burial environments. By coupling these results with a sediment bio-

biosphere. Such records generally are thought to indicate that oxidant availability has increased with each passing geologic eon (12). Although playing prominent roles in sedimentary redox cycles (13), oxidation reactions carry only modest S isotopic fractionations (14, 15).^{*} In typical modern marine sediments, the oxidative region of aerobic organic carbon remineralization is separated from the zone of sulfate reduction (where MSR takes place) by an intermediate layer in which both sulfide oxidation and sulfur disproportionation occur (16, 17). Despite sulfur recycling across that boundary layer, the sulfur that is eventually buried as pyrite



Leavitt et al., 2013



Multiple sulfur isotope constraints on the modern sulfur cycle

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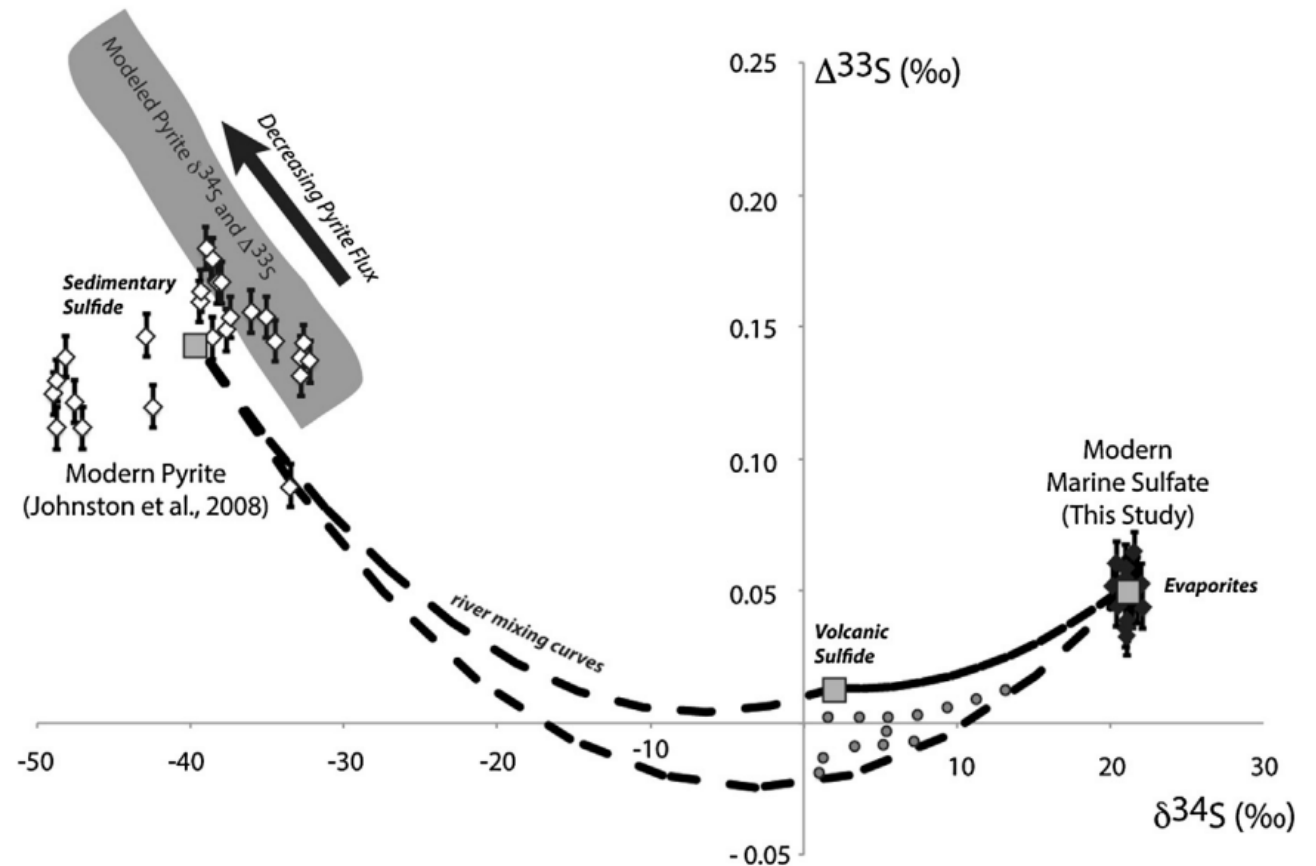
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ABSTRACT

We present 28 multiple sulfur isotope measurements of seawater $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ from the modern ocean over a range of water depths and sites along





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Evaluating the S-isotope fractionation associated with Phanerozoic pyrite burial

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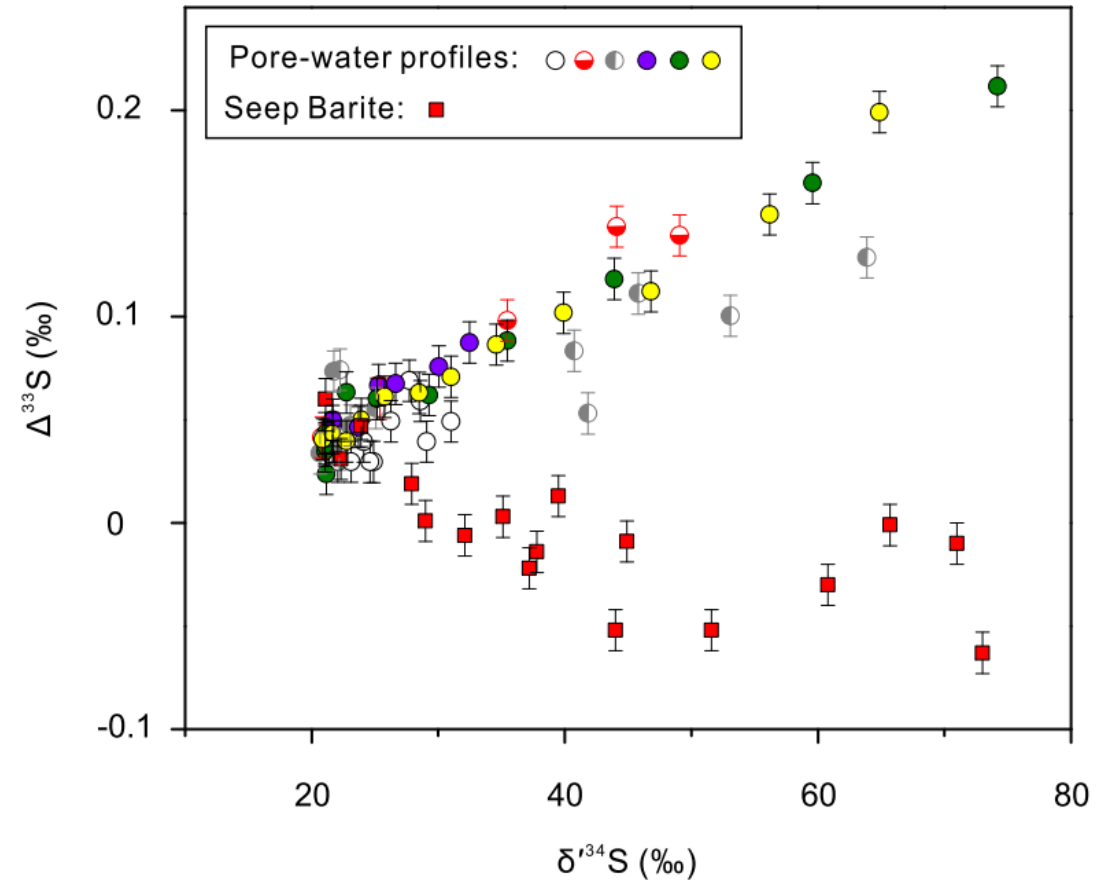
Triple sulfur isotope relationships during sulfate-driven anaerobic oxidation of methane

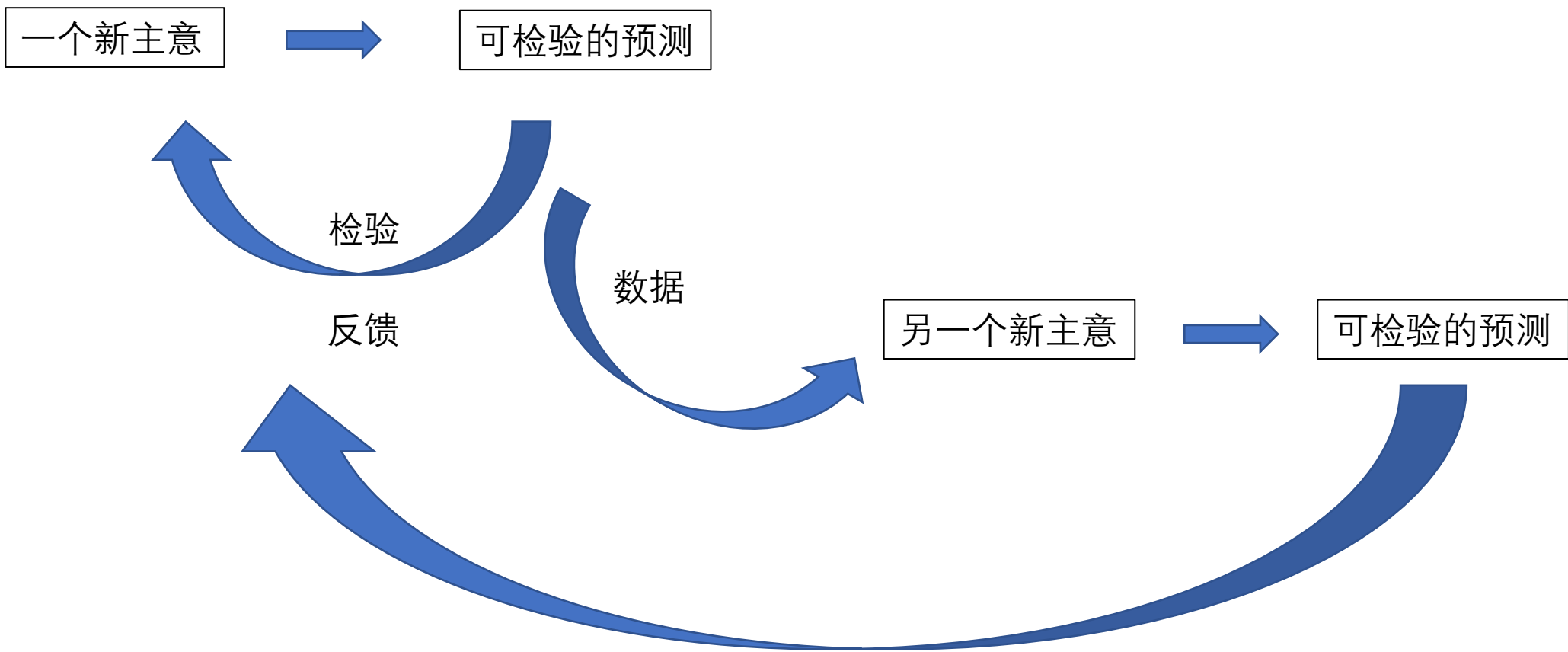
Shanggui Gong^{a,g}, Yongbo Peng^{b,*}, Huiming Bao^{b,*}, Dong Feng^{a,c}, Xiaobin Cao^b,
Peter W. Crockford^{d,e}, Duofu Chen^f

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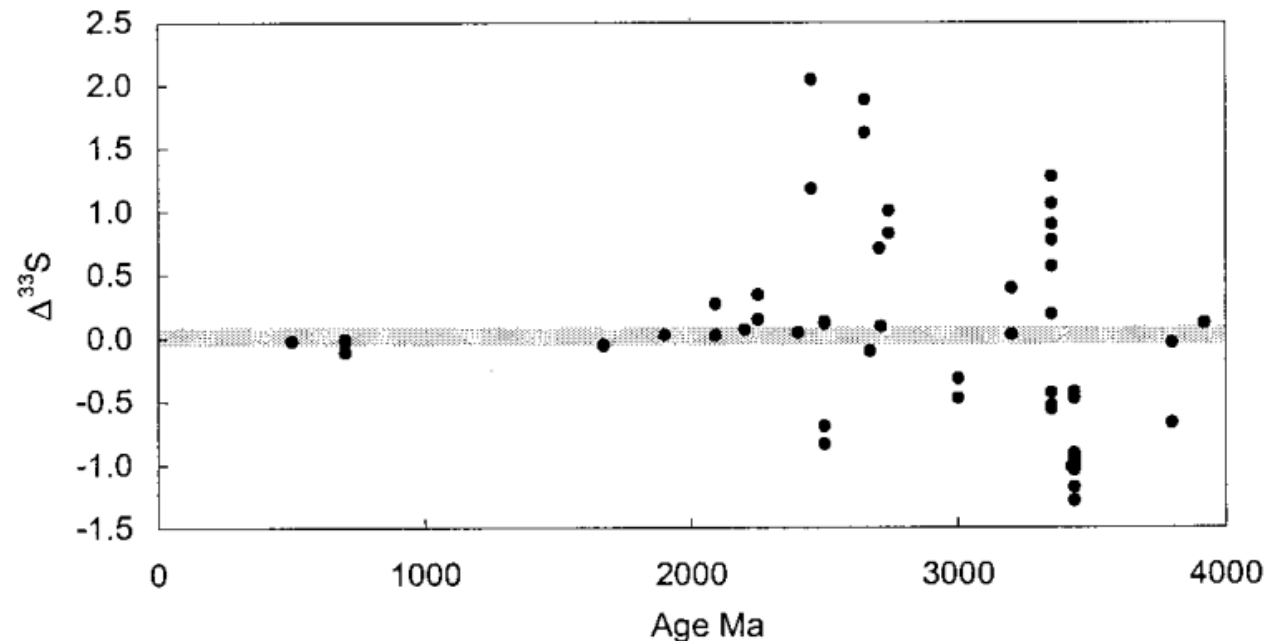




Atmospheric Influence of Earth's Earliest Sulfur Cycle

James Farquhar,* Huiming Bao, Mark Thiemens

Mass-independent isotopic signatures for $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$ from sulfide and sulfate in Precambrian rocks indicate that a change occurred in the sulfur cycle between 2090 and 2450 million years ago (Ma). This change was influenced by gas-phase atmospheric reactions. Atmospheric oxygen partial pressures were low at the time, and weathering and of microbial oxidation and reduction also played a role in determining the oxidation state of sulfur. Atmospheric fractionation processes should be considered to study the onset and consequences of these processes in Earth's early history.



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The five stable isotope compositions of Fig Tree barites: Implications on sulfur cycle in ca. 3.2 Ga oceans

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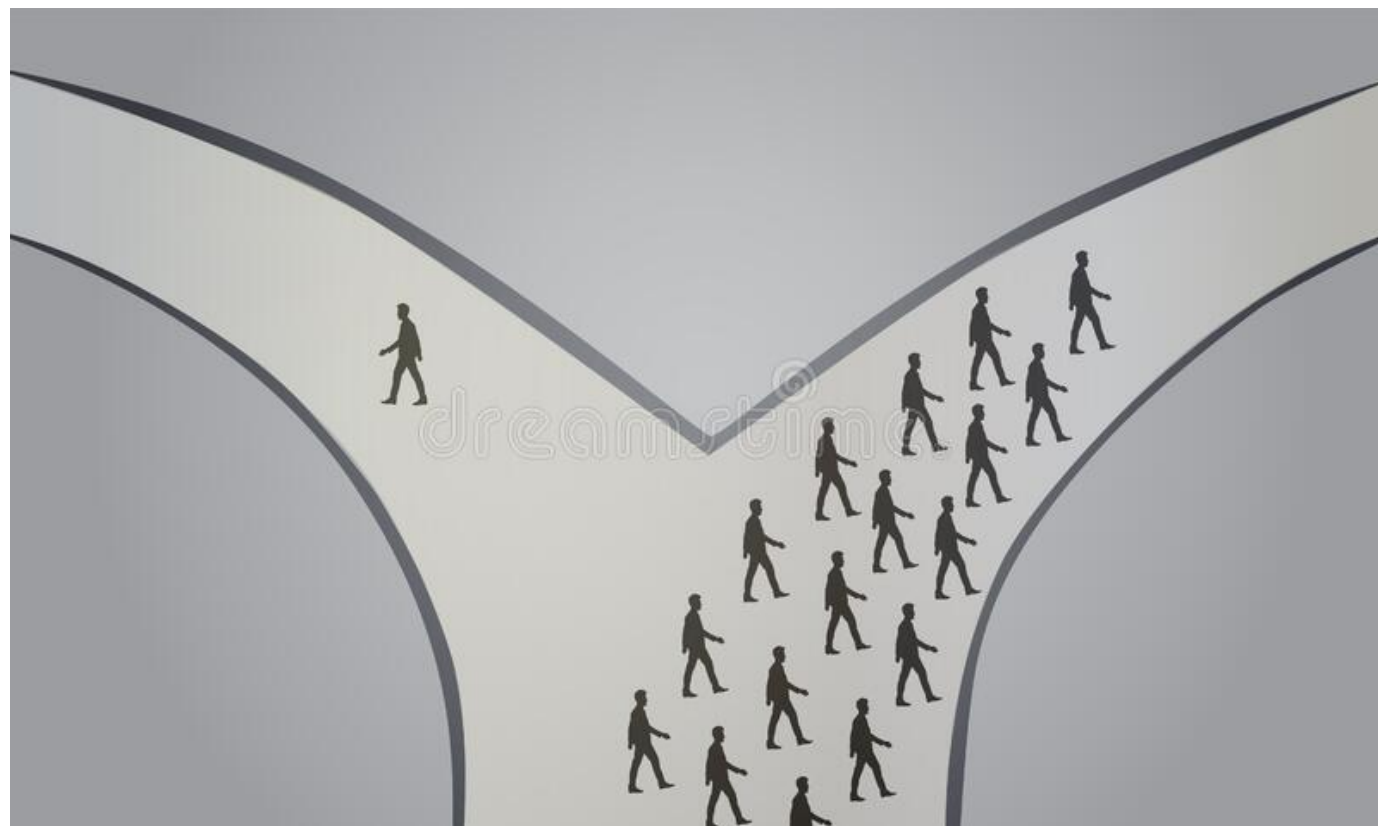
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肆硫。

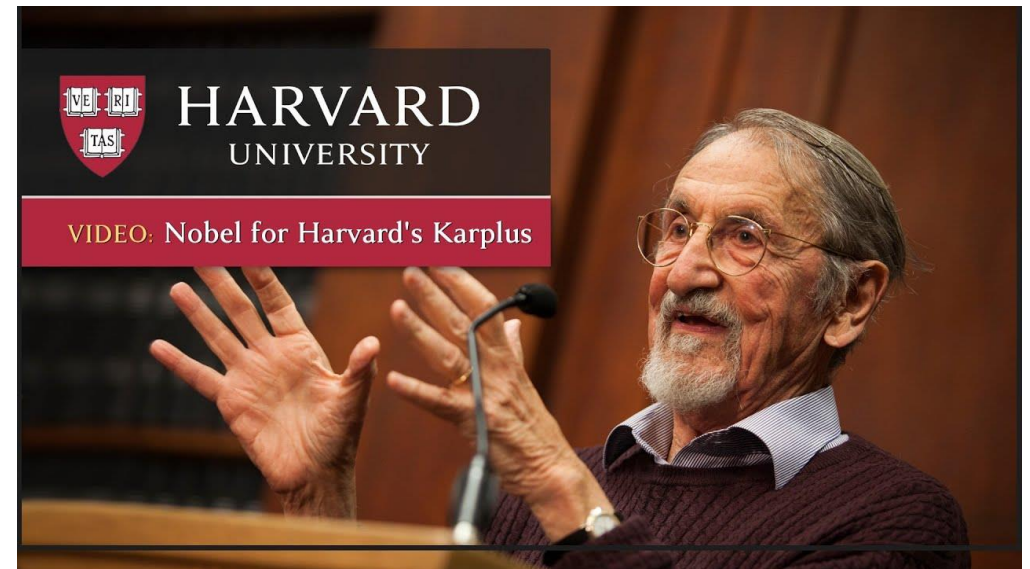
叁氧？



**“Try new things, even if you
don’t know if they’ll work.”**

-- Martin Karplus

But they often lead you to
somewhere new.



Thanks

