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MSG



Sulfur in the Earth system:

From microbes to global cycles through Earth history

V I R T U A L C O N F E R E N C E

16-17 November 2020



Main Convenor:

Dr. Robert Newton (University of Leeds)

Convenors:

Dr. Andrea Burke (St. Andrews)

Geochemistry SG

Prof. Graham Shields (UCL) Chair,
Earth System Science SG

Dr. Sasha Turchyn (Cambridge)
Chair, Marine Studies SG

Keynote Speakers:

Tamsin Mather (University of Oxford)

Ben Mills (University of Leeds)

Itay Halevy (Weizmann Institute of Science)

Emma Liu (University College London)



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VIRTUAL CONFERENCE PROGRAMME

16 November	
11.55	Sign in & brief welcome to the conference and rules of attendance - Rob Newton
Session 1: Sulfur in the Mantle and Volcanic Systems - Chaired Sasha Turchyn	
12.00	KEYNOTE: Subduction zone volcanoes and the Sulphur cycle Tamsin Mather – Oxford University
12.30	Exploring the behaviour of sulfur during magmatic degassing using a thermodynamic model Ery Hughes – California Institute of Technology
12.45	Using S isotopes of alkaline magmas to unlock long-term records of crustal recycling on Earth William Hutchison – University of St Andrews
13.00	Chalcophile elements track sulfide saturation, sulfide resorption and magmatic degassing at Kīlauea Volcano, Hawai'i Penny Wieser – University of Cambridge
13.15	Sulfur isotope systematic of granitoids from the Yilgarn Craton. New insights into the reservoirs of Archean orogenic gold deposits Stefano Caruso – The University of Western Australia
13.30	KEYNOTE: Sulfur in volcanic systems: Transport and reactions from mantle to atmosphere Emma Liu – University College London
14.00	Break
Session 2: Sulfur in the Environment - Chaired Graham Shields	
14.30	New insights on the ~74 ka Toba eruption from sulfur isotopes of polar ice cores Laura Crick – University of St Andrews
14.45	Understanding the hydrothermal influence on seawater sulfate Eleanor Hughes – Harvard University
15.00	Microbial sulfur disproportionation at marine hydrothermal vents: a reconsideration of the global biological sulfur cycle? Maxima Allieux - Ifremer
15.15	Microscale $\delta^{34}\text{S}$ heterogeneities in cold seep barites record variable methane flux off the Lofoten-Veståralen Continental Margin, Norway Seth Wood - Washington St Louis
15.30	Fossil fuels and sulfur: implications for industrial sulfuric acid availability during the transition to a low-carbon future. Simon Day – University College London
15.45	Triple oxygen isotopes ($\Delta^{17}\text{O}$) as records of sulfur cycle drivers Anna Waldeck - Harvard University
16.00	20-year record of sulfuric acid weathering in a High Arctic watershed Emily Stevenson – University of Cambridge
16.15	Organic sulfur fluxes and geomorphic control of sulfur isotope ratios in rivers Preston Cosslett Kemeny - California Institute of Technology
16.30	Poster Flash Talks

Sulfur in the Earth system: From microbes to global cycles through Earth history

Poster presentation	
17.00	<ul style="list-style-type: none"> • Ery Hughes (Joseph Biasi) - Modelling the behaviour of sulfur in magmatic systems from source to surface • Giulia Consuma - Sulfur and carbon in deep Earth: new insights from orogenic garnet-bearing peridotite (Eastern Alps, Italy) • Jesse Walters - The fate of subducted sulfur: Insights from phase equilibrium modeling and petrographic observations • Zoltan Taracsak - Sulfur isotope ratios measured in El Hierro melt inclusions suggest recycled volatiles play a role in melt generation at ocean islands • Lotta Kempainen - Characterisation of sulphide inclusions in diamonds using synchrotron X-ray microfluorescence (s-XRF) • Ursula Jongebloed - Effect of Sea Ice Decline on Arctic Sulfate Aerosols Based on Ice Core Observations and Model Simulations • Angus Fotherby - Modelling the effects of non-steady state transport dynamics on the sulfur and oxygen isotope composition of sulfate in sedimentary pore fluids • Dan James - Does microbial sulfate reduction drive carbonate precipitation in the sedimentary boundary layer? • Eloise Matthews - Geochemical conditions favoring the formation of elemental sulfur nodules in Lake Peten Itza, Guatemala" • Khoren Avetisyan - Eutrophication leads to formation of sulfide-rich deep water layer in Lake Sevan (Armenia) • Maddie Petersen - Characterizing the Sulfur Budget within Lake Superior: Significant Role of Organic Sulfur in Oligotrophic Settings • Man Yin Tsang - Seawater contamination in ODP/IODP porewater samples and its quantitative effects on studies of microbial sulfate reduction • Mourice Czerewko - Implications of sulfur mineralogy and consequences of pyrite oxidation for ground engineering. • Andrey Ilin - Acidophiles' impact on the sulfur cycling at low pH and low temperature environments: An incubation column experiment. • Malcolm S.W. Hodgskiss - Feast then famine: a productivity collapse to end Earth's Great Oxidation Event • Weiqi Yao - Ocean internal sulfur reservoirs: A case study from the Paleocene-Eocene Thermal Maximum • Haley Olson - Predicting primary triple oxygen isotope signatures from altered sulfate • Alec Hutchings - The effect of early diagenetic sulfur geochemistry on paleoredox proxies • Charlotte Spruzen - Evolution of the sulfur isotopic composition of pyrite over the Cenozoic • Huan CUI - Methanogenic outburst in a sulfate-depleted basin? A sulfur isotope perspective for the origin of the middle Bambuí carbon cycle anomaly in Brazil • Kärt Paiste - Testing the global significance of the sulfur isotope record of the c. 2.0 Ga Zaonega Formation: a micro-scale S isotope and trace element investigation • Zheyu Tian - New Experimental Comparisons of Carbonate-associated Sulfate Extraction Methods • Chao Li - Decoupled atmospheric and marine oxidation in the Ediacaran
18.30	Day one close

17 November	
08.55	Sign In Brief welcome and rules of attendance

Sulfur in the Earth system: From microbes to global cycles through Earth history

Session 3: Sulfur in the Environment Part II - Chaired Andrea Burke	
09.00	Records of past permafrost thaw preserved in fossil bone sulfur isotope signatures? Rhiannon Stevens - University College London
09.15	Biogeochemical Cycling of Sulfur, Manganese and Iron in Ferruginous Limnic Analog of Archean Ocean Alexey Kamyshny – Ben-Gurion University
09.30	Sulfur isotope compositions of framboidal pyrites and micropyrites from modern microbial mats pinpoint the influence of local environment Johanna Marin Carbonne - University of Lausanne
09.45	Strong local, not global, controls on marine pyrite sulfur isotopes over glacial-interglacial cycles Virgil Pasquier – Weizmann Institute of Science
10.00	Quadruple Sulfur Isotope biosignatures from terrestrial Mars- analogue systems Arola Moreras-Marti – University of St Andrews
10.15	The carbon-sulfur link in the remineralization of organic carbon in surface sediments Hal Bradbury – University of Cambridge
10.30	KEYNOTE: Multiple local controls on pyrite sulfur isotopes and implications for reading the sedimentary pyrite record Itay Halevy - Weizmann Institute of Science
11.00	Break
Session 4: Sulfur in Earth History - Chaired Rob Newton	
11.30	KEYNOTE: Sulfur cycle controls on Earth's habitability. Ben Mills – University of Leeds
12.00	Global seawater sulfate isotope composition and atmospheric–biospheric evolution constrained at 605 Ma by pyrite Re-Os dating and $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ analyses of the Aberfeldy stratiform barite Norman Moles – The University of Brighton
12.15	Enormous sulfur isotope excursions indicate marine anoxia and large-scale pyrite burial during the end-Triassic mass extinction Tianchen He – University of Leeds
12.30	Bioturbation and the Phanerozoic Sulfur Cycle: A Model Approach Sidney Reimer - The Inter-University Institute for Marine Sciences
12.45	Lithospheric-scale transfer of sulfur through Earth's earliest Wilson Cycle Crystal Laflamme- Université Laval
13.00	Impact of sequence stratigraphy and depositional facies on marine sedimentary pyrite sulfur isotopes: insights from bulk and micro-scale SIMS analyses David Fike – Washington University in St. Louis
13.15	KEYNOTE: Quadruple sulfur isotopes: Windows into sulfur cycling in the Earth system Aubrey Zerkle- University of St Andrews
13.45	Closing remarks
13.55	Conference Close

GSL CODE OF CONDUCT FOR MEETINGS AND OTHER EVENTS

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It also applies to members of the Society attending externally organised events, wherever the venue or online platform (virtual event).

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Harassment includes sustained disruption of talks or other events, inappropriate physical contact, sexual attention or innuendo, deliberate intimidation, stalking, and intrusive photography or recording of an individual without consent. It also includes discrimination or offensive comments related to age, gender identity, sexual orientation, disability, physical appearance, language, citizenship, ethnic origin, race or religion.

The Geological Society expects and requires all participants to abide by and uphold the principles of this Code of Conduct and transgressions or violations will not be tolerated.

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Presentation Abstracts (Presentation order)

Monday 16 November
Session 1 - Sulfur in the Mantle and Volcanic Systems

KEYNOTE: SUBDUCTION ZONE VOLCANOES AND THE SULFUR CYCLE

Tamsin A. Mather¹, Zoltan Taracsak¹, Terry Plank² and Alessandro Aiuppa³

¹ Department of Earth Sciences, University of Oxford, UK ² LDEO, Columbia University, NY, USA ³ University of Palermo, Italy

Understanding sulphur cycling through global subduction zones has important implications for the evolution of Earth's climate and the redox state of different planetary reservoirs. Yet, the inputs, processing and recycling of S throughout the subduction system are still inaccurately known. While volcanic SO₂ is one of the best monitored emissions, on the arc-scale, total emissions still show a high degree of temporal variability making simple subduction zone input/output calculations challenging in anything but the broadest sense. As the fluxes of other volcanic emissions such as halogens and CO₂ are often calculated with reference to SO₂ this is therefore an issue for all volcanic volatile cycling calculations. Further, for S, its relatively complex sedimentary chemistry has meant that the subduction zone input, namely the concentration, oxidation state and isotopic composition, of S in sediments on the downgoing slab, remains largely unconstrained. This strongly hampers the development of a process understanding of S cycling through subduction zones. This presentation will assess what we know and key unknowns regarding the arc S subduction cycle and outline potential future work to tackle these issues.

EXPLORING THE BEHAVIOUR OF SULFUR DURING MAGMATIC DEGASSING USING A THERMODYNAMIC MODEL

Ery C. Hughes¹, Lee M. Saper¹, Philippa Liggins², and Edward M. Stolper¹, ¹Division of Geological and Planetary Sciences, Caltech, CA USA, ²Department of Earth Sciences, University of Cambridge, UK

The behaviour of sulfur in igneous systems is more complex than the other major volatile components (H₂O and CO₂) because sulfur can occur in multiple oxidation states (from S⁶⁺ to S²⁻), species (e.g., SO₄²⁻, SO₂, FeS, etc.), and phases (gas, silicate melt, immiscible liquid, anhydrite, etc.). Such variations in the form of sulfur cause sulfur's behaviour to be influenced by (and sometimes have significant impact on) the redox evolution of magmatic systems. These variations also cause igneous fractionation to lead to changes in the sulfur isotope composition ($\delta^{34}\text{S}$) of coexisting phases. Quantitative interpretation of the volatile concentrations and isotopic compositions of gas, silicate melt, and immiscible sulfides requires magmatic degassing models that explicitly deal with the speciation of sulfur in the silicate melt and the gas phase, the effects of $f\text{O}_2$, and the importance of H₂O and CO₂ in the system, and we present such models here.

We use a thermodynamic model to calculate the equilibrium concentrations, speciation, and isotopic composition of COHS in melt \pm gas systems. We use the concepts of sulfide and sulfate capacity – which relate dissolved sulfide (S²⁻) and sulfate (SO₄²⁻) concentrations in the melt to gas $f\text{O}_2$ and $f\text{S}_2$ — to model melt sulfur solubility and speciation (i.e., S⁶⁺/S²⁻). We simultaneously solve for melt Fe³⁺/Fe²⁺, which is coupled to the speciation and oxidation state of sulfur. Assimilation of crustal sulfate has been modelled using a similar approach^{1,2}, but we focus on the example of hydrous, oxidised, basaltic magmas degassing on decompression. This approach also leads to a simple way to calculate vapour saturation pressures for a given melt volatile content. We find the evolution of total sulfur content in the melt is sensitive to bulk H₂O content, initial $f\text{O}_2$, and sulfate capacity during closed-system degassing. For instance, sulfur can behave either as a compatible or incompatible element in the melt relative to the gas phase, and iron can either oxidise or reduce during ascent. We compare our results to other degassing models, multi-volatile solubility experiments, and literature melt inclusion and matrix glass data where S⁶⁺/S²⁻ and/or $\delta^{34}\text{S}$ have been measured in addition to volatile concentrations.

USING S ISOTOPES OF ALKALINE MAGMAS TO UNLOCK LONG-TERM RECORDS OF CRUSTAL RECYCLING ON EARTH

William Hutchison*¹, Adrian A. Finch¹, Anouk M. Borst¹, Eva E. Stüeken¹, Aubrey L. Zerkle¹, and Adrian J. Boyce²

1. School of Earth and Environmental Sciences, University of St. Andrews, UK , 2. Scottish Universities Environmental Research Centre, UK.

Earth's surface and mantle S reservoirs are connected via subduction, crustal recycling, and volcanism. The most significant insights into the connections between the surface and mantle S reservoirs have been gained from studies of oceanic hotspots, particularly ocean island basalts (OIBs), which often contain recycled subducted material in their mantle source. However, a major limitation is that the oceanic record only extends back ~200 Ma and thus, OIBs cannot reveal temporal variations in crustal recycling over the vast majority of Earth history. S-rich alkaline magmas erupted in continental settings offer a solution to this problem because they are associated with recycled sources (i.e. metasomatized lithospheric mantle and plumes) and, crucially, are found throughout the geological record. Here we undertake a detailed study of S isotopes ($\delta^{34}\text{S}$) in a Mesoproterozoic alkaline province in Greenland to evaluate whether evolved alkaline magmatic suites constrain the mantle source $\delta^{34}\text{S}$. We show that while crustal contamination and changes in oxidation state at low temperature generate large $\delta^{34}\text{S}$ fluctuations, all our samples from Greenland evidence an enriched lithospheric mantle source with $\delta^{34}\text{S}$ of 1–5 ‰. A comprehensive global compilation of S isotopes in alkaline igneous suites shows both positive and negative S isotope signatures, akin to OIB, and provides evidence of recycled surface S in their mantle source. Our compilation also shows a temporal trend with Proterozoic alkaline magmas largely restricted to positive $\delta^{34}\text{S}$ values (0–5 ‰) and Phanerozoic suites showing greater $\delta^{34}\text{S}$ diversity (–5 to 4 ‰). These data record variations in S cycling over Earth history and support changes in the composition of the lithospheric mantle and/or Ga timescales for deep crustal recycling. Thus, alkaline magmas represent a powerful yet underutilised repository for interrogating crustal recycling and mantle evolution through geological time.

CHALCOPHILE ELEMENTS TRACK SULFIDE SATURATION, SULFIDE RESORPTION AND MAGMATIC DEGASSING AT KĪLAUEA VOLCANO, HAWAII

Penny E. Wieser¹, Frances Jenner², Marie Edmonds¹, John Maclennan¹, and Barbara E. Kunz².

¹ Department of Earth Sciences, University of Cambridge, UK, ²School of Environment, Earth and Ecosystem Sciences, The Open University, UK

The concentration of chalcophile (sulfur-loving) elements in volcanic products can be used to track the behaviour of S and sulfides throughout the entire magmatic system; from the generation of melts within the mantle source to low pressure degassing at the eruptive vent. Here, we analyse a large suite of chalcophile elements (e.g., Cu, Ni, Se, Bi, S) in lavas and melt inclusions from Kīlauea Volcano, Hawai'i. The presence of residual sulfides in the mantle source throughout the melting interval accounts for the high S concentrations in Kīlauean primary melts (1387–1600 ppm). Decompression associated with magma ascent through the thick Hawaiian lithosphere drives an increase in the solubility of sulfur, resulting in ascending magmas becoming sulfide undersaturated by the time they enter the crust. A drop in temperature, coupled with major element changes during the fractionation of olivine, causes the solubility of S to decrease once more. Combined with an increase in melt S contents during fractionation, this initiates a second stage of sulfide saturation at relatively high MgO contents (~12 wt% MgO). Syn-eruptive degassing of S as the magma ascends to lower pressures drives the resorption of sulfides in contact with the carrier liquid. The covariance structure of Cu, MgO and Ni contents in melt inclusions and matrix glasses indicates that the dissolution of sulfides effectively liberates sulfide-hosted Cu and Ni back into the melt, rather than the vapour phase. The contrasting behaviour of Cu, Ni, Se and S during sulfide resorption indicates that the chalcophile element signature of the Kīlauean plume is largely controlled by silicate melt-vapour partitioning, rather than sulfide-vapour partitioning. The participation of dense sulfide liquids in shallow degassing processes may result from their direct attachment to buoyant vapour bubbles or remobilized olivine crystals. Sulfide resorption obscures the textural and chemical record of sulfide saturation in matrix glasses, but not in melt inclusions, which are isolated from this late-stage release of chalcophile elements. The partitioning of S between the dissolving sulfide, melt and the vapour phase accounts for ~20% of the total S release into the atmosphere.

SULFUR ISOTOPE SYSTEMATIC OF GRANITOIDS FROM THE YILGARN CRATON.

NEW INSIGHTS INTO THE RESERVOIRS OF ARCHEAN OROGENIC GOLD DEPOSITS

Stefano Caruso^{1,2}, Marco L. Fiorentini¹, Yuichiro Ueno³

1 – Centre for Exploration Targeting, School of Earth Sciences, The University of Western Australia, Australia, 2 – Australian Centre for Astrobiology, School of Biological, Earth and Environmental Sciences, The University of New South Wales, Australia, 3 – Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan

The advent of the analysis of multiple sulfur isotopes (^{32}S , ^{33}S , ^{34}S , ^{36}S) has revolutionised the investigation of Archean and Proterozoic terranes. Recent studies have shed new light to the cycle of sulfur through the lithosphere (LaFlamme et al., 2018), and improved our understanding of the sulfur reservoirs which are critical to the formation of Archean mineral deposits (e.g. Fiorentini et al., 2012). These recent advances are based on the ability to accurately measure the effects of the mass-independent fraction of sulfur (MIF-S), which were largely produced and preserved through photochemical reactions of volcanic SO_2 in the oxygen-poor Archean atmosphere (Farquhar and Wing, 2003). The geological significance, and the chemically conservative nature of MIF-S signatures have since been utilised to recognise crustal sources, and to trace the fluid pathways in ore-forming processes.

This approach has been applied to the study of Archean orogenic gold deposits with the aims of (1) constraining the processes of gold precipitation, and (2) establishing the origin of sulfur that transports gold in the ore-forming fluids. Although, there have been important progresses in the understanding of the mechanisms governing gold precipitation, the identification of the source(s) of sulfur remains problematic. Recent studies have revealed that most of the orogenic gold deposits of Yilgarn Craton host sulfides with non-zero MIF-S signatures, thus suggesting that part of that sulfur had once interacted with the Archean atmosphere (Selvaraja et al., 2017). However, the quantification of the crustal input into the ore-forming fluids remains problematic due to the difficulties to accurately identify the signatures of the sulfur reservoirs. Therefore, it is still unclear whether sulfur in orogenic gold deposits originated from subduction-related metamorphic fluids, lower crust / mantle reservoirs, or from the devolatilisation of supracrustal rocks.

In this study, we analyse the multiple isotope composition of over fifty sulfur-poor granitoids coeval with the main orogenic gold event, and distributed throughout the Yilgarn Craton. We utilise this exceptional dataset to investigate the cycle of sulfur through the lithosphere in the late-Archean, and to address the existing knowledge gaps on the origin of sulfur in orogenic gold deposits.

KEYNOTE: SULFUR IN VOLCANIC SYSTEMS: TRANSPORT AND REACTIONS FROM MANTLE TO ATMOSPHERE

Emma J. Liu¹, Marie Edmonds², Penny Wieser², and Tamsin Mather³

¹ Department of Earth Sciences, University College London, UK, ² Department of Earth Sciences, University of Cambridge, UK, ³ Department of Earth Sciences, University of Oxford, UK

Volcanoes and their magmatic systems play a key role in the Earth's sulfur cycle, transporting sulfur from the mantle, through the crust, and into the atmosphere. Volcanic sulfur emissions, and the subsequent conversion to sulfate aerosol, have important implications for climate and regional air quality. However, the pathway of sulfur to the Earth's surface varies between ocean island and subduction settings due to the sensitivity of sulfur chemistry to melt composition, magmatic water content and oxidation state. Remote sensing techniques, on the ground and from space, have improved our ability to detect and monitor volcanic SO₂ emissions, refining our understanding of the long-term outgassing behaviour of volcanoes globally. This presentation will discuss the contrasting evolution of sulfur in magmas from different tectonic settings, and the resulting impact on atmospheric emissions. In particular, we will focus on the 2014-2015 Holuhraun eruption in Iceland, where petrological constraints and atmospheric measurements together provide key insights into sulfur behaviour during magma ascent and early plume evolution in ocean island settings.

Session 2 - Sulfur in the Environment

NEW INSIGHTS ON THE ~74 KA TOBA ERUPTION FROM SULFUR ISOTOPES OF POLAR ICE CORES

Laura Crick^{1*}, A. Burke¹, W. Hutchison¹, S. Sparks², S. Mahony², E. W. Wolff³, E. A. Doyle³, J. W. B. Rae¹, J. Savarino⁴, and M. Kohno⁵

¹School of Earth and Environmental Sciences, University of St Andrews, Scotland; ² School of Earth Sciences, University of Bristol; ³Department of Earth Sciences, University of Cambridge UK; ⁴Institut des Géosciences de l'Environnement,, France; ⁵ Department of Geochemistry, Georg-August-Universität Göttingen, Germany

The ~74ka Toba eruption in Indonesia was one of the largest volcanic events of the Quaternary and loaded an estimated 100 million tonnes of H₂SO₄ into the atmosphere. Understanding the precise timing of this colossal eruption is vital to unravelling the climatic and environmental impacts of the largest volcanic events on Earth. Sulfur aerosols injected into the stratosphere following large volcanic events reflect incoming radiation and lead to global cooling, and in the case of Toba it has been suggested that it led to cooling of 1 – 5°C and extinctions of some local hominin populations. One of the most enigmatic features of the Toba eruption is that the S peak has yet to be identified in the ice core records, although numerous candidate sulfate peaks have been identified in both Arctic and Antarctic ice cores. To address this, we analysed the sulfur isotope fingerprint ($\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) of 11 Toba candidates from two Antarctic ice cores by multi-collector inductively coupled plasma mass spectrometry. This approach allows us to evaluate injection altitudes and to distinguish large tropical eruptions from proximal eruptions because stratospheric sulfur aerosols undergo UV photochemical reactions that impart a sulfur mass-independent isotopic fractionation (S-MIF). In contrast, tropospheric sulfur aerosols do not exhibit S-MIF because they are shielded from the relevant UV radiation by the ozone layer.

We identify three stratospheric, tropical eruption candidates with two recording the largest $\Delta^{33}\text{S}$ signals measured to date in the ice core archives. The largest of these $\Delta^{33}\text{S}$ signals is >2 ‰ more negative than previous measurements of the 1257 Samalas eruption (the largest eruption of the last 2000 years), despite having a similar integrated sulfate flux for this event to the ice core. These three candidates are within uncertainty of the Ar⁴⁰/Ar³⁹ age estimates for the Toba eruption and when considered with other paleoclimate proxies place the event during the transition into Greenland Stadial 20. Finally, we further analyse the relationship between the Toba eruption candidates and these proxies to determine the precise timing and potential climatic impacts of one of the largest eruptions of the Quaternary period.

UNDERSTANDING THE HYDROTHERMAL INFLUENCE ON SEAWATER SULFATE

Eleanor Hughes¹, Anna Waldeck¹, Sarah Moriarty², John Jamieson², Peter Scheuermann³, Drew Syverson⁴, William Seyfried⁵ & David Johnston¹

¹Harvard University USA, ²Memorial University of Newfoundland Canada, ³University of British Columbia Canada, ⁴Yale University USA, ⁵University of Minnesota USA

Long-term records of the isotopic composition of seawater sulfate are a powerful biogeochemical resource, revealing changes in key fluxes into and out of the seawater sulfate reservoir through time. Microbial, riverine and evaporitic sulfate fluxes have been extensively studied, but the importance of hydrothermal systems remains controversial. Here, we investigate the potential influence of a hydrothermal sulfate flux on the seawater sulfate reservoir. In the first application of triple-oxygen isotope analyses to hydrothermal sulfate, we find that anhydrite (CaSO_4) from a globally distributed set of hydrothermal systems is significantly offset in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ relative to seawater, in large part due to equilibrium oxygen isotope exchange with hydrothermal fluid at elevated temperatures. A flux of hydrothermally-influenced sulfate back into the seawater reservoir may thus significantly affect its isotopic composition. Incorporation of these new isotopic constraints into a model of the global sulfur cycle indicates that the magnitude of this hydrothermal flux may be comparable to riverine inputs (on the order of $10^{11} - 10^{12}$ mol S/yr); however, at present this estimate is highly uncertain. As our understanding of the triple-oxygen isotope composition of riverine and microbial sulfate fluxes improves, the importance of hydrothermal sulfate cycling to the seawater sulfate reservoir will be better constrained. This approach, combining modeling and isotopic constraints, may also help to resolve present debate surrounding long-term sulfate storage in oceanic crust.

MICROBIAL SULFUR DISPROPORTIONATION AT MARINE HYDROTHERMAL VENTS: A RECONSIDERATION OF THE GLOBAL BIOLOGICAL SULFUR CYCLE?

Maxime Allieux,

Université de Bretagne Occidentale, France

Disproportionation corresponds to a chemical or biological reaction where the same mineral or organic compound serves as both an electron donor and as a terminal electron acceptor. In the case of inorganic sulfur compounds such as thiosulfate, sulfite, and elemental sulfur, each one may be oxidized to sulfate and reduced to sulfide. Microorganisms capable of disproportionating sulfur-compounds originate from a large range of environments such as marine and freshwater sediments, anaerobic digestors, terrestrial and marine hydrothermal vents, and acidic and alkaline lakes. Furthermore, they appear to be phylogenetically widespread, particularly in the bacterial domain. Isotopic data on sulfur derived from early Archaean rocks and the presence of microfossils from 3.4 billion-year-old geological formations suggest that sulfur disproportionation could be one of the earliest modes of microbial metabolism and may be associated with the early production of sulfate in the sea, but remains highly controversial. In *Bacteria*, inorganic sulfur compounds appear to be disproportionated via a reverse sulfate reduction pathway to produce ATP directly. However, it is likely that many diverse independent disproportionation mechanisms exist. The current state of knowledge converges on the hypotheses that disproportionation of elemental sulfur, could occur using a complete dissimilatory sulfate reduction pathway including adenylylsulfate reductase, the sulfite reductase system and the involvement of rhodanese-like sulfurtransferases, heterodisulfide reductases and molybdopterin. This work aims to fully identify the path of elemental sulfur disproportionation, notably the oxidative branch, and then those of other sulfur substrates. The hydrothermal vents, studied in this work using physiological, genomic and proteomic approaches are relevant models because of their characteristic high temperature, allowing rapid microbial growth and the sulfur compounds which are ubiquitous in these environments, representing major energy sources for the microorganisms that inhabit them. Currently, potential associated genes had been found by comparative genomics and could be highly associated to elemental sulfur disproportionation. Genetic markers associated to the sulfur disproportionation could lead to a total reconsideration of the biological sulfur cycle in all ecosystems.

MICROSCALE $\delta^{34}\text{S}$ HETEROGENEITIES IN COLD SEEP BARITES RECORD VARIABLE METHANE FLUX OFF THE LOFOTEN-VESTÅRALEN CONTINENTAL MARGIN, NORWAY

R. Seth Wood¹, Aivo Lepland², Ryan C. Ogliore³, Jennifer Houghton¹, Clive Jones¹, and David A. Fike¹

¹Department of Earth & Planetary Sciences, Washington University in St. Louis, USA, ²Geological Survey of Norway (NGU), Norway³Department of Physics, Washington University in St. Louis, USA

Methane seeps are a critical component of the global carbon cycle. In marine environments, sulfate-coupled anaerobic oxidation of methane (AOM-SR) modulates methane release into the overlying water column. Two methane cold seeps were recently discovered on the Lofoten-Vestårelen (LV) continental margin, and U-Th age dates suggest methane-derived authigenic carbonate (MDAC) began precipitating near the end of the Last Glacial Maximum (LGM). Below the sulfate methane transition zone (SMTZ), methane and barium concentrations are variably high, up to 5 mM and 1 mM, respectively. Here, we use secondary electron microscopy (SEM) and secondary ion mass spectrometry (SIMS) to petrographically assess and measure microscale $\delta^{34}\text{S}$ variability of authigenic barite, respectively. The mean $\delta^{34}\text{S}_{\text{BaSO}_4}$ value from SIMS spot analyses is 70.3‰ (n = 300), and $\delta^{34}\text{S}_{\text{BaSO}_4}$ values can range more than 40‰ within individual barite aggregates. SIMS spot measurements were spatially referenced to SEM images to infer the relative timing of $\delta^{34}\text{S}_{\text{BaSO}_4}$ fluctuations, and $\delta^{34}\text{S}_{\text{BaSO}_4}$ ion imaging transects were collected parallel to barite growth axes and provide a semi-continuous record of porewater sulfate evolution during barite precipitation. $\delta^{34}\text{S}_{\text{BaSO}_4}$ values imply the assessed barites precipitated from highly distilled porewater sulfate and precipitated over extended periods under non-steady state conditions. We suggest the primary forcing affecting intragranular $\delta^{34}\text{S}_{\text{BaSO}_4}$ variability is variable AOM-SR activity during precipitation due to changes in cold seep methane flux. Our findings provide a semi-continuous geologic proxy for paleo-methane flux and suggest methane advection rates have gradually decreased at the LV seep sites. However, cyclical changes in $\delta^{34}\text{S}$ values along barite growth axes and periodic dissolution features suggest methane advection rates did not decrease monotonically and that there may have been two or more abrupt episodes of enhanced methane emissions since the LGM.

FOSSIL FUELS AND SULFUR: IMPLICATIONS FOR INDUSTRIAL SULFURIC ACID AVAILABILITY DURING THE TRANSITION TO A LOW-CARBON FUTURE

Day, S., 1; Van Heerde, L. 2; Maslin, M. 2

1 Institute of Risk and Disaster Reduction, University College London. 2 Department of Geography, University College London.

Discussions of anthropogenic influences on the sulfur cycle in the Earth System generally center upon sulfur dioxide emissions to the atmosphere from fossil fuel combustion, producing acid rain that inhibits plant growth and CO₂ uptake by vegetation. However, the industrial uses of sulfuric acid link the carbon, sulfur and phosphorus cycles in other ways.

Efforts to reduce anthropogenic emissions of SO₂ to the atmosphere mean that more than 80% of global sulfur production – most of which is converted to sulfuric acid – is now a byproduct of oil and natural gas desulfurization. The advantages of sulfur production from fossil fuel processing have largely eliminated other industrial sulfur sources. An emerging critical disadvantage, however, is that continued cheap production and widespread use of sulfuric acid now depends upon the profitability of fossil fuel production. Industries that rely on cheap and abundant sulfuric acid therefore also depend upon continued use of fossil fuels and are linked to anthropogenic carbon emissions. These industries include phosphate fertilizer production, upon which intensive food production depends and which uses >80% of sulfuric acid production; and processing of the laterite and deep-sea nodule ores that are considered to be critical reserves of key metals for the anticipated transition to zero-emissions technologies over the next few decades.

Our study indicates that global sulfur demand and sulfur supply from oil and gas desulfurization are presently close to being in balance. However, the implication of a fast transition from fossil fuels (RCP2.6) and early peak oil is that sulfur demand would outstrip supply within the next decade and become an important issue in maintaining global food production and transiting to a low carbon economy. Indeed, the rate at which alternative sources of sulfur can be developed may become a rate-determining step for that transition.

TRIPLE OXYGEN ISOTOPES ($\Delta^{17}\text{O}$) AS RECORDS OF SULFUR CYCLE DRIVERS

Anna Waldeck¹, Weiqi Yao^{1,2}, Adina Paytan³, David Johnston¹

¹Department of Earth and Planetary Sciences, Harvard University, Cambridge, USA, ²Department of Earth Sciences, University of Toronto, Canada, ³Institute of Marine Sciences, University of California Santa Cruz, Santa Cruz, USA

Here we introduce a novel, emerging record of the ^{17}O isotopic composition of seawater sulfate recorded in marine barites (spanning 134 million years ago to present). Using a recently published model - calibrated against the composition of the modern ocean - we interpret the sulfate ^{17}O composition in seawater as recording the relative balance of sulfur cycle processes that are both mass-independent (or impart large anomalies in ^{17}O – meaning $\Delta^{17}\text{O} \neq 0$) and mass-dependent (largely wash away these large ^{17}O anomalies).

Mass-independent isotope effects are sourced from high energy reactions in the atmosphere. Two subsequent processes can thus be considered relative to their MIF consequences. First, the weathering of sulfide minerals has been proposed to incorporate atmospheric O_2 ($\Delta^{17}\text{O} \ll 0$) into product sulfate. The size of $\Delta^{17}\text{O}$ anomaly in atmospheric O_2 is thought to scale to the atmospheric ratio of $p\text{CO}_2:p\text{O}_2$ over time, with an unknown fraction of O_2 being incorporated into sulfate. New work on river systems and sulfate generation (Hemingway et al., 2020, PNAS) challenges these direct interpretations, lessening the straightforward relationship to O_2 . The second means of gaining MIF is via the oxidation of volcanic SO_2 following the injection of S via large igneous provinces ($\Delta^{17}\text{O} > 0$). A sulfur cycle model hypothesizes that large igneous provinces directly influenced the sulfur cycle over the last 120 million years by injecting significant amounts of SO_2 into the atmosphere (Laakso et al, 2020). If this model correctly predicts that SO_2 outgassing was significant during LIP emplacement, then this may be observable in the triple oxygen isotope composition of marine sulfate across these intervals.

The degree to which these anomalies alter seawater sulfate oxygen isotope composition reflects the size of the marine sulfate reservoir as well as the extent of mass-dependent processes like biological recycling of sulfate that also act to augment or even erase these primary effects (Waldeck et al., 2019, EPSL). In our analysis of this new Cenozoic/Cretaceous dataset, we constrain the extent to which these processes (atmospheric influence, weathering, and biology) each shaped the ^{17}O composition of marine sulfate.

20-YEAR RECORD OF SULFURIC ACID WEATHERING IN A HIGH ARCTIC WATERSHED

E.i. Stevenson^{1*}, M.I. Murphy², K.E. Relph¹, E.T. Tipper¹, A.V. Turchyn¹, P.A. .E. Pogge Von Strandmann³, T.R. Christensen⁴

¹Department of Earth Sciences, University of Cambridge, UK, ²Institut for Geovidenskab og Naturforvaltning, Københavns Universitet, Denmark, ³Institute of Earth and Planetary Sciences, UCL and Birkbeck, University of London, UK, ⁴Department of Bioscience, Aarhus University, Denmark

Earth's temperature is thought to be regulated by a negative feedback between atmospheric CO₂ levels and chemical weathering of silicate rocks over million-year time scales. Enhanced physical weathering in the Arctic through glacial retreat, permafrost thaw and collapse is exposing and mobilising vast amounts of finely-ground sediment to the agents of weathering. Elevated pyrite mineral oxidation caused by the exposure of sulfide minerals during physical erosion can generate sulfuric acid which can weather freshly exposed carbonate minerals and release CO₂ to the atmosphere.

Here we present new coupled oxygen-sulfur isotopic data for a high Arctic River (Zackenberg River, Northeast Greenland) to partition the sources of dissolved sulfate from gypsum and pyrite end members. High frequency water chemistry data from the Zackenberg River shows how these chemical weathering reactions have evolved seasonally and annually over the past 20 years. The extent of release and sequestration of CO₂ from the Zackenberg River watershed is highly dependent on the time of the season, erosional and precipitation events. The compiled datasets demonstrate that the release of CO₂ from the sulfuric acid weathering of carbonate minerals is widespread. The total flux of which can, at times, outweigh that from the long-term sequestration of atmospheric CO₂ via silicate weathering. This scenario could represent a possible modern-day positive climate feedback loop, which is unaccounted for in coupled CO₂-climate models.

ORGANIC SULFUR FLUXES AND GEOMORPHIC CONTROL OF SULFUR ISOTOPE RATIOS IN RIVERS

Preston C. Kemeny^a, Mark A. Torres^b, Michael P. Lamb^a, Samuel M. Webb^c, Nathan Dalleska^a, Trevor Cole^b, Yi Hou^b, Jared Marske^a, Jess F. Adkins^a, Woodward W. Fischer^a

^a Geological and Planetary Sciences, California Institute of Technology, California US, ^b Earth, Environmental, and Planetary Sciences, Rice University, Texas US, ^c Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, California US

Pyrite oxidation plays a critical role in the relationship between weathering and climate, and its impact on the global carbon cycle has previously been constrained through inversion models utilizing observations of riverine sulfate (SO_4^{2-}) and sulfur isotope ratios ($\delta^{34}\text{S}$). However, observations from some rivers have suggested that SO_4^{2-} $\delta^{34}\text{S}$ reflects processes such as microbial SO_4^{2-} reduction or organic sulfur cycling, rather than lithology. To study the prevalence and controls of SO_4^{2-} transformations, we measured dissolved major element concentrations, SO_4^{2-} $\delta^{34}\text{S}$, and sediment $\delta^{34}\text{S}$, and made spectroscopic observations of sediment and vegetation from a small catchment in Western Iceland with relatively uniform and isotopically constrained basaltic bedrock. Dissolved SO_4^{2-} $\delta^{34}\text{S}$ ranged from 2.5‰ to 23.7‰ and correlation with $\text{Cl}^-/\text{SO}_4^{2-}$ indicated that SO_4^{2-} predominantly derived from basalt weathering and precipitation. The lower range of SO_4^{2-} $\delta^{34}\text{S}$ values were focused in V-shaped, fluvial valleys incising into bedrock, while higher values occurred in U-shaped, glacially eroded valleys currently alluviated. Spectroscopic observations identified organic S phases in suspended river sediment, floodplain deposits, and vegetation, and mass balance calculations quantified the organic S flux as less than approximately 10% of SO_4^{2-} export. Sediment $\delta^{34}\text{S}$ values were comparable to SO_4^{2-} $\delta^{34}\text{S}$. The isotopic patterns reflected the coupling between erosion, bedrock mineral supply, and oxidative weathering, in contrast to fractionation from S cycling along alluvial reaches. Together the results validated the application of river inversion models for constraining weathering fluxes and affirmed that global pyrite oxidation, even in the presence of terrestrial S cycling, modulates the atmospheric concentration of carbon dioxide. Motivated by these observations, we developed a flexible MATLAB model, called MEANDIR, for customizable Monte Carlo inversion of dissolved river chemistry data. MEANDIR extended former inversion efforts by representing chemical processes as independent end-members, including pyrite oxidation, petrogenic organic carbon oxidation, and carbon dioxide exchange between the river and atmosphere.

17 November

**Session 3 - Sulfur in the Environment Part II - Chaired Andrea
Burke**

RECORDS OF PAST PERMAFROST THAW PRESERVED IN FOSSIL BONE SULPHUR ISOTOPE SIGNATURES?

Rhiannon E Stevens, Hazel Reade, Kerry L Sayle, Jennifer A. Tripp, Thomas Higham.

1: Institute of Archaeology, University College London, 2: Department of Chemistry, University of San Francisco, USA., 3: Scottish Universities Environmental Research Centre, United Kingdom., 4: Research Laboratory for Archaeology and the History of Art, University of Oxford, United Kingdom.

We report here high-magnitude temporal changes in animal bone collagen $\delta^{34}\text{S}$ at the end of the last ice age that are unidirectional, occur in multiple species (with differing dietary niches and mobility behaviours) and in multiple different geographic areas. These records are observed in regions of known permafrost presence during the Last Glacial Maximum, and the high-magnitude excursions appear to coincide with the suspected timing of localised permafrost development and thaw, and with global temperature changes. The magnitude of change observed in the bone collagen $\delta^{34}\text{S}$ data is well beyond that reported from other environmental settings. The commonly invoked interpretations of changing animal diet and mobility fail to adequately explain the data; the continental wide pattern of change can only be adequately explained through regional scale environmental drivers. We hypothesise the high-magnitude changes in faunal bone $\delta^{34}\text{S}$ from these palaeo-permafrost environments are driven by biogeochemical cycling related to soil redox and permafrost thaw. Faunal collagen can preserve unaltered for several hundred thousand years and for samples from the last c. 50,000 years can be directly radiocarbon dated, thus offering an unrivalled prospect for developing high-resolution, tightly chronologically-constrained records of past permafrost change. Furthermore, our findings indicate terrestrial herbivore $\delta^{34}\text{S}$ values can reflect local hydrological conditions, complicating the use of sulphur isotopes as a tool for food origin, animal migration, and archaeological mobility research.

BIOGEOCHEMICAL CYCLING OF SULFUR, MANGANESE AND IRON IN FERRUGINOUS LIMNIC ANALOG OF ARCHEAN OCEAN

Alexey Kamyshny^a, Valeria Boyko^a, Khoren Avetisyan^a, Alyssa Findlay^a, Qingjun Guo^b, Xi Yang^b, André Pellerin^{a,c}

^a Department of Geological and Environmental Sciences, Faculty of Natural Sciences, Ben-Gurion University of the Negev, Israel, ^b Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, China, ^c Department of Biology - Microbiology, Aarhus University, Denmark

The early evolution of life on Earth was intimately coupled with the evolution of ocean chemical composition and redox conditions in Archean ocean. However, the measurements of chemical and isotopic compositions of Archean sedimentary rocks does not provide sufficient information for understanding the biogeochemical processes that characterized oceans during this period. In this research, the cycling of the redox-sensitive elements in the water column and sediments of the seasonally stratified Lake Sihailongwan, China, was studied. It was found that during the stratification, the concentrations of sulfate ions in the epilimnion were $<100 \mu\text{mol L}^{-1}$. The hypolimnion of the lake becomes anoxic and contains iron, manganese and low concentrations of hydrogen sulfide. These conditions are similar to those suggested to exist in the Archean ocean, and therefore the biogeochemical cycles in Lake Sihailongwan may be analogous to those in the Archean ocean. In Lake Sihailongwan, the chemocline is always deeper than the thermocline. The hypolimnion is supersaturated with respect to iron sulfide in August, while in May and October, this supersaturation is present only in the lower hypolimnion. The concentration profiles of the redox species in the water column and in the sediments show that dissolved iron(II) and manganese(II) diffuse from the sediments into the water column, while hydrogen sulfide and sulfate diffuse into the sediment. At the hypolimnion, the sulfur isotope fractionation values are consistent with microbial sulfate reduction, possibly combined, to a minor extent, with disproportionation of zero-valent sulfur. The absolute sulfur isotope fractionation factor increases between spring and autumn and decreases with water depth, possibly due to precipitation of iron sulfide in the lower hypolimnion. The fraction of highly reactive iron in the sediments is mainly composed of iron(II) carbonates and the most reactive iron(III) (hydr)oxide phases. Iron-based paleoproxies are consistent with sediment deposition under ferruginous water column. In the sediment, concentrations of sulfate and hydrogen sulfide are low, and sulfur isotope composition of sedimentary pyrite is equal to that of the epilimnetic sulfate. The obtained results demonstrated that despite a low sulfate concentration in the water column, sulfur isotope fractionation is high. However, due to the complete consumption of the sulfate reservoir, the large isotope fractionation is not preserved in the sedimentary record.

SULFUR ISOTOPE COMPOSITIONS OF FRAMBOIDAL PYRITES AND MICROPYRITES FROM MODERN MICROBIAL MATS PINPOINT THE INFLUENCE OF LOCAL ENVIRONMENT

J Marin-Carbone (UNIL), M-N Decraene (UNIL), Ch Thomazo (Biogéosciences), Laurent Remusat (IMPMC), Stephane Escrig (EPFL), Anders Meibom (EPFL), Emmanuelle Vennin (Biogéosciences) and Karim Benzerara (IMPMC)

Microbial mats are laminated layers of diverse microbial communities that exist across strong geochemical and redox gradients (1,2). The relationships between the diverse microbial metabolic activities and the isotopic signatures in associated biominerals formed in these mats are key to understand the modern biogeochemical cycle(s) and to interpret the geological record. Previous studies have documented in detail the locus of sulfate reduction processes in microbial mats (2,3,4), primarily through identification of soluble sulfur species captured using silver disks. Here we investigate micrometric pyrites in two different microbialites, one from a hypersaline environment (Cayo Coco, Cuba) and one from a volcanic alkaline lake (Atexcac, Mexico). Both environments exhibit two distinct pyrite morphologies: framboidal with sizes ranging from 2 to 15 μm and micropyrates with dimensions less than 3 μm . Sulfur isotope compositions of 60 framboidal pyrites and 40 micropyrates from these two environments were measured by NanoSIMS (5). Using pyrite standards to determine quasi-simultaneous arrival correction factors and instrumental mass fractionation, the analytical reproducibility during analytical sessions was better than 1.6 ‰. Framboid pyrites displayed $\delta^{34}\text{S}$ values from -38 to -11 ‰ (average of $-19.6 \pm 6\text{‰}$ and $-28.6 \pm 6\text{‰}$ for Cayo Coco and Atexcac respectively), while micropyrates were characterized by lighter sulfur isotopic compositions with $\delta^{34}\text{S}$ between -59 to -22 ‰ (average of $-35 \pm 10\text{‰}$ and $-42 \pm 8\text{‰}$ for Cayo Coco and Atexcac respectively). We observe a significant difference in average sulfur isotope composition in framboidal pyrite which we ascribe to a difference in isotopic composition of local water sulfate between these two mats. Sulfate reduction through microbial metabolic activity is strongly suggested by the light isotope signatures and typical shape of these framboid pyrites. However, the more homogeneous morphology, size and isotope distribution of the micropyrates point to multiple step of redox processing of the sulfur pool. Unfortunately, our current analytical protocol cannot permit precise measurement of $\delta^{33}\text{S}$ that is necessary for better assessment of microbial metabolic pathways. Our study thus highlights the importance of understanding at micrometer scale pyrite formation processes in microbial mats to strengthen the basis for interpretation of the rock record.

STRONG LOCAL, NOT GLOBAL, CONTROLS ON MARINE PYRITE SULFUR ISOTOPES OVER GLACIAL-INTERGLACIAL CYCLES

Virgil Pasquier¹, David. A. Fike², Itay Halevy¹

¹Earth and Planetary Sciences, Weizmann Institute of Sciences, Rehovot, Israel, ²Earth and Planetary Sciences, Washington University in St. Louis, USA

Understanding variation in the isotopic composition of sulfur in sedimentary pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) is motivated by the key role of sulfur biogeochemistry regulating Earth's surface oxidation state. Until recently, the impact of local depositional conditions on $\delta^{34}\text{S}_{\text{pyr}}$ has remained underappreciated, and stratigraphic variations in $\delta^{34}\text{S}_{\text{pyr}}$ were interpreted mostly to reflect global changes in biogeochemical cycling. The relative importance of local drivers of variation in $\delta^{34}\text{S}_{\text{pyr}}$ records can be assessed by studying well-dated, well-understood sequences that span periods during which we know components of the sulfur cycle to have been relatively invariant. To this end, we examined four glacial-interglacial $\delta^{34}\text{S}_{\text{pyr}}$ records from the Gulf of Lion, the New-Zealand shelf, the South China shelf and the Peru margin. Despite the maintenance of a well-mixed, oxygenated and sulfate-rich ocean in all of these locations over the study period, all of the studied cores display radically different behaviors, characterized not only by divergent $\delta^{34}\text{S}_{\text{pyr}}$ values, but also by different sense and magnitude of temporal isotopic variability. Variations in the local depositional environment and microbial activity appear to play a major role in generating and modifying the sulfur isotopic composition of pyrite during early diagenesis. Further, we suggest that by controlling the depositional properties (organic carbon and iron loading, sedimentation rate, porosity, among others), global sea-level changes are directly responsible for coeval but discordant $\delta^{34}\text{S}_{\text{pyr}}$ between sedimentary basins. Together, these results highlight strong local controls on $\delta^{34}\text{S}_{\text{pyr}}$, calling for reevaluation of the current practice of using $\delta^{34}\text{S}_{\text{pyr}}$ stratigraphic variations to infer global changes in Earth's surface environment.

QUADRUPLE SULFUR ISOTOPE BIOSIGNATURES FROM TERRESTRIAL MARS- ANALOGUE SYSTEMS

Arola Moreras-Marti, M. Fox-Powell, T. Di Rocco, T.galloway, E.Stüeken, C.R.Cousins, A.I. Zerkle

School of Earth and Environmental Sciences and Centre for Exoplanet Science, St Andrews University, UK.

Quadruple sulfur isotope values (QSI: ^{32}S , ^{33}S , ^{34}S , ^{36}S) preserved in sulfur compounds in the environment and in sedimentary rocks provide evidence of mass-dependent fractionation from biological processes [1-3]. In particular, minor S isotopes show small biologically-induced deviations (termed mass conservation effects) that can be used to unravel complex S cycling processes even when traditional $\delta^{34}\text{S}$ values overlap. Sedimentary QSI records have thus been used to infer the timing of oxygenation and evolution of S-based metabolisms over Earth history.

More recently, S isotopes have also been proposed as a diagnostic tool for recognizing evidence of life on Mars, given the ubiquitous occurrence of sulfur on the Martian surface [4-6]. The widespread volcanic release of S during the Noachian-Hesperian periods together with the variety of S species found on Mars point towards sulfur being implicated in any putative Martian biochemistry. Recent discoveries by the NASA Curiosity rover have confirmed that Mars' surface contains the electron donors and acceptors required for microbial sulfide oxidation and sulfate reduction, suggesting that S metabolisms, and resulting S isotope biosignatures, could be central to the search for martian life.

In order to explore the habitability of S-rich Mars ecosystems and their implications for preserving S isotope biosignatures, we examined QSI values in two S-dominated Mars analogue ecosystems. These included glacially-fed hydrothermal pools in Iceland (Kerlingarfjöll and Kverkfjöll), and the Lost Hammer (LH) hypersaline spring from Axel Heiberg Island (LH), Nunavut, Canada. These two settings preserve distinct QSI biosignatures reflective of different sulfur cycling processes. Our results demonstrate the strong potential for QSI values to be used as biosignatures in the search for S-based life on Mars.

THE CARBON-SULFUR LINK IN THE REMINERALIZATION OF ORGANIC CARBON IN SURFACE SEDIMENTS

Harold J. Bradbury¹, Alexandra V. Turchyn¹, Adam Bateson¹, Gilad Antler², Angus Fotherby¹, Jennifer L. Druhan³, Mervyn Greaves¹, David A. Hodell¹

1: Department of Earth Sciences, University of Cambridge, UK, 2: Department of Geological and Environmental Sciences, Ben Gurion University of the Negev, Israel, 3: Department of Geology, University of Illinois at Urbana Champaign, USA

Microbial sulfate reduction dominates the oxidation of organic matter in many marine sediments due to the relatively high concentration of sulfate in seawater. This oxidation of organic carbon is a key process in the global carbon cycle because it prevents the burial of reduced carbon from Earth's surface. We present carbon and sulfur isotope ratio measurements and concentrations in marine pore fluids from a series of sites located along a depth transect on the Iberian Margin. The combined use of carbon and sulfur isotope ratios provides unique insight into microbial metabolism during sulfate reduction, the anaerobic oxidation of methane and methanogenesis. We show systemic changes in the carbon and sulfur isotopic composition of the pore fluids whereby there are similar changes in one isotope system prior to another that persist across a range of different environments and sediment depths. This behaviour is explored using a reactive-transport modelling approach to investigate how changes in the relative proportion of sulfate reduction and methanogenesis can be interpreted using the combination of carbon and sulfur isotope ratios.

KEYNOTE: MULTIPLE LOCAL CONTROLS ON PYRITE SULFUR ISOTOPES AND IMPLICATIONS FOR READING THE SEDIMENTARY PYRITE RECORD

Itay Halevy¹

¹Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel

Sulfur isotope ratios in modern marine and sedimentary pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) have been extensively used in investigations of sub-seafloor microbial activity, in reconstructions of the biogeochemical sulfur cycle and the tightly coupled cycles of carbon and oxygen, and in reconstructions of the redox evolution of Earth's surface environment. These applications are guided by the assumption that $\delta^{34}\text{S}_{\text{pyr}}$ variation is related to drivers in the global sulfur cycle and the aggregate fractionation imparted by microbial sulfur metabolisms. A growing number of observations from a wide range of natural environments, however, suggest that major $\delta^{34}\text{S}_{\text{pyr}}$ variation is often related to neither of these factors.

To elucidate the controls on $\delta^{34}\text{S}_{\text{pyr}}$ values, we combine (i) studies of well-dated, well-understood Pleistocene marine sediments, during the deposition of which the ocean's chemical composition has varied negligibly, and (ii) a coupled microbial-diagenetic model, which accounts for the transport and reaction of sulfur and iron species, and which is capable of predicting the fractionation imparted by microbial sulfate reduction. Rather than global sulfur-cycle drivers of major $\delta^{34}\text{S}_{\text{pyr}}$ variation, the studied sediment cores clearly demonstrate controls by local variations in sedimentation rate, organic matter and reactive iron content, and reworking by currents, on timescales between tens of thousands of years and tens of millions of years.

Using gridded ($1^\circ \times 1^\circ$) datasets of the relevant sedimentary and environmental factors (e.g., sedimentation rate, organic matter content, reactive iron content, porosity), our model reproduces $\delta^{34}\text{S}_{\text{pyr}}$ distributions compiled from modern marine sediments. The microbial fractionation remains uniformly large under the vast majority of modern marine conditions, and the main determinant of $\delta^{34}\text{S}_{\text{pyr}}$ is the sedimentation rate, which controls the relative importance of sulfur species' diffusion, advection and reaction ("openness"). The abundance and reactivity of organic matter and iron are important secondary controls on $\delta^{34}\text{S}_{\text{pyr}}$. Another important determinant of $\delta^{34}\text{S}_{\text{pyr}}$ values is the concentration of seawater sulfate, and we suggest that the trend of increasing Archean-Proterozoic-Phanerozoic sulfate-pyrite $\delta^{34}\text{S}$ offset reflects increasing sulfate concentrations, which affect the openness of the sedimentary system.

With this new framework, we understand the tectonic, biological and oceanographic factors that have governed $\delta^{34}\text{S}_{\text{pyr}}$ values in marine sedimentary rocks through time.

Session 4 - Sulfur in Earth History

KEYNOTE: QUADRUPLE SULFUR ISOTOPES: WINDOWS INTO SULFUR CYCLING IN THE EARTH SYSTEM

Aubrey L Zeckle

School of Earth & Environmental Sciences and Centre for Exoplanet Science, University of St Andrews, UK.

Quadruple sulfur isotope values (^{32}S , ^{34}S , ^{33}S , ^{36}S) in sedimentary rocks preserve evidence of mass-dependent (MDF) and mass-independent fractionations (MIF) produced during the cycling of sulfur through the Earth system. S-MIF mainly forms in the atmosphere, via UV-driven photochemical transformations that are blocked in the presence of an ozone layer. Thus the disappearance of S-MIF in the early Paleoproterozoic is widely used to define the rise of atmospheric oxygen to above trace levels during the Great Oxidation Event. Older sedimentary records of S-MIF show variations in sign and magnitude that have generally been linked to changes in atmospheric chemistry and sulfur exit channels from the atmosphere. However, once deposited on Earth's surface these sulfur compounds are subject to S-MDF during biogeochemical sulfur cycling in the water column and sediments that can mix or mute sedimentary S-MIF values. Despite the importance of local processes on preservation of S isotope signals, studies of the relative importance of global versus local controls on the incorporation and preservation of S-MIF into sediments remain largely theoretical. I will present new quadruple sulfur isotope data that show large stratigraphic variations in S-MIF within Late Archean sedimentary rocks. Consideration of these changes within the context of additional multi-proxy data suggest that local water column redox and biological S cycling control preservation of S-MIF records in these sediments, rather than changes in global atmospheric chemistry.

GLOBAL SEAWATER SULFATE ISOTOPE COMPOSITION AND ATMOSPHERIC–BIOSPHERIC EVOLUTION CONSTRAINED AT 605 MA BY PYRITE RE-OS DATING AND $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ AND $\Delta^{17}\text{O}$ ANALYSES OF THE ABERFELDY STRATIFORM BARITE DEPOSITS, SCOTLAND

Moles, N.R.¹, Boyce, A.J.², Selby D.³, Warke, M.R.⁴, Gregory, B.⁴, and Claire, M.W.⁴

¹ School of Environment and Technology, University of Brighton, UK² Scottish Universities Environmental Research Centre (SUERC), UK, ³ Department of Earth Sciences, Durham University, UK,⁴ School of Earth and Environmental Sciences, University of St Andrews UK.

The Aberfeldy deposits comprise commercially valuable bedded barite rock (Coats et al. 1981) hosted by graphitic mica schists of the Dalradian (Easdale Subgroup) Ben Eagach Schist Formation in the Grampian Highlands of Scotland. Extensive isotopic ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) studies of the barite have been reported previously (Hall et al. 1991; Moles et al. 2015) and here we report new $\Delta^{17}\text{O}$ results for barite and Re-Os geochronology using associated pyrite. Pyrite Re-Os dates for the separate Foss and the Ben Eagach–Duntanlich deposits are indistinguishable within uncertainty giving a combined age of 605.4 ± 7.0 Ma. Statistically consistent radiogenic age estimates for the stratigraphically overlying formations (e.g. 601 ± 4 Ma for a tuff bed in the Tayvallich Volcanics: Dempster et al. 2002) suggests that the original pyrite Re-Os system has survived amphibolite-facies metamorphism and that the date represents sedimentation. Combined with relatively uniform initial $^{187}\text{Os}/^{188}\text{Os}$ (Os-i) ratios, our results support a syngenetic ('SEDEX') or possibly syn-early-diagenetic depositional model for the mineralization. Early diagenetic alteration while the barite sediment was fine-grained and porous accounts for pronounced decimetre-scale vertical variations in barite $\delta^{34}\text{S}$ (+32 to +41 ‰) and $\delta^{18}\text{O}$ (+8 to +21 ‰) at bed margins (Moles and Boyce 2019). Conversely, in central parts of thicker (1-10 m) barite beds, relatively uniform $\delta^{34}\text{S}_{\text{barite}}$ of $+36 \pm 1.5$ ‰ represent the isotopic composition of contemporaneous open marine sulfate (Moles et al. 2015). In these thicker beds, the barite records $\Delta^{17}\text{O}$ values of -0.249 to -0.084 ‰ (mean: -0.179 ‰; $n=7$) indicating preservation of mass-independently fractionated oxygen isotope (O-MIF) signals. Though these $\Delta^{17}\text{O}$ values do not approach the pronounced negative $\Delta^{17}\text{O}$ excursion at the end of the Marinoan glaciation, they constitute an unambiguous atmospheric signal within the Aberfeldy barite deposits. Assuming 8 % of sulfate-oxygen is derived from tropospheric O_2 (Balci et al. 2007), and that $p\text{CO}_2$ levels were similar to the modern atmosphere, photochemical modelling suggests these $\Delta^{17}\text{O}$ values correspond to $p\text{O}_2$ concentrations >5 % of modern levels. If, however, mid-Ediacaran $p\text{CO}_2$ levels were considerably higher than at present, atmospheric $p\text{O}_2$ levels may have been closer to the modern atmosphere.

ENORMOUS SULFUR ISOTOPE EXCURSIONS INDICATE MARINE ANOXIA AND LARGE-SCALE PYRITE BURIAL DURING THE END-TRIASSIC MASS EXTINCTION

Tianchen He¹, Jacopo Dal Corso^{1,2}, Robert J. Newton¹, Paul B. Wignall¹, Benjamin J. W. Mills¹, Simona Todaro³, Pietro Di Stefano³, Emily C. Turner¹, Robert A. Jamieson¹, Vincenzo Randazzo³, Manuel Rigo⁴, Rosemary E. Jones⁵, Alexander M. Dunhill¹

¹School of Earth and Environment, University of Leeds, Leeds, UK. ²State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, China, ³Department of Earth and Marine Sciences, University of Palermo, Italy. ⁴Department of Geosciences, University of Padova, Italy, ⁵Department of Earth Sciences, University of Oxford, UK.

The relationship between oceanic oxygen deficiency and end-Triassic mass extinction (~201.5 Myr ago) is widely debated. A convincing link between contemporaneous development of marine anoxia/euxinia and the end-Rhaetian biotic crisis has hitherto been lacking. The exact timing, extent and marine ecosystem response of the proposed oceanic anoxic event (OAE) in the latest Triassic remain uncertain. Here we present carbonate-associated sulfate S-isotope data from three sections from both Tethyan and Panthalassan locations spanning the Late Triassic–Early Jurassic transition, which document synchronous large positive S-isotope excursions on a global scale. Our age model suggests that these excursions occurred in as little as ~50 Kyr. Biogeochemical modelling demonstrates that S-isotope perturbation can be explained by a five-time increase in pyrite burial driven by large-scale marine anoxia. Significantly, this anoxic event was exactly synchronous with the main phase of the end-Triassic mass extinction. Thus, the new data identify a short-lived but widespread OAE in the late Rhaetian that may be responsible for the collapse of the global late Triassic marine ecosystem. Modelling also indicates that the pre-event ocean sulfate concentration was low (<1 mM), underscoring this as a common feature of many Phanerozoic deoxygenation events. We suggest this preconditioned the oceans for deoxygenation via an increased net benthic methane flux.

BIOTURBATION AND THE PHANEROZOIC SULFUR CYCLE: A MODEL APPROACH

Gilad Antler^{1,2}, Sydney Riemer¹, Alexandra V. Turchyn³

¹Department of Earth and Environmental Sciences, BenGurion University of the Negev, Israel, ²The Interuniversity Institute for Marine Sciences in Eilat, Israel, ³Department of Earth Sciences, Cambridge University, Cambridge, UK

Bioturbation is the range of processes that occur when organisms burrow through sediments, flushing their burrows with overlying seawater and mixing sediment particles. It is an ecological innovation that evolved during the late Neoproterozoic and became subsequently more prevalent throughout the Phanerozoic. Bioturbation increases mixing across the sediment-water interface, influencing the redox state of the sediment and the cycling of redox-sensitive elements such as sulfur. Throughout Earth history, the fractionation between the sulfur isotopes of sulfate and sulfide has increased intermittently; the second significant increase occurred during the Precambrian-Cambrian transition. The impact of bioturbation on the sulfur isotope record during this second interval of change has been documented by previous studies, but there has been little consensus on what the exact mechanism for the change in the sulfur isotope record is at this time.

Using a simple two-box model, we modelled the concentrations and stable isotope compositions of sulfate and sulfide in bioturbated and non-bioturbated sediment, and the overlying water column. We used results from bioturbation experiments to guide our model results and obtain values for the fluxes of components into and out of the sediment, the sulfate reduction rate, and the sulfur isotope fractionation. We found that, rather than increasing the sulfate concentration of the overlying water due to enhanced sulfate recycling, bioturbation draws down sulfate from the water column and into the sediment, where it is then reduced. Additionally, we found that the fractionation between sulfate and sulfide is greater in the bioturbated sediment. These results support the conclusion that the evolution of bioturbation at the beginning of the Phanerozoic didn't necessarily change the sulfur cycle through the reoxidation of sulfide and subsequent recycling of sulfate back to the ocean, but rather opened up the system to allow for a continuous supply of sulfate to the sediment.

EVOLUTION OF THE SULFUR ISOTOPIC COMPOSITION OF PYRITE OVER THE CENOZOIC

Charlotte Spruzen and Alexandra V. Turchyn

The University of Cambridge, UK

The isotopic composition of sulfur can be used to understand the biogeochemical sulfur cycle, and therefore the redox state of the oceans, over geological time. The primary sinks of sulfur in the biogeochemical sulfur cycle are pyrite (FeS_2) and evaporite (mostly gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) minerals with some estimates suggesting pyrite is responsible for between 70-90% of total removal of sulfur from the surface. Over the last 150 million years there have been large changes in the sulfur isotopic composition of the ocean, which have been attributed to changes in the amount of pyrite buried, changes in the amount of evaporite minerals deposited or weathered, and changes in the volcanic input. Pyrite is formed from the hydrogen sulfide produced during microbial sulfate reduction, which has a large sulfur isotope fractionation (between 3 and 73‰). However, the sulfur isotopic composition of pyrite is often assumed to be constant in box models of the global biogeochemical sulfur cycle, or constantly offset from seawater. This paradigm has been recently challenged. For example, recent studies have shown that depositional environment is a major factor in the efficiency of pyrite burial, and therefore the sulfur isotopic composition of the reduced sulfur preserved in the geological record. This is due in part to the variable availability of highly reactive iron to promote efficient pyrite formation and burial. It has been suggested that tectonically-driven changes in the depositional environments where pyrite could be buried may influence the sulfur isotopic composition of pyrite, and thus the sulfur isotopic composition of global marine sulfate. We are examining the relationship between isotopic pyrite composition and environment of deposition throughout the Cenozoic, by recording the location and depth of deposition of published sulfur isotope data to see if there is a statistically significant relationship between them. We will present the initial work and data from this compilation.

LITHOSPHERIC-SCALE TRANSFER OF SULFUR THROUGH EARTH'S EARLIEST WILSON CYCLE

Crystal LaFlamme^{1,2}, Marco Fiorentini²

¹Département de géologie et génie géologique, centre E4M, Université Laval, Québec, Canada, ²Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia, Western Australia, Australia

Fundamentally, life on Earth comprises 6 major elements, namely H, C, N, O, S and P. Fluxes in these elemental cycles are dependent on microbially catalyzed, energy converting, redox reactions, and are maintained on Earth by movement of substrates and products through the atmosphere and hydrosphere. Oxygen is highly reactive and without a continuous source by way of photosynthesis would become depleted in our atmosphere. However, a long-term net accumulation of oxygen production in turn requires a net sink for reductants such as H, C, Fe, S. The complete removal of reductants (other than hydrogen) depends on their lithospheric-scale transfer under a Global Plate Tectonics regime. Here, we investigate the transfer of reductants through one of the Earth's earliest identifiable Wilson Cycles that followed the greatest geobiological event in Earth history: The Great Oxidation Event. At this time, surficial reduced sulfur was at an all-time high. Using multiple sulfur isotopes, sulfur is tracked from surficial sediments to the mantle and back to the stable crust over a period of 300 million years during the formation of the Paleoproterozoic supercontinent Nuna. This is the earliest evidence of lithospheric-scale transport of sulfur, indicating that Global Plate Tectonics played a role in stabilization of oxygen contents in the atmosphere.

IMPACT OF SEQUENCE STRATIGRAPHY AND DEPOSITIONAL FACIES ON MARINE SEDIMENTARY PYRITE SULFUR ISOTOPES: INSIGHTS FROM BULK AND MICRO-SCALE SIMS ANALYSES

David A. Fike¹, Jennifer Houghton¹, Clive Jones¹, Roger Bryant^{1,2}, Daniele Scarponi³, Virgil Pasquier⁴, & Itay Halevy⁴

¹Earth and Planetary Sciences, Washington University in St. Louis, USA; ²Department of the Geophysical Sciences, University of Chicago, USA. ³Dipartimento di Scienze Biologiche Geologiche e Ambientali, University of Bologna, Italy. ⁴Earth and Planetary Sciences, Weizmann Institute of Sciences, Israel.

Variations in the isotopic composition of sulfur in sedimentary pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) are often used to reconstruct global sulfur biogeochemical cycling and Earth's surface oxidation state over Earth history. Recent work, however, has shown that $\delta^{34}\text{S}_{\text{pyr}}$ is strongly impacted by local depositional conditions, which both confounds attempts to reconstruct global sulfur cycling and provides a new proxy for investigating local paleoenvironmental conditions. Here we present chemostratigraphic records of bulk sedimentary $\delta^{34}\text{S}_{\text{pyr}}$ in a detailed sedimentological and sequence stratigraphic framework from a range of Pleistocene to modern sediments in diverse depositional environments, with a focus on the Early-Mid Pleistocene transition from Valle di Manche, Calabria, Italy. Bulk $\delta^{34}\text{S}_{\text{pyr}}$ data is influenced by sequence stratigraphic tracts and transgressive-regressive cycles, where $\delta^{34}\text{S}_{\text{pyr}}$ values decrease toward -50‰ as accommodation space increases and become more positive and variable during deposition in shallower environments. In addition to bulk sedimentary $\delta^{34}\text{S}_{\text{pyr}}$ data, we collected micron-scale $\delta^{34}\text{S}_{\text{pyr}}$ data via secondary ion mass spectrometry (SIMS) from populations of these pyrites that together give rise to the bulk $\delta^{34}\text{S}_{\text{pyr}}$ values. These SIMS results identify discrete populations of pyrites with distinctive isotopic signatures within these sediment samples. The relative abundance of these different populations is controlled by depositional environment and corresponding syndepositional processes that regulate continued pyrite formation within the porewaters. In turn, it is the relative abundance of these different populations that determines the resulting bulk $\delta^{34}\text{S}_{\text{pyr}}$ value within the sediments. These results demonstrate the value of combined bulk and microscale analysis in investigating $\delta^{34}\text{S}_{\text{pyr}}$ records and highlight the role of local conditions in controlling sedimentary $\delta^{34}\text{S}_{\text{pyr}}$ records. Moreover, this work also illustrates how these isotopic data can be used to reconstruct key parameters of the sedimentary environment that might not be otherwise accessible, especially in deep-time strata.

KEYNOTE: SULFUR CYCLE CONTROLS ON EARTH'S HABITABILITY

Benjamin Mills

School of Earth and Environment University of Leeds, UK.

When considering the habitability of the Earth, two key criteria are the temperature of the planet's surface and the availability of oxygen in its atmosphere and oceans. These are commonly both linked to the global carbon cycle, which controls the amount of CO₂ in the atmosphere and the resulting greenhouse effect, and which also involves the major oxygen-producing reaction photosynthesis. Thus, many attempts at reconstructing Earth's redox and temperature histories from first principles utilize only the cycle of carbon. In this talk I will summarize several new ideas that put the sulfur cycle at the centre of major events in Earth's past. In summary, changes in the sulfur cycle can lead to substantial changes in climate, atmospheric oxygen and marine redox, and the sulfur cycle may have been instrumental in driving Earth's Great Oxidation Event. However, despite its important role, it remains difficult to model the sulfur cycle in deep time.

Poster Session

MODELLING THE BEHAVIOUR OF SULFUR IN MAGMATIC SYSTEMS FROM SOURCE TO SURFACE

Ery Hughes (Joseph Biasi)

Joseph Biasi¹, Isabel Fendley², Ery Hughes¹, Kristen Rahilly^{3,4}, Tyler Schlieder⁵, Heather Winslow⁶, Tobias Fischer³, and Paul Wallace⁷

¹California Institute of Technology, ²University of California, Berkeley, ³University of New Mexico, ⁴Columbia University, ⁵University of California, Davis, ⁶University of Nevada, Reno, ⁷University of Oregon

Identifying changes in the sulfur flux at volcanoes is commonly used as an indicator of magmatic input and can indicate increased likelihood of eruption. However, the behavior of sulfur within magmatic systems from source (parent magma) to surface (outgassing) is poorly understood, particularly with respect to the role of hydrothermal scrubbing in modulating the eventual output of sulfur at the surface. Here we attempt to constrain sulfur inputs and outputs, the extent of hydrothermal scrubbing for volcanoes with either minimal or highly active hydrothermal systems, and the scrubbing effects of shallow water through the presence of a crater lake. Our objectives are to (1) evaluate whether sulfur flux at the surface can be broadly balanced by sulfur flux derived from the parent magma into the system, and (2) constrain how the presence of a hydrothermal system affects sulfur flux at the surface.

We use two volcanoes with available literature data as case studies to constrain the evolution of sulfur: (1) Whakāri/White Island, Aotearoa New Zealand, which contains an active hydrothermal system and a crater lake; and (2) Mt. Etna, Italy, which has an active hydrothermal system but contains no crater lake. Magmatic sulfur inputs were determined via a combination of whole-rock/melt-inclusion data and MELTS modeling. The effects of degassing were modelled using D-Compress and SolEx. We used CHIM-XPT and EQ3/6 geochemical models to constrain the effects of scrubbing by titrating magmatic gases (using high temperature fumarole compositions) through hydrothermal systems of varying sizes, temperatures, and water chemistries. Sulfur outputs were compared to high and low temperature fumarole and plume measurements.

We find that long-term inputs of sulfur into these volcanic systems are broadly balanced by sulfur outputs over geologic timescales. A compilation of C/S ratios from volcanoes with high-temperature emissions shows generally higher values when a hydrothermal system is present, potentially due to sulfur scrubbing. The extent of scrubbing is dependent on size and chemistry of the hydrothermal system and can significantly affect sulfur outputs over shorter timescales. We put our results into a wider context using a global compilation of volcanic sulfur isotope data.

SULFUR AND CARBON IN DEEP EARTH: NEW INSIGHTS FROM OROGENIC GARNET-BEARING PERIDOTITE (EASTERN ALPS, ITALY)

Giulia Consuma, Sonja Aulbach^{b,c}, Roberto Braga^a, Laure A.J. Martin^d, Peter Tropper^e, and Marco L. Fiorentini^f

^a Department of Biological, Geological and Environmental Sciences, University of Bologna, Italy.

^b Institute for Geosciences, Goethe University, Germany.

^c Frankfurt Isotope and Element Research Center (FIERCE), Goethe-Universität Germany.

^d Centre for Microscopy, Characterisation and Analysis (CMCA), Australian Research Council Centre of Excellence for Core to Crust Fluid Systems (CCFS), The University of Western Australia, Western Australia,

^e Institute of Mineralogy and Petrology, University of Innsbruck, Innsbruck

^f Centre for Exploration Targeting, ARC Centre of Excellence for Core to Crust Fluid Systems, The University of Western Australia, Australia.

Sulfur is a minor component in the upper mantle, yet it exerts key control over ore-forming processes and possibly mantle redox conditions. Convergent settings are loci of significant crust-to-mantle mass transfer. Despite major recent advances in constraining sulfur mobility throughout the mantle-crust interface, the evidence from natural samples and thermodynamic models regarding the speciation and behavior of sulfur in various slab components remains conflicting and is currently a hotly debated topic.

Here we present a detailed multi-method investigation of the poorly known sulfur speciation and isotopic composition of orogenic mantle as an integral component of the global sulfur cycle, with the aim to foster understanding on the origin, nature and evolution of C-O-H-S-bearing liquids during their interaction with the mantle wedge under high-pressure eclogite-facies and retrograde conditions. We obtained bulk rock, *in situ* trace elements and sulfur isotope data for sulfides coexisting with multiple generations of carbonate and hydrous minerals, in a suite of well-characterized orogenic garnet-bearing peridotites from a tectonic mélange in the Variscan Ulten Zone (Eastern Alps, Italy). Sulfides are dominantly pentlandite, frequently intimately associated with carbonates, and sulfate is not observed.

Estimates of partial melt extracted (~15-25%) indicate that little sulfur remained in the lithospheric mantle after its initial stabilization, depending on concentration in the source and redox conditions. Thus, peridotite sulfur contents of 40-290 ppm indicate at least partial re-addition throughout the peridotite metamorphic evolution. Despite the relatively restricted sulfur isotope composition of sulfide in peridotites ($\delta^{34}\text{S} = -1.62 \pm 0.42\text{‰}$ to $+3.76 \pm 0.36\text{‰}$ versus Vienna Canyon Diablo Troilite), detailed petrographic information and *in situ* data indicate multi-stage sulfur mobility. Formation by reduction of sulfate may have occurred during early, high-temperature metasomatism by continental crust-derived melt, followed by limited interaction with isotopically heavy crustal fluids under eclogite-facies conditions. Conversely, the final ascent of the mélange into shallow structural levels involved interaction at high fluid:rock ratios and moderate serpentinization, which removed light sulfur and CO₂ from peridotites, indicated by the formation of heazlewoodite at the expense of pentlandite, and brucite-calcite intergrowths at the expense of dolomite.

THE FATE OF SUBDUCTED SULFUR: INSIGHTS FROM PHASE EQUILIBRIUM MODELING AND PETROGRAPHIC OBSERVATIONS

Jesse B. Walters^{1,2}, Horst R. Marschall¹, Alicia M. Cruz-Uribe²

¹Institut für Geowissenschaften, Goethe Universität, Altenhöferallee 1, Frankfurt am Main, DE 60438

²School of Earth and Climate Science, University of Maine, 5790 Bryand Global Sciences Center, Orono, ME 04469

With an 8e⁻ range in oxidation states (S²⁻ to S⁶⁺), sulfur is a potent agent of redox reactions and its exchange between the surface and interior during subduction likely influences the redox characteristics of the deep Earth. Sulfur, largely as sulfide, is a ubiquitous element in the oceanic lithosphere. Prior to subduction, the oceanic lithosphere is altered and oxidized at the seafloor. Previous studies have identified elevated Fe³⁺/SFe and *f*O₂ of arc magmas and subarc mantle xenoliths and suggested that oxidized components may be transferred in slab fluids or melts to the arc. Sulfur is the prime candidate to represent that oxidized component.

Here we conducted phase equilibrium models of sulfur loss using *Perple_X*. Our models show a progressive oxidation of sulfur from S¹⁻ in pyrite or S²⁻ in pyrrhotite, to S⁶⁺ in anhydrite and aqueous SO_x species. Sulfur oxidation is coupled to iron reduction, driving a nearly 50 % decrease in Fe³⁺/SFe in the dehydrating rock. Observations of natural rocks show that sulfides, which are present as inclusions of pyrite, pyrrhotite, and chalcopyrite in garnet and omphacite, are largely absent from the peak metamorphic assemblage of most eclogites. Additionally, eclogites exhibit lower bulk rock Fe³⁺/SFe relative to the altered oceanic crust. These natural observations are consistent with our model predictions. Sulfate-bearing fluids are anticipated to flux the mantle wedge and are capable of raising the *f*O₂ of mantle peridotite up to 2 log units above the quartz-fayalite-magnetite buffer, consistent with the observed *f*O₂ of subarc mantle xenoliths.

SULFUR CYCLE CONTROLS ON EARTH'S HABITABILITY

Zoltán Taracsák^{1,2}, Margaret E. Hartley¹, Ray Burgess¹, Marie Edmonds³, Marc-Antoine Longpré⁴, Romain Tartèse¹, Alexandra V. Turchyn³

¹University of Manchester, ²University of Oxford, ³University of Cambridge, ⁴Queens College, City University of New York, USA.

El Hierro, located in the western Canary Islands, is known to erupt extremely carbon- and sulfur-rich magmas. The sulfur contents of undegassed El Hierro magmas is typically >4000 ppm, akin to those erupting at volcanic arcs. However, the origin of this volatile enrichment is ambiguous. The high sulfur contents of El Hierro magmas may be the result of: low (~5%) degree partial melting of a mantle with bulk silicate Earth (BSE) composition accompanied by total mantle sulfide exhaustion, or the melting of a mantle source which contains excess sulfur added from a previously subducted and then recycled oceanic lithosphere. To better constrain processes governing volatile enrichment at El Hierro we analysed sulfur isotope ratios in extremely sulfur-rich melt inclusions from El Hierro. Our results suggest that El Hierro primary melts contain ~5000 ppm sulfur and that they are enriched in heavy ³⁴S compared to the upper mantle ($\delta^{34}\text{S} = -1.3\text{‰}$), with $\delta^{34}\text{S}$ value of $+4 \pm 0.75\text{‰}$. The primary melt S/Dy ratio is estimated at 870 ± 194 , which lies above the value estimated for BSE (280-460). Assuming S and Dy behave similarly during mantle melting, a mantle source S content of 690 ± 170 ppm can be inferred for El Hierro, which is 2.5-3 times higher than the S content of the BSE (200-250 ppm). Modelling suggests that metasomatism by a sulfur-rich fluid phase originating from a recycled oceanic lithosphere can explain both the mantle S content we infer and the positive $\delta^{34}\text{S}$ values observed in El Hierro melt inclusions. The sulfur budget of the recycled lithosphere is dominated by hydrothermally-formed sulfur bearing phases. Heavy sulfur enrichment of the mantle source implies ³⁴S-rich sulfate, as opposed to sulfide, may have been present in the recycled component. The fingerprint of recycled sulfate in the El Hierro mantle source suggests that oxidising, volatile-rich nature of magmas erupting at various ocean islands (Canary Islands, Cape Verde) derive from the addition of recycled volatiles into the asthenospheric mantle. If sulfate can survive dissolution during slab subduction it may provide a pathway for oxidised surface sulfur to be transferred into the mantle, resulting in widespread redox heterogeneity in the deeper mantle.

CHARACTERISATION OF SULPHIDE INCLUSIONS IN DIAMONDS USING SYNCHROTRON X-RAY MICROFLUORESCENCE (S-XRF)

Lotta I.M. Kemppinen¹, Marion Louvel², Simon C. Kohn¹

¹, School of Earth Sciences, University of Bristol, UK, Institute for Mineralogy, WWU Münster, Germany

Sulphide inclusions are common features of natural diamonds, offering unique insights into the global sulphur cycle. As well as controlling the behaviour of chalcophile and siderophile elements in diamond-forming regions of the Earth's mantle, sulphides can be used in Re-Os radiometric dating of their host diamonds, providing valuable information about continental growth and volatile recycling processes through time (1). The compositions of sulphides captured in diamonds can be used to establish their origin, explore the reasons for their apparent overabundance in diamond growth environments and determine whether the diamonds grew in an eclogite- or peridotite-dominated mantle substrate (e.g. 2).

Sulphides typically exist as immiscible Fe-Ni-Cu monosulphide solid solution or melts in diamond-forming regions of the upper mantle (e.g. 2, 3). Upon their uptake in diamond and upon their ascent to the surface via kimberlite eruption, sulphides undergo sub-solidus exsolution into a heterogeneous assemblage of pyrrhotite, pentlandite and chalcopyrite. A characteristic set of rosette fractures will develop around the inclusions, and sulphide material is commonly injected into these (4). The difficulties of studying sulphide inclusions in diamonds arise from their small size (~120 µm) and their internal complexity. Traditional techniques involving scanning electron microscopy and electron microprobe analyses required for chemical characterisation of the inclusions prior to Re-Os dating inevitably pose the risk of losing material from the inclusions such as peripheral molybdenite (5) during the extraction of the inclusions from the diamonds.

We have performed synchrotron-based x-ray microfluorescence (s-XRF) analyses at the I18 beamline of Diamond Light Source (UK) to investigate the major (Fe, Ni, Cu) and minor (Cr, Zn, Mo ± Pt, As, Se, Pb...) element compositions of unexposed sulphide inclusions in diamonds. We specifically explore the capabilities of the technique for non-destructively acquiring information about the internal chemical heterogeneity and bulk compositions of the inclusions. Our results show that s-XRF provides a relatively fast and efficient means for determining the paragenesis of sulphide inclusions in diamonds based on their Ni and Cr contents, identifying Mo-enrichment in the inclusions, as well as allowing rapid 2D mapping of sulphide exsolution features.

EFFECT OF SEA ICE DECLINE ON ARCTIC SULFATE AEROSOLS BASED ON ICE CORE OBSERVATIONS AND MODEL SIMULATIONS

Ursula Jongbloed¹, Becky Alexander¹, Andrew Schauer¹, Sara Salimi¹, Jihong Cole-Dai², Carleigh Larrick², Joshua Kennedy², Edward Blanchard-Wrigglesworth¹,

¹University of Washington, ²South Dakota State University

The Arctic has warmed at a rate of twice the global average in recent decades, causing profound changes in the region. About 20% of recent Arctic warming is estimated to have been caused by decreasing aerosol abundance in the Arctic due to decreasing anthropogenic pollution resulting from clean air policies from North America and Europe. While anthropogenic emissions of aerosols have decreased, it is unclear how declining sea-ice extent will affect biogenic aerosols, which contribute to particle formation events in the atmosphere and thus influence Arctic climate. The prevailing hypothesis is that the change in composition and quantity of Arctic primary production under rapidly declining sea-ice extent will result in an increase in biogenic aerosols, which is supported by several Arctic ice cores. However, the decline of sea-ice extent will also reduce several key habitats for DMS-producing biota, such as bottom-ice algae, and could result in a decrease in DMS emissions. This hypothesis is supported by a negative correlation between MSA and SST in three other Arctic ice cores. Here we use measured concentrations of non-sea salt sulfate (nssSO_4^{2-}) and $\delta^{34}\text{S}(\text{nssSO}_4^{2-})$ in an ice core from Summit, Greenland to separate biogenic sulfate from other sources of sulfate aerosols in the Arctic. We compare ice core observations to GEOS-Chem simulations of the sensitivity of sulfate decrease in the Arctic to various drivers, including meteorology, anthropogenic emissions, and climate. Through the comparison of model results, ice core observations, and emissions data, we aim to understand the response of biogenic sulfate emissions to sea ice decline to improve understanding of how the retreat of sea ice will influence the Arctic atmosphere. Due to the influence of aerosols on radiative forcing and as cloud condensation nuclei (CCN), the answer to these questions hold implications for the future of Arctic amplification and global climate.

MODELLING THE EFFECTS OF NON-STEADY STATE TRANSPORT DYNAMICS ON THE SULFUR AND OXYGEN ISOTOPE COMPOSITION OF SULFATE IN SEDIMENTARY PORE FLUIDS

Angus Fotherby^{1*}, Harold J. Bradbury¹, Gilad Antler², Xiaole Sun³, Jennifer L. Druhan⁴, Alexandra V. Turchyn¹

1 Department of Earth Sciences, University of Cambridge, UK, 2 Department of Geological and Environmental Sciences, Ben Gurion University of the Negev, Beersheba, Israel. 3 Baltic Sea Center, Stockholm University, Sweden. 4Department of Geology, University of Illinois, USA

We present the results of an isotope-enabled reactive transport model of a sediment column undergoing active microbial sulfate reduction to explore the response of the sulfur and oxygen isotopic composition of sulfate under perturbations to steady state. In particular, we test how perturbations to steady state influence the cross plot of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for sulfate. The slope of the apparent linear phase (SALP) in the cross plot of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for sulfate has been used to infer the mechanism, or metabolic rate, of microbial metabolism, making it important that we understand how transient changes might influence this slope. Tested perturbations include changes in boundary conditions and changes in the rate of microbial sulfate reduction in the sediment. Our results suggest that perturbations to steady state influence the pore fluid concentration of sulfate and the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate but have a minimal effect on SALP. Furthermore, we demonstrate that a constant advective flux in the sediment column has no measurable effect on SALP. We conclude that changes in the SALP after a perturbation are not analytically resolvable after the first 5% of the total equilibration time. This suggests that in sedimentary environments the SALP can be interpreted in terms of microbial metabolism and not in terms of environmental parameters.

DOES MICROBIAL SULFATE REDUCTION DRIVE CARBONATE PRECIPITATION IN THE SEDIMENTARY BOUNDARY LAYER?

Daniel H. James¹, Harold J. Bradbury¹, Gilad Antler^{2,3}, Zvi Steiner^{4,1}, Alec M. Hutchings¹, Xiaole Sun⁵, Raoul Saar³, Mervyn Greaves¹, Alexandra V. Turchyn¹

1 Department of Earth Sciences, University of Cambridge, UK.. 2 Department of Earth and Environmental Sciences, Ben-Gurion University of the Negev, Israel. 3 The Interuniversity Institute for Marine Sciences in Eilat, Israel. 4 GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany. 5 Baltic Sea Center, Stockholm University, Sweden

We present pore fluid geochemistry, including major ion and trace metal concentrations and the isotopic composition of pore fluid calcium and sulfate, from the uppermost meter of sediments from the Gulf of Aqaba (northeast Red Sea) and the Iberian Margin (North Atlantic Ocean). In both locations, we observe strong correlations between sulfate, calcium, magnesium, and strontium concentrations as well as alkalinity and the sulfur isotopic composition of sulfate, suggestive of active changes in redox state - most likely related to microbial sulfate reduction - that should lead to carbonate mineral precipitation and dissolution. The calcium isotope composition of pore fluid calcium ($d^{44}\text{Ca}$), which is a very sensitive tracer to carbonate mineral precipitation and dissolution, is invariant in our measured profiles. We suggest that, despite active alkalinity generation via microbial sulfate reduction, a confluence of factors either inhibit calcium carbonate mineral precipitation or its influence on pore fluid calcium isotope composition; including mixing between the surface and deeper precipitation, and interaction with active iron and manganese cycling. Our results suggest that active metabolically induced changes in calcium carbonate saturation state and associated carbonate dissolution and precipitation may not be as easily recorded by changes in pore fluid $d^{44}\text{Ca}$ as previously thought, particularly in the boundary layer of the sediment column.

GEOCHEMICAL CONDITIONS FAVORING THE FORMATION OF ELEMENTAL SULFUR NODULES IN LAKE PETEN ITZA, GUATEMALA

Eloise Matthews*, Charlotte Spruzen*, Verity A.S. Bennett, Adrian Gilli, David A. Hodell, Alexandra V. Turchyn

Department of Earth Sciences, University of Cambridge, UK.

The presence of elemental sulfur nodules in sediment cores extracted from Lake Peten Itza in Guatemala has been a subject of interest since their discovery in 2006. Elemental sulfur is rare to find in large quantities in the natural environment and its formation in nodules in sediments remains enigmatic. There are two dominant hypotheses for the formation of elemental sulfur: one that it forms from the incomplete oxidation of hydrogen sulfide, and two that it forms from the incomplete reduction of sulfate. One issue is that there are few modern environments where elemental sulfur nodules are currently forming, and therefore there are few places where its formation can be placed in a diagenetic context. Here we present pore fluid concentrations as well as sulfur and oxygen isotope data to explore the conditions that favor the formation of sulfur nodules in Lake Peten Itza, which are commonly found at the lithological transitions between gypsum sand and clay. We combine this with the sulfur isotopic composition of the various nodules extracted from the sediment. The sulfur isotopic composition of the nodules ranges from -10 to +5‰, and up to 10‰ in a single nodule. This is compared with the sulfur isotopic composition of gypsum in the sediment that is +19‰ and pore fluid sulfate that is +50‰, strongly suggesting active microbial sulfate reduction in these sediments. This is supported by correlation matrices produced from the pore fluid data, heatmaps demonstrate that some pore fluid elements, such as sodium and chlorine, have profiles that result from diffusion after the last glacial maximum, while others, such as sulfate and magnesium, are influenced by in situ dissolution and precipitation. A reactive-transport model is used to show that the salinity of the glacial lake is not able to explain the pore fluid sulfate data, which suggests an active cycle of gypsum dissolution, microbial sulfate reduction, and elemental sulfur formation. Our results largely lend support to the first hypothesis for the formation, although a combination of both the incomplete oxidation of hydrogen sulfide and also the incomplete reduction of sulfate is likely the case. We particularly suggest that gypsum diagenesis in an organic carbon poor environment leads to the oversaturation necessary to explain the presence of elemental sulfur.

EUTROPHICATION LEADS TO FORMATION OF SULFIDE-RICH DEEP WATER LAYER IN LAKE SEVAN (ARMENIA)

Avetisyan K.^a, Mirzoyan N.^b, Payne R.^c, Hayrapetyan V.^{b,d} and Kamyshny, Jr. A.^a

^a Department of Earth and Environmental Sciences, Faculty of Natural Sciences, Ben-Gurion University of the Negev, Israel ^b Acopian Center for the Environment, American University of Armenia, Republic of Armenia. ^c Institute of Marine & Environmental Technology, Center for Environmental Science, University of Maryland, USA ^d Center for Responsible Mining, American University of Armenia,, Republic of Armenia

Lake Sevan is the largest freshwater body of Caucasus area, which is of immense cultural, historical, ecological, and industrial importance for Armenia. It is a meso-eutrophic water body, which was severely impacted by anthropogenic level decrease, pollution and eutrophication during the last century. Starting in 1970s, these processes, resulted in formation of oxygen-depleted hypolimnion during summer-autumn stratification of the lake.

In this work, we demonstrate that eutrophication of the lake leads not only to the full oxygen depletion in the hypolimnion, but to the presence of toxic hydrogen sulfide as well as sulfate reducing microorganisms. For the first time hydrogen sulfide was quantified in the water column of both parts of the lake. The thickness of hydrogen sulfide-rich layer was found to be 6 m and 17 m in the Major and Minor Sevan, respectively. We attribute formation of sulfidic deep-water layer to a combination of microbial sulfate reduction in the water column and diffusion of hydrogen sulfide from the sediments. Concentrations of hydrogen sulfide in the hypolimnion of Major and Minor Sevan in October were up to 9 μM and 39 μM , respectively. In October 2019, 66% of lake's bottom is covered by sulfidic waters, while fraction of sulfidic water volume reaches 19%. Diffusion of hydrogen sulfide from the sediment is based on small absolute difference between $\delta^{34}\text{S}$ values of hypolimnetic sulfide and epilimnetic sulfate. Sulfate isotopic composition is homogenous in epilimnion and variability in its $\delta^{34}\text{S}$ values in the hypolimnion is 2.6‰. Variability in $\delta^{34}\text{S}$ values of hydrogen sulfide is about 1.5‰ in each of the basins. Sulfide is isotopically lighter than sulfate with ϵ in the ranges of -7‰ to -9‰ and -11‰ to -12‰ in the Major and Minor Sevan. We suggest, that mixing of relatively isotopically heavy hydrogen sulfide, which diffuses from the sediments with hydrogen sulfide produced in the hypolimnion, results in observed isotopic composition.

**CHARACTERIZING THE SULFUR BUDGET WITHIN LAKE SUPERIOR:
SIGNIFICANT ROLE OF ORGANIC SULFUR IN OLIGOTROPHIC SETTINGS**

Madelyn Petersen, Janna Quick, Kathryn Schreiner, Emily Hyde, Cody Sheik, Sergei Katsev

University of Minnesota-Duluth, USA

Microbially mediated sulfate reduction is important in lake sediment due to its impact on numerous other biogeochemical cycles, including phosphorus, iron, and mercury, and its contribution to carbon remineralization in lake settings. Recently, modelling studies in oligotrophic lake settings have demonstrated that organic sulfur is a significant portion of the total sulfur pool, capable of sustaining cryptic sulfur cycling within the sediment. Organic sulfur consists of freshly deposited biogenic sulfur-containing molecules, their degradation products, and abiotic “sulfurized” non-labile organic matter, which may play a significant role in organic matter preservation. Few, if any, studies have quantified these organic forms of sulfur to the total sulfur cycle in oligotrophic lake settings, indicating that characterization of the total sulfur budget in a low-nutrient lacustrine system is warranted. Here, organic and inorganic species of sulfur are characterized in Lake Superior sediment from four offshore locations. Inorganic contributions to the sulfur pool consist of sulfate in porewater, and sulfides, elemental sulfur, and pyrite in the sediments. Organic contributions are determined by difference from total sulfur by mass. Contributions from organic and inorganic sources of sulfur are evaluated from the surface of the sediment at 1-cm depths to 12 cm, then again at 15, 20, and 25 cm. Results show that in low-deposition settings, organic sulfur comprises up to 90% of total sulfur in Lake Superior sediment, indicating the necessity of further exploration of the contribution of organic sulfur to carbon sequestration in oligotrophic lacustrine settings.

SEAWATER CONTAMINATION IN ODP/IODP POREWATER SAMPLES AND ITS QUANTITATIVE EFFECTS ON STUDIES OF MICROBIAL SULFATE REDUCTION

Man-Yin Tsang, Ulrich G. Wortmann

University of Toronto, Canada.

It is a standard procedure on expeditions of the International Ocean Discovery Program (IODP) to measure concentrations of common ions in the interstitial water of core samples. These measurements allow scientists to discern microbial activities, water-rock interactions, and diagenetic processes. However, porewater samples are easily contaminated by seawater, which is used as the drilling fluid. Since seawater contains around 28 mM of sulfate, it is often used as a contamination tracer. However, once sulfate occurs naturally in porewater, it is challenging to identify seawater contamination. Porewater data from ODP/IODP sites, which have been sampled repeatedly, reveal differences often up to about 5 mM sulfate. This is equivalent to seawater contamination of up to 30% (by volume) and significantly larger than the uncertainty from shipboard analytical procedures.

The presence of seawater sulfate in porewater samples is of particular concern for studies investigating microbial sulfate reduction. We use a reaction-transport model to explore how seawater contamination affects the interpretation of sulfate reduction rates and sulfur isotope fractionation. We show that seawater contamination results in underestimating sulfate reduction rates, but the derived rates are still in the correct orders of magnitude. We further show that a 5% (by volume) seawater contamination will reduce the derived sulfur isotope fractionation factor by about 10‰. However, as we have no a-priory knowledge of whether a sample is contaminated, we also have to consider the case that we assume contamination where there is none. If we falsely assume a 5% contamination, we will slightly overestimate the sulfate reduction rates but significantly overestimate the fractionation by almost 20‰.

IMPLICATIONS OF SULFUR MINERALOGY AND CONSEQUENCES OF PYRITE OXIDATION FOR GROUND ENGINEERING

Mourice A. Czerewko¹, John C. Cripps², J Murray Reid³, Ian Longworth⁴

1 AECOM, UK, 2 Department of Civil and Structural Engineering UK, 3 University of Sheffield, UK, 4 Formerly with TRL, Crowthorne, 4 Formerly with the Building Research Establishment, UK.

Aggressive ground conditions and physical deterioration of ground and engineering material are attributed to a wide range of factors although a high proportion of occurrences in the engineering environment may be attributed by the presence of sulfur minerals, particularly pyrite.

Pyrite is stable under the anoxic reducing conditions in which it forms in geological strata, but when exposed to weathering, oxidising and damp atmospheric conditions can cause break down, in some cases rapidly, giving rise to sulfate rich and acidic chemical conditions. These conditions are aggressive to construction materials and can result in foundation heave, as well as being detrimental to the biological environment.

The rate and products of pyrite oxidation depend on its crystalline form and dimension as well as the host mineralogy and rock fabric, framboidal pyrite in sedimentary rocks being the most susceptible. These factors are coupled with the change in environment brought about during engineering works.

Hence, consideration is needed both of the pre-construction characteristics of the ground and of changes that can take place during and subsequent to construction, especially those caused by engineering disturbance and exposure of the pyrite host material. In some cases, historic groundwater conditions and biological processes have affected the distribution and speciation of sulfur within natural ground sequences and characteristic weathering profiles can be recognised.

Damage to buried concrete and metal structures caused by the oxidation of pyrite in structural backfill and the surrounding natural ground affected a number of British highway schemes during the late 1990's. Accordingly, new test methods, guidance and appraisal strategies were developed for assessing and managing pyrite-related potentially aggressive ground conditions. However, in spite of this and previous guidance for avoiding problems, it is apparent that many practitioners do not appreciate the origin of the sulfur species or their implications leaving much scope for confusion and significant risk that inappropriate materials and/or construction practices will be used.

The aim of this presentation is to review the implications of sulfur minerals associated with pyrite in geomaterials, with emphasis on the effects brought about during the construction processes affecting the behaviour of ground material and aggregates.

ACIDOPHILES' IMPACT ON THE SULFUR CYCLING AT LOW PH AND LOW TEMPERATURE ENVIRONMENTS: AN INCUBATION COLUMN EXPERIMENT

A. Ilin^{1*}, I. Yusta¹, J. Sánchez-España²

¹ University of the Basque Country, Spain ² Spanish Geological Survey (IGME), Spain.

Opencast sulfide mining sites, flooded after cessation of activity, can generate highly acidic (generally between 2.2 and 4.5), sulfate and metal-rich (e.g. Fe, Al, Cu, Zn, As, Cd) waters. These acidic pit lakes (APLs) may develop permanent stratification (meromixis), being excellent model systems for the study of biogeochemical dynamics at low pH and oxic-anoxic regimes. In order to evaluate the impact of biologically driven processes on metal mobility under acidic and anaerobic conditions, natural sediments and waters were obtained from diverse APLs and acidic streams from the Iberian Pyrite Belt (Huelva, Spain) and La Unión (Murcia, Spain) mining districts. These materials were filled into pre-perforated plastic tubes (Winogradsky-type columns) and incubated for 15 months (mo) under different conditions (glycerol-amended at room temperature, untreated columns at room temperature and cool-preserved at 4 °C).

In the organic-rich acidic stream system, the biogeochemical dynamics was shown to be very fast. A strong pH neutralization took place between 2 and 6 cm depth below the water-sediment interface of the column (initial pH was 3.7, which increased to 4.0 after 20 days and 4.9 after 1.5 mo) and expanded vertically upwards and downwards. Simultaneously, ORP dropped from 441 mV to 194 mV in the water column and down to 96 mV (1.5 mo) and -151 mV (12 mo) at the pH maximum, showing to be inversely proportional to pH. Under such reduced conditions, the interaction between biogenic H₂S, formed as a result of sulfate-reducing bacteria (SRB) activity, and dissolved metals led to abundant spherical Cu and Zn sulfide neoformation.

Contrastingly, columns from oligotrophic APLs systems showed virtually no evolution. However, the single addition of 19 mmol/L of glycerol to selected columns provoked extensive biological activity driving pH from 2.3-2.6 up to 3.7-6.1 in only 3 mo followed by slight gradual acidification, possibly due to organic exhaustion. ORP dropped as low as -67.9 mV or -184.2 mV (initial sediment contain detrital carbonates). The columns built with material from deep anoxic parts of APLs showed faster neutralization than the ones representative of upper oxygenated layers. Furthermore, the presence of carbonates in some of these sediments proved to catalyze the bacterial metabolisms by creating a more appropriate niche for SRB proliferation also expressed as more abundant reduced sulfur immobilization via metallic sulfide precipitation.

The results show that biosulfidogenesis in the sediments of the studied acidic systems is strongly carbon-limited. If supplied with a suitable external carbon source, the indigenous SRB inhabiting these sediments may have a profound impact on the cycling of sulfur and metals, as well as on acidity neutralization.

FEAST THEN FAMINE: A PRODUCTIVITY COLLAPSE TO END EARTH'S GREAT OXIDATION EVENT

Malcolm S.W. Hodgskiss¹, Peter W. Crockford², Yongbo Peng³, Boswell A. Wing⁴, and Tristan J. Horner⁵

¹Department of Earth Sciences, University of Cambridge, U.K. ²Department of Earth and Planetary Sciences, Weizmann Institute of Science, Israel. ³School of Earth Sciences and Engineering, Nanjing University, China. ⁴Department of Geological Sciences, University of Colorado Boulder, U.S.A.

⁵Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, U.S.A.

It has been hypothesized that the overall size of — or efficiency of carbon export from — the biosphere decreased at the end of the Great Oxidation Event (GOE) (ca. 2,400 to 2,050 Ma). However, the timing, tempo, and trigger for this decrease remain poorly constrained. Here we test this hypothesis by studying the isotope geochemistry of sulfate minerals from the Belcher Group, in subarctic Canada. Using insights from sulfur and barium isotope measurements, combined with radiometric ages from bracketing strata, we infer that the sulfate minerals studied here record ambient sulfate in the immediate aftermath of the GOE (ca. 2,018 Ma). These sulfate minerals captured negative triple-oxygen isotope anomalies as low as $\sim -0.8\%$. Such negative values occurring shortly after the GOE require a rapid reduction in primary productivity of $>80\%$, although even larger reductions are plausible. Given that these data imply a collapse in primary productivity rather than export efficiency, the trigger for this shift in the Earth system must reflect a change in the availability of nutrients, such as phosphorus. Cumulatively, these data highlight that Earth's GOE is a tale of feast and famine: a geologically unprecedented reduction in the size of the biosphere occurred across the end-GOE transition.

OCEAN INTERNAL SULFUR RESERVOIRS: A CASE STUDY FROM THE PALEOCENE-EOCENE THERMAL MAXIMUM

Weiqi Yao ^{1,*}, Adina Paytan ², Ulrich G. Wortmann ¹

¹ Department of Earth Sciences, University of Toronto, Canada, ² Institute of Marine Science, University of California–Santa Cruz, USA

For the longest time, the marine S-isotope ratio has been considered to vary only over long timescales (million years). This view is supported by the fact that the steady-state sulfur fluxes in and out of the ocean are small compared to the standing stock of sulfate in the ocean. However, we now understand that not only the net fluxes matter but also the gross fluxes (e.g., burial versus reduction and reoxidation). There is also more and more evidence showing that sulfur input and output fluxes can undergo short-lived but drastic changes, with the ability to affect the marine S-isotope ratio on considerably shorter timescales. Moreover, with a sulfate concentration substantially smaller in the past, the sulfur cycle may have been more dynamic than in the modern ocean where the marine sulfate residence time is long (10 to 20 million years). Here we extend this line of thinking by analyzing seawater S-isotope ratios during the Paleocene-Eocene Thermal Maximum (PETM) with a time resolution of five thousand years. Our data show clear changes in the marine S-isotope ratio (+1‰ excursion and recovery) within less than 100 thousand years. Weathering and burial flux variations would need to exceed their current values by one order of magnitude to explain such rapid changes. In the absence of geological evidence supporting the required flux changes, we argue that we must consider the idea of an ocean internal sulfide reservoir. While there is no such reservoir in the modern ocean, we contend that fluctuations in the size of oxygen minimum zones may explain the observed S-isotope signal. Specifically, we propose that once dissolved oxygen drops below a threshold value, sulfate reduction will commence in the water column. Unlike oxic respiration, organoclastic sulfate reduction is not limited by its electron acceptor concentration, and the resulting hydrogen sulfide will further deplete oxygen, reinforcing the internal sulfur cycle. However, this process is limited by the organic matter rain rate (i.e., export production from the photic zone). Box modeling suggests that during the PETM, 10-20% of the global ocean volume must have become sulfidic, with gross reduction and reoxidation rates two orders of magnitude higher than those in modern marine sediments.

PREDICTING PRIMARY TRIPLE OXYGEN ISOTOPE SIGNATURES FROM ALTERED SULFATE

Haley Olson, Anna Waldeck, Weiqi Yao, Clara Blättler, David Hodell, and David Johnston

Sulfate-bearing minerals such as gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) can be used as proxies for atmospheric conditions ($p\text{O}_2:p\text{CO}_2$) at the time of mineral precipitation. This information is captured by the triple oxygen isotope composition (denoted $\Delta^{17}\text{O}$) of the sulfate, which contains atmospheric O_2 ($\Delta^{17}\text{O} < 0\text{‰}$) that is incorporated into the sulfate during pyrite oxidation. The magnitude of the original atmospheric O_2 anomaly scales with contemporaneous $p\text{O}_2:p\text{CO}_2$ and gross primary production (GPP). Here, we explore the effect of post-depositional sulfate oxygen isotope exchange on ancient gypsum $\Delta^{17}\text{O}$ values and the associated uncertainties of predictions for contemporaneous $p\text{O}_2:p\text{CO}_2$ ratios and GPP. To do this, we use gypsum from three sub-basins in the Western Mediterranean Basin deposited during the Messinian Salinity Crisis (5.96-5.33 Ma) to characterize the distribution of $\Delta^{17}\text{O}$ values in a relatively unaltered evaporite basin. The mean of this distribution reflects Messinian seawater sulfate and the compositional distribution encompasses natural early diagenetic processes. This distribution is paired with a model of oxygen isotope exchange between sulfate and alteration fluids, which we use to unwind the alteration of 8 Proterozoic evaporite units (2308 Ma to 790 Ma, $n > 12$). The model predicts that all of the Proterozoic evaporite units have experienced oxygen isotope exchange with alteration fluids and that the mean $\Delta^{17}\text{O}$ value of the initial sulfate population is likely to be more negative than the most negative measured value. This model output predicts lower $p\text{O}_2:p\text{CO}_2$ ratios and GPP during the Proterozoic than previous studies.

THE EFFECT OF EARLY DIAGENETIC SULFUR GEOCHEMISTRY ON PALEOREDOX PROXIES

Alec M. Hutchings¹ and Alexandra V. Turchyn¹

¹Department of Earth Sciences, University of Cambridge, UK

Mid-Proterozoic oceans are thought to have contained both euxinic conditions—anoxic water with dissolved aqueous sulfide—and ferruginous conditions—anoxic water containing aqueous iron. Estimates of the relative proportion of these two conditions can be gleaned from geochemical proxies, however there is disagreement among nearly all of these proxies. Here, we explain this discrepancy by highlighting the hitherto under-acknowledged effect of early diagenetic effects with aqueous sulfide on certain paleoredox proxies in the rock record. In particular we examine the effect of sulfidation on previously deposited iron mineralogy, and how this may alter the geochemical signal which is ultimately measured. Using a previously compiled iron speciation dataset, we find that between 75–80% of samples classified as euxinic could be reasonably explained by this diagenetic process. Samples with a higher sedimentary iron content are less susceptible to this effect and are thus a more faithful recorder of the paleoredox conditions of the water column. The results of this study indicate that euxinia has been wildly overestimated in mid-Proterozoic oceans.

EVOLUTION OF THE SULFUR ISOTOPIC COMPOSITION OF PYRITE OVER THE CENOZOIC

Charlotte Spruzen and Alexandra V. Turchyn

¹Department of Earth Sciences, University of Cambridge, UK

The isotopic composition of sulfur can be used to understand the biogeochemical sulfur cycle, and therefore the redox state of the oceans, over geological time. The primary sinks of sulfur in the biogeochemical sulfur cycle are pyrite (FeS_2) and evaporite (mostly gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) minerals with some estimates suggesting pyrite is responsible for between 70-90% of total removal of sulfur from the surface. Over the last 150 million years there have been large changes in the sulfur isotopic composition of the ocean, which have been attributed to changes in the amount of pyrite buried, changes in the amount of evaporite minerals deposited or weathered, and changes in the volcanic input. Pyrite is formed from the hydrogen sulfide produced during microbial sulfate reduction, which has a large sulfur isotope fractionation (between 3 and 73‰). However, the sulfur isotopic composition of pyrite is often assumed to be constant in box models of the global biogeochemical sulfur cycle, or constantly offset from seawater. This paradigm has been recently challenged. For example, recent studies have shown that depositional environment is a major factor in the efficiency of pyrite burial, and therefore the sulfur isotopic composition of the reduced sulfur preserved in the geological record. This is due in part to the variable availability of highly reactive iron to promote efficient pyrite formation and burial. It has been suggested that tectonically-driven changes in the depositional environments where pyrite could be buried may influence the sulfur isotopic composition of pyrite, and thus the sulfur isotopic composition of global marine sulfate. We are examining the relationship between isotopic pyrite composition and environment of deposition throughout the Cenozoic, by recording the location and depth of deposition of published sulfur isotope data to see if there is a statistically significant relationship between them. We will present the initial work and data from this compilation.

METHANOGENIC OUTBURST IN A SULFATE-DEPLETED BASIN? A SULFUR ISOTOPE PERSPECTIVE FOR THE ORIGIN OF THE MIDDLE BAMBUÍ CARBON CYCLE ANOMALY IN BRAZIL

Huan Cui^{1,2*}, Lucas Veríssimo Warren³, Gabriel J. Uehlein⁴, Juliana Okubo³, Xiao-Ming Liu⁵, Rebecca E. Plummer⁶, Jean-Marc Baele⁷, Steven Goderis⁸, Philippe Claeys⁸, Fei Li⁹

¹ Geomicrobiology Group, Institut de Physique du Globe de Paris (IPGP), University of Paris, France. ² Department of Earth Sciences, University of Toronto, Canada. ³ Department of Geology, Institute of Geosciences and Exact Sciences, São Paulo State University Brazil. ⁴ Centro de Pesquisas Manoel Teixeira da Costa, Instituto de Geociências, Universidade Federal de Minas Gerais, Brazil. ⁵ Department of Geological Sciences, University of North Carolina, USA. ⁶ Hydrology and Remote Sensing Laboratory, Beltsville Agricultural Research Center, US Department of Agriculture, USA. ⁷ Department of Geology, Faculty of Engineering, University of Mons, Belgium. ⁸ Analytical, Environmental and Geo- Chemistry Group, Vrije Universiteit Brussel, Belgium. ⁹ State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, School of Geoscience and Technology, Southwest Petroleum University, China

The Ediacaran-Cambrian Bambuí Group in Brazil records an anomalously positive excursion in carbonate carbon isotopes ($\delta^{13}\text{C}_{\text{carb}}$) with a sustained plateau of ca. +15‰ (aka the Middle Bambuí positive Excursion–MIBE). Considering that the $\delta^{13}\text{C}_{\text{carb}}$ signals in Ediacaran-Cambrian seawaters do not typically exceed +6‰, the MIBE therefore represents a profound carbon cycle anomaly in Earth's history. Although intensive studies have been done on the Bambuí Group, origins of the MIBE remain enigmatic. In order to better constrain the biogeochemical carbon and sulfur cycles during the MIBE, high-resolution chemostratigraphic analysis was conducted for both the plateau (i.e., Lagoa do Jacaré Formation) and the recovery part (i.e., lower Serra da Saudade Formation) of the MIBE. Chemostratigraphic profiles reveal remarkably different values in $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{18}\text{O}_{\text{carb}}$, and $\delta^{34}\text{S}_{\text{pyrite}}$ between these two studied MIBE intervals. The new data show that the plateau of the MIBE is characterized by coupled higher $\delta^{13}\text{C}_{\text{carb}}$, higher $\delta^{13}\text{C}_{\text{org}}$, and higher $\delta^{34}\text{S}_{\text{pyrite}}$ signals compared with the recovery part of the MIBE. Based on multiple lines of sedimentological, geochemical, and modelling evidence, we propose that the possibilities of enhanced organic

TESTING THE GLOBAL SIGNIFICANCE OF THE SULFUR ISOTOPE RECORD OF THE C. 2.0 GA ZAONEGA FORMATION: A MICRO-SCALE S ISOTOPE AND TRACE ELEMENT INVESTIGATION

K. Paiste^{a,b}, D. A. Fike^a, K. Kirsimäe^b, P. Paiste^b, C. Jones^a

^a Department of Earth & Planetary Sciences, Washington University in St Louis, USA ^b Department of Geology, University of Tartu, Estonia

According to the current paradigm, the initial oxygenation of Earth's atmosphere at c. 2.4 Ga (the Great Oxidation Event – GOE) was followed by global changes that led to low-oxygen environments and temporally fluctuating ocean redox conditions that persisted until the Neoproterozoic. The metasedimentary rocks of the c. 2.0 Ga Onega Basin (Russia) have figured prominently in this concept, particularly the exceptionally organic- and pyrite-rich shales of the Zaonega Formation. However, a growing body of evidence shows that local depositional processes impacted the geochemical records of the Onega succession, thus calling for careful assessment of the global significance of the preserved geochemical information. In order to test former interpretations of large-scale excursions inferred from bulk sulfur isotope ($\delta^{34}\text{S}$) data (and concomitant implications for global redox changes) we used a micron-scale investigation of pyrite petrography, trace element (TE) and S-isotope composition in organic-rich metasediments of the Zaonega Formation.

Several generations of pyrites that formed at various stages of lithogenesis were identified in the analysed samples and their $\delta^{34}\text{S}$ and TE composition were determined by secondary ion mass spectrometry and laser ablation inductively coupled plasma mass spectrometry. Most samples from the Zaonega Formation display inter-grain $\delta^{34}\text{S}$ variability with earlier formed small (<20 μm) pyrite crystallites carrying typically less positive $\delta^{34}\text{S}$ values than large (>100 μm) inclusion-rich later formed pyrites. We also identified pyrite pseudomorphs replacing other precursor minerals, such as marcasite, anhydrite or barite. In comparison to the diagenetic pyrites, the pyrite pseudomorphs have distinct TE compositions and likely precipitated from different mineralising fluids. Overall, the TE composition of all analysed pyrites implies a sedimentary origin (e.g., Co/Ni ratios <2), yet morphological evidence implies that most pyrites have experienced some degree of alteration. Large euhedral crystallites and pyrite pseudomorphs commonly have $\delta^{34}\text{S}$ values >20‰ (up to ~50‰). It is doubtful that they preserve a seawater isotopic signature but rather reflect porewater conditions. These results call into question the previous interpretation that the anomalously positive pyrite $\delta^{34}\text{S}$ reflect fluctuations in the seawater sulfate reservoir and provide a deeper understanding of the mechanisms that govern S-isotope fractionations in sediments and how these signatures are preserved over geologic time.

NEW EXPERIMENTAL COMPARISONS OF CARBONATE-ASSOCIATED SULFATE EXTRACTION METHODS

Zheyu Tian¹, Graham A Shields², Ying Zhou²

¹2Department of Earth Sciences, University College London, UK

Carbonate-associated sulfate (CAS) refers to trace amounts of sulfate, which is incorporated into carbonate minerals during precipitation. CAS has long been used as a powerful proxy to recover the paleo seawater sulfate sulfur isotope value ($\delta^{34}\text{S}_{\text{sw}}$) as it occurs more widely and in less restricted marine environments than alternative minerals. However, uncertainties remain about the fidelity of preparation techniques due to the inadvertent inclusion of contaminant sulfur-bearing species. In this study, we selected four representative Ediacaran carbonate samples with different lithology. Their carbonate content ranging from 91.63% to 50.36%. Three new CAS extraction methods have been designed using aqueous solutions of: (1) 10% H_2O_2 followed by 10% NaCl; (2) 12% NaOCl followed by 10% NaCl; (3) Combined NaOCl and H_2O_2 followed by 10% NaCl. We compared these three newly designed methods together with the refined single 10% NaCl (aq) leaching method (He et al., 2019) and used 6 M HCl (aq) for the final dissolution step for all these testing methods. Reaction times were minimized to no more than 30 mins. 200g/L BaCl_2 (aq) was added to the solution in order to precipitate released trace sulfate. All the leachates and the final CAS fractions were analyzed for S isotope values and purity. Our work shows that the third method might be a superior method for handling organic and pyrite-rich limestone samples. The final CAS sulfur isotope values ($\delta^{34}\text{S}_{\text{CAS}}$) of the third method was between 0.65‰ and 0.9‰ than rival methods. We recommend that published and future $\delta^{34}\text{S}$ studies consider such effects in future.

DECOUPLED ATMOSPHERIC AND MARINE OXIDATION IN THE EDIACARAN

Wei Shi¹, Benjamin J. W. Mills², **Chao Li**^{1*}, Simon W. Poulton², Meng Cheng¹, Alexander J. Krause², Ying Zhou³, Tianchen He², Graham A. Shields³

¹State Key Laboratory of Biogeology and Environment Geology, China University of Geosciences, China. ²School of Earth and Environment, University of Leeds, LS2 9JT, UK.. ³Department of Earth Sciences, University College London, UK,

The Ediacaran Period (~635 to ~540 Ma) witnessed the early radiation of metazoans, in the form of the Ediacara Biota, at ~575 Ma. This biological revolution has been attributed to a temporally restricted episode of deeper ocean oxygenation possibly caused by a contemporaneous rise in atmospheric oxygen levels. However, this cause-and-effect assumption remains largely speculative. Here, we present an isotope mass balance model for Ediacaran atmospheric oxygen and oceanic sulfate evolution, based on paired carbon and sulfur isotope records from South China, Oman and USA-Mexico. Our results indicate that Ediacaran atmospheric oxygen levels rose monotonically from a lower limit of ~0.01 Present Atmospheric Level (PAL) between ~630 Ma and 575 Ma, and subsequently remained stable at ~0.55 PAL. By contrast, the marine sulfate reservoir did not increase until ~575 Ma, indicating decoupled atmospheric and marine oxidation. We propose that the initial rise of Ediacaran atmospheric oxygen levels established an ocean on the brink of widespread oxygenation. Subsequent transient changes in the input of oxidizing power (mainly sulfate) from continents drove dynamic oxygenation of deeper waters, triggering the evolution of the Ediacara Biota.