3 Stable and radiogenic isotope geochemistry

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3.1 Clay-mineral extraction and purification for reconstructing silicate weathering

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By serving as a negative feedback mechanism capable of attenuating climate and carbon-cycle perturbations, silicate weathering has acted as a major driver of global climate stability throughout Earth’s history. However, it is currently not possible to accurately describe silicate weathering responses to past climate changes, primarily due to a lack of direct observations regarding temperature and hydrologic conditions at which the process took place. In this context, we suggest that triple-oxygen isotope compositions (Δ¹⁷O and Δ¹⁸O) of pedogenic clays can provide such direct paleotemperature and paleohydrology constraints.

To harness this proxy effectively, the initial step necessitates extraction of high-purity clay-mineral fractions from soils and sediments. Indeed, sample purity is critical to the precise determination of Δ¹⁷O and Δ¹⁸O, since the presence of other oxygen-bearing phases, whether organic or inorganic, may significantly shift measured isotope compositions, thereby leading to potentially erroneous interpretations. In this respect, we developed a clay purification protocol that combines different chemical and physical steps. Chemical steps aim to remove organic matter, carbonates, soluble sulfates, salts, and iron oxides, whereas physical steps are indispensable for the elimination of micro quartz particles. We place particular emphasis on the removal of oxides and quartz; we adopt and subsequently compare three distinct techniques for oxide removal and two for quartz removal.

This protocol successfully separates clays with high purity from soils and sediments samples, as confirmed by petrographic techniques (i.e., XRD). Such an achievement will contribute to more precise and accurate triple-oxygen isotope analysis of clays from natural samples, thus substantially mitigating the potential for misinterpretations and enhancing our capacity to ascertain the temperature and hydrological conditions governing silicate weathering events in Earth’s geologic past. Finally, we will present preliminary clay triple-oxygen isotope results from well constrained modern soil samples.
3.2 Spatial and temporal isotopic changes in Cordilleran magmatism: The Antarctic Peninsula, an alternative case

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Spatial and temporal changes in the radiogenic isotopic composition of arc magmatism is a fundamental tool for studying the interactions between the crust and the lithosphere in convergent margins (e.g. Ducea and Barton, 2007; Chapman et al., 2017). These changes have been used to interpret diverse tectonic phenomena including continental subduction (e.g. Bouilhol et al., 2013), subduction erosion (Kay et al., 2005), delamination (Kay et al., 1994), changes in crustal thickness (Haschke et al., 2002), and lithospheric extension (DePaolo and Daley, 2000) among others. Spatial trends in the radiogenic isotopic composition of arc magmatism have been interpreted as an intrinsic feature of Cordilleran-style orogenic systems (Chapman et al., 2017) and likely imply a fundamental change in the dynamics governing the formation of their igneous rocks. A consistent trend has been observed in arc magmas from the Central Andes, U.S. Cordillera and Tibet, whereby more isotopically juvenile compositions are encountered near the trench (i.e. radiogenic or enriched 176Hf/177Hf and 143Nd/144Nd) and increasingly evolved landward (unradiogenic or depleted 176Hf/177Hf and 143Nd/144Nd; Chapman et al., 2017). Furthermore, these Cordilleran systems are well-studied examples of both modern and ancient active margins, which suggest that this spatial-compositional trend is long-lived and persists throughout the life of a given continental arc. Additionally, these spatial trends are observed in a broad spectrum of geochemical compositions. These spatial isotopic trends for Cordilleran magmatism have been explained by the mantle lithosphere thinning towards the trench due to sub-lithospheric processes, such as delamination or subduction erosion, allowing the magmas to be sourced from isotopically juvenile asthenospheric mantle with minimal lithospheric interaction. Conversely, isotopically evolved arc magmas are founded landward, where the absence of lithospheric thinning permits the development of a thicker continental mantle lithosphere, producing isotopically evolved arc magmas. The Antarctic Peninsula represents the southern continuation of the Andes convergent margin and although difficult access has partially hindered its understanding and characterisation, a plethora of recent data now permits a more robust characterisation of this Mesozoic-Cenozoic continental margin (e.g. Bastías et al., 2021, 2022; Riley et al., 2020, 2022; Burton-Johnson et al., 2023). The Antarctic Peninsula thus makes an excellent natural laboratory for both testing and revising the dynamics in Cordilleran convergent margins. We combine these existing datasets with newly presented geochemistry (elemental and isotopic) and geochronology from the Cenozoic arc record, providing key information for a poorly constrained period of the Antarctic Peninsula. We use these combined datasets to test the model proposed for other Cordilleran-active margins and examine the magmatic and tectonic history of the Antarctic Peninsula in comparison with the Central Andes, U.S. Cordillera and Tibet (cf Chapman et al., 2017).

REFERENCES

3.3
A detailed look at organic carbon cycling across the Early Triassic (Smithian - Spathian) using compound specific n-alkane carbon isotope compositions


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After the largest mass extinction in Earth’s history at the Permian-Triassic boundary ca. 252 million years ago, the Early Triassic epoch is noted to have a series of dramatic carbon isotope excursions. The underlying factors driving these isotopic fluctuations remain a matter of contention consequent to limited data differentiating between terrestrial and marine carbon cycles. This study concentrates on the Smithian-Spathian boundary (SSB), around 2 million years after the commencement of carbon cycle disruptions at the Permian-Triassic boundary, which is marked by a global positive $\delta^{13}C_{\text{bulk}}$ excursion of approximately 5 ‰ (e.g., Widmann et al 2020). Our study focuses on analyses of organic-rich shales from Spitsbergen for n-alkane molecular distributions and their compound-specific carbon isotopic compositions ($\delta^{13}C_{\text{n-alkane}}$). Measured $\delta^{13}C_{\text{n-alkane}}$ values suggest that both marine and terrestrial systems were impacted by carbon cycle disturbances as evidenced by >6 ‰ fluctuations in associated biomarker n-alkane records. For the marine system, $\delta^{13}C$ values predominantly mirror variations in dissolved organic carbon $\delta^{13}C$, influenced by local fluvial influx, atmospheric carbon dioxide levels, primary productivity, and changes in temperature. Terrestrial ecosystems also experienced notable changes as vegetation shifted from lycophytes to gymnosperms (Hermann et al. 2011), influencing the overall carbon isotopic fractionation between vegetation and atmospheric CO$_2$. Overall, these findings shed light on the complex interplay between terrestrial and marine carbon cycle dynamics during the Smithian-Spathian in the Early Triassic.

REFERENCES
Formation of subcontinental lithospheric mantle was enabled by subduction driven recycling of surface derived material in the Paleoarchean

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Earth is unique among the rocky planets in the solar system in terms of having a bimodal distribution of thick felsic continental crust and thin mafic oceanic crust. Formation and stabilization of this thick felsic crust was a fundamental process in Earth’s history as it lead to formation of a stable landmass on the early Earth. Coupled formation, evolution and stabilization of a thick subcontinental lithospheric mantle (SCLM) was critical in ensuring the stability of the thick continental crust. Hence, a way to study the evolution of Archean felsic crust is to understand the co-evolution of the lithospheric mantle beneath it. Large-scale dyke swarms that intrude Archean cratons can provide information on the formation of the sub crustonic lithosphere and efficiently track its secular evolution (Bartels et al., 2015; Pandey & Paul, 2022). Dyke swarms that intruded the Paleoarchean felsic crustal nucleus of the Singhbhum Craton are of Neoarchean to Paleoproterozoic age. The parental magma of these mafic-ultramafic dykes were enriched in incompatible elements that indicate the presence of a “crustal component” in their source (Pandey et al., 2021). Mobility and stable isotope fractionation of the redox-sensitive element Mo combined with radiogenic isotopes (Nd, Hf), have the potential to track the petrogenesis of the different dyke swarms and the composition of their source(s) (Skora et al., 2017; Ahmad et al., 2022).

Four dyke swarms that intruded between 2.8 Ga and 1.765 Ga were studied to derive constraints on the chemical evolution of their mantle source region. Trace element abundance combined with stable Mo and radiogenic Hf and Nd isotope signatures of these primitive dyke swarms indicate that the crustal enrichment signature in the dykes’ parental magma is not due to assimilation and fractional crystallization processes during magma emplacement, but rather due to mantle source enrichment. The covariation of (δ98/95Mo with immobile element ratios indicate the involvement of hydrous melts originating from surface-derived materials, in the metasomatism of dykes’ parental magma source region in the lithospheric mantle. A redox dependent multicomponent element (Mo, Ce) and isotope (δMo, εHf, εNd) mixing model affirms that the metasomatism of lithosphere underlying the Singhbhum Craton was facilitated by low degree anoxic melts coming from sediments and hydrated mafic crust, during their subduction driven recycling. The mixing model further predicts that the Singhbhum cratonic lithosphere was metasomatized in the Paleoarchean around 3.44 Ga, which is coeval with the formation of Singhbhum granitoids.

REFERENCES
3.5
Dissolved chromium concentrations and stable isotopes in marine pore waters from the equatorial Pacific Ocean

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The interaction between pore water and sediments can result in the scavenging or release of elements, influencing sedimentary and water column chemistry. Therefore, pore water can play a significant role in the chemical composition of marine sediments and deep seawater, with potential implications for sediment proxies. Cr concentration ([Cr]) and stable isotope composition (δ⁵³Cr) have been used as a paleoproxy for atmospheric oxygen content from records in sedimentary deposits e.g. (Frei et al., 2009; Planavsky et al., 2018). This study focuses on the analysis of pore water to better understand the processes driving isotopic shifts and Cr dynamics in marine sediments to refine our understanding of Cr behavior as a paleoproxy.

Early water column-based studies suggested benthic fluxes of Cr play a significant role in shaping dissolved Cr distributions (e.g. Achterberg & Van den Berg, 1997; Jeandel & Minster, 1987; Murray et al., 1983), although pore water data to assess these suggestions are scarce. Recent pore water data, showing fluxes of Cr into deep waters (Bruggmann et al., 2023; Janssen et al., 2021) help to give direct constraints on the magnitude of benthic fluxes and their impact on the oceanic Cr cycle; however, these localized data cover only small sections of the global ocean. To address this knowledge gap, three sets of sediment cores paired with water column depth profiles were collected during the Kilo Moana expedition KM2012 in October and November 2020 in the equatorial Pacific. These sites were chosen to cover sedimentary regimes of high spatial significance in the global ocean.

Our preliminary results indicate that pore water [Cr] range from 5.0 to 7.3 nmol/kg and δ⁵³Cr varies from 0.43 ± 0.06 to 0.68 ± 0.08 ‰ (2SEM). These data indicate higher and isotopically lighter pore water [Cr] and δ⁵³Cr, respectively, compared to seawater, in agreement with limited available field data (Janssen et al., 2021). These data, in combination with available literature data, give an opportunity to assess controls on benthic Cr fluxes as well as their significance across diverse sediment regimes. This provides new insights into the interactions governing Cr cycling between sediments, seawater, and pore water, contributing to a more comprehensive understanding of how Cr records are preserved in sedimentary rocks and helping improve future Cr paleoproxy applications.

REFERENCES
3.6 Natural gas of radiolytic origin: Insights from carbon isotopes

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Natural gas is extracted from conventional and unconventional reservoirs, and the composition and isotopic signatures of gas components provide useful proxies of gas origin and maturity. Several types of gases have been distinguished so far: microbial (primary and secondary), thermogenic (early mature, oil-associated, late mature), and abiotic (Milkov et al., 2020). However, in many cases, assessing the origin may be hindered due to different post-sedimentary processes like mixing, migration, sorption, etc. (e.g., Bernard et al., 1976; Bernard et al., 1977; Chung et al., 1988; Milkov and Etiope, 2018).

Additionally, a recent irradiation laboratory experiment conducted by Silva et al. (2019) demonstrated the possibility of the production of measurable quantities of radiolytic gases including methane, ethane, and propane with very distinct δ13C values. This leads to the question: Does the process of radiolysis create considerable amounts of radiolytic natural gases? For example, the Alum Shale formation (Mid-Cambrian to Tremadoc, Northern Europe) is a prominent example of uranium-rich black shales, that were formed ~500 Ma ago and where the radiation dose obtained by the organic matter is significant. The irradiation in the shale causes changes in the structure and properties of organic matter, such as an increase in aromaticity, condensation degree, vitrinite reflectance, and, to some extent, carbon isotope signatures. These changes are explained by radiation-initiated cross-linking of organic molecules that results in aromatization and polymerization in the kerogens (Schovsbo, 2002; Lewan & Buchardt, 1989; Yang et al., 2019).

Our study (Naumenko-Dèzes et al., 2022) investigated whether radiolytic methane, ethane, and propane constitute a previously overlooked component of natural gas, especially in organic-rich shale gas plays. We demonstrate that light alkanes derived from the irradiation of kerogen and oil make a non-negligible contribution to natural gas mixtures from unconventional hydrocarbon reservoirs. By using an isotopic maturation-mixing model on a large set of natural gas data we quantify the effect of the admixture of light alkanes of radiolytic origin to gases of thermogenic and microbial origin. We also demonstrate that the resulting isotope signatures can lead to misinterpretation of gas origin and maturation levels and we provide a novel explanation of the so-called isotope reversals in natural gas from unconventional hydrocarbon reservoirs. We conclude that radiolytic gas derived from organic matter constitutes a previously not recognized type of natural gas, that needs to be considered especially in organic-rich unconventional hydrocarbon reservoirs that frequently contain uranium (U) in substantial quantities.

REFERENCES
Yang, S.Y., Schulz, H.M., Schovsbo, N. and Mayanna, S., 2019. The organic geochemistry of “Kolm”, a unique analogue for the understanding of molecular changes after significant uranium irradiation. International Journal of Coal Geology, 209: 89-93
3.7

Use of Rb-Sr and Sm-Nd isotope systems in determining diamond crystallisation ages

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Diamonds and their inclusions provide rare, direct and unaltered insights into deep Earth geochemical and geodynamic processes. Diamond crystallisation ages are an essential tool in determining when such processes occur, as well as in better understanding how and why diamonds form. Dating the crystallisation of diamond relies on mineral/fluid inclusions, which are protected - by their inert diamond host - from isotopic exchange with the surrounding mantle. Yet, Rb-Sr and Sm-Nd isotope systematics of silicate inclusions in diamonds rarely yield consistent ages. Further, radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are often unsupported by their low Rb/Sr ratios (Smit et al. 2022 and references therein).

Here, we present Rb-Sr and Sm-Nd isotopic data of lherzolitic clinopyroxene and garnet inclusions of diamonds from Victor, Canada. The main inclusion population yields a Sm-Nd isochron age within error of the $\sim 720$ Ma Re-Os age of sulphide inclusions of diamonds from the same mine, indicating that diamond crystallisation was likely triggered by the Franklin magmatic event (Aulbach et al. 2018). Rb-Sr isotope systematics appear to suffer from various degrees of Rb loss and indicate a younger age. The cause of the Rb-Sr complexity and its implications will be discussed in the context of diamond exploration.

REFERENCES
Assessing mechanisms of argon isotope redistribution in muscovite:
Preliminary results from the Black Hills, South Dakota

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Several key assumptions form the basis of extracting continuous thermal history information from the Ar isotopic compositions of minerals. Recent in-situ ⁴⁰Ar/³⁹Ar and geochemical analyses have shown that argon distributions are frequently a consequence of fluid-associated retrograde reactions, even in gem-quality mica (Naumenko-Dèzes et al., 2021). Mica can retain ⁴⁰Ar/³⁹Ar crystallisation ages at temperatures above 500°C (Airaghi et al., 2018), despite predicted closure temperatures. However, retrograde re-equilibration often occurs, rendering mica useful for hygrochronometry (Villa, 2016). We test the hypothesis that diffusion profiles in white mica can remain over geological timescales, despite the effects of partial retrograde re-equilibration.

A Mesoproterozoic metasedimentary sequence is intruded by a granitic core in the Black Hills. The metasedimentary rocks yield white mica ⁴⁰Ar/³⁹Ar total-fusion dates that increase with distance from the granite, span several 100 Ma and have been interpreted to record cooling (Dahl & Foland 2008). However, the role of fluid interaction on the Ar isotopic compositions has not been thoroughly assessed. To test the hypothesis, we have re-sampled the metasedimentary units and the Harney Peak Granite. White micas are initially classified using optical light petrology and QEMSCAN, before detailed characterisation using EPMA, EBSD, TEM, SIMS - δ¹⁸O and in-situ Rb-Sr dating to add a petrographic and temporal context for the in-situ Ar isotopic data. In-situ Ar isotope analyses will be compared to Ar isotopic data acquired using furnace step-heating to assess the causes of inflexions in Arrhenius trajectories. By studying a range of textures to provide recommendations for interpreting ⁴⁰Ar/³⁹Ar mica ages.

REFERENCES
P 3.2
Resolving Earth’s Lead Paradox

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Following the accretion and differentiation of the Earth into core and silicate mantle, the formation of crust initiated a process of depletion in incompatible elements via partial melting of the mantle. With the posterior onset of plate tectonics, the mass exchange between geochemical reservoirs drives the continuous compositional evolution of the crust and mantle, and the bio-chemical cycles that ultimately control Earth’s surface habitability.

Amongst the diverse isotope systems, the U-Th-Pb system has been widely employed to study our planet’s differentiation and evolutionary history. Its key significance is based on the refractory and lithophile behaviour of U-Th and the volatile and chalcophile behaviour of Pb, their different oxidation states, and the different half-lives of the radioactive parent isotopes (²³⁸U→²⁰⁶Pb; t₁/₂=4.468 Gyr; ²³⁵U→²⁰⁷Pb; t₁/₂=703.8 Myr; ²³²Th→²⁰⁸Pb; t₁/₂=14.05 Gyr).

Bulk Silicate Earth (BSE) should plot on the so-called Geochron (Patterson 1956) in a ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁷Pb/²⁰⁴Pb plot. However, the Pb isotope ratios of rocks from mantle and crustal reservoirs both lie on the right side of the Geochron. This skewed distribution was termed the 1st Pb Paradox (e.g., Hofmann, 2008; Burton et al., 2012).

Multiple solutions to this apparent paradox have been proposed throughout the years. The most straightforward solution would be the existence of a reservoir that counterbalances the radiogenic accessible reservoirs (e.g., Hofmann, 2008). Unradiogenic Pb (i.e., low ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb) is found in abyssal and cratonic peridotites (e.g., Burton et al., 2012; Warren and Shirey, 2012; Aulbach et al., 2019), indicating that Earth asthenospheric or subcontinental lithospheric mantle may be significant repositories for unradiogenic Pb.

A review of Pb and U contents and Pb isotope ratios in mineral phases (silicates and sulphides) of mantle xenoliths and abyssal peridotites from the literature will be presented to assess - through mass balance modelling - the potential of the asthenospheric and lithospheric mantle as the unradiogenic Pb reservoir.

REFERENCES
P 3.3
Constraining oceanic lithosphere depletion through non-traditional stable isotope analyses

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Archaean cratonic harzburgites are highly depleted in incompatible elements, a feature that resulted from major melt depletion creating the depleted, buoyant lithospheric mantle beneath Archaean cratonic nuclei. Yet, the mantle unit (harzburgites/dunites) of the Papua New Guinea (PNG) ophiolites are some of the most depleted rocks, but are only Cretaceous in age (Barrett et al., 2022). We look to isolate the contribution partial melting had to create such depleted rocks in a modern setting by presenting a model of Fe-Ti isotopic fractionation through two PNG ophiolite sequences.

The PNG ophiolites consist of the Marum Ophiolite (upper mantle unit + cumulates) and the Papuan Ultramafic Belt (upper mantle unit + cumulates + basalt) and record cogenetic sequences based on major and trace element compositions (Davies and Jaques, 1984). Based on known mineral modes and Fe-Ti concentrations, we develop a theoretical model for the expected Fe-Ti isotope fractionation and will test this against analyses of the natural rock record. As Ti isotope systematics readily record magmatic differentiation, we expect to see a correlation with typical differentiation indices (e.g. MgO) (Millet et al., 2016; Storck et al., 2023). Further, we expect heavier Fe isotope ratios with melt evolution, consequently becoming more enriched in Fe\textsuperscript{3+}, since earlier forming minerals favour Fe\textsuperscript{2+} and lighter isotopes (Williams et al., 2018).

Future work in the project will focus on how fluid activity may cause further depletion.

REFERENCES
Tracing the source of fluids in the Archean crust factory: an example from the Lewisian Gneiss Complex (NW Scotland)

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In the early Earth, significant production of sodic continental crust (i.e., trondhjemite–tonalite–granodiorite—TTG) occurred during the Archean eon by partial melting of basaltic (mafic) crust, at depth between 25 and 50 kilometres. Fluid-fluxed melting has recently been invoked as an important trigger for TTGs formation1, but the geodynamic settings and processes involved are highly debated. Important questions about the source of the melt-triggering fluids and how they were transported to deeper crustal levels have remained difficult to ascertain.

In this contribution, we combine petrographic observations, major and trace element whole-rock geochemical data, in-situ oxygen isotope analysis, and U-Pb dating of zircon from TTG gneisses from the Lewisian Gneiss Complex (LGC), in NW Scotland, to highlight the differences between two distinct groups of TTGs present in this region: hornblende-bearing (i.e., central region of the LGC) and biotite-bearing (northern and southern regions) TTGs.

Our results show that hornblende-TTGs are commonly primitive, Na-rich tonalitic magmas derived from partial melting of low-K mafic rocks and yield δ18O values of 5–6‰ indicating that these magmas were hydrated by mantle-derived fluids rather than from a sedimentary or hydrothermal source. By contrast, less sodic, more "mature", biotite-TTGs reflect more evolved trondhjemite to granodiorite compositions. The biotite-TTGs yield δ18O values that, in places, are slightly above that of the average mantle zircon (5.3 ± 0.6‰ 2SD)2. This may indicate that TTG magma production in the northern and southern regions of the Lewisian Gneiss Complex was triggered by mantle-derived fluids that were previously contaminated with a supracrustal source to account for the small positive O isotopic excursions. These results highlight the hybrid sources of fluids which play an important role in the evolution of intracrustal recycling and crust-mantle interaction during crust formation in the Archean.

REFERENCES
P 3.5
Optimizing Experimental Conditions for Accurate Oxygen Diffusion Measurements in Biominerals

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Oxygen isotope compositions from pristine biominerals are the foundational proxies for paleoseawater temperatures spanning from the Paleozoic to the present. Recent research; however, has identified potential temperature biases introduced by low-temperature oxygen solid-state diffusion, particularly in calcitic biominerals e.g., foraminifera (Cisneros-Lazaro, et al., 2022; Adams et al., 2023). The extent of this diffusion-related effect on the paleotemperature record remains incompletely assessed due to challenges in determining accurate diffusion coefficients in (bio)minerals at low temperatures, yet its significance even under ambient ocean burial conditions may be substantial.

In this study, we address the formidable challenges of measuring and understanding diffusive phenomena in mineral systems at low temperatures (≤ 300 °C). We incubated foraminifera tests in autoclaves in four oxygen isotope exchange mediums: (1) 18O-labeled calcite-saturated liquid water between 30–190 °C, (2) 18O-labeled Na2CO3 fluids at 190–300 °C, (3) 97 atom% H218O vapour at 190–300 °C, and (4) C18O2 gas at 190–300 °C. The resulting rates and ultrastructural patterns of isotope exchange in foraminifera tests were examined using bulk isotope measurements and NanoSIMS mapping.

At low temperatures no recrystallization took place and the results were consistent with a grain-boundary diffusion mechanism. However, at higher temperatures in aqueous fluids, biomineral nanocrystallites become prone to recrystallization despite calcite-saturated incubation fluids. In contrast, foraminifera tests did not recrystallize at high temperatures in water-vapour or CO2, but NanoSIMS mapping revealed isotope exchange patterns that differed from lower temperature experiments. While the rates of diffusive processes have been conventionally considered too slow to be detectable at low temperatures, our experiments demonstrate their capacity to influence isotopic compositions in biocarbonate minerals even over short experimental timeframes. By exploring a range of experimental conditions, we illuminate the complexity of these processes and their implications for accurate paleoclimatic interpretations.

REFERENCES
Productivity changes from the Holocene to the ice age evidenced by chromium isotopes

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Chromium (Cr) and the processes controlling its stable isotope fractionation are sensitive to redox conditions and/or biological productivity in modern marine environments. However, there is an ongoing debate related to the preservation and interpretation of Cr isotope compositions (δ⁵³Cr) in the sedimentary record. While the database on Cr isotope compositions in seawater, as well as in ancient sedimentary rocks is growing, the Cr isotope system has yet barely been applied to marine sediments from Earth’s recent past. Such sedimentary records can provide useful archives to explore Cr isotope systematics across arguably well-characterised climate intervals of the past, such as the Last Glacial Maximum (LGM). Here, we provide a new data set on Cr isotope compositions in a marine sediment core from the Crozet Plateau (MD19-3580) to unravel the biogeochemical controls on the δ⁵³Cr values since the last ice age.

The downcore sedimentary leachate data show that δ⁵³Cr values generally follow sea surface temperatures (SST). The highest δ⁵³Cr values are found in sediments deposited during the Holocene, where the biogenic carbonate content is at its maximum. Samples deposited during the LGM, on the other hand, show the lowest δ⁵³Cr values. These data can be interpreted as primarily reflecting changes in biogenic productivity, rather than changes in deep ocean oxygenation, suggesting that changes in export production exert a strong control on the marine biogeochemical cycling of Cr in modern and past environments.
P 3.7
Stable and radiogenic isotopes as weathering regime proxies: The source-to-sink response to the Paleocene-Eocene Thermal Maximum in the Spanish Pyrenees

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Global warming and the associated hydrological cycle variations are known to disrupt the weathering regime over geological timescales. Enhanced weathering and erosion, which constitute denudation, serve as feedback mechanisms for regulating Earth’s temperature over multi-million-year timescales. Weathering can draw down CO$_2$ from the atmosphere, while enhanced physical transport of clay particles can accelerate organic carbon sedimentation and, hence, carbon sequestration. In this study, we aimed to uncover changes to the denudation regime accompanying a massive climatic disturbance in deep time, the Paleocene-Eocene Thermal Maximum (PETM). The global warming of 5-8 °C due to the PETM has been documented to have increased the magnitude and intensity of precipitation events in the Spanish Pyrenees. But how did weathering respond to such a climatic and hydrological disturbance?

We investigated the lithium (Li), hafnium (Hf), and neodymium (Nd) isotopic composition of the <2 μm clay size-fraction in three sections in the Spanish Pyrenees, from source to sink: the Esplugafreda, Campo, and Zumaia localities. The Li isotope record at Esplugafreda in the terrestrial domain shows a positive δ$^{7}$Li excursion during the onset and body of the event (syn-PETM) and a negative excursion during the recovery (post-PETM), with no variation in the ΔeHf, the εHf corrected for provenance changes with the εNd record. The Campo transitional section shows a negative Li isotope excursion during the body of the event. In the Zumaia deep marine section, the body of the event was characterized by a positive δ$^{7}$Li excursion, coeval with a negative excursion in ΔeHf.

Overall, these results suggest a relative decrease in weathering (W) to denudation (D = W+E, where E is erosion) from pre-PETM to syn-PETM. The terrestrial section (Esplugafreda) indicates a local decrease in clay formation relative to erosion (E). The transitional section (Campo) integrates over a larger catchment area and could reflect an absolute increase in weathering. Finally, the “sink” deep-marine (Zumaia) section could indicate a relative decrease in regional weathering to denudation (W/D), consistent with the positive Li isotope and negative ΔεHf excursions. This source-to-sink approach suggests that, although weathering in the Pyrenees increased in absolute amounts during the PETM, the amount of physical erosion of sediments increased substantially more than the chemical weathering, controlling the denudation regime in the region. These changes imply a trend towards a kinetically-limited regime in the region, with local variations in the weathering efficiency. The next step in this project will aim to quantify the relative importance of weathering to erosion during the PETM and, therefore, the share of each of these denudational processes in the climate recovery.