ISONOSE ISOTOPIC TOOLS AS NOVEL SENSORS OF EARTH SURFACE RESOURCES

Metal Stable Isotope Geochemistry Workshop

Final Workshop of the ITN IsoNose

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The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

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17:45 - 18:00	**Marie Küssner**	17:45 - 18:00	**Rasesh Pokharel**		
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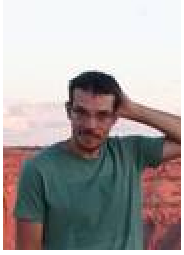
20:00 – 22:00	Dinner	19:30 –	Wine tasting		
		20:00 – 22:00	Dinner		

Organising Committee



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Invited Talks

Isotope-enabled reactive transport models of critical zone structure and reactivity

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The chemical weathering rates and patterns which shape the structure of the Critical Zone are often inferred from fluid samples that are the flux-weighted average of these heterogeneous systems. Metal stable isotope ratios of these dissolved solutes are utilized to partition between sources and a suite of reactive pathways with characteristic mass-dependent partitioning. While much work has been devoted to the identification and parameterization of these fractionating reactions, samples collected from physically heterogeneous CZ systems are often still interpreted through simplified distillation models that inherently assume a homogeneous fluid residence time. Here, I will present the application of two modeling approaches designed to treat the relationship between fractionation and flow-field heterogeneity in open, through-flowing physically heterogeneous systems. The first is an analytical derivation which merges a non-uniform fluid travel time with a fractionating reaction, resulting in a modified Rayleigh equation. The second is a multi-component isotope-enabled numerical reactive transport model. The two approaches both demonstrate that the observed fractionation factor is predictably linked to the fluid residence time distribution.

Metal isotopes in the hydrological cycle: Where do we go?

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This talk aims at giving an overview of where we are, and where we need to move forward, in the use of metal isotopes to better constrain water rock interactions at the global scale.

Metal isotopes are fractionated along the hydrological cycles and a precise measure of their abundance adds constraints on the water-rock interaction processes.

New isotopic tracers must be developed showing which isotopes are fractionated by weathering and/or transport processes. The measurement of « insoluble » elements is particularly challenging as they may exist in very small amounts in water and may be affected by colloids.

The isotopic composition of river sediments has to be more systematically investigated, in particular in large river sediments that integrate over large surface areas and will survive once deposited in sedimentary basins, thus providing geological archives. The drawback of using sediments is that they have a longer residence time in watershed compared to the dissolved products of weathering and may contain a significant bedrock component.

More work should be also be conducted experimentally to constrain the fractionating mechanisms at the crystal scale.

Finally, one of the most promising avenues is to couple different isotopic systems in catchments whose hydrology and geomorphology is well constrained. This can typically be done in CZOs by refining the frequency of sampling.

We will exemplify these different promising directions.

Seasonal variation of lithium and magnesium isotopes in the dissolved and suspended load of the Amazon River Basin

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The volume of water and suspended sediment delivered to the ocean from the Amazon River is significantly different between the dry and wet seasons. Discharge is 50% lower in November (dry season than it is in June (wet season), which increases the residence time of water in the hydrological system and enhances the extent fluid-rock interactions. Both lithium (Li) and magnesium (Mg) isotopes respond to changes in weathering conditions such as the formation and dissolution of secondary minerals that are intimately linked to these seasonal weather variations. As the Amazon supplies ~20% of the freshwater input to the ocean, it is crucial to assess the effects of these seasonal variations on Li and Mg concentrations and isotope compositions (δ^7Li and δ^{26}Mg) to properly interpret past variations in the δ^7Li and δ^{26}Mg composition of seawater. In support of this, we have sampled the dissolved and suspended load in the Amazon River basin during both the dry and wet season. The δ^7Li value of the dissolved load is higher in the dry season than it is in the wet season ($\delta^7\mathrm{Li}_{\mathrm{Nov}} - \delta^7\mathrm{Li}_{\mathrm{Jun}}$ = 0.7 to 8.7‰) both in the main stem of the Amazon and its tributaries, but there is little different in the δ^{26}Mg value of the dissolved phase ($\delta^{26}\mathrm{Mg}_{\mathrm{Nov}} - \delta^{26}\mathrm{Mg}_{\mathrm{Jun}}$ = -0.10 to 0.49‰). The difference in the δ^7Li values can largely be explained by secondary mineral formation in the dry season as suggested by Al/Li and Li/Na ratios, rather than a change in the source of Li. The Li and Mg isotope composition of the suspended material is not significantly affected by seasonal variations. Our results demonstrate that seasonal changes in the Li isotope composition of river water may be important for setting the Li isotopic composition of seawater. On the contrary, not impacted by secondary minerals formation, seasonal variations in the Mg isotopic composition of river water are insignificant.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Metal stable isotope tracers of the hydrological cycle

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The release and transport of metals from weathering to the oceans is a major control on the chemical composition of seawater that, in turn, regulates primary productivity and uptake of atmospheric carbon dioxide. For this reason, knowledge of the controls on the weathering flux to the oceans is critical for assessing how climate has varied in the past, and for predicting how it may change in the future. Weathering flux estimates for many elements, however, can vary by orders of magnitude, and there is an urgent need to better quantify fluxes at the catchment scale and determine the processes that modify weathering signals as water moves through soils into rivers and into the ocean.

The aim of this talk is to demonstrate the importance of the development of new instrumentation and techniques for the accurate and precise analysis of metal stable isotopes for addressing these issues. I will show for example that the lithium isotopic composition of river water allows the relative contributions of metals released from carbonate vs silicate sources to be quantified, and has provided new information on past changes in weathering intensity that can be linked to changes in Earth's climate. By contrast, analyses of molybdenum isotopes can be used to assess redox controls on weathering fluxes. Especially, I will highlight the contributions of ISONOSE researchers to the generation of new knowledge in this emerging and buoyant field of research.

Anthropogenic depletion and contamination of trace metals in the environment: the example of Zn

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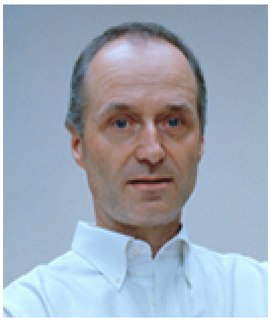

The anthropogenic disturbance of metal cycles in the Earth surface environment dates back several millennia but three factors conspire to potentially magnify these issues in our century. Firstly, the deployment of new technology fuelling the digital revolution exposes the environment to rare metals that occur at very low abundance in the continental crust. This issue will be illustrated with an environmental study in a protected national park, in which elevated indium was identified. This element has widespread applications in LEDS and thin film solar cells and may become a significant environmental pollutant. Secondly, the pervasive use of transition metals in plastics (e.g. as stabilisers) and the dispersion of plastics in the environment lead to increased environmental pollution of certain metals. This will be illustrated with the element Zn in an Irish peat bog. Finally, the growing world population puts ever greater demands on soil resources for food production. The over-use of agricultural soil can lead to essential metal deficiency in food and eventually in human, contributing to unnecessarily high mortality. Little is know about the relative roles of inherent vital metal deficiency in soils vs. human-induced depletion. The last example will illustrate the natural loss of Zn from tropical soils through advanced weathering and the close geological correspondence between geology and Zn malnutrition.

The behaviour of Cr and its isotopes during Ni laterite formation: A case study from the Piauí Ni laterite deposit

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Atmospheric weathering of ultramafic landmasses is mainly driven by redox–controlled hydrolysis that transforms Mg–rich rock to Fe–rich soil within the Critical Zone. Under favourable climate conditions (i.e. warm and humid climates) the alteration process can lead to the formation of a Ni laterite deposit. The Piauí Ni deposit (NE Brazil) is a clay–rich Fe–oxide laterite that developed over a serpentinised dunite parent rock under changing climate conditions, which silicified the deposit and prevented collapse and erosion of the profile. Garnierite is the main Ni ore. Oxidative weathering leads to redox–controlled Cr release from Mg–silicates and Fe–oxides that produces alteration products with low δ^{53}Cr values (as low as –1.699 ± 0.038 ‰) compared to the parent rock (δ^{53}Cr = –0.177 ± 0.009 ‰). Secondary Cr that was mobilised from the breakdown of primary minerals is incorporated into clays (e.g. montmorillonite, kaolinite) that also have low δ^{53}Cr values, between –0.6 ‰ and –1.8 ‰. The loss of heavy Cr isotopes (^{53}Cr) during rock weathering is heterogeneously developed within the laterite profile, as incongruent mineral dissolution, Mn availability, and fracture–controlled fluid pathways significantly influence the Cr isotope fingerprint during lateritisation. Enduring Cr release is an effective tracer of the redox–controlled evolution of the laterite, in particular during extreme lateritisation, where Cr is derived from the sluggish breakdown of oxides. Cr isotopes of catchment and pore waters show the late stage weathering effect of Cr released predominantly under today's arid climate conditions that are characterised by a strong seasonality with short intense rain periods. The weathering limited transport of Cr gives insights into the impact of the Cr isotope fingerprint that is exported to the riverine system and contributes to the global Cr cycle.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Control of groundwater fluctuations on river chemistry, insights from river dissolved concentrations and Li isotopes during flood events

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Water flow exerts a strong control on weathering reactions in the Critical Zone (CZ). Solute export responds strongly to storm events [1] and investigating the concentration and isotope composition of trace elements in river catchments can advance our understanding of the processes governing water-rock interactions and provide information on the water flow paths during these "hot moments". Especially, Li and its isotopes are sensitive to the balance between mineral dissolution and precipitation in the subsurface and therefore, a powerful tool to characterize the response of chemical weathering to hydrology [2]. Hence, high-frequency stream chemistry yields valuable insight into the hydrological processes within the catchment during "hot moments".

This study focuses on a CZ Observatory (French Research Infrastructure OZCAR). The granitic catchment Sapine (0.54 km^2, southern France) is afflicted by big rain events and therefore, it is an appropriate location to study stormflows. The relationships between concentrations and discharge indicate differential responses of dissolved elements to the hydrological forcing. Especially, systematic changes are observed for Li and its isotopes as a function of water discharge depending on the hydrological conditions (dry vs. wet), suggesting maximum secondary mineral formation at intermediate discharge. We suggest that Li dynamics are chiefly influenced by the depth at which water is flowing with, e.g. dissolution of primary minerals in deeper groundwater flows, and water-secondary mineral interaction at shallower depths. The combination of elemental concentrations and Li isotopes in river dissolved load tracing chemical weathering, with hydrogeophysical methods mapping water flows and pools, provides us with a time-resolved image of the CZ, improving our knowledge of the impact of hydrological changes on the chemical mass budgets in catchments.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

[1] Kirchner et al. (2010), Hydrol. Processes. [3] Liu et al. (2015), Earth Planet. Sci. Lett.

Boron isotope fractionation in the Critical Zone

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Boron has chemical properties that make it particularly suitable to investigate interactions between the biosphere, the hydrosphere and the lithosphere. It is present in trace amounts in most of the rock-forming minerals, it is highly soluble and is an important micronutrient for all living organisms. Because of its light mass and its trigonal or tetrahedral speciation, its two stable isotopes (^{10}B and ^{11}B) are greatly fractionated during all biogeochemical reactions leading to large isotopic variations in nature. In this presentation, the main reactions leading to the fractionation of boron isotopes in the Critical Zone will be discussed with particular focus on both the water/rock and soil/plant interactions. In particular, insights of boron isotopes into the weathering regime (dissolution vs. precipitation), the identification of the chemically active horizons in the soil and the source of nutrients for the plant (weathering vs. cycling) will be presented in more details.

From the surface to the ore: applications of copper isotope fractionation for identifying hidden resources in exploration geology

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The discussion will focus on how copper isotope variations in waters, soils, plants, weathered rocks and sulfide minerals can be used to find buried metal ore deposits. The talk will develop and explore how the copper isotope fractionation observed in laboratory experiments is applied to variations seen in nature. Examples from various deposits world ranging from porphyry copper deposits in the USA, China and Chile, sedimentary copper deposits in Canada and Africa, massive sulfide deposits in Europe, and skarns in China.

Computing equilibrium isotopic fractionation: advances and future developments. The case of Lithium and Silicon

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Thermodynamical calculations based on statistical mechanics provide a mean to access to the fractionation properties of isotopes. Because they are a purely quantum mechanical phenomenon, exact calculation of fractionation factors is nontrivial. Consequently, a severe approximation is often made, in which it is assumed that the system can be decomposed into a set of independent harmonic oscillators. This approximation can be applied to solids and gaseous systems, and has for long constituted a mean to have an idea of fractionation factors of natural phases, starting from the necessary knowledge of their dynamical (vibrational) properties. The development of atomistic modeling approaches in the last 20 years permitted to enlarge the computation of fractionation properties to any system, even those badly characterized for their dynamical properties. Liquid systems are particularly concerned, as they are both more difficult to study experimentally for their dynamic properties, and involved in many fractionation processes in Nature. As such, they have motivated numerous studies in recent years, most of them based on the harmonic approximation and on a simplified description of dissolved species. However, liquids exhibit complex dynamical behavior, which could make this approximate approach fail, shedding doubt on these studies. Indeed, recent studies showed that for liquids, another approach must be used. This approach, called "path integral molecular dynamics", is based upon the formulation of quantum mechanics developed in the 1940s by Richard Feynman, 1965 Nobel Prize in Physics, and allows the computation of isotopic enrichment between solids and dissolved species accurately. It thus lifts the last remaining lock to our theoretical understanding of the mechanisms of equilibrium isotopic fractionation, covering the case of liquids.

To be announced

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Abstract

The influence of weathering processes on Si, Mg, Fe, Zn, and Mo stable isotope fractionation in the Critical Zone: a case study from Icelandic soils

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Soils play a crucial role in mineral nutrient production and export to terrestrial and aquatic ecosystems. To improve our knowledge of the sources and processes which govern these vital functions, .i.e., disentangling the complex biogeochemical interactions in soils inaccessible to the observation, understanding the controls on stable isotope fractionation of mineral nutrients in the Critical Zone is essential. For example, as it will be illustrated with a case study in Icelandic soils, combining Si stable isotopes with other stable isotope systems such as Mg, Fe, Zn and Mo can provide new insights into important soil reactions, such as silicate weathering, ion exchanges, redox reactions, organic matter-mineral interactions, and plant recycling.

Magnesium-Isotope Fractionation During Microbial Uptake

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The model rock-inhabiting microcolonial fungus *Knufia petricola* fractionates stable Mg isotopes in a time- and pH-dependent manner. During growth, the increase of ^{26}Mg/^{24}Mg in the fungal cells relative to the growth media amounted to 0.65 ± 0.14 ‰ at pH 6 and 1.11 ± 0.35 ‰ at pH 3. We suggest a constant equilibrium fractionation factor during incorporation of Mg into ribosomes and ATP as a cause of enrichment of ^{26}Mg in the cells. We suggest too that the proton gradient across the cell wall and cytoplasmic membrane controls Mg^{2+} transport into the fungal cell. As the strength of this gradient is a function of extracellular solution pH, the pH-dependence on Mg isotope fractionation is thus due to differences in fungal cell mass fluxes. Through a mass balance model we show that Mg uptake into the fungal cell is not associated with a unique Mg isotope fractionation factor. This Mg isotope fractionation dependence on pH might also be observed in any organism with cells that follow similar Mg uptake and metabolic pathways, and serves to reveal Mg cycling in ecosystems.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Anthropogenic Zn isotopes fractionation: an overview of the Zn-Pb metallurgical industry as source of contamination

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Zn and Pb smelters are the major contributors to Zn and Pb emissions among all anthropogenic sources. Thus, it is essential to understand Zn isotopic variations within the context of metallurgical industries, as well as its isotopic fractionation in environmental media impacted by smelter activities. In this work is outlined the current state of knowledge on Zn isotopic fractionation during the high-temperature roasting and electrolytic processes in Zn refineries; δ^{66}Zn values variations in air emissions, slags, slags alteration and effluents from the smelters in comparison to geogenic Zn isotopic signature of ores formation and weathering. In order to assess the environmental impact of these smelters, the available and measured δ^{66}Zn values are compiled for smelter impacted natural water bodies (groundwater, stream and river water), sediments (lake and reservoir), soil (peat bog soil, inland soil) and plant uptake. Finally, a special focus is given on the isotopic fractionation induced by numerous physicochemical reactions and transformations, i.e. bio-uptake, surface adsorption, precipitation as well as both inorganic and organic surface complexation. The final aim is to provide a framework on δ^{66}Zn variations and fractionation in different environmental compartments (air, water, soil, plants) impacted only by Zn and Pb metallurgical activities (staring from ore mining until final metal products). By compiling the variations, and understanding the processes, Zn isotopes are useful environmental tracers of metallurgical industries.

Linking Mg and Li isotope fractionation and secondary mineral formation in both field and laboratory settings

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Chemical weathering mediates Earth's carbon cycle and hence global climate over geological time-scales. Ca and Mg from silicate minerals are released to the solute phase during dissolution with carbonic acid and subsequenty buried as marine carbonate. This mechanism has provided the climatic feedback that has maintained Earth's climate equable over geological history. Quantitative models of contemporary silicate weathering processes coupled to estimates of modern day carbon fluxes associated with silicate weathering are therefore fundamental to understanding Earth's carbon cycle, and the feedbacks between the carbon cycle, climate and chemical weathering. However, such quantitative models have proved elusive in part because of the many controlling parameters. Isotope ratios, both radiogenic and stable, of many different elements have provided invaluable contraints on both weathering sources and processes.

Over the last 15 years it has become apparent that stable isotope ratios of elements such as Mg and Li may provide promise to better fingerprint the weathering reactions taking place and to provide valuable quantitative constraints. Several studies have made links between the isotope ratios sand secondary minerals such as clays. This fractionation could be related to both mineral surfaces (cation exchange processes) or structural incorporation into the clays. Here we will discuss Mg and Li isotope analyses on dissolved, exchangeable and structural Mg and Li from field settings and compare them to data on synthetic clays synthesised in a laboratory. In field settings it has been known for some time that river waters are enriched in 7Li over 6Li compared to the silicate rocks they drain. For Mg isotopes, there would appear to be a more significant source control than for Li isotopes with most river waters having intermediate 26Mg/24Mg ratios between the carbonate and silicate rocks that contribute to the solute load. However, small rivers draining only silicate rock have typically shown an enrichment in the 24Mg relative to the silicate rock. Also seawater is enriched in 24Mg relative to silcate rocks leading to the suggestion that 26Mg is retained by secondary minerals on the continents such as clays. These field observations will be contrasted with new experimental data on clays and literature experimental data on clays in an attempt to better understand the controlling processes at a global scale.

Metal Iso-Phytology and the Plant Mineral Nutrient Balance

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with past and present members of „Earth Surface Geochemistry" at GFZ Potsdam
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Of the many uses of metal isotopes their application in element cycling through higher plants is the one that has been least-developed, yet perhaps has the highest potential. Successful "Isotope-Phytology" requires a backbone, and a playing field. The backbone requires hard work away from the limelight: the α's. However, a first set of fractionation factors on plants and the cells that build them have now been established *in vitro*, in the field, and by *ab-initio* models. Of many metals, plants and cells prefer the lighter isotopes during uptake. Only for Mg stable isotopes, plants seem to prefer the heavy isotopes. A closer look at this contrast reveals substantial detail in cell-physiological mechanisms, and shows the utility of metal isotopes as process markers of cell membrane transporters and of cell-internal and -external binding processes.

The playing field, often in beautiful landscapes, lies the use of metal isotope differences between the compartments of natural and agricultural ecosystem to obtain quantitative budgets of metal nutrient cycles. Simple mass balance equations describe the metal uptake into plants relative to metal release from rock and soil. We used this formalism to explore element cycles in two natural endmember ecosystems: nutrient-depleted and nutrient-rich regolith. In the nutrient-depeted tropical forest mountain in the Highlands of Sri Lanka we find no isotope ratio shift in ^{26}Mg/^{24}Mg between trees and soil water. Thus isotope mass balance requires complete uptake of Mg into trees, and a high recycling rate. In the nutrient-rich mountain forest of the Southern Sierra Critical Zone Observatory, California, Mg stable isotope mass balance shows that 50-100% of the Mg released by chemical weathering is taken up by forest trees from a depth of up to 7m, and is discarded after uptake in plant debris with minimal recycling. Collectively, these results show how a ecosystem mineral nutrient balance can be established rapidly with a small set of rather simple isotope measurements.

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Ge and Si isotope geochemistry in global rivers: element-specific response to weathering intensity

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We present a global overview of a novel tracer – Ge isotope ratios (δ^{74}Ge) – in a number of large and small rivers around the world. Dissolved δ^{74}Ge values range from 0.9 to 5.5‰ with a global discharge-weighted average of 2.6 ± 0.5‰. Riverine suspended and bedload sediments range from 0.5 to 0.7‰, indistinguishable from silicate source rocks. A direct comparison of δ^{74}Ge, δ^{30}Si, and Ge/Si signatures analyzed on the same set of samples shows that they are all primarily fractionated by secondary phase precipitation. In some cases, δ^{30}Si and Ge/Si can be strongly modified by biological uptake (vegetation, diatoms) but δ^{74}Ge appears unaffected.

Lastly, we show that dissolved riverine δ^{74}Ge, δ^{30}Si, and δ^{7}Li each have a different relationship with silicate weathering intensity globally. Furthermore, δ^{74}Ge and δ^{7}Li (and to a lesser extent δ^{30}Si) dissolved signatures are primarily controlled by the degree of solute removal via secondary phase precipitation. Thus, we propose that the distinct Ge, Si, and Li isotope relationships with weathering intensity may stem from different affinity of each element to the dominant weathering products at a given weathering regime (e.g., refractory oxides vs. aluminosilicate clays). We suggest that future studies could utilize these differences in chemical (and as a result, isotopic) behavior to more accurately determine weathering intensity of the studied setting.

Applications of Uranium Isotope Fractionation: Groundwater, Ore deposits, and Oceans

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Uranium (U) isotope ratio has emerged as a powerful tool to investigate a range of geochemical problems from contaminant remediation to the extent of ocean anoxia. Here, we present our recent work on U isotope ratios to understand 1) the environmental U mobility in groundwater at in situ recovery (ISR) U mines, 2) the formation and evolution of roll-front U ores 3) the role of aqueous U speciation on isotopic fractionation with implications for U isotope ratio as a palaeo-redox proxy.

We demonstrate naturally occurring U reduction at ISR U mines using U isotope ratios of groundwater samples collected from wells drilled within, upgradient and downgradient of mined U ore. Along the hydraulic gradient, the δ^{238}U values measured in groundwater samples range from 0.6‰ to −2.5‰ at Rosita, TX, USA, and from −0.9‰ to −2.8‰ at Smith Ranch, WY, USA. Enrichment in ^{238}U in groundwater samples may be attributed to the dissolution of U ore while the depletion of ^{238}U suggest U(VI) reduction by the downgradient sediments. We also report U isotopic characterization ((^{234}U/^{238}U) and δ^{238}U) of a roll-front U deposit to assess the relative contributions of groundwater hydrology and pore-scale chemical reactions. Our results show a systematic pattern of decreasing δ^{238}U along the hydraulic gradient at the center of the mineralized zone, caused by reactive transport of U across the redox gradient. This predictable pattern helps understand the formation and evolution of roll-fronts as well as aids in U exploration and efficient mining. The results from our recent experiments reveal the dependence of U isotopic fractionation on aqueous U speciation where fractionation increases with increasing Ca concentration. These results help interpret existing U isotope data from Black Sea, modern oceans and rock record, and establish U isotope ratios as an excellent proxy for both microbial and abiotic U reduction.

Stable Iron Isotope Fractionation in Magmatic Systems: Insights into Ore-Forming Processes

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Stable Fe isotope fractionation at magmatic conditions (temperatures >700°C) is predictably small but confidently measured due to advances in multi-collector inductively coupled plasma mass spectrometry. Studies published over the past decade indicate that stable Fe isotope ratios can elucidate magmatic processes such as partial melting, fractional crystallization, redox changes, fluid exsolution, thermal diffusion, and sub-solidus re-equilibration. The Fe isotope composition of whole rocks and minerals can be used to constrain the formation and evolution of magmatic systems. Due to the widespread occurrence and abundance of Fe in magmatic/magmatic-hydrothermal ore deposits, Fe isotopes have become a robust geochemical tool within Economic Geology.

We present detailed Fe isotope datasets in the context of three types of ore deposits: 1) layered intrusions; 2) magmatic Ni-Cu deposits; 3) iron oxide-apatite/iron oxide-copper-gold deposits. Fractionation of Fe isotopes throughout an igneous intrusion or in individual minerals (mineral-mineral, mineral-melt, mineral-fluid fractionation) can be large relative to the average range in typical igneous whole rock values (~<0.6‰). Whole rock and mineral Fe isotope compositions reflect processes common to each ore deposit type and provide key information about their origin and formation over time. Alteration events are also recorded in Fe-bearing minerals. Iron isotope ratios of ore deposit samples are both powerful alone and when paired with more “traditional” stable (O, H, S) or radiogenic (Pb, Sr) isotopes for a new perspective on established “fingerprinting” methods.

Our exponentially growing knowledge of the behavior of Fe isotopes in magmatic systems has significantly improved our understanding of the origin and life cycle of Fe-bearing ore deposits. Stable Fe isotopes have the potential to contribute to exploration efforts by constraining the ranges of expected Fe isotope values and variations produced by ore-forming processes.

Chromium mobility in ultramafic areas: an isotopic study

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Ultramafic rocks may display high chromium (Cr) concentrations, which could be naturally leached to surface and groundwater. However, mining and metallurgical activities may considerably increase the amount of both Cr(III) and Cr(VI) released into the environment, the later being highly soluble in water, bioavailable and toxic. In the present study, a nickel mining area was studied in Goiás State, Brazil (Barro Alto, BA) in order to determine the potential release of Cr, its pathway from solids to surface and ground waters, and the associated isotopic compositions in those matrices. The chemically and isotopically exchangeable pool of Cr(VI) (ECr(VI)) was significant in BA ores with values up to 104.09 ± 7.70 mg kg-1. In deep soils (160 cm), the ECr(VI) was up to 30 and 8 fold higher than in the surface. This was accompanied by an increase of δ^{53}Cr, which varied from -0.28 ± 0.01‰ to -0.05 ± 0.01‰. In addition, extracted Cr(VI) (0.1 M KH2PO4) displayed positively fractionated δ^{53}Cr (1.69 ±0.03 ‰) in the same range of isotopic compositions measured in the fresh waters. These results suggest that in weathered materials, Cr is mainly release as the toxic Cr(VI) specie, which availability increases from the soil profile to the ores and mining residues. The differences observed in the Cr isotopic composition suggest that δ^{53}Cr could be used as a tracer of Cr leaching in environmental studies.

Experimental studies of uranium isotope fractionation

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We present results from recent inorganic and microbial U reduction experiments designed to elucidate the important mechanisms controlling the direction and magnitude of 238U/235U fractionation. All experiments were conducted at anerobic conditions in a N2-H2±CO2 atmosphere.

Inorganic reduction experiments were conducted with synthetic makinawite and solutions containing fixed amounts of U and NaHCO3. Varying amounts of CaCl2 were added to experiments to shift the amount of neutrally charged U-Ca-CO3 species. Residual aqueous U concentrations and isotopic compositions were characterized by MC-ICP-MS. U isotopic compositions are reported as δ238U normalized to the starting U solution. The U concentration and isotopic data were used to calculate the reaction order and the isotopic fractionation factors. All experiments are consistent with first order reaction kinetics with reaction rate constants between 0.050-0.257 (h-1) and total durations of up to 48 hours. Isotopic fractionation factors (α) range from 1.00023-1.00084 and are correlated with U speciation. The results demonstrate that inorganic and microbial U isotope fractionation can have similar magnitudes and direction of fractionation. Our results are then used to predict the U isotopic fractionation factors for a roll front U deposit and the Black Sea.

We also investigated the variations of U isotopic fractionations during microbial U isotopic fractionation. Microbial U isotopic fractionation is reported to vary from 0.7‰ to ~1‰. Our results show that U isotopic fractionation by Shewanella sp. (NR) is dependent on the rate of U(VI) reduction. The magnitude of fractionation decreases with increasing U reduction rate. We attribute this rate dependence of fractionation to reactive transport of U to the enzymes and present a numerical model that adequately simulates our experimental data. These results suggest a mechanistic link between bacterial metabolism with the observed isotopic fractionation.

Nickel isotope fractionation during Ni coprecipitation with calcite at 25 °C

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Nickel speciation in seawater-type solutions is dominated by $NiCO_3°$, $NiHCO_3^+$, $NiSO_4°$ along with $Ni^{2+}_{(aq)}$ whereas Ni substitutes for Ca in calcite as octahedral Ni^{2+} . As a result, the Ni isotopic composition of sedimentary calcite can provide precious information on the chemical composition, pH and pCO_2 of past oceans. In an attempt to calibrate this new proxy, we have investigated Ni isotope fractionation at 25°C during Ni coprecipitation with calcite using a mixed-flow reactor. The experiments have been performed as a function of calcite growth rate (from log r_p = -8.2 to -7.3 mol m^{-2} s^{-1}).

Nickel has then been separated from the matrix elements using a 4-step anion-exchange procedure, and Ni isotopes were measured by MC-ICPMS.

Our results are in good agreement with previous work where Ni incorporation in calcite does not seem to be affected by growth rate [1]. Our preliminary data shows a preferential incorporation of light Ni isotopes in calcite. Owing to its strong hydration in the aqueous phase, it is expected that Ni isotope fractionation decreases as precipitation rate increases, as is the case for Mg.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

[1] Lakshtanov and Stipp (2007), GCA 71, 3686-3697.

δ^{137}Ba of two large river systems

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Oceanic geochemistry of barium has been studied for tracing biological productivity. However only few data has been reported on large rivers system which is the main input of dissolved barium to the ocean. These river data show significant difference in δ^{137}Ba [1], it implies that earth surface processes can fractionate barium isotopes from rocks weathering to input in ocean. Thus the ocean record of δ^{137}Ba evolves with the variation of continental weathering, as a consequence, it is more challenging to reconstruct paleobiological productivity.

For this reason we proposed here isotopic composition of two large and different river systems in term of lithology, relief, erosion and climate in order to investigate Ba continental geochemical cycle. Data showed δ^{137}Ba variations from 0.08 to 0.45‰.

Linear correlation can be observed in Ca/Ba Z^-/Ba and $HCO3^-$/Ba vs δ^{137}Ba plots which can be interpreted as a binary mixing probably between silicates and carbonates-gypsum end members. Moreover, a significant difference of δ^{137}Ba can be observed between the two catchments: Mackenzie has the higher δ^{137}Ba whereas Amazonas has lower δ^{137}Ba. This different could be also the fact of i) difference in weathering intensity ii) A source rocks effect iii) a possible link between gypsum dissolution and pyrite oxidation could explain link between δ^{137}Ba and SO_4^{2-} abundance.

[1] Cao, Z., Siebert, C., Hathorne, E. C., Dai, M., & Frank, M. (2016). *Earth and Planetary Science Letters*, *434*, 1-9.

Characterisation of the deposition of organolead compounds in the Irish peatlands by GC-MC-ICP-MS

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From the Industrial Revolution to the present, smelting and refining of metal-bearing ores in Ireland has released lead-containing particles into the atmosphere. Due to their unique characteristics, ombrotrophic (rain-fed) peat bogs offer exceptional opportunities to study the long term atmospheric deposition of metals from various sources.

Pb isotope analysis of peat subsamples from the Liffey peat bog in the Wicklow Mountains, Ireland, has revealed mixing trends between Pb enriched sources with different signatures[1]. Some of those sources are undoubtebly organolead compounds, added to fuels since the 1930's; the organolead compounds released by burnt fuels have been detected within Greenland ice cores[2].

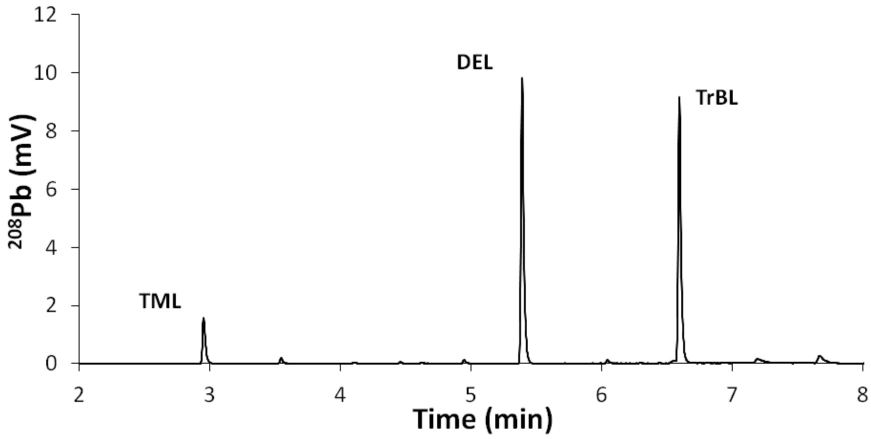

Figure 1: Separation of trimethylead (TML), diethelylead (DEL) and tetrabutyllead (TrBL) by GC-MC-ICP-MS.

Peat cores were taken at two bog locations in Ireland, Liffey Head and Brackloon Wood (Figure 1). The cores were subsequently sub-divided into 1 cm spits. Each subsample from the Liffey Head bog was analysed by ^{210}Pb-^{241}Am dating, in order to construct chronologies of the changing elemental and isotopic composition. The bulk trace elemental, zinc [3], and lead isotopic composition has already been reported for each of these subsamples.

The bulk Pb isotopic composition of the Liffey Head changed markedly over the course of the 20th Century. It was hypothesised this was due to the blending of two or more Pb sources with differing isotopic composition, with organolead compounds one likely source. Isotopic speciation analysis has recently been made much easier by the release of the GCI-300 (Figure 2), a new commercially available GC-MC-ICP-MS interface by Thermo Scientific [4]. Using GC-MC-ICP-MS the Pb isotopic composition of the organic and inorganic lead compounds were individually measured and compared. The high reproducibility of the new interface allowed four individual organolead compounds to be identified on the basis of their retention times. For one site, Liffey Head, the evolution of the organolead composition measured over time was found to correlate well with the phasing out of leaded fuel in the European Union.

1. Rosca *et al* (2016) *59th Irish Geologicial Research Meeting, Galway, Ireland*
2. Hong *et al* (1994) *Science*, **265**, 1841-1843
3. Rosca *et al* (2017) *Goldschmidt Abstracts*, **2017**
4. Craig *et al* (2016) *Thermo Scientific Technical Note*, **TN30383**

In situ stable silicon isotope composition of single phytoliths

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Silicon, one of the most abundant elements, is not only abiotically cycled through the Critical Zone, but also incorporated into plants. This cycling is accompanied by a mass-dependent isotope fractionation.[1] Previous studies investigated the Si fractionation between soil and plants on a bulk scale. Although the uptake of Si into plants is significant in terms of mass, the plant specific Si isotope fractionation is not well constrained[2], and a large range of isotope composition has been reported (δ^{30}Si ≈ -2 – 6 ‰).[1,3]

Silicon is deposited as microscopic silica in different plant compartments. These deposits, called phytoliths, differ greatly in shape and size, and are characteristics for various plant species. Biogenic opal is very stable, and persists during the decay of plants. Under ideal conditions phytoliths are preserved through time and can be used in paleo-climate research and archaeology.[4] However, an *in situ* analytical routine is needed for sparsely available phytoliths.

We developed an *in situ* routine based on femtosecond laser ablation analysis (fs-LA) to make the information stored in a single phytoliths available. To establish the analytical routine, a set of 7 different phytolith samples from 6 different species were collected. The species included grasses (common reed, bushgrass), trees (European beech, Norway spruce) and ferns (common and rough horsetail). Single phytoliths were fixed with lacquer on a PMMA substrate and analysed by standard sample bracketing technique. The results were compared to bulk digestion, chromatographic separation and solution analysis. Within uncertainty there is no differences in the silicon isotope composition analysis between bulk solution and fs-LA. The solution method is favoured in terms of precision achievable (typically < 0.1 ‰ 2 S.E.). The method however, cannot unravel inhomogeneity within a bulk population. Our developed routine, using fs-LA, offers a clear advantage for this type of analysis.

[1] Opfergelt & Delmelle (2012) *C. R. Geoscience* 344 723–738. [2] Ma & Yamaji (2006) *Trends Plant Sci.* 11, 392–397. [3] Ding *et al.* (2005) *Chem. Geol.* 218, 41–50. [4] Piperno, (2006) Phytoliths: a comprehensive guide for archaeologists and paleoecologists, *AltaMira Press*.

Silicon isotopes along an erodosequence: implications for their use as a weathering proxy

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Interpretation of metal(loid) stable isotope compositions in the Critical Zone (CZ) is often predicated on the assumption that the CZ can be treated as a steady-state batch reactor with only a limited number of important processes. Recently formalised as a series of mass-balance equations, this approach predicts that the isotopic composition of a river solute is directly related to the fraction of an element solubilised during weathering that is exported as a fractionated solid, which might be expected to vary as a function of erosion rate. It further suggests sedimentary isotope records should reflect palaeoweathering intensity, i.e. the ratio of chemical to total denudation.

To validate the palaeoweathering proxy, we explore these issues and the underlying assumptions further with a detailed silicon isotope mass balance at three sites defining a gradient of weathering intensity. These run from the tectonically inactive and supply-limited Sri Lankan highlands to the kinetically limited Rhone Valley in the Swiss Alps, via Providence Creek in the Sierra Nevada Mountains. At each site, we develop a mass-balance model using silicon isotope ratios of bedrock, bulk soil and clay separates, long-term denudation rates from cosmogenic ^{10}Be, and Zr-normalised elemental depletion profiles. Supplemented with previously published weathering zone Si isotope mass-balances, this allows us to assess the extent to which silicon isotope ratios in dissolved Si or secondary clays reflect the weathering regime and therefore hold utility as weathering or palaeoweathering proxies. A large river concentration-discharge dataset from the USGS adds more insight by allowing the relationship between Si removal from solution (i.e. into secondary clays or plant biomass) and catchment characteristics (derived from GIS) to be elucidated.

Assessing the contribution of hydrothermal alteration to element fluxes from volcanic island arcs using dissolved Ge/Si ratios in rivers

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Volcanic island arcs display the highest silicate weathering rates on Earth, thereby playing an important role in global chemical fluxes to the ocean. However, in these regions, uncertainties remain regarding the significance of hydrothermal alteration in contributing to the chemical fluxes. This impedes accurate assessments of weathering fluxes and associated atmospheric CO_2 consumption. Germanium, a trace element, behaves as a chemical analog to Si. However, it is fractionated relative to Si in surface processes. According to a few studies, the dissolved Ge/Si ratios of terrestrial hydrothermal springs are higher (2-1000 µmol/mol) than to those found in river waters worldwide (0.2-2.8 µmol/mol). This suggests that the Ge/Si ratio may be used as a tracer of hydrothermal inputs to rivers. However, additional work is needed to better constrain the range of Ge/Si values in terrestrial hydrothermal systems.

Here we report the Ge/Si ratio values of hydrothermal spring and river waters from three different volcanic island arcs with active hydrothermal systems: La Soufrière volcano (Guadeloupe), Kawah Ijen volcano (Indonesia) and Aso volcano (Japan). La Soufrière's hydrothermal system is characterised by chloride alkaline, acid-sulphate, and acid-sulphate-chloride waters, and the system from Aso by $Ca\text{-}SO_4$ waters; pH value in waters from these two hydrothermal systems ranges between 3 and 9. Kawah Ijen's magmatic hydrothermal system is characterised by acid-sulphate-chloride waters with extremely low pH values (< 0.5).

The highest measured Ge/Si ratios (10-508 µmol/mol) were found in Kawah Ijen springs. The hydrothermal springs from La Soufrière and Aso displayed significantly lower Ge/Si values in the ranges, respectively, of 0.3-15 and 0.2-21 µmol/mol. The Ge/Si fingerprint of hydrothermal contribution to rivers is higher in hydrothermal system with extremely low pH (4-514 µmol/mol, Kawah Ijen) than in other sites (0.2-5 µmol/mol, La Soufrière; 0.2-2 µmol/mol, Aso).

This study highlights that the use of Ge/Si ratio to assess hydrothermal contribution to rivers should carefully consider local variability of Ge/Si ratio in hydrothermal springs.

Olivine weathering by rock-inhabiting fungi: microbially-induced effects measured with geochemical precision

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Fungi are significant geoactive agents – especially since fungi-dominated biofilms are ubiquitous on air-exposed surfaces of our planet. In Earth's history, these surfaces always used to be rocks, but in the recent past this weathering-related niche expanded to anthropogenic environments like solar panels where fungi-dominated biofilms block radiation and decrease the energy yield. The mechanisms of biofilm establishment and quantification of its deteriorating effect on any substrate can be studied in simplified, well-controlled laboratory experiments.

Our geobiological experimental system includes a model rock-inhabiting strain *K. petricola* A95 along with its melanin-deficient mutant (A95 ΔPKS). The model mineral used is forsteritic olivine. Both batch and a mixed flow experiment were performed in triplicates to study the ability of both fungal strains to dissolve olivine. Geochemical analysis of dissolved and solid mineral components was done by a combination of ICP-OES, SEM-EDX, TEM/FIB as well as XPS.

Time series ICP-OES elemental concentration analysis of the medium solution showed that the olivine dissolution rate was highest for the wild type *K. petricola* A95, followed by the mutant and the abiotic control. The wild type's rate 3.9 and 5.5 times higher for batch and mixed flow experiments respectively as compared to the mutant's. SEM-EDX analysis of the weathered olivine showed that the melanin-deficient mutant produces more Extracellular Polymeric Substances (EPS) than the wild type but on the other hand is unable to establish direct contact with the olivine surface. TEM and XPS analysis show the presence of an amorphous silica layer together with an oxidised iron phase on the weathered olivine. The higher dissolution rate of the wild type is probably caused by its direct contact with the olivine. If this contact is enabled by the presence of melanin or its thinner layer of EPS remains a question. Future experiments will study the effect of a static biofilm in which prolong biofilm-mineral contact is guaranteed.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Genetics of rock-inhabiting fungi as a tool in geochemistry

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Although the influence of rock-inhabiting microbial communities on weathering of minerals is well known, full understanding of the processes that shape these interactions can only be obtained by combining advanced biological and geological methods. Here we report a method for targeted gene disruption in the model rock-inhabiting fungus *K. petricola* A95. The resulting library of different genetically modified strains is available, with a spectrum of added and knocked-out weathering-relevant qualities.

Strains from this model rock-inhabiting fungus mutant library were subsequently tested for their ability to adhere to and weather olivine. Fungi and olivine were tested in (i) batch, (ii) mixed-flow reactors as well as (iii) flow-through chambers. Mineral alteration processes were analysed with a combination of ICP-OES, SEM-EDS, TEM/FIB as well as XPS analyses.

A distinct ability to leach Mg from olivine was demonstrated for the wild type *K. petricola* A95 as well as for the melanin-deficient strain Kpdpks. Further melanin presence was influencing adhesion processes: melanised (black, wild type) strain was universally capable of adhering to mineral grains, while the melanin-deficient mutant Kpdpks failed to establish close contact with olivine surface.

With the now available mutant library of a model rock-inhabiting fungus we can reach a totally new level of geochemical and geomicrobiological analysis. Targeted disruption of selected genes will permit elucidation of the role of specific cell components (e.g. carotenoids and melanins, other cell wall components) in biodeterioration, mineral weathering and soil formation processes.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Characterizing nutrient fluxes in Quebec vineyards:
Insight from stable and radiogenic strontium isotopes

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Recent studies have demonstrated that it is possible to establish direct and unambiguous relationships between the radiogenic ^{87}Sr/^{86}Sr ratio of bioavailable Sr in soils and the plants growing on it. While this allows authenticating the origin of agro food products, such as wine, it says little about how Sr is transferred from the soil to the grapes/wine. With that in mind, we investigated stable ($\delta^{88/86}$Sr) and radiogenic ($^{87/86}$Sr) isotopes of strontium in total and exchangeable fractions of Sr in soils, grapes, mash pulps of grape and wines from 5 vineyards from Quebec, Canada.

The $^{87/86}$Sr ratios showed a strong correlation between the soil labile fraction, the grape and the wine confirming its potential as a proxy for geographic provenance and for wine authentication. However, the $^{87/86}$Sr ratios of mash pulp were all significantly lower than those of the exchangeable fractions, grapes and wines. This suggests that the sources of nutrients available for plant uptake vary during the vegetative cycle of the vine. The seeds and skin form in the early vegetative cycle that is characterized by enhanced rhizosphere activity, higher nutrient levels and rapid growth. Acids released by the rhizosphere activity enhances mineral solubility, resulting in higher $^{87/86}$Sr ratios. The pulp develops late in the cycle when rhizosphere activity and mineral solubility is reduced, leading to lower $^{87/86}$Sr ratios.

$\Delta^{88/86}\text{Sr}_{\text{total-labile}}$ ratios show a strong negative correlation with $\delta^{88/86}$Sr of the labile fraction that implies an enrichment of the labile fraction through pedogenic mineral precipitation. The $\delta^{88/86}$Sr values of grapes suggest that preferential uptake of lighter isotopes by plants is increased in soils showing higher secondary mineral precipitation. Furthermore, $\delta^{88/86}$Sr of wine are depleted in ^{88}Sr compared to mash pulp and enriched against grapes, suggesting preferential transfer of lighter isotopes to skin and seeds compared to the pulp. The $\delta^{88/86}$Sr values of wine, mash pulp and grape correlate with the Sr concentrations of these components underlining the importance of grape pulp, seeds and skin to the making of wine.

Effect of CdS precipitation on the partitioning of Cd isotopes: implications for Cd oceanic cycle

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The biogeochemical cycling of cadmium and its isotopes in the ocean is mainly ascribed to the assimilation-remineralization cycle occurring in phytoplankton [1, 2]. Recently, several studies reported an alternative Cd scavenging through CdS precipitation in Oxygen Minimum Zones (OMZ) based on the decrease of Cd/PO_4 ratio and of a concomitant positive Cd isotope excursion in dissolved seawater compared to sinking particles [3, 4,5]. To identify if CdS precipitation effectively engenders a Cd isotope fractionation, we performed cadmium-sulphide precipitation experiments under controlled atmosphere at low (MilliQ-water) and high ionic strengths (synthetic seawater) by varying reaction time as well as cadmium/sulphide ratio.

Enrichment in light Cd isotopes is observed in the precipitated CdS phase, in agreement with *ab initio* simulations performed between the various speciation of Cd in aqueous solution [6]. The data follow a closed-system Rayleigh fractionation model with the fractionation factor ($\alpha_{Cdsol\text{-}CdS}$) decreasing with increasing salinity (from 1.00026 for Milli-Q to 1.00014 for a salinity twice that of modern seawater). We propose that this fractionation is directly controlled by an isotope equilibrium between the various Cd aqueous species with preferential involvement of Cd^{2+} in CdS formation.

The magnitude of the Cd isotope fractionation determined in our study is in excellent agreement with the Cd isotope shift observed in modern oceanic OMZ and attributed to CdS precipitation [3,4,5], witnessing the impact of this scavenging process. In restricted euxinic basins such as the Black Sea, Cd isotopes may be useful tracer of the near-quantitative sequestration of cadmium sulphides.

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Metal stable isotopes as paleoenvironmental indicators: Defining ancient sources of natural metal toxicity

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Multiple metal stable isotopes are increasingly used to define paleoenvironments, principally as indicators of paleoredox conditions. Here we document the importance of multiple proxies and, importantly, their isotopic compositions to establish cause and effect in paleoenvironmental processes.

The Global Stratotype Section and Point (GSSP) at Meishan, China, defines the Permo-Triassic extinction. U-Pb geochronology of ash beds bracketing the extinction horizon at the highly condensed Meishan section tightly constrain the extinction event to 252 Ma. The condensed section, however, provides little detail on the lead-up to this extreme event. Our multiple-isotopic study of the same event in East Greenland and NW Norway shows that this was indeed a singular event in Earth history, not confined temporally to the toxic Tethyan realm. Re-Os geochronology documents temporal correlation with the 252 Ma Meishan event, while sharp increases in Re, Mo, Cd, and Se *precede* the extinction. The expanded section permits trace metal evidence of hot, acidic, anoxic conditions, but concentration data alone do not distinguish between increased metal input to seawater and increased drawdown and preservation in the sedimentary section. By adding data for stable isotopes of Cd and N, we are able to define causes for the trace metal enrichment*. $\delta^{114/110}$Cd and $\delta^{15/14}$N distinguish nutrient upwelling and increased productivity from oceanic stagnation as a driver of environmental change in the lead-up to the Permo-Triassic extinction. Further, Se isotopic analyses on the same samples are expected to strengthen this conclusion.

The take-home message? No single set of trace element data, nor any single isotopic system can firmly define paleogeographic setting and marine conditions. Multiple geochemical and isotopic proxies must be combined with geochronology and solid geologic observations to link cause and effect on a global scale.

*Georgiev et al. (2015) Earth and Planetary Science Letters 410: 84-96.

Mg isotope fractionation during mineral phase transformations

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The isotopic compositions of carbonate minerals are routinely used to help reconstruct environmental conditions that occurred in the geologic past, such as temperature and ocean pH, and can be used to track reaction processes and element sources. The robust interpretation of the measured isotopic compositions requires knowledge of the mechanism of isotopic fractionation and the factors that influence its degree between minerals and forming fluids. The length or strength of the metal-oxygen bond in the mineral compared to that of the aqueous ion, which can be accompanied by changes in coordination, and the mineral growth rate are known to influence the fractionation of isotopes. The pathway of mineral formation, for example via direct precipitation versus transformation of a precursor, is therefore a potentially important factor controlling the isotopic composition of the stable phase. In this study, we investigate the isotopic fractionation of Mg and C isotopes in hydrous Mg-carbonates. These minerals are of interest because they form in ultramafic weathering terrains, can be used to sequester CO_2, and have numerous metastable phases that transform at low temperature. The fractionation of both Mg and C isotopes during the transformation of nesquehonite [$MgCO_3·3H_2O$] to the thermodynamically more stable phase, dypingite [$Mg_5(CO_3)_4(OH)_2·{\sim}5H_2O$] was tracked at 25°C and 35°C in experiments. Although the rates and mechanism of the transformation differ between 25°C and 35°C, as shown by X-ray diffraction and electron microscopy, a similar equilibrium distribution of Mg and C isotopomers between dypingite and the fluid is reached at both temperatures. During the phase transformation, solids were progressively enriched in ^{13}C relative to fluids, resulting in an equilibrium fractionation factor between dypingite and dissolved inorganic carbon (DIC) of $\Delta^{13}C_{dyp\text{-}DIC} \approx +4.65 \pm 0.06‰$ at 25°C, and $+4.47 \pm 0.16‰$ at 35°C. Conversely, $\delta^{26}Mg$ of the solids decreased during the mineral phase transformation, with a $\Delta^{26}Mg_{dyp\text{-}fluid} \approx -0.76 \pm 0.07‰$ and $-0.97 \pm 0.18‰$ at 25°C and 35°C, respectively. A smaller fractionation factor between $Mg_{(aq)}$ and nesquehonite was documented than for dypingite, at only $\Delta^{26}Mg_{nsq\text{-}fluid} \approx -0.18 \pm 0.05‰$ and $-0.11 \pm 0.08‰$ at 25°C and 35°C, respectively, suggesting a crystallographic control on isotopic fractionation. These experimental results provide insights to the factors controlling fractionation of Mg and C in different Mg-carbonate minerals, and allow more robust interpretation of isotopic signatures measured in the field.

New perspectives on the Cenozoic δ^7Li record

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The driving mechanisms behind light lithium isotope ratios (δ^7Li) in early Cenozoic seawater, and their subsequent rise to heavy values today[1], have been the focus of intense debate and scientific investigation. Much of this work has focussed on the input fluxes from land [e.g. 2-5]. However, relatively little attention has been paid to the fidelity of the seawater signal in the archive used to construct these records: the planktic foraminifera. In the modern ocean alone, planktonic foraminifera reveal δ^7Li values of between 25 and 31‰[6], but the drivers of this interspecific variation are largely unknown.

Here we present results from Holocene core-tops that span a wide range of hydrographic settings, also revealing considerable variability in δ^7Li across species and between sites. By combining these data with new laboratory culture experiments and downcore measurements, we identify some of the key controlling factors that influence foraminiferal δ^7Li. We interrogate the physiological basis for these geochemical differences, and discuss the potential influence of these vital effects on interpreting published Cenozoic marine records.

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Molybdenum isotope fractionation in a seasonally anoxic fjord

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Determining the mechanisms driving Mo cycling and associated isotope fractionation is required in order to utilize sedimentary Mo as a redox proxy in paleoenvironments. The accumulation of Mo in oxic sediments results from adsorption onto iron (Fe)- and manganese (Mn)- (oxyhydr)oxides, while its accumulation in euxinic sediments results from conversion to the particle-reactive tetrathiomolybdate species *(1)*. Molybdenum isotopes track paleoredox because the isotopic offset between seawater Mo and oxic sediments is 3‰, while it is 0‰ between seawater Mo and euxinic sediments *(2,3)*. However, elemental and isotopic Mo cycling in seasonally anoxic/euxinic environments are not well understood and may complicate the use of Mo as a redox tracer *(4,5)*.

Dissolved Mo was monitored over a nine-month period in the waters of Saanich Inlet, British Columbia—a seasonally anoxic fjord characterized by intense reducing conditions below 120 m, with deep-water ventilation during early Fall. Anoxic subsurface waters have significantly lower Mo concentrations ([Mo] = 6.7 ppb) and significantly heavier Mo isotope ratios (δ^{98}Mo = +2.55‰) than oxic surface waters ([Mo] = 12.1 ppb, δ^{98}Mo = +2.23‰ and +2.03‰) *(6)*. Furthermore, samples collected at the seawater redox boundary have low [Mo] (9.6 ppb) but show both enrichment (δ^{98}Mo = +2.41‰ and +2.45‰) and depletion (δ^{98}Mo = +2.19‰) of heavy isotopes relative to average seawater. These deviations are related to periods of oxygenated seawater renewal and potential changes to the magnitude of freshwater inputs, suggesting that Mo cycling is influenced by seasonal changes. Therefore, Mo cycling cannot be described by the two fractionation mechanisms found in purely oxic or euxinic environments. Instead, multiple mechanisms may generate 'non-conservative' Mo behavior in the water column. Continued monitoring and the analyses of plankton and sediment samples will aid in revealing additional fractionation mechanisms and/or temporal mass balance effects over a wide range of redox conditions.

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COPPER MC-ICP-MS ISOTOPIC ANALYSIS AFTER CHROMATOGRAPHIC PURIFICATION USING CU SPEC AND AG MP-1 RESINS

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Cu isotopic composition is widely applied in different fields of science, such as geochemistry, ecology and biology. The isolation and purification of the target element is a prerequisite step when analyzing isotope ratios by mass-spectrometry.

Sample preparation and analysis were carried out within the class 1,000 clean room facility (IGG UB RAS).

Two chromatographic resins were used for Cu purification and tested with standard multi-element solutions. Elemental concentrations for elution curves were obtained by Q-ICP-MS NexION 300S.

Cu resin (Triskem) was loaded into polypropylene column with layer configuration: D=0.7 cm, h=4 cm, V=1.6 mL. The purification protocol: 5 mL 0.01 M HCl precondition step, 6 mL 0.01 M HCl matrix elution step and 3 mL 8 M HCl for Cu elution step. The scheme provided good purification and yielded 90% of Cu in collected fraction. However, significant amounts (up to 20 % wt.) of Fe, V, Be, Bi and Cr were determined in Cu eluate.

AG MP-1 (Bio-Rad) was loaded into polypropylene column with the same layer configuration. According to [Borrock et al., 2007], the purification protocol included 5 mL 10 M HCl precondition step, 5 mL 10 M HCl matrix elution step, 6 mL 6 M HCl, 5 mL 1M HCl and 5 mL of deionized water. The recovery of Cu, Fe and Zn was up to 100%.

Triskem Cu resin is appropriate for obtaining purified Cu fraction; the advantage of the AG MP-1 resin is the possibility to obtain purified Fe and Zn fractions along with Cu.

Cu isotopic determination was carried out by MC-ICP-MS (Neptune Plus). Standard-sample bracketing approach was applied using Cu NIST SRM 976. Obtained ^{65}Cu/^{63}Cu ratios in BHVO-2 and AGV-2 are 0.14±0.04 (2 SD, n=10) and 0.12±0.04 (2 SD, n=10), respectively, and in a good agreement with GeoReM data.

The study was carried out at the “Geoanalytic” Collective Use Centre and supported by UB RAS Presidium Program No. 18-5-5-54

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Calcium isotopic signatures in three forest catchments with contrasting bedrocks in the Slavkov Forest Critical Zone Observatory

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Calcium isotope systematics of ten ecosystem compartments were compared among three spruce catchments situated in the Slavkov Forest, Czech Republic. δ^{44}Ca differences between individual pools/fluxes were used to identify Ca sources for the bioavailable Ca soil reservoir and for runoff. Base-poor bedrock included granite at Lysina (LYS), base-rich bedrock was formed mostly by serpentinite at Pluhův Bor (PLB) and amphibolite at Na Zeleném (NAZ). LYS was much more acidified than NAZ and PLB due to differences in chemical weathering (Krám et al. 2012 Appl. Geoch. 27: 1854, Dannhaus et al. 2018 GCA in press). At all three sites, Ca in spruce biomass (bark, xylem, fine roots and needles) was isotopically lighter than Ca of atmospheric deposition (open-area bulk precipitation and spruce throughfall). Calcium in plant material was often isotopically lighter than Ca in bedrock and Ca in soil solutions tended to be isotopically heavy. Calcium of open-area precipitation was isotopically similar to Ca of runoff. All catchments had isotopically lighter Ca in silicate bedrock and exported isotopically heavier Ca via runoff. Most runoff Ca at LYS came from atmospheric deposition and residual Ca following plant uptake, while the contribution of granite to runoff was small. This conclusion was corroborated by Ca isotope analysis of rock-forming minerals, including apatite, feldspars and micas. At LYS, Ca in the organic soil horizons was isotopically heavier than Ca in mineral soil horizons, therefore soil-derived Ca in runoff came mostly from the organic soil horizons. Organic Ca cycling, along with atmospheric input of isotopically heavy Ca, were responsible for the high-δ^{44}Ca signature in runoff at LYS. In contrast, contribution of bedrock Ca to runoff at PLB and NAZ was high, but even at these base-rich sites a contribution of biologically-cycled isotopically heavy Ca had to be invoked to explain the high δ^{44}Ca value of runoff.

Insights from stable isotopes into fish life history

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Anthropogenic activities have a dramatic impact on ocean chemistry and marine resources. Theoretical and modelling studies suggest that climate change could exert a large effect on food web structure and dynamics but currently we lack the quantitative data to evaluate these models and determine how the life history of aquatic biota responds to environmental changes. This presentation will cover the application of stable isotopes to the study of the environment and ecology, with an emphasis on our recent advancements using heavy stable isotopes (e.g., lead, mercury, strontium) to understand foraging ecology history, contamination profile, and changes in physical environment for migratory fish. We studied commercially important species like salmon and tuna as well as common prey fish such as herring and smelt. Our results show that these naturally occurring heavy stable isotopes combined with conventional stable isotopes ($\delta^{13}C$, $\delta^{15}N$) can provide insights into dominant foraging habitats over short- and long-time frames and distinguish the habitat differences across ontogenic stages of migratory species. We further investigate the usefulness of heavy stable isotopes to study migratory species' present-day geographic range/routes and foraging conditions, which could provide crucial information for fish conservation and ecosystem management and the baseline for forecasting climate change impacts.

Lithium and silicon isotope dynamics in a carbonate island aquifer system, Rottnest Island, Western Australia

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Lithium (Li) and silicon (Si) isotopes are useful for tracing continental weathering processes. Interpretations of marine Li and Si records typically assume that the stable isotope continental weathering signal of meteoric waters is not modified during seawater mixing. However, silicate dissolution and secondary mineral formation processes appear to continue in seawater and may remove up to 25% of dissolved Li supplied by rivers globally (Pogge von Strandmann et al., 2008), and similar processes may affect Si isotopes. Here we measure Li and Si isotopes from source to sink in a carbonate island aquifer system at Rottnest Island, Western Australia. The δ^{7}Li values of fresh groundwaters ranged from +22 to +32‰. The correlation of Li with calcium and chloride concentrations, and the absence of low δ^{7}Li values suggests that Li is sourced from seawater mixing or carbonate mineral dissolution. The δ^{7}Li values of deeper, more saline groundwaters decreased with depth, and trend towards δ^{7}Li = +15‰, suggesting increased silicate and/or clay mineral dissolution. The δ^{30}Si values of groundwaters generally increased from +0.7 to +3.8‰ with increasing chloride concentrations suggesting seawater mixing predominantly controls Si isotope variations. However, δ^{30}Si values did not follow a simple conservative mixing trend as fresh groundwaters initially increased to a maximum of +2.6‰ and then decreased to +1.7‰ for deeper, more saline groundwaters. These data show that Li and Si isotopes do not undergo simple conservative mixing in coastal carbonate aquifers. Similar to artesian groundwater systems (Pogge von Strandmann et al., 2014), Li isotopes appear to be more sensitive than Si to geochemical changes in the aquifer environment.

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Fingerprinting Metal Signatures in Hawthorn (*Crataegus* sp.) around the Navan Zn-Pb Ore Deposit, Ireland: Developing a Conceptual Model for two Natural Systems using Cu and Zn Isotopes

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We report new results of trace-element geochemistry and metal stable isotopes of native and common Irish plant species including ash, beech, blackberry, hawthorn, oak, poplar and sycamore systematically sampled above the Navan Zn-Pb deposit (Ireland), currently mined by Boliden Tara Mines Limited. Biogeochemical analyses reveal the presence of an anomaly in plants directly above sub-cropping mineralisation, representing a natural metal anomaly.

Based on trace metal data on a wider selection of plant species, focus was placed on studying hawthorn and oak as representative plant species for spatial and temporal exploration vectoring. In order to better understand the source and pathway of the metal anomaly, stable metal isotopes were measured to investigate typical ranges of Zn and Cu isotopes in two large natural systems. For this purpose we analysed twelve plants, four wood samples and nine soil samples collected above mineralisation at Navan and in surrounding unmineralised areas. The Zn isotope composition of hawthorn growing on unmineralised ground exhibits enrichment in heavy isotopes ($\delta^{66}Zn_{JMC}$ of 0.15‰ to 0.48‰). By contrast, above the ore-body, much lighter Zn isotopes ($\delta^{66}Zn_{JMC}$ of -0.12‰ to -0.62‰) were detected in the same plant species. Copper isotopic composition showed a similar pattern of relative differentiation, though in absolute terms, all data were isotopically heavy ($\delta^{65}Cu_{NIST976}$ of +0.09‰ to +0.67‰). Investigating the soil isotopic composition for the two studied areas, we have determined slightly lighter Zn isotopes in the mining area ($\delta^{66}Zn_{JMC}$ of +0.19‰, on average) compared to the control site ($\delta^{66}Zn_{JMC}$ of +0.35‰, on average). The differences in plants and soil can be interpreted as representing two possible Zn sources: with signatures imparted on soil from Zn mineralisation (sphalerite) or from Zn contents in carbonate minerals in the host limestone sequences.

This study is resulting in a better understanding of biogeochemical metal cycling and for development of new geobotanical tools for Zn-Pb exploration in temperate European climates.

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Variations of Si cycling in the Chesapeake Bay during the Holocene

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Investigations within the last decades demonstrated the importance of the silicon (Si) cycle for the climate system by highlighting the role of diatoms – siliceous phytoplankton – in transporting carbon and other nutrients to the deep ocean (the 'biological pump'). Si isotopes can be used to detect changes in Si fluxes and utilization influenced by climate variations and human impacts. However, the transfer of Si from the continents to the ocean is still not fully understood and needs more attention.

Coastal marine ecosystems are sensitive to changes in nutrient loads and climate variations and can be seen as the linkage between the terrestrial and the marine Si cycles. The Chesapeake Bay, an estuary at the East Coast of North America, is a well-studied environment with a constrained settlement history (European settlement around 250 years BP). A suite of different sedimentary proxies reveal the influence of climate variations, land use changes and altered nutrient fluxes on the Chesapeake Bay ecosystem.

The terrestrial Si pool drained by rivers and ground water flows regulates the availability of dissolved silica (DSi) in the Chesapeake Bay. Changes in catchment Si pools and fluxes caused by e.g. variations in precipitation patterns or land use changes are likely to have a significant effect on Si inputs to the estuary. To investigate variations in Si fluxes in the Chesapeake Bay during the Holocene we measured biogenic silica (BSi) and δ^{30}Si in diatom frustules of two sediment cores. One site is located proximal to the main inflow, the Susquehanna River, while the other is closer to the Atlantic Ocean. A comparative approach will allow us to disentangle the effect of changing mixing conditions vs. changing end-member composition (i.e. to extract the signals of climate and human activity on terrestrial Si cycling).

Our first results show BSi fluxes increase simultaneously with European settlement, and also at around 7000 BP when the estuarine ecosystem evolved. The results indicate superimposed mechanisms (variations in precipitation pattern and erosion) that control the Si isotope signal in the Chesapeake Bay throughout the Holocene. Changes in δ^{30}Si correlate with changes in BSi and indicate a strong link to human activity during the last ~300 years. However, human impact on coastal ecosystems is diverse and needs further investigation.

Element mapping of silicate and sulfide minerals

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The element mapping of major and trace elements in silicate or sulfide minerals by LA-ICP-MS has be shown to be particularly useful in documenting the distribution of certain elements that rarely form their own minerals but instead substituting into the lattice of other sulfide minerals (e.g. gold in pyrite).

At the German Centre for Geosciences GFZ Potsdam, we operate an *Analyte Excite* 193nm excimer laser coupled to a *Thermo iCAP* quadrupole ICP-MS to quantitatively determine element concentration in various matrices (silicates, sulfides, carbonates, etc.). For coupling these two devices we use the Aerosol Rapid Introduction System (ARIS) to be able to map at much greater speed and higher spatial resolution than conventional LA-ICP-MS systems. We are able to use small (1 µm) laser spot diameters and high repetition rates of up to 300 Hz. By using the former mentioned instrumental setup we are able to increase the speed of data acquisition and therefore decrease the time mapping by a factor of up to 5. For example the time for mapping minerals with diameters of 300 µm will go down from 2-3 h to 50 min.

One application in our laboratory is the differentiation of distinct pyrite groups with divergent sulfur isotope compositions and individual trace element composition. We therefore coupled the Laser system simultaneously to the *Thermo iCAP* quadrupole ICP-MS to measure the trace element composition and to the sector field *Thermo Element* ICP-MS where we determined the sulfur isotope ratios. With this setup we reach a precision on the sulfur isotope ratios of ~2‰.

Tin column chromatography for isotope analysis of granite, sediment and coal

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Tin has 10 stable isotopes with masses from 112 to 124. It is the element that naturally has the largest number of stable isotopes. The variation of Sn stable isotope compositions in geomaterials is potentially of use in provenance studies. Therefore, in this study, three different geomaterials, granite, sediment and coal, are selected to develop a method of tin purification for further isotope composition measurements.

Standards of granite (AC-2), sediment (PACS-2) and coal (SARM-20) are first digested using microwave acid digestion. Then two sequential chromatography column separations are applied: the AG-1-X8 resin for major element elimination and the TRU spec resin for further tin separation.

By using the two-column separation, tin can be effectively separated from their original matrix. The recovery of Sn purification generally is around 80 %.

Deciphering sources of present day Zn pollution of the Earth surface environment from the geochemistry of ombrotrophic peat bogs

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Atmospheric heavy metal pollution is a global phenomenon of an increasing order. Despite regulatory actions, concentrations of heavy metals, and specifically zinc (Zn) remain elevated in the sub-surface level of different natural archives across the northern hemisphere.

In this study, we combine metal ratios, radiogenic Pb isotopes, and stable Zn isotopes in ombrotrophic peat bogs from the east and west coast of Ireland to reconstruct sources of atmospheric pollution over the last century. This time sequence comprises periods of historic mining and smelting, leaded gasoline, into recent times. A special focus is set on understanding the origin of the increasing load of atmospheric Zn observed today.

The isotopic composition of Zn the peat bog from the east coast shows an evolution from heavy (0.72‰±0.02) to lighter (0.18‰±0.02) $\delta^{66}Zn_{JMCLyon}$ values towards the top, in agreement with findings of other studies of peat cores. Strong correlations between Pb and Zn isotopes, as well as metal ratios (e.g., Zn/Cd, Cr/Cd, Ni/Cd) and Zn isotopes point towards a mixing from two major polluting sources: a geographically restricted (local mining) and a more diffuse recent source composed of emissions from fossil fuel burning, in particular from the widespread use of coal, diesel and oil. Metal ratios in the peat from the west coast of Ireland suggest a strong influence from coal combustion only, with insignificant depositions from vehicular emissions. This is due to the location of this site close to the Atlantic Ocean and remote to major urban settings with intense traffic.

Our study shows that: i) upward increase in Zn contamination observed at both sites represent a real pollution signal and not a manifestation of post-depositional redistribution within the peat bogs and, ii) Zn pollution shows a strong local activity control, whereby important contributors to the hemispheric pollution can be successfully identified.

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Cu isotopes in grey copper ores of Berezovsky ore field

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Berezovskoe ore field (Middle Urals, Russia), associated with vein gold-sulfide-quartz mineralization in altered sub-volcanic granitoid dykes among metamorphosed volcanites and serpentinites, covers a great area (ca. 60 km^2). Mineralogical zonality is revealed across the ore field, manifesting through the alteration of grey copper ores composition from antimonitic in the Southern to arsenic in the North.

The aim of the work is to obtain new data on Cu isotopic composition of Berezovskoe ore field and to trace its alteration on the example of minerals of tennantite-tetrahedrite series (23 samples of grey copper ores and bournonite) and Cu-minerals of weathering crust.

Sample preparation and analysis were carried out within the class 1,000 clean room facility (IGG UB RAS, Ekaterinburg).

Small monomineral samples (0.00n mg) were weighted under binocular in Savillex vials, then dissolved in 0.5 ml of concentrated HNO_3 and evaporated until dryness on a hot plate. After that the residuals were diluted by 3% HNO_3 so that the resulting Cu concentrations do not exceed 200 ppb. Cu isotopic analysis was carried out by MC-ICP-MS (Neptune Plus). Standard-sample bracketing approach was applied using Cu NIST SRM 976.

Obtained results indicate little variations of $^{65}Cu/^{63}Cu$. Most of the Cu isotopic ratios of Berezovskoe deposit and Blagodatnye Mines (the central part and the North of ore field) are grouped around the average value of $0.4725^{0}/_{00} \pm 0.0003^{0}/_{00}$. The samples from the Southern part are characterized by a slightly heavier Cu isotopic composition (0.4728-$0.4749^{0}/_{00}$). Thus, a weak dependence, connected with the temperature of mineral formation, is observed. A few samples with lowered $^{65}Cu/^{63}Cu$ ratios have the traces of hypergenic alterations, while the malachite and azurite from the same part of the deposit have slightly increased Cu ratios, which are in agreement with [Maher, 2005].

The study was carried out at the "Geoanalytic" Collective Use Centre and supported by UB RAS Presidium Programs No. 18-5-5-8 and 18-5-5-54.

Experimental determination of equilibrium Mg isotope fractionation between aqueous fluid and brucite, and among Mg aqueous species

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Due to their high concentrations in rock-forming minerals and natural fluids, magnesium (Mg) plays a key role in many processes taking place in the Earth's crust, the surface of continents and the oceans. Investigating Mg isotope signatures in solids and fluids can thus provide insights on the temporal evolution of continental weathering, sedimentary carbonates formation and seawater chemistry. Such an approach requires knowing the equilibrium isotope fractionation factors between a Mg-bearing solid phases and fluids, and among the important species controlling Mg aqueous speciation in natural fluids.

For this purpose we performed isotope exchange experiments at *bulk chemical* equilibrium between brucite ($Mg(OH)_2$) and aqueous fluids of various compositions and pH enriched in ^{25}Mg. Experiments were run up to 365 days. The 'three isotope method'[1] was used to quantify the advancement of the isotope exchange reaction and thus derive the equilibrium fractionation factors between brucite and Mg^{2+}(aq), Mg^{2+}(aq) and the $MgCitrate^{-}$complex, and Mg^{2+}(aq) and $MgSO_4^{\circ}$.

The results of this study are compared with ab initio calculated fractionation factors and discussed in terms of the mechanisms controlling chemical and isotopic exchanges at the soild-solution interface.

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Elemental and isotopic behaviour of Zn in Deccan basalt weathering profiles: Chemical weathering from bedrock to laterite and links to Zn deficiency in tropical soils

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Zinc (Zn) is a micronutrient for organisms and essential for plant growth, therefore knowledge of its elemental cycling in the surface environment is important regarding wider aspects of human nutrition and health. To explore the nature of Zn cycling, we compared its weathering behaviour in a sub-recent regolith versus an ancient laterite profile of the Deccan Traps, India. We demonstrate that progressive breakdown of primary minerals and the associated formation of phyllosilicates and iron oxides leads to a depletion in Zn, ultimately resulting in a loss of 80% in lateritic residues. This residue is mainly composed of resistant iron oxides ultimately delivering insufficient amounts of bio-available Zn. Moreover, (sub)-tropical weathering in regions experiencing extended tectonic quiescence (e.g., cratons) further enhance the development of old and deep soil profiles that become deficient in Zn. This situation is clearly revealed by the spatial correlation of the global distribution of laterites, cratons (Africa, India, South America, and Australia) and known regions of Zn deficient soils that result in health problems for humans whose diet is derived from such land.

We also investigate whether this elemental depletion of Zn is accompanied by isotope fractionation. In the saprolitic horizons of both weathering profiles, compositions of $\delta^{66}Zn_{JMC\text{-}Lyon}$ lie within the "crustal average" of +0.27 ± 0.07‰ $\delta^{66}Zn_{JMC\text{-}Lyon}$. By contrast, soil horizons enriched in secondary oxides show lighter isotope compositions. The isotopic signature of Zn ($\Delta^{66}Zn_{sample\text{-}protolith}$ up to ~ -0.65‰) during the formation of the ferruginous-lateritic weathering profile likely resulted from a combination of biotically- and kinetically-controlled sorption reactions on Fe-oxyhydroxides. This isotopic behaviour invites a broader study of global soils to test whether light isotope composition alone could serve as an indicator for reduced bioavailability of Zn.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° [608069].

Redox reactions in U-ore deposits: insights from U, Mo and Tl isotopes

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Mobility of U in natural systems is greatly influenced by redox state. U^{VI} forms oxyanions that will be highly mobile in oxidizing environments whereas in more reducing conditions, U^{IV} is immobile and precipitates in U-rich minerals such as uraninites (UO_2). Developing proxies of redox conditions is thus of prime importance, as these will give insights on the formation of U-ore deposits, on the long-term evolution of nuclear waste repositories and mine tailings, but also on potential new pathfinders for U exploration.

In this study, we focused on the MacArthur River deposit, in the Athabasca basin (Northern Saskatchewan, Canada). This massive unconformity-related U deposit exhibits some of the highest grades in the world (>15 wt% U_3O_8) and offers a unique geological context, with the deposit being overlain by a thick silicified layer strongly channeling fluids circulating through the system.

The objective of this study was to use clay minerals sampled throughout the stratigraphic profile to assess the evolution of the isotopic signature of several redox sensitive elements – U ($\delta^{238}U$, $\delta^{234}U$), Mo ($\delta^{97}Mo$) and Tl ($\varepsilon^{205}Tl$) – from the formation of the deposit at depth to the remobilization by later alteration fluids.

The $\delta^{97}Mo$ and $\varepsilon^{205}Tl$ results have a wide range of isotopic compositions in the U-ore minerals ($\delta^{97}Mo$ from -7 to +3‰, $\varepsilon^{205}Tl$ from -10 to +5 ε-units), and show variations in good agreement with what is observed in other redox-controlled systems. During remobilization, because of their very contrasted chemistry, Mo and Tl isotopes exhibit very different behavior, the former showing significant fractionation related to partial remobilziation by oxidizing fluids, whereas the signature of the latter is being preserved in clay minerals, likely due to its incorporation in interlayer sites.

Experimental investigation of Li behaviour during mineral-seawater interaction

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The inputs and outputs to the oceans drive the composition of seawater. Noticing the apparently unbalanced budget of major elements in the oceans, which should have led much saltier oceans than observed today, Mackenzie and Garrels (1966) proposed a process taking up cations from the seawater into authigenic sediments and liberating carbon dioxide compensating for CO_2 consumption on land *via* weathering. This process is termed "reverse weathering". Later Michalopoulos and Aller, (1995) showed such process exists using experimental evidence. Based on this work, Mackenzie and Kump, (1995) generalized reverse weathering reaction as：

Silica + degraded aluminous clays + iron oxide + organic carbon + soluble cations + bicarbonate → new clay minerals + water + carbon dioxide

Reverse is a viable candidate to explain the isotope mass balance of Li cycle in the ocean (Misra and Froelich, 2012), where it was suggested that reverse weathering accompanied by a Li isotope fractionation factor of 16‰ ((Δ^7Li=δ^7Li$_{\text{Seawater}}$- δ^7Li$_{\text{Sediments}}$). In this study, we conduct experiments to explore this effect by studying the Li concentration and δ^7Li during interaction between seawater like fluid and two minerals: kaolinite and basalt glass, representing clays and primary minerals, respectively.

In our study, we observe that ^{6}Li is preferentially leached out first during the dissolution of kaolinite in synthetic seawater. During an experiment time of ~160 days, the basaltic glass experiment leads to a 10% Li removal with little variation of δ^7Li in the solution; however the kaolinite experiment led to the removal of up to 85% doped Li with a significant elevation of δ^7Li (δ^7Li$_{\text{terminal}}$-δ^7Li$_{\text{initial}}$- = 25‰) in the dissolved load.

Altogether, these experiments show the potential of the interactions between seawater and detrital material to drive the Li isotope cycle of the ocean and more generally suggest their influence on the budgets of major alkali elements in seawater.

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Silicon Isotope Doping Method for Measuring Silicate Reaction Rates in the Critical Zone

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Our Si isotope doping experiments demonstrated that this is a robust technique for measuring silicate reaction rates at ambient temperature, near neutral pH, and close to equilibrium conditions, which are unattainable with the traditional Si concentration-based method. The isotope doping technique introduces an enriched rare isotope of an element to an experimental solution that is interacting with a mineral or a suite of minerals that have normal or natural isotopic compositions (Gaillardet, 2008). Although the method itself is not new, MC-ICP-MS technology now makes the measurement of a large number of non-traditional isotopes accessible, presenting a new opportunity to utilize the isotope doping method to advance the field of geochemical kinetics.

Results from experiments for albite, K-feldspar, and quartz (Liu et al., 2016; Zhu et al., 2016) demonstrated that the isotopic contrast and analytical precision allow detection of the dissolution of a minute amount of silicate. Because the precipitation of Si-containing secondary phases or the reverse reaction consume silica but leaves the ^{29}Si /^{28}Si ratios essentially unchanged in experimental solutions, dissolution rates were still measurable when secondary phase precipitation took place in experiments. This old story of “isotope ratio versus concentration” allowed our measurements of the simultaneous dissolution and precipitation rates at equilibrium, independently, and permitted testing of the applicability of the Principle of Detailed Balance. Many challenges remain in the discipline of geochemical kinetics. Innovation of the non-traditional stable isotope shows great promise for meeting some of the long-standing challenges.

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ISONOSE ISOTOPIC TOOLS AS NOVEL SENSORS OF EARTH SURFACE RESOURCES

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