



Isotopes in Biogenic Silica (IBiS) 2024

Abstract Booklet

Session 1- New Frontiers in Analytical Methods,
Data Modeling and Biotechnologies

How to measure Si isotopic signatures in specific phases of suspended particles?

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Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

Presenter Name: Damien Cardinal

Presenter Preference: Oral presentation

To be clear, this presentation will not answer the question posed in the title. Rather, its aim is to open the discussion on different practices and perspectives focusing on Si isotopes and the specificities of suspended particles in marine environments close to the continental margin or in freshwater. These particles are characterised by a highly variable mixture of amorphous (biogenic or not) and crystalline Si phases, while Si adsorption adds a level of complexity to such matrices. For decades, the silicon community has debated the best way(s) to measure amorphous silicon concentrations in water, soils or sediments, and the jury is still out. Silicotopists have now successfully applied a combination of physical and chemical separation steps to measure Si isotopes in sediments or soils. However, due to the limited amount of material available in suspended particles, these methods are generally not directly applicable to such samples. Recently, some studies have reported promising Si isotopic compositions of suspended amorphous phases, mostly in glacial environments where mechanical erosion tends to produce fine particles with a high contribution of amorphous silicon. Here we review different methods used and propose some perspectives to start a constructive discussion with the IBiS community in order to identify best practices.

Culturing Radiolarians for Isotope Geochemistry

by Sophie Westacott | Emmeline Gray | Bernát Heszler | Lisa Friberg | Michael Henehan | University of Bristol | University of Bristol | University of Bristol | University of Bristol | University of Bristol

Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

Presenter Name: Sophie Westacott

Presenter Preference: Oral presentation

Radiolarians have not been used extensively for geochemistry, in spite of a fossil record dating back to the Cambrian. One reason for this is their apparent reluctance to being grown in controlled laboratory conditions. Breaking down this barrier would allow for experimental calibration of silicon and oxygen isotope fractionation by radiolarians, including the effect of dissolved Si concentration and species-specific vital effects.

Here, we present insights from a three-month field season maintaining radiolaria under different pH regimes for the purpose of testing their potential as a novel taxonomic medium for the boron isotope-pH proxy. Boron isotopes in planktonic foraminifera have long been used as a pH (and thus atmospheric CO₂) proxy, and expanding their application to radiolarians could fill in spatial and temporal gaps in the Mesozoic and Cenozoic CO₂ record. Preliminary data suggests radiolarian tests contain substantial boron, but controls on its isotopic fractionation are as yet unexplored. We identify a spumellarian genus that is abundant in near-surface waters at Villefranche-sur-mer (southern France), easy to distinguish, and hardy. We find they are readily kept alive for multiple weeks, in contrast to previous assumptions, and exhibit comparatively limited sensitivity to pH.

What can we learn from the oldest and first $d^{30}\text{Si}$ diatom taxa specific record?

by Lucie Cassarino | Karolina Brylka | Yuhao Dai | Rebecca A. Pickering | Sylvain Richoz | Daniel J. Conley | Université Bretagne Occidentale - Lund University | Lund University | Australian National University | Lund University | Lund University | Lund University

Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

Presenter Name: Lucie Cassarino

Presenter Preference: Oral presentation

Silicon isotopic signatures ($d^{30}\text{Si}$) of diatoms is an increasingly common tool in palaeoceanographic studies, used to constrain the marine silica cycle, including past productivity and carbon sequestration through the biological pump. Diatoms have influenced the marine silica cycle for at least the past 120 Ma, but most diatom $d^{30}\text{Si}$ records have focused on the more recent ocean history. Here we present the oldest known $d^{30}\text{Si}$ record from diatoms, spanning from 76.3 Ma to 66.3 Ma (Late Cretaceous). Our samples come from Deep Sea Drilling Project site 275, located on the Campbell Plateau, South Pacific Ocean. In addition to producing the oldest $d^{30}\text{Si}$ measurements of diatoms, we add a new dimension to our results by comparing bulk $d^{30}\text{Si}$ with three mono-taxa $d^{30}\text{Si}$ records: *Coscinodiscus* sp., *Hemiaulus polymorphus* and *Tricancria excavata*. These three taxa were the most abundant in our samples and morphologically different between each other, showing significant $d^{30}\text{Si}_{\text{BSi}}$ differences, with $d^{30}\text{Si}_{\text{Cosci}} = 1.90 \pm 0.18\text{‰}$, $d^{30}\text{Si}_{\text{Hemiaulus}} = 0.47 \pm 0.24\text{‰}$ and $d^{30}\text{Si}_{\text{Tricancria}} = 0.71 \pm 0.63\text{‰}$ over the 10 Ma studied here. The average bulk $d^{30}\text{Si}$ of $0.67 \pm 0.63\text{‰}$, which is in accordance with *Hemiaulus polymorphus* and *Tricancria excavata* species, however it does not align with *Coscinodiscus* sp. $d^{30}\text{Si}$ record. The most striking result of our study is the divergence of the different $d^{30}\text{Si}_{\text{diatoms}}$ records through time. Our study raises the question of bulk diatom $d^{30}\text{Si}$ records interpretation but also add new avenues to interpret these records by adding new ecological information due to the different genus identified.

Silicon stable isotopes of phytoliths to reconstruct past water availability in *Sorghum bicolor*

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Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

Presenter Name: Francesca D'Agostini

Presenter Preference: Oral presentation

In this study we examine the potential of silicon isotopic discrimination of phytoliths to detect water availability in *Sorghum bicolor* during plant growth. We focused our analysis on $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ in BULLIFORM, ELONGATE, and STOMA morphotypes with varied deposition locations and functions both as living cells and phytoliths. *Sorghum* was chosen because it is characterised by an active mechanism of Si transport and is a versatile plant that thrives both wild and cultivated in many diverse geographic areas with arid and temperate climates around the globe. Moreover, it is also one of the first crops that has been domesticated in Africa, and is currently a staple for over 500 million people.

Landraces of sorghum were cultivated under varied water regimes in lysimeters, simulating conditions varying from water abundance to water stress. Phytoliths from leaves and chaff were analyzed using femtosecond laser ablation multi-collector inductively coupled plasma-mass spectrometry, allowing for precise measurements of individual silica bodies. Analysis of 717 data points of phytoliths revealed significant differences between morphotypes and plant parts under different water treatments. BULLIFORMS, in particular, show a silicon isotopic discrimination in $\delta^{30}\text{Si}$, sensitive to watering, enabling us to develop a model to predict water availability. In conclusion, the results of our analysis of sensitive phytoliths for their $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ content demonstrates a tangible connection between the deposition of specific morphotypes and the plant's response to drought, thereby opening up a new realm of potential hypotheses regarding the utilization of phytoliths for archaeological and paleo-environmental reconstruction.

Exploring triple-silicon isotope behaviour during amorphous silica precipitation

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Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

Presenter Name: Patrick Frings

Presenter Preference: Poster presentation

Kinetic and equilibrium isotope effects make subtly different predictions about the mass-dependent scaling between the silicon (Si) isotope ratios $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$. The mass-dependencies of kinetic vs. equilibrium fractionations are typically not resolvably different during analysis, but recent work [1,2] demonstrates that with high-precision, high-resolution analyses deviations from a fractionation line are in fact quantifiable. This opens up a new analytical frontier of 'triple silicon isotopes' that can build on frameworks developed for e.g. the oxygen and sulfur isotope systems, to provide a new constraint on Si sources and processing. Here we present the results of preliminary experiments designed to capture a transition from kinetic to equilibrium fractionation during amorphous silica precipitation. Using educt-product (rather than standard-sample) bracketing on a Neptune HR-MC-ICP-MS, we investigate optimal measurement strategies for improved precision of triple silicon isotopes. We also present evidence for mass-independent silicon isotope fractionation during MC-ICP-MS analyses, and discuss the extent to which this might confound measurement and interpretation of triple silicon isotopes.

1. Sun et al. 2023, EPSL 607 <https://doi.org/10.1016/j.epsl.2023.118069>
2. Pack et al. 2023, GGG 24 <https://doi.org/10.1029/2023GC011243>

Silica determination assessment in seagrass leaves

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Topic: session 1: New Frontiers in Analytical Methods, Data Modeling and Biotechnologies

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Presenter Preference: Poster presentation

The biogeochemical cycle of silicon has been extensively studied in terrestrial plants, revealing three beneficial effects of biogenic silica accumulation for this vegetation: structural, physiological and protective. However, its importance in marine plants, particularly seagrasses, which are essential for biogeochemical coupling between terrestrial and coastal ecosystems, remains largely unexplored. Our research aims to fill this gap by assessing for the first time the wet-alkaline digestion and hydrofluoric-acid digestion methods to determine the silicon content in the leaves of a common seagrass species, *Zostera marina*. Leaves of *Z. marina* contained 0.26% silicon:dry-weight, consistent with the only two existent studies in seagrasses to date. Our results indicated that *Z. marina* incorporates silica in two forms: a labile form, digested by the alkaline method, and a more resistant form, digested only by acid digestion. These findings support chemical digestions for silicon quantification and provide insights into the impact of seagrasses on the marine silicon cycle: labile silica will be recycled, benefiting siliceous organisms upon leaf degradation, and the refractory form will contribute to the ecosystem's buried silica stock and coupled carbon sequestration. This study also provides a methodological basis for exploring silicon functionality in seagrass physiology and ecology.

Session 2 - Biogeochemical Cycling in the Oceans

Silicon cycling from ice-sheet to coastal ocean: insights from isotope geochemistry

by Katharine Hendry | Felipe Sales de Freitas | Sandra Arndt | Lisa Friberg | Jade Hatton | Jonathan Hawkings | Jeffrey Krause | Lorenz Meire | Hong Chin Ng | Helena Pryer | Tong Wang | E. Malcolm S. Woodward | British Antarctic Survey | Universite Libre de Bruxelles | Universite Libre de Bruxelles | University of Bristol | Charles University | University of Pennsylvania | Dauphin Laboratory & University of South Alabama | Greenland Institute of Natural Resources | University of York | University of Cambridge | University of Bristol | Plymouth Marine Laboratory

Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Katharine Hendry

Presenter Preference: Oral presentation

The polar regions are biologically productive and play a disproportionate role in regional and global biogeochemical cycling. One important nutrient is dissolved silicon, required for the growth of siliceous phytoplankton, diatoms, which form a key component of the biological production in the polar seas. Glacial weathering is a thought to be source of dissolved silicon, or silicic acid, to coastal waters, especially in regions of the Arctic that experience silicon limitation of algal growth at least on a seasonal basis. However, there are several complex interactions in fjords and coastal regions that can impact the supply of dissolved and particulate nutrients, including silicon, from glacial sources. Here, I will review the insight that silicon isotope geochemistry offers into Si cycling in glaciated ocean margins. We show that stable and radioisotopic geochemical methods can provide us with a mechanistic understanding of subglacial silica formation and its cycling across the land-ocean continuum. Biogeochemical modelling is an important complementary tool for constraining all the influencing processes acting upon these complex environments. Looking forward, outstanding questions about Si cycling in these vulnerable ecosystems will only be answered through novel techniques and collaborative cross-discipline research that overcomes traditional ecosystem boundaries in these interface environments.

Seafloor nutrient factories: investigating the benthic cycling of silicon in fjords along the West Antarctic Peninsula

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Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Lisa Friberg

Presenter Preference: Oral presentation

The release of silicon (Si) into marine ecosystems during early diagenesis across the sediment - water interface plays a vital role in supporting primary production and driving the marine carbon cycle. This process is particularly significant in the shelf regions of the West Antarctic Peninsula (WAP), where diatoms are the predominant phytoplankton group. The widespread diatom blooms during the austral summer results in extensive deposits of siliceous sediment, which replenishes the Si content in the water column and alters the composition of deep waters upwelling onto the shelf. The benthic cycling within fjord systems along the WAP can therefore influence the distribution of Si and other essential nutrients, impacting their availability to the wider ocean.

To understand the fate of Si and the potential impacts on nutrient cycling within fjords experiencing glacial retreat, we analysed three fjord systems along the WAP: Marian Cove, Børgen Bay and Sheldon Cove. Sediment porewater was collected at sites proximal and distal to the glacier and analysed for silicon isotopic composition ($\delta^{30}\text{Si}$) and DSi concentration. Additionally, a temporal analysis was conducted in Sheldon Cove to enhance our understanding of seasonal patterns and estimate the seasonal benthic flux of Si. Our results reveal ongoing benthic recycling of Si and provide insights into how glacial retreat might affect the Si supply in fjords.

Evolution of particles composition along a glacier-ocean continuum

by Mathis Guyomard | Damien Cardinal | Sandrine Caquineau | Edwin Cotard | LOCEAN - Laboratoire d'Océanographie et du Climat : Expérimentations et Approches Numériques (Sorbonne Université, CNRS, IRD, MNHN) | LOCEAN - Laboratoire d'Océanographie et du Climat : Expérimentations et Approches Numériques (Sorbonne Université, CNRS, IRD, MNHN) | LOCEAN - Laboratoire d'Océanographie et du Climat : Expérimentations et Approches Numériques (Sorbonne Université, CNRS, IRD, MNHN) | LOCEAN - Laboratoire d'Océanographie et du Climat : Expérimentations et Approches Numériques (Sorbonne Université, CNRS, IRD, MNHN)

Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Mathis GUYOMARD

Presenter Preference: Oral presentation

Silicon (Si) is a key element for silicifying marine organisms. In the Southern Ocean, diatoms are the main phytoplanktonic group, in particular around the Kerguelen plateau with seasonal blooms, an area naturally enriched in iron. Diatoms play a major role on the carbon cycle through the biological carbon pump (BCP) and Si cycle via their frustules made of biogenic silica (BSi). Silicic acid (DSi) supply from water below the surface generally controls the production of diatoms, but since few years, some studies report subglacial amorphous silica (ASi) as a potential source of DSi to the polar oceans. Since ASi can be both biogenic and non-biogenic, it is difficult to identify the Si source. In addition, clay particles can play a role in the DSi pool via Si adsorption - desorption along the salinity gradient in estuaries. The identification and nature of particles (primary, secondary mineral and ASi) is essential to assess the bioavailability of silicon. Different freshwater, estuarine, coastal and oceanic environments were sampled in late summer 2024 during the MARGO campaign around the Kerguelen plateau. Filtration at 3 μ m and 0.2 μ m was processed in order to study the coarse and fine particles by scanning electron microscopy (SEM) and X-Ray diffraction (XRD). Different chemical leaching steps were also tested with the aim of measuring Si isotopes. We will discuss the evolution of the particulate fraction composition along the glacier-ocean continuum with samples collected from a melting glacier (glacial flour), glacial and non-glacial lakes, estuary and coast.

Silicon isotopic contrast between Southern Ocean fertilized and HNLC (High Nutrients Low Chlorophyll) areas around Kerguelen and Heard Islands

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Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Edwin Cotard

Presenter Preference: Oral presentation

Silicon (Si) is a key element for silicifying marine organisms. Silicic acid (DSi), controls the production of diatoms, predominant in the Southern Ocean. Diatoms are main contributors to the biological carbon pump, which is particularly active in the Southern Ocean and in areas naturally enriched in iron such as around the Kerguelen and Heard plateau.

The objective of this study is to better understand the factors controlling the biogeochemical cycle of Si and its dynamics in the Southern Ocean and how it might be impacted by island mass effect. We use Si isotopic signatures combined with several parameters: DSi, BSi, LSi concentrations and, SEM observations of suspended particles. Different oceanic environments were sampled in late summer 2021 during the SWINGS campaign. Here, we focus exclusively around the Kerguelen and Heard plateau.

Surface $\delta^{30}\text{Si}$ values are not homogeneous among stations likely resulting from different DSi water mass sources. Nevertheless, other significant variations are observed for areas under shelf influence. Around Heard the $\delta^{30}\text{Si}_{\text{DSi}}$ data are homogeneous and lighter by 0.5 to 1‰, along with high LSi concentrations, suggesting a significant contribution of LSi to the DSi pool. This is consistent with SEM observations showing the presence of volcanic ashes. We also observe variations in the $\delta^{30}\text{Si}_{\text{BSi}}$ signatures. The surface $\delta^{30}\text{Si}_{\text{BSi}}$ vary strongly ranging from 2.5‰ to 1.0‰ coupled with high BSi concentrations above the shelf (>5 μM at Heard and at Kerguelen). We will discuss this data with the degree of Si utilization and its sources in the mixed layer.

Deglacial stratification of the polar Southern Ocean

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Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: François Fripiat

Presenter Preference: Oral presentation

The effect of global warming on the circulation of the Southern Ocean is complicated by the potential for interactions between wind-driven upwelling and ice sheet melting. Here, we investigate the changes of the Southern Ocean surface across the last two deglaciations, when the globe warmed rapidly. In a sediment core from the polar Antarctic Zone, we analyzed diatom-bound nitrogen isotopes to reconstruct surface nitrate concentration, which reflects the balance between biological productivity and the flux of subsurface nitrate into the Antarctic surface waters. Early in each deglaciation, there is a transient decline in surface nitrate concentration, reflecting a rise in density stratification. This is followed by an increase in nutrient supply in each of the two interglacials, signaling more vigorous surface-subsurface exchange. Combining the data with other Antarctic records further from the continent, the deglacial changes echo model simulations of ongoing global warming, in which upwelling increases near the Polar Front, while subsurface influx to the surface closer to the Antarctic continent decreases in response to ice sheet melting. The findings have implications for the cause of the observed rise in atmospheric CO₂ concentrations during deglaciations as well as for the future of the ocean's uptake of global warming heat and fossil fuel-derived CO₂.

Estuaries as modulators of tropical riverine Si fluxes

by Sarath Pullyottum Kavil | K.R. Mangalaa | Ramananda Chakrabarti | Jean Riotte | Arnaud Dapoigny | V.V.S.S. Sarma | Damien Cardinal | LOCEAN-IPSL (Sorbonne Universite, IRD, CNRS, MNHN) Paris,75005, France, | LOCEAN-IPSL (Sorbonne Universite, IRD, CNRS, MNHN) Paris,75005, France | Centre for Earth Sciences, Indian Institute of Science, Bangalore, 560012, India | GET-OMP, IRD, Toulouse, 31400, France | LSCE-IPSL, CEA-CNRS-UVSQ, Gif-sur-Yvette, 91190, France | NIO-CSIR, Visakhapatnam, 530017, India | LOCEAN-IPSL (Sorbonne Universite, IRD, CNRS, MNHN) Paris,75005, France

Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Sarath Pullyottum Kavil

Presenter Preference: Poster presentation

The alterations of riverine dissolved and particulate matter through estuarine processes can significantly alter the silicon fluxes along the land-to-ocean continuum. However, the impact of abiotic and biotic processes occurring along the salinity gradient in estuaries on Si supply and isotopic composition remains overlooked. The study presents DSi and $\delta^{30}\text{Si}$ composition from 19 tropical estuaries and groundwater from the Indian subcontinent, covering a wide range of climatic and lithological zones. The river water endmember (salinity <1) in studied estuaries exhibits a wide range of DSi from 105 to 445mM and $\delta^{30}\text{Si}$ values from 0.4 to 2.1‰. The Southwestern Indian rivers with high documented silicate weathering rates exhibit a lower DSi ($121\pm 13\text{mM}$) and lighter $\delta^{30}\text{Si}$ ($0.6\pm 0.2\text{‰}$) compared to the rest of the peninsular rivers. The $\delta^{30}\text{Si}$ of the high salinity end members were comparable to the previously observed values from surface Bay of Bengal Sea. Based on DSi, we observed signatures of non-conservative mixing in 11 of the 19 studied estuaries, with 8 estuaries exhibiting a DSi depletion. Majority of the observed DSi depletion occurs with an enrichment in $\delta^{30}\text{Si}$ of the estuary waters compared to simple freshwater-seawater mixing, consistent with the diatom uptake. Overall, groundwater samples exhibit highly heterogenous DSi ($490\pm 225\text{mM}$) and $\delta^{30}\text{Si}$ ($0.8\pm 0.6\text{‰}$), with typically higher DSi and lighter $\delta^{30}\text{Si}$ compared to river water, forming a source of lighter DSi. Annually, Indian peninsular rivers supply 102 ± 6 Gmol Si with an isotopic composition of $1.7\pm 0.1\text{‰}$ to North Indian Ocean, out of which 18 Gmol is lost in estuarine processes.

Isotopic approaches to exploring coupling of marine silica and carbon cycling in the Southern Ocean

by *Laura Taylor* | *Clara Manno* | *Kate Hendry* | *Helen Williams* | *British Antarctic Survey/ University of Cambridge* | *British Antarctic Survey* | *British Antarctic Survey* | *University of Cambridge*

Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Laura Taylor

Presenter Preference: Poster presentation

Diatoms contribute over 75 % of annual primary production in the Southern Ocean, resulting in a strong coupling of silica and carbon cycles in the region. However, a mechanistic understanding of the full extent of these interactions in the modern-day ocean is still not fully developed. Si fractionation by diatoms in the formation of siliceous frustules is the primary process controlling seawater $\delta^{30}\text{Si}$ variations and can therefore be used as a tool to shed light on the interactions of diatoms with carbon export processes in the marine environment.

This work aims to uncover linkages between carbon and silica cycling across different temporal and geographical scales in the Southern Ocean. This includes examination of $\delta^{30}\text{Si}$ of sinking particulate material on the Western Antarctic Peninsula shelf, through the water column over a long transect across the Scotia and Weddell Seas, and around the perimeter of a giant iceberg in the south Scotia Sea. The use of other stable isotope analyses will provide information on phytoplankton community composition (using $\delta^{13}\text{C}$), trophic transfer and community structure (using $\delta^{15}\text{N}$), and water mass composition and nutrient supply (using $\delta^{18}\text{O}$).

This work will contribute to developing a mechanistic understanding of silica and carbon cycle linkages, allowing consideration of the impact of changes to the Southern Ocean silica cycle on the future state of the ocean carbon sink and climate.

Marine silicate weathering drives exceptionally strong benthic silicon fluxes in Icelandic fjords

by Katharine Hendry | Cedric Goossens | Cathrin Wittig | Mikhail Kononets | Per Hall | Sebastiaan van de Velde | British Antarctic Survey | University of Antwerp | University of Ghent | University of Gothenburg | University of Gothenburg | University of Antwerp

Topic: session 2: Biogeochemical Cycling in the Oceans

Presenter Name: Katharine Hendry

Presenter Preference: Poster presentation

The polar regions are experiencing the most rapid environmental changes observed in recent decades. Diatoms are carbon-fixing marine algae that are at the base of these polar ecosystems and are sensitive indicators of the state of nutrient cycling. Diatoms precipitate biogenic opal as amorphous silica and, as such, require dissolved silicon (DSi) as a critical nutrient in their lifecycle. The main sources of DSi to the surface polar oceans are from glacial weathering, marine sediments, groundwater discharge, and the physical mixing and upwelling of deeper waters within fjords. However, the rates of these inputs in fjord and coastal environments, and the impact of subglacial and catchment lithology, are poorly constrained.

Here, we investigate the fluxes of DSi from sediments in Icelandic fjords and coastal environments using a range of methodologies, including core incubations, and in situ benthic lander incubations, and diffusion calculations based on pore fluid profiles. Calculated DSi fluxes from the different methodological approaches agree well. We show that Icelandic fjords have exceptionally high DSi benthic fluxes compared to other (sub)polar environments, likely driven by marine weathering of basaltic sediments. We will use the stable silicon isotopic composition of the pore fluid and incubation samples, and sediments, to assess the relative control over DSi build up in sediments from marine silicate weathering, dissolution and authigenic mineral precipitation. These key processes that supply DSi to productive coastal waters are climate sensitive and likely to change into the future, with significant impacts on regional biological productivity and throughout the global ocean.

Session 3 - Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Does biology matter for the coupling of the long-term carbon and silicon cycles?

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Patrick J. Frings

Presenter Preference: Oral presentation

The concept of coupled biogeochemical cycles implies that the flux of one element can be used to infer that of another. A long-standing paradigm asserts that the long-term ($>10^5$ yrs) cycles of carbon and silicon are coupled through the silicate-weathering feedback, where weathering of silicate minerals is a *source* of dissolved Si and bicarbonate alkalinity. More recently, attention has also focused on clay mineral authigenesis - 'reverse weathering' - in marine sediments as an important *sink* for dissolved Si and bicarbonate alkalinity. It is also well established that the biological fluxes of silicon and carbon associated with terrestrial and marine ecosystem primary production are orders of magnitude higher than the fluxes associated with weathering or reverse weathering. But to what extent do these biological fluxes influence the rates or pathways of the weathering or reverse weathering reactions? Expressed alternatively, how different would the coupling between carbon and silicon during weathering and reverse weathering look in an abiogenic world? I discuss why this is a difficult question to address, and why the answer is probably 'not very much'.

Examining silicon cycling in abyssal marine sediments using silicon isotopes

by Manyu Chen | Jianghui Du | Colin Maden | Gregory F. de Souza | ETH Zurich, Institute of Geochemistry and Petrology | Peking University | ETH Zurich, Institute of Geochemistry and Petrology | ETH Zurich, Institute of Geochemistry and Petrology

Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Manyu Chen

Presenter Preference: Oral presentation

The influence of early diagenesis on the cycle of silicon (Si) and its isotopes has received increasing interest in recent years. We have investigated benthic silicon cycling in abyssal red clays at two sites in the central equatorial Pacific Ocean, by analyzing the concentration ([Si]) and stable isotope composition of Si ($\delta^{30}\text{Si}$) in porewaters and sedimentary reactive silica pools extracted by sequential leaching. The Na_2CO_3 targeting biogenic silica (bSi) is isotopically heavy ($\delta^{30}\text{Si}$ from +1.98‰ to +2.37‰), the HCl leach targeting authigenic silica and metal oxides is very light (-2.53‰ to -2.06‰), while the NaOH leach targeting lithogenic silica (LSi) is intermediate (-0.09‰ to +0.35‰).

Porewater [Si] increases to more than double of bottom water concentrations within 10 cmbsf with $\delta^{30}\text{Si}$ varying from +1.18‰ to 1.48‰. Porewater $\delta^{30}\text{Si}$ values are thus intermediate between bSi and LSi and increase slightly as [Si] increases. Covariation of $\delta^{30}\text{Si}$ and [Si] indicates that porewaters must be influenced by the combined dissolution of bSi and LSi, and suggests that sedimentary dissolution of bSi (or extraction of the bSi reactive pool) may be associated with isotope fractionation. Elemental data from the sediment leaches indicates that the HCl leach likely attacked both authigenic phases and lithogenic detrital material at our sites, suggesting that the $\delta^{30}\text{Si}$ value of non-lithogenic Si extracted in this leach could be as low as -4‰. We will discuss the potential sedimentary carriers of this extremely low $\delta^{30}\text{Si}$ value in the context of porewater and reactive pool chemistry.

Oxygen isotopes in cherts record decreasing paleo-heat flow on Shatsky Rise (W' Pacific)

by Oskar Schramm | Geoscience Center, Georg-August-Universität Göttingen

Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Oskar Schramm

Presenter Preference: Oral presentation

Oxygen isotopes in cherts record decreasing paleo-heat flow on Shatsky Rise (W' Pacific)

Oskar Schramm¹, Tommaso DiRocco¹, Andreas Pack¹, Patrick, J. Frings², Michael Tatzel¹

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Sedimentary cherts form by the crystallization of amorphous silica during burial diagenesis. Their $^{18}\text{O}/^{16}\text{O}$ isotope ratio ($\delta^{18}\text{O}_{\text{chert}}$) is conventionally thought to record the combined influence of paleo-seawater temperatures and the $\delta^{18}\text{O}$ of paleo-seawater. However, a recent model study argued that the kinetics of silica diagenesis control the temperatures at which quartz precipitates, such that $\delta^{18}\text{O}_{\text{chert}}$ depends on paleo-heat flow during silica diagenesis. To provide an empirical underpinning to this interpretation, we investigated O-isotopes in the chert layers on top of the basalts on Shatsky Rise, a large igneous plateau in the Pacific Ocean. Here, we demonstrate that a $\sim 5\text{‰}$ $\delta^{18}\text{O}_{\text{chert}}$ increase in these cherts going stratigraphically upwards was controlled by a decreasing heat flow over tens of millions of years, as predicted by a numerical model for silica diagenesis. Smaller variations within the overall trend can be explained by minor changes in sedimentation rate. This work provides evidence that $\delta^{18}\text{O}_{\text{chert}}$ is sensitive to paleo-heat flow and that $\delta^{18}\text{O}_{\text{chert}}$ discloses the prograde thermal histories of sedimentary basins and Earth's thermal evolution.

Silicon and oxygen isotope fractionation in a silicified carbonate

by Michael Tatzel | Marcus Oelze | Daniel A. Frick | Tommaso DiRocco | Moritz Liesegang | Maria Stuff | Michael Wiedenbeck | Uni Göttingen | Bundesanstalt für Materialforschung und -prüfung | Uni Kiel | Uni Göttingen | RMS Foundation | Geoforschungszentrum Potsdam

Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Michael Tatzel

Presenter Preference: Oral presentation

Silicon isotope fractionation during silicification has not yet been investigated and impedes paleoenvironmental reconstructions from silicon- and oxygen isotopes in ancient cherts. We investigated the microscale silicon- ($\delta^{30}\text{Si}$) and oxygen isotope ratios ($\delta^{18}\text{O}$) in different silica phases within a Lower Cambrian silicified zebra dolostone to investigate isotope fractionation during silica-for-carbonate replacement. The successive replacement of carbonate layers coincides with decreasing $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values. This trend can be explained by i) changes in fluid $\delta^{30}\text{Si}$, ii) changing $\epsilon^{30/28}\text{Si}$ during precipitation or iii) by near-complete silica precipitation in an open system with limited silicon availability. We scrutinize the latter explanation using a Rayleigh distillation model that suggests positive $\epsilon^{30/28}\text{Si}$ values, consistent with predictions from *ab-initio* models for isotope distribution at chemical equilibrium. Applying the $\epsilon^{30}\text{Si}$ -temperature relationship from *ab-initio* models, we obtain silicification temperatures of ca. 50°C. To reconcile $\delta^{18}\text{O}_{\text{chert}}$ compositions with these temperatures, the fluids' $\delta^{18}\text{O}$ must have been between -2.5 and -4‰, compositions that match recent reconstructions for the early Phanerozoic oceans. Diagenetic carbonate-for-silica replacement appears to occur in oxygen- and silicon isotopic equilibrium and suggest that crystallization temperatures and paleo-fluid $\delta^{18}\text{O}$ can be reconstructed in silicified carbonates.

HAS-Li isotope fractionations? Investigating how and when geochemical signatures of rock-water interactions are archived within secondary phases.

by Xu Zhang | Andrea Billarent Cedillo | David Wilson | Oliver Plümer | Philip Pogge von Strandmann | Helen E. King | Utrecht University | Utrecht University | University College London | Utrecht University | Johannes Gutenberg University Mainz | Utrecht University

Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

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Presenter Preference: Oral presentation

The lithium isotope system has been used to study Earth's surface processes (Pogge von Strandmann et al., 2020). During rock-fluid interactions, light Li isotopes (${}^6\text{Li}$) are preferentially taken up by secondary phases. Clay precursors such as allophone can have high Al/Si ratios and carry isotope signatures similar to advanced weathering conditions such as low $\delta^{30}\text{Si}$ and low $\delta^7\text{Li}$ values (Opfergelt et al., 2012; Zhang et al., 2023). A fundamental question can be raised: when are the geochemical signatures recorded in secondary phases and can they evolve during clay crystallization/transformation?

In this study, we synthesized amorphous hydroxylaluminosilicates (HAS) by mixing AlCl_3 with Li-doped Na_2SiO_3 solutions. Elemental concentrations and $\delta^7\text{Li}$ were monitored. Preliminary results from XRD and Raman spectroscopy suggest the formation of amorphous phases. Chemical fluctuations observed in the fluids indicate that reprecipitation occurs within hours of the experiment with no Li isotope fractionation. $\delta^7\text{Li}$ fractionation is observed when Al is precipitated suggesting the fractionation is associated with Al content. These results suggest Li isotope fractionation archived in secondary phases evolve with crystallization process, implying different roles of weathering regimes (mountains vs. floodplains) on geochemical signals in nature.

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Extremely high alkalinity due to dissolution of mica-group silicate in the pelagic sediments of the Ulleung Basin (East Sea): stable Si isotopes evidence and reactive transport modelling

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Tzu-Hao Huang

Presenter Preference: Oral presentation

Marine silicate alteration affects long-term carbon cycling by combining lithogenic silicate (LSi) dissolution and secondary clay formation. However, the net H_2CO_3 consumption and production ability of marine silicate alteration remains highly uncertain. Critical factors such as silicate types and rates of marine silicate alteration have not yet been studied thoroughly. This study aims to identify silicate types and quantify rates of marine silicate alteration using sequential leaching, elemental abundance, Si isotopic signature and numerical modelling in Ulleung Basin drill cores, in which porewater alkalinity is up to 130 meq/L caused by active LSi dissolution. A decreased porewater dissolved Si (DSi) concentration and increased $\delta^{30}\text{Si}_{\text{porewater}}$ value found from 0-9 meter below seafloor (mbsf) are attributed to the formation of secondary clay, which is mainly smectite suggested by numerical modelling. Below the sulfate-methane transition zone (9-32 mbsf), increased DSi concentration and decreased $\delta^{30}\text{Si}_{\text{porewater}}$ value result from LSi dissolution, likely mica-group minerals and albite suggested by elemental abundance of separated LSi phase and modelling. Further, sensitivity tests using various organic matter degradation rates show that alkalinity, Mg and K concentrations in porewater are affected majorly by smectite formation rate, while mica and vermiculite dissolution rates are constant. The decreased contribution of LSi dissolution and an increased contribution of BSi dissolution from 32 to 218 mbsf are indicated by increased DSi concentration and $\delta^{30}\text{Si}_{\text{pw}}$ values and rate results output by modelling.

Silicon isotope fractionation during the formation of amorphous silica, amorphous hydroxyaluminosilicates and amorphous hydrous ferric silicate phases

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Franziska M. Stamm

Presenter Preference: Poster presentation

Silicon (Si) plays a critical role during mineral dissolution and neo-formation processes in Earth's near-surface environments and is mobilized during continental and seafloor silicate weathering and subsequently transported or released as silicic acid ($\text{Si}(\text{OH})_4$) to the ocean. In the modern ocean, $\text{Si}(\text{OH})_4$ is sequestered by silicifying organisms and various silicate minerals, such as authigenic clay minerals. The Si cycle is of particular interest within the critical zone (CZ), where Si is suspected to first precipitate as amorphous, gel-like phases, such as short-range ordered hydroxyaluminosilicates (HAS: e.g., allophane) and hydrous ferric silicates (HFS: e.g., hisingerite). These highly reactive minerals serve as precursors to the formation of important soil clay minerals, such as those of the smectite and kaolinite group. To decode the reaction paths and the environmental controls underlying HAS and HFS formation, the use of Si isotope fractionation can be a powerful tool. Therefore, a series of silica and allophane-hisingerite precipitation experiments at high temporal resolution has been performed to investigate and assess the kinetic Si isotope fractionation between the reactive fluid and the precipitating solid phase at room temperature. The kinetics of the precipitation reaction increased from amorphous Si < HAS < HFS. Further, large Si isotope fractionation followed by highly dynamic Si isotope exchange during HAS and HFS formation and structural re-organization was observed, following a Rayleigh-type fractionation model. Within 16 days, close to steady state conditions were reached, where the Si isotopic composition of the precipitates approached those found in allophanes and other clay minerals,

Iron-Silicon Interactions in Reactive Silicon Pools: Insights from West Antarctic Fjord Sediments

by Lisa Friberg | Kate Hendry | Amber Annett | University of Bristol | British Antarctic Survey | University of Southampton

Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Lisa Friberg

Presenter Preference: Poster presentation

There is a growing interest to understand how different reactive silicon pools contribute to the marine silicon budget. Quantifying reactive (and potentially bioavailable) silica associated with the different pools - weak acid-leachable Si (Si-HCl), alkaline-leachable Si (Si-Alk) and strong alkaline-leachable Si (Si-NaOH) - is integral for our understanding of early sediment diagenesis. Furthermore, the stable silicon isotopic composition ($\delta^{30}\text{Si}$) of these pools can shed light on their formation processes. However, previous studies using sequential leaching techniques lack $\delta^{30}\text{Si}$ data, thus overlooking potential mechanisms and processes driving silica formation. To date, only a handful of studies have conducted sequential leaching experiments, showing the potential for a link between silica diagenesis and iron cycling within marine sediments. However, these studies are mostly limited to the northern hemisphere and predominantly focused on temperate coastal environments.

Given that iron is a limiting nutrient and silicon is essential for diatom production, which drives primary productivity in the Southern Ocean, unravelling the factors controlling iron and silicon production in sediments and the exchange between sediments and seawater in fjords is essential. Here we present the first results from sequential leaching of sediments from three fjords along the West Antarctic Peninsula. Additionally, we conducted parallel leach experiments for iron and measured the concentration of both Si and Fe in these leaches to assess the association of iron with reactive Si pools and vice versa. Our findings reveal the spatial variability in these pools across the studied fjords, highlighting nuanced differences crucial for understanding sediment diagenesis in polar environments.

The role of marine silicate alteration in regulating carbon cycling

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

Presenter Name: Tzu-Hao Huang

Presenter Preference: Poster presentation

Despite the growing recognition of in-situ silicate alteration (dissolution and formation) in marine sediments, its controlling factors are still poorly understood. By compiling information from scientific ocean drilling programs and applying numerical modelling, we aim to 1) identify silicate phases responsible for the hyper porewater alkalinity (>56 meq/L) commonly observed from productive continental margins, 2) investigate the interplay between silicate dissolution, clay formation, and carbonate authigenesis, and 3) provide constraints on the environmental parameters of silicate dissolution. Using porewater composition, we show that marine silicate weathering is primarily driven by dissolution of K- and Mg silicates. No apparent difference was observed for Ca concentrations when comparing sites with and without hyper alkalinity, which hints for complicated feedbacks through authigenic carbonate formation. Through numerical modeling, we are able to reproduce the observed porewater composition when including several mica- group and smectite-group silicates. When organic matter degradation rate is low to moderate, authigenic carbonate formation is effective in controlling subsurface DIC/alkalinity level and thus only little carbonic acid produced by reverse weathering can diffuse away from sediments. Under a scenario with fast organic matter fermentation, dissolution of Mg- and K-silicates becomes the only pH buffer that neutralizes most of the DIC produced from organic matter fermentation. The analysis of global dataset reveals the potential importance of burial history in controlling submarine silicate alteration. Mg- and K-silicate minerals in sediments with high organic matter reactivity that have been buried sufficiently long and/or high temperature are more susceptible to weathering.

Testing wet-chemical sequential leaching on sediments with modified BSi contents for method improvement to separate and quantify SiO₂ phases in marine sediments

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

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The silicon (Si) phases found in marine sediments, such as biogenic silica (BSi), lithogenic silicate (LSi), and authigenic silica/silicate (ASSi) provide insights into silicon deposition and biogeochemical cycling. DeMaster (1981) was the first to develop Na₂CO₃ leaching to extract diatoms from surficial marine sediments. This protocol has since been widely used and modified, but most leaching protocols fail to completely separate the individual SiO₂ phases. As recent studies have shown, it is especially difficult to separate BSi and LSi phases from deeply-buried and diagenetically-modified sediments, which require longer digestion times to extract BSi via Na₂CO₃ leaching. Hence, there is a need for a robust protocol that allows both for isolation and quantification of the individual phases. To test how much BSi can be extracted with wet-chemical sequential leaching methods (modified after Huang et al. 2023), we perform systematic experiments where PACS-3, a marine sediment certified reference material, is mixed with known amounts of BSi (0, 5, 10, 20 wt%). The extracted leachates are analysed regarding their elemental abundance (Si, Al, K, Fe) and we use the Si/Al molar ratio in the leachate as an indication for the leached Si phases. Still, our results emphasise the need for more systematic studies to make our protocol applicable for different marine sediments at various diagenetic stages and with variable compositions of (B)Si phases.

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Early Diagenesis of Authigenic Silicon in Deep-Sea Sediments from the South Pacific

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Topic: session 3: Relevance of Abiogenic Silica Formation for Sedimentary Cycles

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Presenter Preference: Poster presentation

Preservation of diatom biogenic opal in sediments is strongly influenced by early diagenetic processes such as (partial) dissolution or the formation of authigenic reactive Si-containing phases. The exact conditions leading to the formation of those reactive Si-phases is, however, poorly understood. To improve this, the main goal of our study was to investigate the early diagenetic alteration of Si in deep-sea sediments in two areas differing significantly in their environmental conditions: The oligotrophic South Pacific Gyre (SPG) and sediments east of New Zealand are characterized by e.g. highly variable primary production in surface waters, input of lithogenic material and mineralogical/geochemical sediment composition. Surface sediments (0-5 cm depth) from four stations in each area were analyzed for bulk element composition. Reactive Si phases (biogenic opal, metal oxide-associated Si and authigenic Al-Si phases) were extracted following modified sequential leaching protocols. The results indicate that biogenic opal content is low in both areas. However, surprisingly, in sediments east of New Zealand, 0.6-3% of the total Si is contained in reactive phases, whereas in the SPG up to 13% of the total Si is reactive. This reactive Si in the SPG is largely associated with metal oxide coatings. Overall, this suggests that oligotrophic regions, which have largely been ignored in Si cycling and diagenesis studies, can have significant reactive Si contents, and therefore warrant more attention in the future.

Session 4 - A Window to the Past - Paleo
Investigations of the Silica Cycle

A robust signal in diatom $\delta^{30}\text{Si}$ across the last deglaciation

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Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Gregory de Souza

Presenter Preference: Oral presentation

More than 25 years ago, the first time-series of the silicon stable isotope composition ($\delta^{30}\text{Si}$) of diatoms isolated from Southern Ocean sediment showed higher diatom $\delta^{30}\text{Si}$ in the Holocene relative to the last glacial maximum. Both this and subsequent records have been interpreted to reflect an increase in the utilisation of Si in the Antarctic Zone (AZ) during the Holocene, contrasting with an inferred decrease in nitrate utilisation.

Recent research into the Si isotope systematics of other silicifiers, as well as into the sedimentary cycling of Si, has revealed a wide diversity of $\delta^{30}\text{Si}$ signatures in the components of marine sediment. Particularly relevant are the low $\delta^{30}\text{Si}$ values found for Southern Ocean radiolaria and for a sedimentary pool interpreted to be an authigenic Si-bearing phase, both of which are $>2\text{‰}$ lower than those of diatoms. Given the low primary productivity (and diatomaceous biogenic silica flux) of the glacial AZ, could the deglacial diatom $\delta^{30}\text{Si}$ increase of $\sim 0.5\text{‰}$ be the result of a changing proportion of non-diatom or authigenic, diagenetic Si?

To tackle this question, we have microfiltered and manually purified diatom samples previously analysed for diatom-bound nitrogen isotopes from a sediment core from the Indian AZ. We show that the deglacial diatom $\delta^{30}\text{Si}$ increase of $\sim 0.5\text{‰}$ at our core site is (a) not the result of contamination by other sedimentary components, and (b) step-like within the $\sim 1\text{ka}$ resolution of our sampling, pre-dating the deglacial rise in biogenic silica flux.

Constraining changes in silicate weathering and ocean circulation during the middle-late Eocene: Evidence from silicon and lithium isotopes.

by Ruchi Ruchi | Michael J. Henahan | Patrick J. Frings | Ollie Laub | Donald E. Penman | Daniel A. Frick | Friedhelm von Blanckenburg | Earth Surface Geochemistry, GFZ German Research Centre for Geosciences, Potsdam, Germany | School of Earth Sciences, University of Bristol, Bristol, United Kingdom | Earth Surface Geochemistry, GFZ German Research Centre for Geosciences, Potsdam, Germany | Geosciences Department, Utah State University, USA | Geosciences Department, Utah State University, USA | Institute of Geosciences, University of Kiel, Kiel, Germany | Institute of Geological Sciences, Freie Universität Berlin, Berlin, Germany

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Ruchi

Presenter Preference: Oral presentation

It is well-accepted that the silicate weathering feedback counterbalances CO₂ degassing on timescales of $>10^4$ years. However, ~ 300 kyr period of gradual warming and deep-sea carbonate dissolution at ca. 40 Ma (the Middle Eocene Climate Optimum; MECO) challenges our understanding of this long-term carbon sink. Moreover, the existence of MECO-like events in the middle-late Eocene (with similar durations and carbon and oxygen excursions as the MECO) poses the question of whether these intervals were also driven by the same mechanisms as the MECO. Previous work has invoked 187Os/188O isotopes to infer a weakening of the weathering feedback but this poses its own problems. Further investigation of whether transient weakening of the feedback is feasible, and the potential for its subsequent reinvigoration, is required.

To address these questions, we generate Si isotope data from planktic radiolarians and benthic sponges and Li isotope measurements from single species foraminifera from multiple sites- North Atlantic, South Pacific and South Atlantic oceans spanning the MECO and a later MECO-like event at 37 Ma. Limited change in radiolarian $\delta^{30}\text{Si}$ over the MECO speaks against extreme changes in continental weatherability whereas the sponge $\delta^{30}\text{Si}$ data indicates a change in thermohaline circulation. During a MECO-like event, asynchronous changes in both groups implies changes in productivity and circulation. A new Li isotope data highlights the difference in the weathering intensity proxies. We discuss the implications of the data for reconstructions of silicate weathering feedback strength, ocean circulation, and the marine silicon and lithium cycles.

Physical erosion enhanced silicate weathering stabilized climate after the Paleocene-Eocene Thermal Maximum

by Yuhao Dai | Research School of Earth Sciences, the Australian National University, ACT, Australia

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Yuhao Dai

Presenter Preference: Oral presentation

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The climate recovery from hyperthermal events, such as the Paleocene Eocene Thermal Maximum (PETM), has been thought to be facilitated by carbon removals from the ocean-atmosphere system via chemical weathering of silicate rocks. While hydrology-driven physical erosion can affect silicate weathering, its contribution to post-PETM atmospheric carbon removal remains ambiguous due to its potential to release carbon. Here, we infer silicate weathering changes around the PETM based on surface-ocean silicon isotope signatures ($\delta^{30}\text{Si}$) obtained from mono-taxonomic radiolarians and examine their linkage to contemporary changes in deep-ocean carbonate chemistry. Our data suggest that physical erosion increased continental silica fluxes to the ocean, followed by a longer-term silicate weathering enhancement after the PETM as indicated by a ~600,000-year-long surface-seawater $\delta^{30}\text{Si}$ reduction. Our inferred strengthening of silicate weathering is supported by a coeval increase in deep ocean carbonate saturation. Overall, our results indicate that physical erosion enhanced silicate weathering and thus carbon removal from the ocean-atmosphere system, operating as a critical feedback to stabilize Earth's climate around the PETM.

Primary sources, circulation and Si burial in marine environment of Precambrian-Palaeozoic times

by Agata Jurkowska | AGH University in Krakow

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Agata Jurkowska

Presenter Preference: Oral presentation

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The biogeochemical Si cycle evolves during Earth history and its current mode has been established after Eocene, which correlates with diatoms proliferation. The main actualistic paradigm about the evolution of Si cycle in Earth history is an assumption of its biological control, which comes down to the conclusion, that significant turning points in this biogeochemical cycle are correlated with major evolutionary changes in siliceous organisms. This assumption has been extended into Palaeozoic and Mesozoic times, while during the Precambrian the abiotic control has been assumed due to lack of silicifers (Maliva et al., 1989; Maliva and Siever, 1989a, b; Siever (1991; 1992). However, in a light of new paleontological studies of evolution of silicifers, as well as chert facies distribution analysis in combination with geochemical and isotopic ($\delta^{30}\text{Si}$) studies of siliceous rocks, the biological control of siliceous sponges and radiolarians over the Palaeozoic Si cycle is a phenomenon which is difficult to understand. The literature review, that has been done by us, highlights that the seminal models of Si evolution based on paradigm of biological control over the deposition of siliceous rocks are limited significance, especially in Palaeozoic. The review indicate that the another overlooked primary source of seawater dSi of endogenous dSi of volcano-hydrothermal activity, controlled the dSi seawater concentration and governed the evolution of Si cycle.

Glacially enhanced silicate weathering constrained by Si isotopes and Ge/Si of biogenic silica in Holocene lake sediments

by Yi Hou | Jotis Baronas | Preston Cosslett Kemeny | Julien Bouchez | Áslaug Geirsdóttir | Gifford Miller | Mark A. Torres | ETH Zurich | Durham University | University of Chicago | IPGP | University of Iceland | University of Colorado Boulder | Rice University

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Yi Hou

Presenter Preference: Oral presentation

How glaciation affects CO₂ drawdown by chemical weathering sets the strength of the weathering-climate feedback, which controls the exogenic carbon cycle and planetary habitability. However, the exact role of glaciers remains elusive as glaciation alters multiple factors controlling weathering, the net effect of which is ambiguous even in directionality. While illustrative, modern observations have limited ability to constrain time-dependent behavior, which is thought to be important to glacial weathering. To isolate and quantify the effect of glaciers over millennial timescales, we developed a novel multi-proxy system for constraining catchment-scale fluxes in the past. This approach utilizes the correlation between Ge/Si and Si isotope ratios in modern rivers that tracks chemical weathering congruency and the preservation of these signals in biogenic silica in lake sediments. We report changes in weathering fluxes in two catchments with different glacial histories during the past ten thousand years from two lacustrine records in Iceland. We find that the chemical weathering fluxes are an order of magnitude higher in the same catchment when glaciated compared to when ice free. The synchronous variations in weathering fluxes with the expansion and contraction of glaciers indicate a rapid, positive effect of glaciation that may amplify climatic variations.

The key role of the Archean oceanic Si cycle in the growth of early continental crust

by Luc André | Musée Royal de l'Afrique centrale

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: André

Presenter Preference: Oral presentation

Weaker drainage of the limited continental surface of Eo-Paleoarchean continents was equivalent to a reduced capacity to neutralize the large volume of fluids emitted by the high-temperature vents of mid-ocean ridges. Without this continental runoff and the absence of detrital deposits, the Paleoproterozoic Ocean had very specific characteristics (e.g. high proton and Cl⁻ contents, low alkalinity and low Mg content). Thermodynamic models also show that high-temperature hydrothermal fluids are supersaturated with Si, Ge and K.

In the lack of an efficient biosphere, the oceanic Si oversaturation is therefore equilibrated through the low-temperature (80-150°C) off ridge hydrothermal activity. The percolation of seawater into the seafloor basalts beneath an impermeable layer of cherts gave rise to deep-seated alteration of the oceanic crust, structured in three major layers: silicification at the surface, followed at depth by intense carbonatization and then a classic association of greenschist facies. This alteration manifests itself in a massive transfer of heavy Si ($\delta^{30}\text{Si} > 0$ in the seafloor) and its depletion in Ge relative to Si ($\text{Ge/Si} < 1$).

Similar heavy Si isotopic and low Ge/Si ratio anomalies are systematically observed in all Eo-Paleoproterozoic crustal granitoids, either as batholithic intrusions or transformed into grey gneisses. This demonstrates that the growth of the very first continents originated from the deep interaction between the seafloor and the silica-saturated primitive ocean. The consequences of these results in terms of intracrustal and mantle recycling will be briefly discussed.

The stubborn silica: Why do diatom frustules withstand a sequential leaching protocol?

by Petra Zahajská | Franziska M. Stamm | Andre Baldermann | Christopher M. Schiller | Daniel Conley |
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Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Petra Zahajská

Presenter Preference: Poster presentation

Biogenic silica (bSi) in lake and marine sediments is commonly quantified using sequential alkaline extraction protocols (DeMaster, 1981; Conley and Schelske, 2001). This is based on the faster dissolution rate of highly reactive (amorphous) bSi compared to slowly reacting (semi)crystalline silicon-bearing phases (e.g., feldspar, quartz and phyllosilicates) of the sediment. The standard method involves a 0.1M Na₂CO₃ solution (pH ~ 11) at 85°C with multiple samplings over 1-3-hour intervals to monitor potential clay mineral dissolution. This method was applied to sediments from the (hydro)thermally affected Goose Lake in the Lower Geyser Basin of Yellowstone National Park (Wyoming, USA), but it was proved to be ineffective.

The well-preserved diatom frustules from sediments with bSi ranging from 26-68wt% remained undissolved even after 5h hours of sequential leaching. Scanning electron microscopy and energy-dispersive X-ray spectroscopy analyses revealed no significant compositional changes in the diatom frustules.

The lack of bSi dissolution can be explained by:

1. **Early Diagenetic Effects:** Early diagenetic processes, such as re-crystallization of biogenic opal, may have altered the bSi frustules, making them more resistant to alkaline extraction.
2. **Sequential Leaching Effects:** Bulk sediment composition retards bSi dissolution due to pH buffering and diatom coating phenomena.
3. **Species dependency:** Mineralogy and chemistry of diatom species (Al/Si ratio) affecting the dissolution behaviour/kinetics.

This resistance of diatom frustules to dissolution highlights a potential limitation of the current bSi quantification method in complex sedimentary environments like (hydro)thermally affected lakes. Further research is needed to understand the factors influencing bSi preservation in such settings.

The Silica Cycle during the Upper Cretaceous: A Case Study from a Canadian Continental Shelf

by Kristin Doering | Zhouling Zhang | Yuhao Dai | Wolf Dummann | Tjördis Störling | Claudia Schröder-Adams | Sylvain Richoz | Martin Frank | Jens Herrle | David Harwood | Daniel J. Conley | Aarhus University | GEOMAR Helmholtz Centre for Ocean Research Kiel | The Australian National University | Institute of Geosciences, Goethe-University Frankfurt | Lund University | Department of Earth Sciences, Carleton University | Lund University | GEOMAR Helmholtz Centre for Ocean Research Kiel | Institute of Geosciences, Goethe-University Frankfurt | Department of Earth & Atmospheric Sciences, University of Nebraska-Lincoln | Lund University

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Kristin Doering

Presenter Preference: Poster presentation

The oceanic Silica Cycle, driven by weathering and biosilicification, is important due to its strong link to the biological pump and carbon drawdown. Today, the global DSi concentrations are comparatively low, while higher DSi are thought to have prevailed during the Precambrian and Paleozoic. A significant drawdown in DSi was assumed to have occurred during the Cenozoic, which was attributed to the diversification of diatoms and their high turnover of DSi. However, to test this hypothesis estimates of DSi from the Cretaceous are missing.

To improve our DSi reconstructions over the Cretaceous, we studied a section from the Kanguk Formation on Devon Island, recording Upper Cretaceous shelf sediments (94 Ma to 86 Ma years). To reconstruct the silica cycle in this shelf environment, we analysed silicon (Si) isotope ratios (expressed as $\delta^{30}\text{Si}$) of sponge spicules, radiolaria and diatoms. Different diatom groups were handpicked, resulting in $\delta^{30}\text{Si}$ values between -0.3 and 0.7‰. We suggest these values reflect 0% to 70% surface DSi utilization, assuming mostly light (1-1.2‰) riverine source waters. The $\delta^{30}\text{Si}$ of sponges range from -1.65‰ to -0.4‰, and that of radiolaria from +0.1 to +1.0‰. Overall, the $\delta^{30}\text{Si}$ -sponge values indicate DSi concentrations only slightly heavier than found in the Canadian Arctic today, with DSi concentrations of less than 20 μM . Additionally, we observe higher DSi concentrations of shelf bottom waters before and after the anoxic events. At the same time, higher $\delta^{30}\text{Si}$ -radiolaria suggest lower surface-subsurface DSi concentrations, suggesting stronger stratification during these periods.

Species-specific radiolarian $\delta^{30}\text{Si}$ signals across the last deglaciation

by Joy Schrepfer | Iván Hernández-Almeida | Colin Maden | Gregory F. de Souza | ETH Zurich, Institute of Geochemistry and Petrology, Switzerland | ETH Zurich, Geological Institute, Switzerland. Now at PAGES IPO, University of Bern, Switzerland | ETH Zurich, Institute of Geochemistry and Petrology, Switzerland | ETH Zurich, Institute of Geochemistry and Petrology, Switzerland

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Gregory de Souza

Presenter Preference: Poster presentation

The last deglaciation was a time of major reorganisation of marine carbon and nutrient pools in which the Southern Ocean was a major dynamical and biogeochemical player. As such, it provides an excellent case study for the testing of novel tracers of nutrient cycling in the past ocean. Here, we present species-specific silicon stable isotope ($\delta^{30}\text{Si}$) data for two radiolarian species isolated from IODP Site U1537 in the Atlantic sector of the Southern Ocean (59°S, 41°W; 3713m water depth) across the last deglaciation, i.e. from 42ka to 7ka.

The species we focus on have fundamentally different habitats: *Antarctissa denticulata/strelkovi* live in the shallow subsurface to surface (< 200m), while *Cycladophora davisiana* appears to be a deep-dwelling (>200m) species that favours regions with extensive winter sea ice cover. Average $\delta^{30}\text{Si}$ values across our records are $-0.96\pm 0.45\text{‰}$ and $-2.60\pm 0.95\text{‰}$ (2SD) for *A. denticulata/strelkovi* and *C. davisiana* respectively (the large variance reflects a time-varying signal). This enables two first-order findings: firstly, our species-specific data confirm previous observations from mixed radiolarian samples that Southern Ocean radiolaria are isotopically lighter, by 2‰ or more, than those extracted from core-tops or deglacial sediment at lower latitudes. Secondly, there is a large difference in the $\delta^{30}\text{Si}$ value of the two species we investigate, and the isotopic offset between these two species is variable over our deglacial record (at 0.94 - 2.31‰). This may reflect the combination of a sensitivity to the concentration of ambient dissolved Si as well as its isotopic composition.

Exploring glacial-interglacial nutrient conditions in the Antarctic Zone: Insights from a one-dimensional water column model

by Cédric Dumoulin | François Fripiat | Barbara Hinnenberg | Daniel M. Sigman | Alfredo Martínez-García | Université libre de Bruxelles | Université libre de Bruxelles | Max Planck Institute for Chemistry | Princeton University | Max Planck Institute for Chemistry

Topic: session 4: A Window to the Past - Paleo Investigations of the Silica Cycle

Presenter Name: Cédric Dumoulin

Presenter Preference: Poster presentation

In the Antarctic Zone (AZ), deep nutrient-rich waters ascend to the surface, feeding the Southern Ocean's overturning circulation cells at a rate that exceeds the capacity of phytoplankton to fully consume the dissolved nutrient load. This incomplete consumption results in the release of previously sequestered CO₂ into the atmosphere. It has been suggested that enhanced nutrient consumption contributed to the lowering of atmospheric CO₂ concentrations during ice ages. Diatom-bound δ¹⁵N records in the AZ point to more complete nitrate consumption in surface waters during ice ages. The correspondence of more complete nitrate consumption with lower export production calls for a lower gross nitrate supply to the AZ surface and, therefore, a reduction in the exchange of water between the surface and the deep ocean. However, preliminary reconstructions indicate more than a 5-fold reduction in the rate of gross nitrate supply to match paleo proxy data and nitrate consumption.

Here, we explore more fully the amplitude of the glacial decrease in gross nitrate supply to the AZ surface required to match the N isotope and export production proxy data. We developed a 1D advection-diffusion-reaction model of the water column that accounts for the consumption of nitrate and its isotopes at the surface. The preliminary results of the models match current observations and support an increase in the δ¹⁵N with an ice age reduction of the water supply during ice ages. Consistent with previous models, the system requires a substantial reduction of upwelling to reach the observed glacial δ¹⁵N values.

Session 5 - Silica Dynamics in Terrestrial
Ecosystems: Unveiling the Interplay between
Soil and Plant Systems

Silicon dynamics in terrestrial ecosystems: current knowledge and future prospects

by Félix de Tombeur | CEFÉ, Univ Montpellier, CNRS, EPHE, IRD, Montpellier, France School of Biological Sciences and Institute of Agriculture, The University of Western Australia, Perth, Australia

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Félix de Tombeur

Presenter Preference: Oral presentation

Silicon (Si) is widely recognized as an important regulator of the global carbon cycle on different timescales via its effect on diatom productivity in oceans and the weathering of silicate minerals on continents. Beyond biogeochemical processes, an increasing body of evidence demonstrates the pivotal role of Si as an essential nutrient for terrestrial biota, especially for plants. Understanding the drivers of terrestrial Si biogeochemistry is therefore essential to understand and ultimately predict key biogeochemical and ecological processes. In this talk, I will first give an overview of the seminal works that highlighted the effects of plants on terrestrial Si cycling, and address debates surrounding (1) the key drivers of soil-plant Si cycling (biogenic vs. litho/pedogenic drivers) and (2) the potential effects of plants on Si transfers at the critical zone scale. Better predicting pools and fluxes of biogenic Si in soil-plant systems require a fine understanding of plant Si variation. As such, in a second part, I will discuss different phylogenetic and ecological drivers of plant Si variation, and whether trait-based approaches might help to better understand this variation. I will finally discuss the influence of overlooked soil biotic factors on Si biogeochemistry. Overall, fully integrating living organisms and their pivotal role on Si transformation in soil-plant systems (and beyond!) is highly challenging, probably because of the different time and space scales involved. Scaling-up methods to shift from small to large scales has long been proposed by functional ecologists and could be useful to better understand and predict Si cycling.

Reactive transport modelling reveals changes in properties of tropical soils subjected to enhanced silicate weathering

by Juliette Glorieux | Yves Godd ris | Sylvain Kuppel | Pierre Delmelle | Earth & Life Institute, UCLouvain | G osciences Environnement Toulouse, CNRS-IRD-UPS-CNES | G osciences Environnement Toulouse, CNRS-IRD-UPS-CNES | Earth & Life Institute, UCLouvain

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Juliette Glorieux

Presenter Preference: Oral presentation

Applied regionally to cropland soils, enhanced silicate weathering (ESW) is advocated as a viable technology for enhancing the consumption of atmospheric CO₂, while also providing ancillary benefits to soil fertility and crop growth. However, important uncertainties remain regarding the short- and long-term effects of silicate addition on weathering rate and soil properties. To address this issue, we adapted and used the reactive transport model WITCH¹ to simulate weathering in a tropical soil (Oxisol) amended annually with 50 t ha⁻¹ of crushed basalt over ten years. We monitored the changes in the soil chemical properties, primary and secondary mineralogy and CO₂ consumption rate. The modelling results confirm that the instantaneous CO₂ consumption rate increases with basalt application. Basalt weathering increases the pH of the soil solution, from acidic to alkaline values, and releases Ca, Mg and K in solution, thus serving as a plant nutrient source. We also found that allophanes may form in the Oxisol in response to dissolution of the basalt's glass and plagioclases. As evidenced in volcanic soils, allophanes typically exhibit a significant potential for organic carbon stabilisation. The formation of allophanes in the Oxisol treated with basalt may improve aggregation processes, water retention and hydraulic conductivity, but may decrease phosphate availability further. Our modelling study highlights that the intentional application of basalt to a tropical soil affects various soil properties significantly. The short and long-term impacts of these changes on soil functioning will need to be assessed.

¹Godd ris et al., 2006. GCA 70:1128-1147

Quantifying the loss of silica in the Scheldt river as a result of plastic removal

by Jonas Schoelynck | Silke Van den Eynde | ECOSPHERE Research Group, University of Antwerp, Belgium | ECOSPHERE Research Group, University of Antwerp, Belgium

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Jonas Schoelynck

Presenter Preference: Oral presentation

In recent years, there's been a surge in removing plastic pollution from rivers, yet few studies delve into their unintended catch of organic matter. In the Scheldt river, plastic removal yields mostly common reed (*Phragmites australis*), a significant silica accumulator vital for tidal river functioning. Evaluating silica bycatch during plastic removal informs whether the impact of plastic removal has any impact on estuary silica fluxes.

Sampling occurred monthly for a full year period, at three depths across four locations during full ebb or flood phases. Assessing *P. australis* litter decomposition and silica dissolution from litterbags in the river aided understanding of organic matter's role in estuarine silica cycling.

During all clean-up events together, only 311.6 ± 0.2 g BSi was removed in 50.5 ± 0.1 kgDW organic matter. Extrapolating to the entire river, the average total annual Si flux in transported reed litter was 1242 ± 77 kg BSi year⁻¹, which still is several orders of magnitude lower than the total annual BSi flux. Spatiotemporal variation, however, led sometimes to more substantial fractions. Litterbag experiments show gradual biomass decline (-50% after ~150 days) and fast BSi dissolution (-50% after ~1 week), which explains the low annual Si flux in reed litter.

The research shows that current organic matter removal as a bycatch of plastic removal isn't affecting the Si flux in the Scheldt. The role of reed litter is predominantly quick supply of fresh DSi to the ecosystem, which can be important during periods of low DSi in the channel.

Tracing changes in winter biogeochemical processes in Arctic rivers with amorphous silica precipitation

by Sophie Opfergelt | François Gaspard | Catherine Hirst | Laurence Monin | Juhls Bennet | Anne Morgenstern | Michael Angelopoulos | Paul Overduin | UCLouvain | UCLouvain | Durham University | UCLouvain | AWI | AWI | AWI | AWI

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Sophie Opfergelt

Presenter Preference: Oral presentation

The ice-covered period of large Arctic rivers is shortening. To what extent will this affect biogeochemical processing of key nutrients during winter months? Here we reveal, with silicon isotopes ($\delta^{30}\text{Si}$), a key winter pathway for nutrients under river ice. During colder winter phases in the Lena River catchment, conditions are met for frazil ice accumulation creating microzones. These are conducive for lengthened reaction time for biogeochemical processes under ice. The heavier $\delta^{30}\text{Si}$ values (3.5 ± 0.5 ‰) in river water reflect that $39 \pm 11\%$ of the Lena River discharge went through these microzones. This can be explained by the supersaturation and precipitation of amorphous silica preferentially incorporating the lighter silicon isotopes, leaving the water isotopically heavier. Amorphous silica precipitation concomitant to an increase in ammonium concentration and changes in dissolved organic carbon aromaticity in Lena River water support microbially mediated processing of key nutrients (carbon, nitrogen) in these microzones. In a warming scenario considering shorter ice-covered periods, decreasing winter microbial processes in large Arctic rivers will decrease nitrogen supply to the Arctic Ocean, a key limiting nutrient.

Silicon isotopes as a tool to capture winter biogeochemical processes in permafrost soils

by Maëlle Villani | Catherine Hirst | Eléonore du Bois d'Aische | Maxime Thomas | Erik Lundin | Reiner Giesler | Magnus Mörth | Sophie Opfergelt | Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium | Department of Earth Sciences, Durham University, Durham, United Kingdom | Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium | Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium | Abisko Scientific Research Station, Swedish Polar Research Secretariat, Abisko, Sweden | Climate Impacts Research Centre, Department of Ecology and Environmental Science, Umeå University, Umeå, Sweden | Department of Geological Sciences, Stockholm University, Stockholm, Sweden | Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Maëlle Villani

Presenter Preference: Oral presentation

Silicon isotope fractionation upon amorphous silica precipitation is sensitive to freeze-thaw cycles in arctic soils that are composed of carbon-rich permafrost (i.e. soil layer that remains frozen for at least two consecutive years) covered by an active layer (i.e. soil layer that thaws in summer in freezes in winter). The consequences of permafrost thaw for organic carbon decomposition are mainly studied during the growing season in summer, considering the soil as inert in winter. Here we show that biogeochemical processes involving organic carbon are present in early winter. We couple silicon isotopes with iron and dissolved organic carbon concentration measurements in soil pore water along a natural gradient of permafrost degradation (intact, intermediate, and thawed sites) and on a downstream river in Stordalen (Sweden) collected over two months during late summer and early winter. The data support that: (i) annual freeze-thaw cycles drive soil-water interaction and biogeochemical processes mostly at the intact site; (ii) early winter snowmelt results in soil water infiltration, water table increase and the dissolution of Fe-oxides at the intermediate site; (iii) early winter snow water infiltration increases lateral flow and export of dissolved organic carbon, especially between the thawed site and the downstream river. Combined, we show an extended period of soil-water interaction in early winter that destabilizes iron-organic carbon associations in permafrost soils and increases dissolved organic carbon transport to rivers.

A multi-isotopic study of the role of groundwater in supplying silicon to the ocean: A case study in groundwater from Cardiff, UK.

by Zhe Dong | Katharine Hendry | Hong Chin Ng | Jamie Lewis | David Boon | Christopher Coath | Xiaoning Liu | Gareth Farr | School of Earth Science, University of Bristol | School of Earth Science, University of Bristol | School of Earth Science, University of Bristol | School of Earth Science, University of Bristol | British Geological Survey, Cardiff Office | School of Earth Science, University of Bristol | School of Earth Science, University of Bristol | British Geological Survey, Cardiff Office

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Zhe Dong

Presenter Preference: Oral presentation

Groundwater discharge is a crucial component in supplying various metals and nutrients into the ocean. Here, we carry out the first systematic multi-isotopic analysis of groundwater in Cardiff, UK. Multiple isotopes including stable silicon, magnesium and strontium isotopes and radiogenic strontium isotopes were measured in groundwater, river and estuarine water samples, to investigate (1) processes controlling the groundwater geochemistry, and (2) the role of groundwater in supplying metals and nutrients, especially silicon to the ocean.

The ionic and isotopic data reveal that groundwater geochemistry is influenced by multiple factors. Potential processes that control the groundwater geochemistry include, firstly, the influence of ocean tides. The significant fresh water-seawater mixing trend revealed by the elemental compositions suggests the influence of seawater intrusion. Secondly, the occurrence of carbonate precipitation in groundwaters is indicated by reduced calcium concentrations, as well as the elevated Mg and Sr isotopes. Thirdly, the increased Si concentration and Si isotopes indicates an extra Si source with heavy Si isotopes entering the groundwater, which indicates possible wastewater contamination. Lastly, historic chemistry data show that, after the construction of Cardiff Bay barrage, groundwater chemistry in areas where dewatering actions were conducted have been changing over time.

$^{87}\text{Sr}/^{86}\text{Sr}$ in estuary water is above the freshwater -seawater mixing line, suggesting a third source of Sr in the estuary, which is likely to be the groundwater. Our results reveal that the intricate circumstances could result in complicated groundwater chemistry, and highlight the significant role of groundwater in supplying metals and nutrients into the ocean.

Enhanced Silicate Weathering - A marine perspective for an emerging technique of atmospheric CO₂ removal?

by Winter Bui | Nathalie Roevros | Le Chou | Steeve Bonneville | BGeoSys - Department of Geosciences, Environment & Society Université libre de Bruxelles, Brussels, Belgium | BGeoSys - Department of Geosciences, Environment & Society Université libre de Bruxelles, Brussels, Belgium | BGeoSys - Department of Geosciences, Environment & Society Université libre de Bruxelles, Brussels, Belgium | BGeoSys - Department of Geosciences, Environment & Society Université libre de Bruxelles, Brussels, Belgium

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Winter Bui

Presenter Preference: Poster presentation

Climate change is one of the biggest global challenge of the 21st century and urgently requires ambitious actions to limit global warming. In this context, we address an understudied, yet promising carbon dioxide removal technique (CDR) : enhanced silicate weathering (ESW) in the coastal environment. The core idea of ESW is to apply easily-weatherable silicate minerals - such as olivine - in marine environments conducive to high weathering rates in order to enhance atmospheric CO₂ uptake by increasing the alkalinity of the ocean. Our goal is to explore experimentally the feasibility of ESW under marine, sedimentary conditions, taking advantage of the coastal ocean as a large-scale, natural benthic weathering reactor. To investigate the potential of marine ESW as an approach to sequester atmospheric CO₂, we conducted a geochemical and mineralogical characterisation of the sediment at field sites where silicate minerals are naturally weathered (e.g. Icelandic shelf). Simultaneously, we experimentally studied some factors affecting olivine weathering rates by carrying out controlled lab batch experiments in which olivine is dissolved under close-to-natural conditions. A first set of weathering experiments has been conducted with artificial seawater, investigating the grain size effect of olivine materials from a Norwegian deposit. Further experiments with natural seawater and marine sediments are planned to track olivine weathering reactions under more realistic conditions.

The effect of papyrus and reed wetlands on Si cycling in east African streams

by Patience Ayesiga | Giulia Lodi | Joel Ndayishimiye | Jan Cools | Makarius Ialika | Jonas Schoelynck | ECOSPHERE Research Group, University of Antwerp, Belgium | ECOSPHERE Research Group, University of Antwerp, Belgium | University of Burundi, Burundi | Institute of Environment and Sustainable Development, University of Antwerp, Belgium | Sokoine University of Agriculture, Tanzania | ECOSPHERE Research Group, University of Antwerp, Belgium

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Patience Ayesiga

Presenter Preference: Poster presentation

Wetlands are often dominated by Si-accumulating sedges and grasses. Most of the dissolved silicon (DSi) entering wetlands is first cycled into vegetation, deposited, and released as biogenic silica (BSi) into the sediments. From here, BSi is partially transported further downstream. Hence, wetlands represent an important Si filter between terrestrial and aquatic ecosystems, interacting with river biogeochemistry. Knowledge on tropical wetlands however, is scarce and this study therefore focusses on the Si cycle in three different areas in eastern Africa. The study areas are located within the River Rwizi (Uganda), River Rusizi (Burundi), and River Mara (Tanzania) catchments, which are connected to the Lake Mburo-, Rusizi-, and Serengeti National Parks, respectively.

On its way to Lake Victoria, River Rwizi flows through the southern papyrus (*Cyperus papyrus* L.) wetland of Lake Mburo. River Rusizi flows into Lake Tanganyika, through a reed-dominated wetland (*Phragmites mauritianus* Kunth). River Mara streams through the Mara wetland, dominated by papyrus and common reed (*Phragmites australis* (Cav.) Trin. ex Steud.), before flowing into Lake Victoria.

Water and vegetation samples have been collected in October 2018 and February-March 2024, and analysed for DSi and BSi. Both papyrus and reed are known Si-accumulating species and are expected to have a major influence on the Si cycle. Preliminary results for vegetation indicate high Si accumulation in all plant species with [BSi] up to 5%DW. The first results from water also seem to confirm the vegetation's filtering role as [DSi] are found to decrease going from the rivers into the respective lakes.

The effects of dunite fertilization and precipitation regimes on biogenic silica concentration in the liverwort *Marchantia polymorpha*

by Jonas Schoelynck | Heleen Keirsebelik | Giulia Lodi | Katharina Wilfert | ECOSPHERE Research Group, University of Antwerp, Belgium | ECOSPHERE Research Group, University of Antwerp, Belgium | ECOSPHERE Research Group, University of Antwerp, Belgium | ECOSPHERE Research Group, University of Antwerp, Belgium

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Jonas Schoelynck

Presenter Preference: Poster presentation

Terrestrial plants play a crucial role in the biogeochemical silica cycle by acting as a significant sink for biogenic silica (BSi). While silica uptake in rooted plants has been studied extensively, less is known about unrooted plants such as bryophytes. Earlier research has found silica uptake, biomineralization, and silica deposits within bryophyte tissues. Drivers of Si uptake are however not known. In this study, the model species *Marchantia polymorpha* L. was grown on natural loamy sandy soil containing different dunite grain size fractions (coarse or fine) and experiencing different precipitation regimes (daily or weekly). After exposure for 30 days, three organs (thalli, male, and female gametophytes) were sampled and analyzed colorimetrically for their BSi contents. Although all three organs contained BSi, male gametophytes displayed the highest BSi concentration (0.31-1.77 mg/gDW). Fine dunite application reduced the amount of BSi in all tested organs compared to coarse dunite. No differences in BSi concentration were found between the coarse dunite treatment and the control group. Differences in precipitation regimes were only significant ($p < 0.01$) for the control group to which no dunite was applied. The weekly precipitation regime increased the BSi concentration in all three organs. This study shows that *M. polymorpha* absorbs dissolved silica and deposits it as BSi within its tissue. The deposition varies among organs, consistent with prior research that also describes an increased accumulation in male gametophytes. The experiment has also shown that mineral silica in the soil and precipitation regimes steer Si uptake in liverworts, similar to higher plants.

Rocking heathlands: Exploring silicate rock powder as an alternative to liming in the restoration of acidified heathlands

by Sophia Findeisen | Antwerp University

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

Presenter Name: Sophia Findeisen

Presenter Preference: Poster presentation

High levels of atmospheric acid deposition in Western Europe has caused soil acidification in heathlands, impacting plant and soil biodiversity. Traditional dolomite liming, although effective in restoring base saturation, often results in undesirable pH spikes and excess release of calcium and magnesium. In this study, we explored a novel alternative, slow-release silicate (Si) rock powder, comparing its effects on soil chemistry and the soil microbiome to traditional liming in acidified heathlands nine years after application. Our study comprised 40 large research plots equally divided between wet and dry heathlands, with four treatments nested within: the application of Dolokal (liming with dolomite), Soilfeed (rock powder, K-feldspar/biotite) Biolit (rock powder, chlorite/muscovite), or no application (control). All application treatments caused significant changes in soil chemistry, with largest effects in soils with lowest cation exchange capacity (CEC) (i.e. wet heathlands). Liming resulted in a large increase in soil pH and base saturation and significantly altered bacterial and fungal communities. In contrast, rock powder had minimal impact on soil microbiota. The modest but discernible effects of rock powder treatment suggest potential for improving soil properties without disrupting the existing system. Conversely, liming resulted in a large increase in soil pH triggering shifts towards more grassland-like habitat. This study discusses the potential of Si rock powder application as an alternative to liming for mitigating soil acidification for heathland restoration.

Silicon isotopes in juvenile and mature *Cyperus papyrus* from the Okavango Delta, Botswana

by Giulia Lodi | Julia Cooke | Rebecca A. Pickering | Lucie Cassarino | Mike Murray-Hudson | Keatshephile Mosimane | Daniel J. Conley | University of Antwerp | The Open University | Lund University | Université de Bretagne Occidentale | Okavango Research Institute | Okavango Research Institute | Lund University

Topic: session 5: Silica Dynamics in Terrestrial Ecosystems: Unveiling the Interplay between Soil and Plant Systems

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Presenter Preference: Poster presentation

The three most abundant stable isotopes of Silicon (Si), ^{28}Si , ^{29}Si , and ^{30}Si , all occur in plants. Isotope studies are a potential tool to explore uptake and function of plant Si, and it is a developing field. However, there is a lack of studies from natural environments, and species from the African continent, and all plant parts including reproductive structures. In this study, naturally grown papyrus plants were sampled from the Okavango Delta and divided into five organs, i.e. umbel, culm, scales, rhizome, and roots. Samples were analysed for TN, TOC, BSi, TP concentrations, and for Si isotopes. Each organ of papyrus is represented by two samples, one from juvenile tissue and one mature (apart from the roots where age is difficult to determine). The study confirms that papyrus is a high Si-accumulating species, with BSi ranging from 0.88% in rhizomes to 6.61% in roots. High Si precipitation in the roots leads to an enrichment in heavy Si isotopes in the residual mobile Si pool, as light Si isotopes precipitate in phytoliths in the roots, even though in this study phytoliths were identified for all organs except for roots. In papyrus, shoot organs gradually become enriched in heavy Si isotopes along the transpiration stream, with an increase in heavy isotopes from rhizomes to scales, culm, and umbel, same pattern that has been observed for other plants in literature.