Silica, Al and Pb in atmospheric PM10 and in human lungs in Upper Silesia, Poland

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Upper Silesia (US) is the most densely populated (>1600 people/km²) and the most polluted region of Poland. Annual average of PM10 concentration is still higher than national standards set by the regulators at 40 µg/m³. That situation poses a high risk to human health as evidenced by the medical data. In this study, silica, aluminium and lead were determined in atmospheric PM10 and in human lung tissues. Silica occurs as quartz and amorphous phase, whereas aluminium is in clay minerals, feldspars, amorphous alumino-silicates etc. Lead occurs in the form of galena, lead chloride and lead oxide. All of those mineral particles are abundant in respirable fraction of PM10 and in ultrafine particles.

Fifteen samples of PM10 and 34 samples of lung tissues from autopsy donors from US (13 female and 21 male) were analysed. Silica was determined by colorimetry, and aluminium and lead were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The concentration of silica in PM10 is the range of 1.00 – 34.98 wt. % (the average is 12.11±5.19 wt. %). In human lung tissues the average concentration of silica is 3.03±0.84 wt. % (the minimum value is 0.37 wt. % and the max. 5.65 wt. %). The concentration of aluminium in PM10 ranges from 0.58 wt.% to 2.78 wt. %. The average concentration of Al of 1.69±0.42 wt. % is distinctly higher than the average of Al in human lungs (0.197±0.08 wt. %). The lead content in PM10 ranges from 45 ppm to 1473 ppm, with the average 296±92 ppm. In human lungs the content of lead is 13±3 ppm, (min. 2 ppm, max. 47 ppm).

The presence of abundant Si, Pb, and Al in ultrafine particles is particularly worrisome as it is known, that particles with a diameter less than 0.5 µm immediately infiltrate into blood circulation system similarly to gases [1]. 100% of Pb hosted by ultraparticles is absorbed by lung tissues [2].

References
Helium solubility in ring site bearing minerals and implications for noble gas recycling

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Noble gas solubility in minerals is generally assumed to be low, leading to the assumption that noble gases are not recycled back in to the mantle (e.g. 1). However, applicable experimental data remain scarce. To explore possible mechanisms of noble gas recycling, we conducted a series of experiments defining He solubility in a suite of amphiboles and cyclosilicates using an externally heated, gas-pressure-medium apparatus. Analysis was conducted using by laser-ablation mass spectrometry. Helium was the pressure medium in all experiments. Pressures and temperatures ranged from 50 to 170 MPa and 650 to 800°C, respectively. Helium solubility in both cyclosilicates (tourmaline, beryl, cordierite) and amphibole (richterite, paragasite, actinolite) is remarkably high and correlates with the density of vacant (i.e., unoccupied by a cation) ring sites. Helium is >1,000x more soluble in vacant ring rich cordierite, beryl, and actinolite than in olivine.

The concentration of He dissolved into cordierite and beryl is linearly dependent on Pₜₚₑₛ, demonstrating Henrian behaviour, and thus applicable to natural systems. Depth profiles were completed on each phase investigated and showed that He concentrations are homogenous. This indicates a close approach to equilibrium and an absence of inclusions affecting the analysis. The observed solubilities are independent of experimental duration (7-27 hrs) and temperature (650 to 800°C).

The ring site is a lattice structure constituting six Si/AlO₄ tetrahedra linked in a hexagonal ring. It is large, hosting alkali cations, and has no net charge when vacant. Following lattice strain theory, the ring site is an energetically favorable environment for noble gas dissolution. Excess argon is commonly observed in natural samples of ring-bearing minerals (amphibole, mica, cyclosilicates) (2, 3), corroborating our conclusion that noble gas solubility can be associated with ring sites.

Ring-site-bearing minerals, including mica, serpentine, talc, and amphibole, are common in recycled lithologies (4) and may provide a possible mechanism for widespread recycling of noble gases back into the mantle. Moreover, ring-site bearing minerals are the major minerals responsible for recycling water and halogens. Thus, water and halogen recycling may be mineralogically linked to noble gas recycling.


Trace element composition of a non-chondritic Earth: Potential solutions and geodynamic implications

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The bulk composition of the silicate part of the Earth (BSE) has long been assumed to be tied to chondrites, where refractory, lithophile elements like Sm and Nd are thought to exist in chondritic relative abundances in the Earth. However, recent work exploring the ¹⁴²Nd/¹⁴⁴Nd systematics of modern terrestrial samples identifies ratios that are 18±5 ppm higher than the chondrite reservoir that challenges the traditional BSE model [1]. Here we investigate a hypothesis that this terrestrial ¹⁴²Nd excess is related to a Sm/Nd ratio 6% higher than chondritic. We develop a non-chondritic BSE trace element model in which the elevated Sm/Nd requires a shift of BSE ¹⁴²Nd/¹⁴⁴Nd from 0.51263 to 0.51300 that demands, in turn, corresponding changes to ⁸⁷Sr/⁸⁶Sr and ¹⁷⁶Hf/¹⁷⁷Hf, as well as the associated parent-daughter ratios — Rb/Sr, Lu/Hf. These modified parent-daughter ratios define a normalized trace element pattern, or spidergram, that is depleted in highly incompatible elements relative to the chondrite-based BSE. We use the ⁴⁰Ar abundance of the atmosphere, crust and depleted mantle to constrain the minimum K in the Earth (155 ppm), and anchor the spidergram to this K concentration to determine the concentrations of the other geochemically important incompatible elements, such as U and Th. An upper limit (170 ppm K) is estimated by assuming that abundances of the least incompatible elements (e.g., Lu) do not exceed chondrite-based BSE concentrations. This non-chondritic BSE trace element model requires that >78% of the mantle mass contribute to the formation of continental crust. The reduced concentrations in heat-producing elements U, Th and K in our new BSE compositional model implies a ~30% reduction in the current rate of radiogenic heating and, thus, a proportional increase in the heat flow delivered to Earth’s surface by plate tectonics, the implications of which we explore in parameterized thermal history models.

Mapping element concentrations and Ce⁴⁺/Ce³⁺ ratios in zircon by LA-ICP-MS

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A LA-ICP-MS procedure has been developed for simultaneously generating element, element ratio and isotope ratio maps of individual zircon grains. The instrumentation used was a Photon Machines Analyte.193 laser ablation system and Agilent 7700 quadrupole ICP-MS with addition of a second rotary interface pump that doubles instrument sensitivity. The procedure involves performing lines of individual spot ablations, resulting in true spot size-limited spatial resolution. Each spot ablation is preceded by several laser cleaning pulses and a short period of flushing to remove surface contamination (from condensation and other sources). For each element, signals for each individual spot are integrated into single readings, then calibrated using an external standard (NIST 612) and an internal standard (SiO₂) for element concentration measurements, and against a zircon (GJ-1) for Pb-U isotope ratio measurement. The concentration or ratio data are then presented as colour pixel maps by assigning colours according to concentration (or ratio) using a choice of different colour assignment schemes (linear, logarithmic, percentile).

Zircon (ZrSiO₄) is an abundant accessory mineral in granitoid igneous intrusive rocks that are associated with porphyry and other magmatic-hydrothermal mineral deposits. Using spot sizes as small as 7 microns in diameter, Ce and the REE from Nd-Lu, Pb, Hf, Th and U can be detected routinely in zircons. Measurement of this suite of REE allows, by extrapolation, calculation of Ce⁴⁺/Ce³⁺ ratios, which are a proxy for oxidation state of the source magma which has been linked to its fertility for generation of porphyry-style Cu (±Au±Mo) mineralization [1]. Distribution maps for key trace elements and Ce⁴⁺/Ce³⁺ ratios in single zircons thus allow the geochemical evolution of the magmatic system, including oxidation state, to be visually documented.

The procedure is been applied to zircons from a suite of Jurassic and Cretaceous granitoid intrusions from the Canadian Cordillera, including samples from igneous host rocks to porphyry-style deposits, to determine whether systematic differences exist in the geochemical trends between mineralised and non-mineralised intrusions. Pb/U ratio and age maps for the zircons are also being generated, allowing identification of inherited cores and, potentially, multiple crystallisation ages for zircons that have had a protracted crystallisation history. Also being evaluated is whether zones with anomalous ages can be identified and whether these correlate with the chemistry of the REE, or other elements, as has been proposed [2].


Shale gas and its environmental footprint

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The Marcellus shale is one of the largest natural gas reservoirs in the United States and, like other shale gas reserves, has been developed through advances in drilling technologies and production strategies. Concerns over potential environmental impacts have accompanied natural gas extraction around the country. We have sampled shallow groundwater systems of >200 homeowners in NE Pennsylvania and New York for brines, dissolved gases, and other attributes of water quality for the last two years. In particular, we have exampled possible relationships between water quality and distance to natural gas wells.

In our first study published in May of 2011 [1], we found no evidence of increase salt concentrations or fracturing fluids with distance to gas wells, but dissolved methane concentrations were 17 times higher on average for water wells found within 1km of them. Higher chain hydrocarbons (ethane, propane, and butane) were detected more often in active areas (21, 8, and 3, respectively) compared to non-active areas (3, 0, and 0, respectively), indicating a more thermogenic methane character. The carbon isotope values of 13C-CH4, in active extraction areas were on average less negative (-37±7 ‰) than non-active extraction areas (-54±11 ‰). We conclude from these, and newer follow-up results, that there are important differences in methane concentration, natural gas composition, and 13C-C-CH₄ values in some shallow groundwater wells near natural gas extraction areas. Furthermore, the dissolved gas geochemistry nearer gas wells appears to be consistent with a more thermally mature source of organic matter. New results from additional sampling in 2011 will be presented.

High concentrations of atmospheric ClO$_4^-$, ClO$_3^-$, and NO$_3^-$ occur in the Atacama Desert where dry and oxic conditions allow oxyanions to accumulate near the surface over long periods. We collected sediment samples from vertical profiles (~1-3 m depth) over a 1000 km longitudinal transect along the central depression in the Atacama. ClO$_4^-$/NO$_3^-$ molar ratios (350-3,500) and NO$_3^-$ stable isotopes were relatively consistent both with depth and along the longitudinal transect except for locations receiving ~2 cm of annual precipitation. ClO$_4^-$/ClO$_3^-$ molar ratios were similar for most sites (~1). In contrast, ClO$_4^-$ exhibited substantial variation in its stable isotopic composition ($\delta^{17}$O and $\Delta^{17}$O) with respect to location along the longitudinal transect. In addition, the $\delta^{18}$O and $\Delta^{17}$O of O in ClO$_4^-$ were strongly correlated ($r^2$=0.89). Elevated $\Delta^{17}$O values indicate ClO$_4^-$ formed largely by O$_3$ mediated oxidation of Cl, possibly in the stratosphere. However, substantial variation in $\delta^{18}$O (-25 to -3 per mil) and $\Delta^{17}$O (+4 to +10 per mil) of ClO$_4^-$ is intriguing given the long salt accumulation times (~10^5 years). This isotopic variation may indicate some unknown process is controlling deposition over a large area for long time periods, atmospheric ClO$_4^-$ isotopic composition has varied in geologic time, or some surface process (generation or alteration) that varies spatially is affecting the ClO$_4^-$ isotope composition by transformation, exchange, or dilution. Insights from our work are relevant to models of oxyanion production and accumulation in areas with little biologic activity.

Enstatite Chondrites and the Composition of the Earth

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The nearly identical O isotopic compositions of the enstatite chondrites (EC), Earth's mantle, and Moon were used [1] to argue that the EC provide the best Solar System material for estimating the chemical composition of the Earth. A possible link between the EC and Earth is further supported by recent observations that EC and Earth have the same isotopic compositions for both major and minor elements (O, Ca, Ti, Cr) which exhibit substantial variations among different chondrite groups [e.g., 2-4], with Si being the only exception.

However, there is a huge mismatch in chemical compositions between the EC and Earth. For example, the EC have much too high Rb/Sr and K/U ratios and are depleted in FeO and refractory lithophile elements compared to the composition of Earth's mantle deduced from terrestrial rocks. This discrepancy could be resolved by assuming that the Earth and EC had a common nebular precursor but they have experienced different chemical evolution. Such an assumption is supported by the mineralogy and O isotopic data for the most primitive EH3 chondrites.

The abundant FeO-bearing silicates, compositionally similar to those in other classes of chondrites, are well documented in ECs [5-8], with most silicates having O isotopic compositions of the bulk EC values [7-8]. Recent studies [9-11] showed that the chalcophile behaviour of Ca, Mg, Na, and other elements in EC is due to secondary processing of FeO-bearing silicates in an H-poor environment with high $f_{ce}$ (Fe-FeS buffer) and $f_{co}$ close to the CO$_2$ buffer.

We propose that the nebular reservoir that produced the precursor material for EC has also produced the building blocks for the Earth, chemically similar to the widely accepted Earth’s composition of [12]. Interestingly, the Nd isotope variations in the Earth and EC are consistent with a bulk mantle-crust system that followed the CHUR evolution curve [13].

Investigating cloud absorption effects I and II: Global and Arctic absorption properties of black carbon and tar balls in clouds and aerosols

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This is a study to understand better Cloud Absorption Effects I and II, which are the effects on cloud heating of absorbing inclusions in hydrometeor particles and of absorbing aerosol particles interstitially between hydrometeor particles at their actual relative humidity (RH), respectively [1]. The GATOR-GCMOM model was used to study these effects as well as optical properties and the mixing states of black carbon (BC) and tar balls (TB) in clouds and aerosols. The globally- and annually-averaged modeled 550-nm aerosol mass absorption coefficient (AMAC) of externally-mixed BC was found to be 6.72 (6.3-7.3) m2/g, within the laboratory range (6.3-8.7 m2/g). The global AMAC of externally- plus internally-mixed (IM) BC was 16.2 (13.9-18.2) m2/g, less than the measured maximum at 100% RH (23 m2/g). The resulting AMAC amplification factor due to internal mixing was 2.41 (2-2.9), with highest values in high RH regions. The global 650-nm hydrometeor mass absorption coefficient (HMAC) due to BC inclusions within hydrometeor particles was 17.7 (10.6-19) m2/g, ~9.3% higher than that of the IM-AMAC. The 650-nm HMACs of TBs and SD were half and 1/190th, respectively, of that of BC. Modeled aerosol absorption optical depths were consistent with AERONET and OMI data. In column tests, BC inclusions in low and mid clouds (CAE I) gave column-integrated BC heating rates ~200% and 235%, respectively, those of interstitial BC at the actual cloud RH (CAE II), which itself gave heating rates ~120% and ~130%, respectively, those of interstitial BC at the clear-sky RH. Globally, cloud optical depth increased then decreased with increasing aerosol optical depth, consistent with boomerang curves from satellite studies. Thus, CAEs, which are largely ignored, heat clouds significantly.


Electron Donor Utilization During the Bioreduction of Uranium

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Stimulating microbial reduction of soluble U(VI) to less soluble U(IV) is a promising strategy for remediating uranium contaminated groundwater. Little is known about optimizing the electron donor for promoting this process, nor what fraction of the electron donor is utilized by the target microbial population. Results presented here focus first on the effect of several electron donors on the microbial community and the overall uranium removal efficiency, and then on the specific utilization of acetate by target microorganisms. Acetate and lactate, as well as more complex and commercially used donors such as a hydrogen-releasing compound (HRC) and vegetable oil were examined in terms of their effect on uranium removal and the microbial community, using flow-through column experiments. The composition of the microbial communities was evaluated with quantitative PCR probing specific 16S rRNA genes and functional genes, phospholipid fatty acid analysis, and clone libraries. For equivalent amounts of donor in terms of total organic carbon, acetate was least effective in U(IV) removal, while vegetable oil and donors such as HRC were most effective.

Utilization of acetate was examined closer by utilizing C-13 labeled acetate to determine which microorganisms take up acetate during the biostimulation process, promoting this process, nor what fraction of the electron donor is utilized by the target microbial population. Results presented here focus first on the effect of several electron donors on the microbial community and the overall uranium removal efficiency, and then on the specific utilization of acetate by target microorganisms. Acetate and lactate, as well as more complex and commercially used donors such as a hydrogen-releasing compound (HRC) and vegetable oil were examined in terms of their effect on uranium removal and the microbial community, using flow-through column experiments. The composition of the microbial communities was evaluated with quantitative PCR probing specific 16S rRNA genes and functional genes, phospholipid fatty acid analysis, and clone libraries. For equivalent amounts of donor in terms of total organic carbon, acetate was least effective in U(IV) removal, while vegetable oil and donors such as HRC were most effective.

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The differentiation of continental crust in arcs

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Processes resulting in the chemical stratification of the continental crust have since long been studied but, limited information is available on the extend and origin of stratification of the initial juvenile continental crust formed in arcs. This lack of knowledge renders the quantification of secondary reworking processes in the continental crust difficult. Here we present an extended dataset documenting the magnitude and nature of chemical stratification of the juvenile Kohistan arc crust. The Kohistan arc (NE Pakistan) is the only complete exposed arc section preserved in the geological record, ranging from upper mantle peridotites and ultramafic cumulates at the bottom to unmetamorphosed sediments at its top. The bulk composition of the Kohistan arc, formed during intra oceanic subduction, is andesitic and similar to the bulk continental crust. As postcollisional secondary reworking processes in Kohistan are negligible, the chemical stratification observed of the Kohistan arc represents the best available initial stratification state of the juvenile continental crust formed in arcs.

We used in total ~60 own and published geobarometric results (Al-in-hbl and various net-transfer reactions) to constrain the (re)crystallisation depth of the different plutonic rocks of the entire Kohistan arc. The calculated (re)crystallisation pressures coincide well with inferred intrusion depths of the different units based on magmatic phase relationships and form a regionally consistent pattern of increasing pressures from the unmetamorphosed sediments in the north to the upper mantle peridotites in the south. We thus interpret the geobarometric results to generally reflect magmatic emplacement pressures. Based on these results, we used standard krigging methods to approximate the intrusion depth of > 200 sample for which geochemical whole rock compositions exist. The result is a profound chemical stratification between the lower and upper crust. Whereas the upper part of the crust is internally only weakly stratified and compositional rather homogenous the lower crust section is compositionally strongly stratified and complementary to the upper crust. This indicates that the juvenile continental crust formed in arcs inherits a strong primary compositional stratification before secondary (e.g. remelting) processes may set in.


Multi-tool dating for polymetallic deposits (Antimony Line, RSA)

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The 3.09-2.97 Ga Murchison Greenstone Belt is one of several Archean volcano-sedimentary belts within the Kaapvaal Craton in southern Africa [1]. It hosts a variety of ore deposit types: VMS style Cu-Zn mineralization [2], pegmatite related emerald and orogenic-style Sb-Au deposits along the Antimony Line (AL), the latter an unusual Precambrian Sb-dominant set of deposits located in a major quartz-carbonate altered ductile structure. Various models (magnetic, volcanogenic-derived, orogenic-gold...) have been proposed for the AL, which emphasize its overall complexity.

The Malati Pump mine, at the eastern end of the AL, hosts Au-Sb mineralization in the cupola of one of a number of granodiorite plugs intrusive into the belt. Its U-Pb (Zircon) dating and Pb-Pb dating of the Au-Sb-related sulphides yield an age of 2.97 Ga, identical to the age of the VMS Cu-Zn and the emerald deposits. Thus the granodiorites emplacement was probably the main trigger for this polymetallic metallogenic system at different crustal levels (Fig).

The AL is also clearly related to hydrothermal fluid circulation. Albitites run along the AL, and were developed at the expense of a granodioritic protolith. Their systematic enrichment in Sb highlights a genetic link between the Sb mineralization and the albitization process. U-Pb data on hydrothermal monazites spread along the Concordia from 2.8 down to ca 2.0 Ga. Chemical analyses on the dated monazite allow us to interpret the data as a Discordia (combination of a major fluid circulation at 2.8 Ga followed by a thermal/fluid event at ca 2.0 Ga) rather than as a multi-events system.

Figure: Model for the AL deposit formation and evolution.

Fluid dating is rather complex as is the AL system as a whole. This study illustrates that a combination of conventional U-Pb zircon dating to accurately identify the emplacement ages of the major igneous host rocks, with Pb-Pb dating of sulphide minerals and U-Pb dating of monazites to date stages of mineralization, plus mineral chemistry studies of the various dated phases combined with 40Ar/39Ar geochronology represents a useful methodology for uncovering the history of metallogenically complex regions.

Shear deformation of olivine at high pressures and temperatures: An atomic scale perspective

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Olivine, (Mg,Fe)2SiO4, is assumed to be the most abundant mineral of the Earth’s upper mantle. The knowledge of its physical properties in the relevant range of pressures and temperatures therefore provides important constraints on the dynamic behavior of the upper mantle. Plastic deformation of olivine has been investigated for a long time but recent experimental [1] and computational [2] studies suggest a pressure and strain rate dependence of the dominant olivine dislocation slip system from [100] slip at low pressures and low strain rates to [001] at high pressure and high strain rates.

Here, an atomic scale modeling approach is used to investigate the pressure and temperature dependence of the shear deformation mechanism of the magnesium end member, MgSiO4 forsterite. The simulations combine classical molecular dynamics with metadynamics using the scaled simulation cell box matrix as dynamic variables [3]. The particle interactions are described by an advanced polarizable ion potential [4]. Pressure was varied between atmospheric and 20 GPa, temperature between 1000 K and 2000 K. At high pressures (> 5 GPa), the dominant shear is observed in [001], which is consistent with the experimental studies. The dominant shear plane changes from (100) to (010) with increasing pressure and temperature. At lower pressures (< 5 GPa), both shear in [100] and combined shear in [001] and [100] are observed.

Besides identification of shear plane and direction, insight into the atomic scale mechanism of shear is obtained. The most interesting observation is a change of shear mechanism in [001](010) from a two-step process at lower pressure, in which SiO4 tetrahedra remain intact and the stacking order of oxygens unchanged, to a three-step process, which involves breakage of Si-O bonds and changes in the stacking order of the oxygen sublattice. The latter mechanism is observed at the highest pressure, where the free volume needed for the other shear mechanism becomes energetically too expensive. Finally, possible relations between shear deformation and high pressure phase transitions of single crystal forsterite will be discussed.

The shear deformation observed in these simulations does not describe the process of dislocation creep but it provides useful guidelines and insights that are not available otherwise. The method used in this study may therefore complement other efforts to understand the rheological behavior of mantle minerals, including the very promising multiscale simulation method presented very recently [5].


Mineralogical controls on arsenic bioaccessibility in mine waste and body fluids

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Arsenic associated with ores is typically hosted in arsenopyrite and/or arsenical pyrite. In mine waste, arsenic mineralogy is much more complicated as a result of weathering, ore processing and the ability of As to be incorporated as As(V), As(III) or reduced As in a wide range of secondary minerals. Gastric to intestinal extraction tests indicate decreasing As bioaccessibility from Ca Fe arsenate > lead arsenate > arsenic trioxide > amorphous iron arsenate > As-bearing Fe oxyhydroxide > arsenical pyrite > As sulfide (realgar) > arsenopyrite. There are likely to be additional factors affecting As uptake in the gastro-intestinal system including changes in pH, redox conditions and availability of Fe and S to combine with dissolved As.

Field and laboratory observations of the stability of As secondary minerals in mine waste may provide insight into the anticipated complexities and As phase transformations in the gastro-intestinal system. Arsenopyrite (FeAsS) is typically coarse-grained relative to secondary minerals, explaining why it does not react during bioaccessibility tests which involve exposure to gastric fluids for only an hour or so. Scorodite (FeAsO4 · 2H2O) forms as an oxidation product of arsenopyrite (Fe/As = 1 for both minerals) and is stable in low pH environments which explains why it releases little As to acid gastric fluids, even when the starting solid is nanocrystalline [1]. As pH increases, scorodite is transformed to hydrous ferric arsenate (Fe/As=1), which may explain why more As is released to circum-neutral pH intestinal fluids. Tootleite (Fe(AsO4)(SO4)(OH)4·4H2O) has been recognized only rarely in mine waste but precipitates readily when As(III) is combined with Fe(III) under acid conditions (pH<4) [2] suggesting that if sufficient Fe is available (Fe/As=.66), this phase may form under gastric conditions and limit As bioaccessibility. Arsenic trioxide (As2O3) is a product of ore processing which is stable over a wide range of pH and, in some contaminated soils, persists for many decades. In other situations, arsenic trioxide combines with Fe(III) to form scorodite in acid drainage [3] or with reduced S to form secondary As sulfides [4]. It is possible that similar transformations may occur in the body, both of which would reduce As bioaccessibility. Finally, Ca-Fe arsenate minerals (e.g. yukonite CaFe12(AsO4)11(OH)2·15H2O) have Fe/As>1 form under pH-neutral conditions where carbonate minerals are stable. These minerals are soluble in acid fluids and exhibit high As bioaccessibility in gastric solutions.

Laboratory results indicate that As bioaccessibility can actually be higher per mass in simulated lung fluids than gastric, but the overall dose is smaller due to the lower amounts that reach the lung.

Chromium isotope fractionation during reduction of Cr(VI) under saturated flow conditions

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Chromium (VI) is a pervasive groundwater contaminant that poses a considerable threat to human health. Remediation techniques have focused on the reduction of the highly mobile Cr(VI) to the sparingly soluble Cr(III) species. Reduction has been shown to produce significant Cr isotope fractionation, characterized by an enrichment in the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio in the remaining Cr(VI) pool [1]. Chromium isotopes are promising indicators of Cr(VI) reduction in groundwater; however, the influence of transport on fractionation has not been fully examined.

A laboratory column experiment was conducted to evaluate isotopic fractionation of Cr during Cr(VI) reduction under controlled flow conditions. Simulated groundwater containing 20 mg L⁻¹ Cr(VI) was pumped through a saturated column containing quartz sand with 10% (v/v) organic carbon. Isotope measurements were performed on both effluent and profile samples. Dissolved Cr(VI) concentrations decreased while $^{53}\text{Cr}$ increased, indicating that reduction of Cr(VI) occurred. Solid-phase analysis by scanning electron microscopy (SEM) and X-ray absorption near edge structure (XANES) spectroscopy confirmed the presence of Cr(III) on the surface of the organic carbon. The $\delta^{53}\text{Cr}$ data followed a linear regression equation yielding a fractionation factor ($\alpha$) of 0.9979, whereas previous studies of batch experiments under similar geochemical conditions demonstrated Rayleigh-type isotope fractionation. Both the results of the solid-phase Cr and isotope analyses suggest a combination of Cr(VI) reduction mechanisms, including reduction in solution, and sorption prior to reduction [2]. The linear characteristic of the current $\delta^{53}\text{Cr}$ data may reflect the contribution of transport on Cr isotope fractionation.


Mechanisms of reaction driven porosity and permeability generation

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The evolution of the Earth’s lithosphere is, to a major extent, affected by reactions in which magmatic or metamorphic rocks consume fluid components such as H₂O and CO₂. Examples include serpentinization of the oceanic lithosphere and weathering of continental rocks. The progress of such reactions, as well as many other replacement processes that depend on the presence of a fluid phase, requires that porosity is maintained to keep fluid in contact with reactive solid surfaces.

As most volatilization reactions lead to a reduction in rock density, and thus an increase in the volume of solid, the initial pore volume will tend to become filled with new mineral phases during such processes, in the absence of porosity-generating processes. However, observations at scales ranging from nanometer to outcrop scales, indicate that a variety of porosity generating processes are operating. For example, replacement reactions mediated by dissolution-reprecipitation mechanisms have been observed to produce micro-porous products in a variety of systems [1], while reactions associated with a significant volume increase often lead to fracturing [2]. However, the detailed mechanisms of these porosity-producing processes have been poorly understood.

In this contribution, we review examples of reaction driven fracturing, and propose a new model for how stress is generated at reacting olivine surfaces during serpentinization. This model emphasizes the role of interface coupled dissolution-reprecipitation processes in producing the surface roughness required to generate stress concentration and associated fracturing at the reactive surface. This process results in the hierarchical fracture network [3] represented by the characteristic mesh-structure of partly serpentinized olivine grains. Similar patterns are also observed in a variety of other systems.

The relationship between PM10 and meteorological conditions in Sosnowiec (Poland) in view of potential health hazard

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The aim of this study was to determine concentrations and chemistry of PM10 in one of the major cities in densely populated and industrial region of Upper Silesia, SW Poland, in relation to meteorological conditions. Meteorological conditions and atmospheric circulations play an important role in dispersion of air pollutants [1].

Both concentrations of PM10 and meteorological parameters were monitored from June to December 2011. In addition, the collected PM10 was investigated by analytical scanning and transmission electron microscopies (SEM, TEM). The identification of phases in PM10, their morphology, chemical compositions, structure and particle size enabled the precise pinpointing of the emission sources.

The abundant ultraparticles occur in the PM10 fraction. Those ultraparticles are carriers of heavy metals including Pb, Zn, Cd, U and others. The most common constituent of PM10 is soot. A large number of nano-sized particles containing toxic elements adhered to the soot surface and together with respirable soot particles can be inhaled by the humans.

Quartz, iron oxides, amorphous and crystalline aluminosilicates are also abundant in PM10 and in ultraparticles. Regardless of their size they may have a negative impact on human health as suggested by medical data for this part of Poland. All of the observed mineral phases in PM10 are typical of fossil fuels combustion and of car exhausts.

As expected, the highest concentrations of PM10 was observed during the prevalence of anticyclonic conditions, at low speed winds, and the lack of precipitation. The extremely high concentrations of PM10 were associated with the thermal inversion. The presence of some mineral phases in PM10 (e.g. Zn, Pb, Cd-sulfides, Sn alloys) combined with back-trajectories of air flow allowed precise location of particular sources of dust emissions.

A Physiochemical Analysis of the Transport and Retention of Technetium in Unsaturated Hanford Formation Sediments

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The transport of Tc, like many other radionuclides, is of interest due to the potential for human exposure and impact on ecosystems. Specifically, Tc is a contaminant of concern at several DOE facilities including the Hanford, Oak Ridge, Paducah, Portsmouth, and Savannah River Sites.

Current conceptual models do not fully explain the distribution and persistence of technetium in vadose zone environments such as the Hanford site, Eastern Washington. In an oxic environment with low organic content the residence time of technetium in the soil would be expected to be low, due to its low sorption and high mobility. While Tc(VI)O4 can be reduced, it is also readily oxidized, so temporary reducing environments are not expected to alter the general rapid Tc migration in the subsurface. Inexplicably, nearly 50 years following the release of contamination into the site, a significant fraction of Tc has persisted in the subsurface in the 200 Area.

In these experiments we examined the unsaturated transport of pertechnetate at very low water content using an Unsaturated Flow Apparatus (UFA) to evaluate breakthrough curve behavior and the potential impact of immobile domains, anion exclusion and sorption on the transport and retention of technetium. The analysis confirmed that Tc was transported at pore water velocity and that transport was not altered by the presence of immobile domains, anion exclusion, or sorption. The experimental dispersivity increased with decreasing saturation.

Using borehole sediments from the Hanford site 200 Area where Tc co-disposed with a variety of chemicals and has been in contact with the sediment for decades, a series of sequential extractions was conducted to evaluate the mineral associations of technetium in natural Hanford sediments. The sequential extractions targeted the Tc associated with the ion exchange layer, carbonate minerals, aluminosilicate minerals and iron oxides. The analyses indicated that while most Tc was associated with an aqueous extractable phase, some Tc was associated with oxalic acid and nitric acid extractable phases. The preliminary results indicate a portion of the Tc may be less mobile than originally indicated. EXAFS and XANES will be used to identify Tc surface phases, as the surface Tc may be incorporated in minerals or coated by non-Tc precipitates. Results from extractions and additional geochemical analysis will be presented.

Saline groundwater discharges in the Athabasca oil sands region: a chemical mass balance

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Quantifying water quality impacts of oil sands developments in western Canada will require decoupling natural contributions of organic and inorganic contaminants from potential releases from tailings ponds, oil sands mining, and in-situ bitumen production. Here, we quantify natural saline groundwater contributions to the Athabasca River by applying a chemical mass balance (CMB) to monthly chemical and discharge data collected between 1987 and 2009, using data available from the Long Term River Network.

The results of the chemical mass balance indicate that saline springs are an important control on the chemistry of the Athabasca River, despite comprising <3% of the river’s discharge. The impact of these discharges on the chemistry of the Athabasca River is greatest during periods of low river flow. The shift in chloride concentrations measured between Fort McMurray and the Peace Athabasca Delta can only be explained if saline groundwater along this stretch are in the range of 500 to 3400 L/s. This finding is supported by the subcrop exposure and known seepage of Devonian- and Cretaceous-aged aquifers bearing saline fluids along this reach of the Athabasca River. While this study does not exclude the possibility that tailings discharge to the Athabasca River could be occurring, the observed increase in chloride measured between Fort McMurray and the Peace Athabasca Delta cannot be accounted for using tailings pond seepages alone. The range of chloride concentrations reported for a wide range of tailings ponds are very low in comparison with the groundwater seeps entering the river and the total increase in chloride along this stretch cannot be reconciled using just mixing with tailings pond water.

Given the important role discharges of saline groundwater from Cretaceous and Devonian formations appears to play in the geochemical evolution of the Athabasca River, a more comprehensive evaluation of regional groundwater flowpaths and groundwater surface water interactions is warranted. These results suggest that any future water quality monitoring efforts for the Athabasca River should try to better quantify the contribution of groundwater inflow to changes in river water quality.
Historical atmospheric deposition of PAHs in lakes east of the Athabasca oil sands operations

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The growth of bitumen mining activities in northeastern Alberta poses significant environmental challenges. One of the main concerns is a potential increase in emissions of harmful organic contaminants such as polycyclic aromatic hydrocarbons (PAHs). PAHs are widespread in the environment and result from incomplete organic matter combustion (kinetic process) or maturation (thermodynamic process), which makes them good markers of pyrogenic or petroleum input.

In order to understand the impact of oil sands-related mining activities to the environment it is essential to examine PAH emissions in the context of variability in natural background levels. Here we report geochronological records of PAH atmospheric deposition fluxes over the last century in two headwater lakes located approximately 50 km downwind from the main area of oil sands operations. Assessing PAH levels over the last 100 years allowed us to differentiate the deposition fluxes prior to the modern period of bitumen mining activities (i.e., pre-1970). Concentrations of the 16 EPA priority PAHs in addition to coronene, retene, perylene and 6 alkylated groups were measured in dated cores from both lakes. PAH molecular diagnostics ratios were used in order to discriminate preliminary sources and their variation over time.

Results and conclusion:

Our results showed an increase of parent and alkylated PAHs (2-fold for alkylated PAHs and 0.5-fold for 16 EPA priority PAHs) in both lakes over the past decade. Alkylated PAHs are generally related to petroleum sources. A possible explanation for this increase may be the expansion of open mine pit area resulting in greater sensitivity to wind erosion and transport. PAH molecular diagnostics ratios revealed two distinct groupings using two different sets of ratios: a pre-1980s combustion dominated type, and a post-1980s petroleum dominated one. These results point to an increasing contribution from recent oil sands mining activities, though it should be noted that overall PAH levels in these lakes are relatively low. In light of these results, and taking into consideration the future expansion plans of bitumen mining activities, it is possible that PAH fluxes in this region may continue to rise. Further insight into PAH source apportionment is expected from ongoing work involving compound-specific isotope analysis.

Meridional distribution of the atmospheric $^{3}$He/$^{4}$He isotopic ratio

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Due to the release of crustal helium by natural gas and oil production and by coal mining with a low $^4$He/$^3$He ratio, the atmospheric $^3$He/$^4$He ratio may be decreasing with time. The direct detection of this change is problematic due to the difficulty in finding well preserved ancient air samples and has led to conflicting results. Most of the $^3$He release occurs in the northern hemisphere, therefore it may create an interhemispheric gradient in the atmospheric $^3$He/$^4$He ratio, as already observed for other anthropogenic gases such as CH$_4$, CFC or $^{85}$Kr. We performed precise helium isotope measurements on air samples collected at various latitudes going from 82°30’N (Alert Station) to 78°38’S (Vostok Station). The mean helium isotope ratio (relative to our Saclay air standard) are identical for both hemisphere: 1.0004 ± 0.0005 for the northern hemisphere and 1.0004 ± 0.0009 for the southern hemisphere respectively, thus showing no detectable meridional gradient. However, as shown in Fig. 1, $^3$He/$^4$He values are very homogeneous from the northernmost latitudes to 20°S but the two southernmost data points show diverging trends. Therefore, additional data are needed south of 20°S.

Figure 1: Meridional distribution of the helium isotopic ratio of air

The lower value for Vostok could be due either to the high elevation (3500 m) or to the relative isolation of the air masses over the Antarctic interior. If we consider this latter data point as an outlier, the mean $^3$He/$^4$He value for the southern hemisphere becomes 1.0006 ± 0.0009. The two mean values, $^3$He/$^4$He = 1.0004 for the northern hemisphere and $^3$He/$^4$He ≤ 1.0006 for the southern hemisphere, can be used to estimate the value of the anthropogenic helium flux using a simple two-box model of the atmosphere with an interhemispheric mixing time of about 1 year [1-2] and a anthropogenic helium input function proportional to the world release of fossil carbon since 1850. Model results indicate that the He/C molar ratio may be $\leq 2 \times 10^{-7}$, with a decrease of the atmospheric $^3$He/$^4$He ratio ≤ 0.7% over the industrial period.

Ferric oxyhydroxide microbial mat community metabolic model based on metagenome sequence analysis

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Introduction and Approach

Ferric oxyhydroxide microbial mats in acidic high-temperature springs of Norris Geyser Basin, Yellowstone National Park (Wyoming, USA) are inhabited by an environmentally constrained consortia of archaea. These extreme environments are ideal sites to study microbial interactions in natural communities where gradients in temperature and oxygen occur over spatially resolvable distances. The goal of this study was to generate a stoichiometric metabolic model as an incremental step in describing the microbial ecology within these chemotrophic systems. We obtained a metagenome of a ferric oxyhydroxide mat community in One Hundred Springs Plain via Sanger sequencing (DOE-Joint Genome Institute). De novo assemblies were obtained using the Celera (J. Craig Venter Institute) assembler and evaluated using nucleotide word frequency-principal components analysis. These communities are comprised of several dominant populations including chemolithoautotrophic Thermoprotesales, Desulfofurococcals, and a novel, deeply rooted archaeon (NAG1). De novo assemblies corresponding to these populations were annotated and in silico stoichiometric metabolic models were created for each organism focusing on mass and energy fluxes within and between community members.

Results and Conclusion

Multiscale metabolic systems analysis was used to predict possible modes of microbial interaction where autotrophic metabolism of Metallosphaera yellowstonensis supports Thermoprotesales, Desulfurococcals, and NAG1 growth via metabolic exchange of cofactors as well as different types of reduced carbon. These metabolic exchanges suggest autotroph-heterotroph relationships constrained by fluxes of major electron donors/acceptors and sources of carbon. This work provides a rational, in silico framework for understanding the microbial ecology within a thermophilic ferric oxyhydroxide mat community.
Geochemical characteristics of suspended matters and sediments in a small watershed of the central Guizhou province and its weathering implications

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Southwest China is one of the three biggest karst areas in the world. Over the past few decades, land use changes in this area have resulted in a series of severe ecological and environmental problems. This paper presents data on trace elements and C, N isotopes of suspended matters and sediments collected from the Qianzhong watershed in the central Guizhou province, Southwest China. Results showed that the contents of trace elements are different between rivers and lakes, also between suspended and sedimentary phases; the spatial and temporal distribution of OC contents, Corganic/Ntotal and δ13C in total suspended matter (TSM) and sedimentary matter showed different variation, indicating the transfer and arrival of allochthonous organic matter and the ecosystem changes during past sedimentary period. δ15N ratios reflected the combined results of information of sources and a series of biogeochemical processes. Although δ15N ratios could provide limited information of sources, it can be used to trace some special biogeochemical processes. The conclusion was testified the element characteristics and material conveying status in chemical weathering and physical erosion processes in the small watershed. 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Towards a unifying theory of geomicrobial kinetics

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Geomicrobial kinetics studies how fast microbial metabolism proceeds in natural environments – a key question of low-temperature geochemistry [1]. It differs from microbial kinetics by considering wide spectra of tempetaures, pHs, availabilities of energy sources and growth nutrients, and other environmental factors. Geomicrobial kinetics also differs from geochemical kinetics in that it accounts for life’s essential functions, including energy conservation, growth, and maintenance, and considers how thermodynamics impacts reaction rates.

Geomicrobial rates can be predicted on the basis of rate laws that applicable to natural environments [2]. These rate laws carry relatively large numbers of kinetic and thermodynamic parameters in order to account for various environmental and microbial factors. But application of the rate laws present a special challenge – how to assign values for the parameters.

Jin and Roden propose a best-choice approach to assign parameter values [1]. In theory, microbial parameters can be separated into two groups, extant and intrinsic [3]. Extant parameters describes how rates are influenced by microbial adaptation to the environments, and include half-saturation constants for electron donor oxidation, acceptor reduction, and nutrient consumption, and specific maintenance rate. These parameters vary with the availability of energy and nutrient sources, and should be determined directly using samples from the environment.

Intrinsic parameters describe the dependence of microbial rates on cellular enzymes and pathways, and include rate constant, growth yield, ATP yield, phosphorylation energy, and average stoichiometric number. These parameters bear the relationships determined by microbial physiology. Taking anaerobic respiration as an example, ATP yield and average stoichiometric number vary with electron donors and acceptors, and can be determined on the basis of respiratory pathways. Also, because microbial growth depends on ATP synthesis, growth yield increases linearly with ATP yields. As a result, we can taken intrinsic parameters as constants of microorganisms, and extrapolate the values determined for pure cultures directly to the environment.

Taking the simulation of microbial sulfate reduction and methanogenesis as examples, I demonstrate how to select parameter values that are consistent with our current knowledge of microbial physiology and relevant to the environment of interest. I then apply the parameter sets and simulate microbial metabolism in batch reactors of mixed culture, flow-through sediment columns, and lake sediments. The results demonstrat that the best-choice approach reduces the task of parameter fitting and ensures the quality of simulation.


Experimental study on carbonation of Portland cement in sodium chloride solutions

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Carbonation behavior of cement has been extensively studied because cement carbonation affects the concrete strength and corrosion resistance of the steel reinforcement. Various factors can affect the carbonation of cement. This study presents the influence of salinity on the carbonation behaviors of cement material.

The leaching and carbonation tests were conducted on ordinary Portland cement(OC) using a Teflon reactor at various NaCl concentrations (0 ~ 2.0 M) under ambient temperature and pressure conditions. For the carbonation tests, CO2 gas (99.9%) was injected in the slurry, which was obtained by mixing the soluiton and OPC.

For the leaching tests, the slurry pHs increased to 12.0 ~ 12.9, regardless of the NaCl concentration, after 24-hours leaching due to dissolution of Ca(OH)2. The electrical conductivities (ECs) of the slurries increased steadily during the leaching test at low NaCl concentrations (< 1.0 M), whereas decreased at high NaCl concentrations (> 1.0 M). The Ca concentration in the slurry increased with increasing the NaCl concentration. After the leaching tests, dissolution of C-S and Ca(OH)2; and formation of C-S-H and Friedel’s salt were indentified by XRD, SEM-EDX, and TGA analysis. The NaCl concentration affected the extent of the C-S-H formation during the leaching tests. The C-S-H content in the reacted OPC was the highet at the 1.0 M NaCl solution. During CO2 injection, the pH decreased due to the dissolution of CO2 and the carbonation reaction. Precipitation of well-crystallized calcite (CaCO3) and halite (NaCl) in the reacted OPC obtained after the carbonation tests were identified by XRD, SEM-EDX, and TGA analysis. The C-S-H content decreased but the CaCO3 content increased with increasing the NaCl concentration after the carbonation tests. Theses results suggests that the presence of NaCl enhances the dissolution of Ca(OH)2 in the OPC during hydration and the precipitation of CaCO3 by the elevated dissolution of C-S-H during CO2 injection.
Combined silicon, oxygen isotope and trace element microanalysis of giant spicules of the deep-sea sponge *Monorhaphis chuni* for paleoclimate research

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The deep-sea sponge *Monorhaphis chuni* forms giant spicules, which can reach lengths of 3 m and diameters of 10 mm [1]. Because of the long lifespan of this sponge (several thousands years), the spicules offer a unique opportunity to record environmental change of past oceanic and climatic conditions [2]. To get a detailed time-resolved record over the lifetime of the sponge, analyses at a high resolution in the nm to μm range were performed. We investigated several giant spicules from the East and South China Sea along center-to-surface segments by determining Si isotopes with UV fs-LA-MC-ICP-MS at GFZ, and O isotopes with NanoSIMS and trace elements with LA-ICP-MS at MPI. No clear trend in Si isotope variability outside external analytical reproducibility (+0.2 ‰, 2SD) could be identified in the spicule MC from the East China Sea; average $^{29}\text{Si}$ and $^{30}\text{Si}$ values relative to NBS 28 were -0.67±0.21 and -1.30±0.35 (2SD), respectively. According to [3], the Si isotope fractionation is influenced by seawater Si concentration with lower isotope ratios being associated with sponges collected from waters high in Si. This implies that no significant change in Si concentration in the ambient seawater occurred during the lifetime of the sponge. Average $^{29}\text{Si}$ values for the specimen SCS-3 and Q-E from the South and the East China Sea, respectively, are different: -0.43±0.22 (SCS-3) and -1.28±0.23 (Q-E) indicating different Si contents of the seawater. In contrast to these measurements, oxygen isotope data and Mg/Ca ratios of the spicule MC show a small trend in $^{18}\text{O}_{\text{SMOW}}$ from about 36±1 (rim) to 38.5±0.5 (core) and Mg/Ca from 0.062 (rim) to 0.055 (core), which can be interpreted as an increase in seawater temperature of about 3 °C during the lifespan of this specimen, similar to the results of the giant spicule QB [2].


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Gold, Gilding and gilded marble sculpture in Antiquity: new methods, new results.

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Gilding marble statues in Antiquity was rather a common practice, as testified both by ancient literary and epigraphical sources. However, for a long time, scholars showed some reluctance to admit it, due to the lack of archaeological evidence. Today, on the contrary, new scientific methods of surveying, evidencing and analysing marble surface treatments, by combining for instance videomicroscopy and X-ray fluorescence spectroscopy, confirm without any doubt the success of gilded marble statues in ancient Greece as in Rome[1]. They also give informations about gilding an regilding processes, documenting gold leaf thickness as well as the techniques of applying it on the marble layer by layer. By crossing archeological and archeometrical evidence, it becomes then possible to reconsider both ancient taste and gilded statues functions. For instance, a bright white marble hellenistic copy of the Famous classical Greek sculptor Polycletes, found in Delos [Figure 1] at the beginning of the 20th century was originally wholly gilded [Figure 2], leading to new conclusions as regards the status and functions of such a work[2]. But at the present time, some decisive information remain unknown, as for instance the provenance of the gold itself, a central historical and economic topic for Historians and Archeologists. We need to find the missing link between antique gold mines and gilded or gold artefacts. The present talk aims also at arousing new collaborations focused on this topic.

**Figure 1: The so-called Polycletes’s Diadoumenos at the very time of its discovery (©Faqueut, Bourgeois, Jockey).**

**Figure 2: 3D digital Reconstruction of its original look (©Fauquet, Bourgeois, Jockey).**
Sources of organic matter fueling As mobilization in groundwaters of West Bengal, India: Evidence from reactive transport modeling

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It is generally agreed that microbial reduction of Fe(III) oxides/oxyhydroxides coupled to organic matter (OM) oxidation is an important mechanism by which arsenic (As) is mobilized to groundwaters within the Bengal Basin of Bangladesh and West Bengal, India. Nonetheless, the source of the OM driving the respiratory processes remains contentious [1]. Some researchers argue that recently constructed perennial ponds are a major source of recharge waters, and hence dissolved organic matter (DOM) to the As affected groundwaters, whereas others maintain that the sediments contain sufficient OM to fuel microbial respiration [2, 3]. Here we employ reactive transport modeling to simulate transport of DOM in aquifers from the Murshidabad district of West Bengal, India. Nonetheless, the source of the OM driving the respiratory processes remains contentious [1]. Some researchers argue that recently constructed perennial ponds are a major source of recharge waters, and hence dissolved organic matter (DOM) to the As affected groundwaters, whereas others maintain that the sediments contain sufficient OM to fuel microbial respiration [2, 3]. Here we employ reactive transport modeling to simulate transport of DOM in aquifers from the Murshidabad district of West Bengal, India. The goal was to assess the possibility that OM originating in surface waters would require at least 1000 years to reach the top of groundwater at these depths (e.g., ~ 50 years). Instead, DOM from surface waters would require at least 1000 years to reach the top of the As affected aquifers in Murshidabad. Results of the modelling support an in situ, sediment source for the DOM.


A triple-proxy approach to reconstructing seawater δ18O

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Reconstructing changes in the oxygen isotopic composition of seawater (δ18Oseawater) through geologic times is a high-value target as this proxy informs us on the evolution of Earth’s cryosphere (waxing and waning of ice sheets), changes in ocean currents (with subtle differences in δ18Oseawater) and salinity effects related to the amount of evaporation of surface waters (the lighter 16O isotope being preferentially fractionated in the water-vapor phase during evaporation). Unfortunately, geologic samples of biogenic marine calcite (δ18Ocalcite) record the combined effects of changes in δ18Oseawater and changing water temperature. For instance, a phase of expended high-latitude ice sheets during a glaciation will result in heavier δ18Oseawater (due to 16O preferentially stored in the continental ice) but would also be associated with a global cooling of the ocean, thus further increasing the δ18Ocalcite values. This makes assessing the relative impact of each mechanism on δ18Ocalcite difficult, and hinders quantitative assessments of changes in δ18Oseawater.

The paleoceanography community has tried to come around this limitation by pairing δ18Ocalcite with other temperature proxies independent of δ18Oseawater. One of the most successful proxies to date is the Mg/Ca ratio of benthic foraminifers. Foramiferal Mg/Ca ratio has been shown to be temperature dependent for many species, and the Mg/Ca ratio of seawater is thought to be conservative on the timescale of 1 million years. However, on timescales greater than a million year the Mg/Ca ratio of seawater is likely to change, implying that this proxy is a good proxy for relative temperature changes, but that it cannot unambiguously resolve absolute seawater temperatures for periods older than the Pleistocene. Furthermore, the concentration of carbonate ions seem to impact Mg/Ca intake in benthic foraminifers, and thus changes in carbonate ion concentrations in the ocean could impact on the temperature estimates from foraminiferal Mg/Ca.

This review talk will highlight how adding a third, novel proxy (clumped isotopes) could resolve some of the issues at hand. The “Clumped isotope paleothermometer” is based on thermodynamics, and thus is independent of δ18Oseawater. Calibrations have shown that clumped isotopes are independent of nearly all changes in ocean chemistry, though some exceptions occur (for instance, in hypersaline conditions). Clumped isotopes suffer from their own set of limitations, notably because the measurements require a significant amount of time and sample material (up to 25 mg if three replicates are made). However, we will show through some preliminary data what strategies can be put in place to overcome this limitation, and how a “triple-proxy” approach based on high-resolution δ18Ocalcite measurements, medium resolution foraminiferal Mg/Ca measurements and low-resolution clumped isotope measurements could help resolve some of the issues currently faced by the paleoclimate community.
The role of nano-components in contaminated mine water outflow crossing a redox boundary

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Especially in the last 15 years, Earth scientists have been exploring the role of nano-sized materials in a number of environment-related processes, including the transport and transformation of organic and inorganic contaminants. In this study, with both the geochemistry and microbiology in mind, we chose to study a highly dynamic environmental system (Ronneburg Mining District, Germany) where groundwater outflow from a former uranium mine is negatively impacting the downstream environment. The outflow contains high amounts of Fe(II) and, upon exposure to air at pH 5.8-6.0, iron oxyhydroxide particles form. Our principal goal was to determine the role that nanoparticulate formation has on the (bio)geochemistry of this complex and dynamic system. From June to October of 2011, water and sediment was carefully collected at four sites along portions of the flow path of greatest interest: at the groundwater outflow point, at rust-colored terraces where the outflow water flowed over a creek bank, from the creek adjacent to the terrace, and from the creek about 1 km downstream. A multi-scale approach was used to analyze the samples including XRD, ICP-MS, SEM and analytical TEM (HR-TEM, EDS, and SAED).

The first indication of nanocrystalline particles comes from the broad XRD peaks of the sediment samples, many of which match goethite and akaganite. XRD of suspended particles shows even broader diffraction maxima that cannot readily be indentified, but do indicate the predominance of nano- and/or very poorly crystalline or amorphous particles. TEM corroborates this to a point, but also reveals very important details. For example, suspended particles (40-300 nm) in terrace and creek sites tend to be roughly spherical, and found in aggregates of amorphous iron oxyhydroxides intimately mixed with and sometimes coated by amorphous silica. Various types of nanocrystalline phases were found in the sediment samples as well, including nanoneedles of goethite growing from 100-300 nm spherical particles, and even smaller and smoother spherical particles that are clearly mixtures of amorphous silica and the very earliest stages of iron oxyhydroxide crystallization manifested by uniform lattice fringes that can be traced over only 2 to 5 nanometers. Interestingly, in the groundwater outflow, suspended nanometer-thin ferrous sulfate pseudo-hexagonal platelets (containing small amounts of Zn) were discovered. We have tentatively identified these as the mineral rozenite using electron diffraction analysis.

As these rozenite particles in the outflow become unstable, they are an important source of Zn, which is the metal with the fourth-highest concentration downstream. Zn and Ni were not primarily associated with larger suspended particles (> 0.1 μm), unlike the metals at trace concentrations (U, Cu, Cr, and Pb). Interestingly, Sn oxide oval-shaped nanoparticles (5-20 nm) were found multiple times in terrace site water samples, and their significance is presently being investigated.

In this ongoing study, we have shown again why knowledge of the formation, transformation, reactivity, and dissolution of the nano-components are important in understanding the behavior and evolution of the entire system.

From mineral interfaces to 200 million tons per year: A geologic perspective of the surface-catalyzed iron redox cycle

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Evidence for redox-driven reactions at the mineral-fluid interface of iron oxides may be found in the largest iron deposits on Earth, banded iron formations (BIFs), which were largely deposited in the Neoarchean and Paleoproterozoic. The insights gained by detailed, mechanistic studies of mineral-fluid reactions demonstrate that the major volume of BIF deposits was not formed by “passive” accumulation of iron oxide minerals on the seafloor but instead record an extensive redox history during formation and early diagenesis prior to lithification. Redox-driven reactions are the fundamental process that inhibits iron oxides from behaving as “inert” particles, and, in fact determine not only the isotopic compositions of redox-sensitive elements such as Fe, but also the O isotope compositions through breakage of Fe-O bonds. In addition, the structural changes that occur in iron oxides upon subersituation of Si, an important component in marine environments in the Precambrian, produce significant changes in stable isotope compositions. Redox-driven reactions between aqueous Fe(II) and Fe(III) oxides that are catalyzed by biology may produce significantly different end products and elemental mass balance than abiologic Fe(II)-Fe(III) oxide interactions, and this contrast may be expressed as distinct isotopic compositions. In the case of BIFs, the isotopic fingerprints of microbially-catalyzed redox cycling is expressed in fine-scale isotopic heterogeneity that produces compositions out of equilibrium with ambient seawater. Importantly, the end product of extensive biological reduction of Fe(III) oxides are not mixed Fe(II)-Fe(III) minerals such as magnetite, which are produced at moderate extents of reduction, but Fe(II)-bearing carbonates ( siderite, ankerite). Although perhaps not immediately obvious, iron carbonates actually contain the best evidence for the magnitude of microbially-catalyzed redox cycling of iron oxides in BIFs, and C, O, and Fe isotope compositions clearly indicate significant differences in the elements mass balance than that of abiotic Fe(II)-Fe(III) oxide interactions, and this contrast may be expressed as distinct isotopic compositions. In the case of BIFs, the isotopic fingerprints of microbially-catalyzed redox cycling is expressed in fine-scale isotopic heterogeneity that produces compositions out of equilibrium with ambient seawater. Importantly, the end product of extensive biological reduction of Fe(III) oxides are not mixed Fe(II)-Fe(III) minerals such as magnetite, which are produced at moderate extents of reduction, but Fe(II)-bearing carbonates ( siderite, ankerite). Although perhaps not immediately obvious, iron carbonates actually contain the best evidence for the magnitude of microbially-catalyzed redox cycling of iron oxides in BIFs, and C, O, and Fe isotope compositions clearly indicate biological Fe(III) reduction. The C, O, and Fe isotope compositions of the largest BIFs, the 2.5 Ga Brockman (Pilbara craton, Australia) and Kuruman (Kaapvaal craton, South Africa) iron formations, indicate that virtually all of the Fe in these deposits has been cycled by microbes. These BIFs provide the majority of the world’s iron, in economic deposits that reflect later hydrothermal mobilization, oxidation, and deposition. These BIFs are mined at a rate of ~200 million tons per year in the Pilbara craton alone, an impressive testament to the importance of surface-catalyzed redox cycling.

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Rapid early- to mid-Holocene thinning of Pine Island Glacier detected using cosmogenic exposure dating

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The West Antarctic Ice Sheet is thought to be inherently unstable and has the potential to contribute up to 3.3 metres to sea level rise. Recent years have seen dramatic rates of thinning of major ice streams flowing into the Amundsen Sea, and in particular Pine Island Glacier. Onshore measurements of these changes are restricted to decadal timescales and in particular the satellite era, which makes it difficult to judge their significance and whether such changes are unprecedented. One way to place these events in a longer-term context is to study the geological record of past ice sheet change. This approach also provides data that are critical for building reliable ice sheet models that will predict the magnitude and timing of sea level change.

Recent advances in exposure dating afford new approaches for dating Holocene ice sheet thinning: we present the first study combining precise \(^{10}\)Be and in-situ \(^{14}\)C surface exposure ages from Antarctica. We used glacially-transported erratic cobbles as a vertical ‘dipstick’ for tracing past fluctuations in thickness of the West Antarctic Ice Sheet, focusing on the lower elevations of three nunataks in the Hudson Mountains (immediately north of Pine Island Glacier and close to its present-day grounding line). Exposure ages from the lowermost 100 m of two nunataks (Mt Moses and Maish Nunatak) suggest that rapid thinning was sustained there over a few hundred years in the early- to mid-Holocene, and brought the ice sheet surface close to its present elevation by ~6 ka. We also report exposure ages from within 40 m of the modern ice surface at Meyers Nunatak.

Formation of the Si-rich layer on olivine surfaces during carbonation under in-situ conditions

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Olivine dissolution releases divalent cations (Mg\(^{2+}\), Fe\(^{2+}\)) into solution and in the presence of dissolved CO\(_2\) will result in the precipitation of carbonate minerals. This process, known as mineral carbonation, has the potential to safely store CO\(_2\) in the subsurface over geologic time. Although the reaction is thermodynamically favored and occurs naturally, the kinetics are typically slow at temperatures < 100°C and thus limit industrial applications of the process. Previous results from this group and others have shown that the dissolution rate of olivine drops over two orders of magnitude as the reaction solution approaches saturation with respect to amorphous silica (a by-product of metal silicate carbonation). This study aims to understand why and how the rate drop occurs, using a series of batch reactions in a three-phase system (water, solid, and supercritical CO\(_2\)) at conditions relevant to in-situ carbonation (60°C, 100 bar P\(_{\text{CO}_2}\)). Analysis of the mineral reaction products indicates the formation of a Si-rich, Mg-depleted layer on the olivine surface as soon as 2 days after reaction is started and before the bulk solution reaches silica saturation. Ion probe analysis of olivine grain surfaces produced by reaction with a \(^{29}\)Si-spiked, CO\(_2\)-containing aqueous solution suggests that a Si-rich layer up to 1.5 \(\mu\)m deep forms on the grain surfaces, and that after 2 weeks of reaction this layer is primarily due to preferential removal of cations (leaching) rather than re-precipitation of silica. At t<20 days and pH<5, the Si-rich layer appears to control the rate of olivine dissolution. After 20 days, the layer no longer controls the dissolution rate, the rate increases, and carbonation occurs. Although Mg-carbonate precipitation requires significant oversaturation with respect to magnesite, the overall rate-limiting step for olivine carbonation as measured in our experiments involves the formation and subsequent break-down of the Si-rich layer. Current work is aimed at preventing the formation of the leached layer.
Interrogating the mechanisms controlling sulfur isotope fractionation during sulfate reduction

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The sedimentary sulfur isotope record represents a unique opportunity to learn about Earth’s environmental history. This great interpretability is related to the fact that the sulfur cycle captures the interplay of numerous redox sensitive biological processes and preserves an extraordinary geological signal, both of which are accessible with a multiple isotope system. The precision with which we can tell these stories, however, rests with the quality of our calibrations. To date, isotopic calibrations have targeted microbial sulfate reduction; an anaerobic metabolism that is both the dominant contributor to the preserved sulfur isotope variability and provides the tight, quantitative links between the sulfur, oxygen and carbon cycles. Decades of classic batch experiments with whole cells of sulfate reducers underpin our understanding of the fractionation capacity of this metabolism, coarsely linking cellular and volumetric rates of reduction to the inverse of the magnitude of $^{34}S/^{32}S$ fractionation ($\Delta$). Although informative, it is possible to both place tighter quantitative constraints on this relationship as well as to develop a more fundamental understanding of the physiological mechanisms driving the observed fractionation patterns. With this level of calibration, and through the inclusion of minor isotope fractionation patterns, a more refined picture of Earth surface evolution is possible.

In what follows we present data from a suite of continuous culture experiments with two pure Desulfovibrio strains of sulfate reducer: D. vulgaris Hildenborough and D. alaskensis G20. Through these experiments we varied sulfate concentrations from 1-100% of modern values and modulated the electron delivery rate over an order of magnitude in order to induce varying degrees of limitation in electron availability. These experiments thus target the two primary controls on sulfate reduction – electron donation rate (lactate flux) and reception (sulfate availability) – and map onto distinct geological questions. For example, in the case of sulfate availability, the difference in isotopic composition between Proterozoic sulfates and sulfides is often inferred as related to $[SO_4^{2-}]$: our experiments directly address this assumption as they span the presumed $[SO_4^{2-}]$ for that time interval (0.5-5 mM). Our entire data set presents fractionation that in $^{34}S/^{32}S$ range from the ordinary ($<25\%$) to the extraordinary ($>50\%$), and can be contoured by electron consumption rates. When paired with the minor isotope data, the flux of sulfur through a bacterium can be more specifically solved.

This work also helps to open the ‘black box’ of large fractionations related to $[SO_4^{2-}]$ for that time interval (0.5-5 mM). Our entire data set presents fractionation that in $^{34}S/^{32}S$ range from the ordinary ($<25\%$) to the extraordinary ($>50\%$), and can be contoured by electron consumption rates. When paired with the minor isotope data, the flux of sulfur through a bacterium can be more specifically solved. For example, the case of sulfate availability, the difference in isotopic composition between Proterozoic sulfates and sulfides is often inferred as related to $[SO_4^{2-}]$: our experiments directly address this assumption as they span the presumed $[SO_4^{2-}]$ for that time interval (0.5-5 mM). Our entire data set presents fractionation that in $^{34}S/^{32}S$ range from the ordinary ($<25\%$) to the extraordinary ($>50\%$), and can be contoured by electron consumption rates. When paired with the minor isotope data, the flux of sulfur through a bacterium can be more specifically solved.

To detect changes in the conformation of MerR, which in turn propagate through DNA contacts to its operator DNA (MerOP) is unknown. In this study we investigate Hg(II)-induced conformational changes of MerOP in complex with its regulator MerR. Experimentally, we purified MerR and prepared a complex with a 23bp MerOP dsDNA construct. In vivo, MerR tightly binds to MerOP in a region of dyad symmetry between the -10 and -35 RNA polymerase recognition sites. In the absence of Hg(II), RNA polymerase binds to its promoter and forms a stable pre-initiation complex with dimeric MerR acting as a repressor preventing RNA polymerase from accessing the -10 recognition site. In the experiments, we examined the MerR-MerOP complex in the presence and absence of Hg(II) using small-angle neutron scattering (SANS) (Fig. 1). A contrast variation series allowed us to detect changes in the conformation of MerR and MerOP, respectively. Homology modeling and molecular dynamics simulations were used to generate atomic resolution models to interpret the data. The results provide insights on the allosteric change in MerR triggered by Hg(II), which causes a reorientation of the -10 recognition site and ultimately initiation of transcription by RNA polymerase [3].

Figure 1: Small angle neutron scattering intensities $I(q)$ vs momentum transfer $q$ in 100% D2O buffer and a model of the MerR-MerOP complex.

Are River Basins affected by Climatic Variations?: A study from a major river in Central Mexico, Mexico.

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Variations in climatic cycle during different periods often affect various aspects in the earth, especially it shows more diversity in the aquatic region. Our study focuses mainly on the geochemical aspects of river sediments from River Amajac, Panuco and its lagoons which are located in the north eastern part of the Mexico. The whole system runs through the Sierra Madre Oriental in Central part of Mexico and finally drains into the Gulf of Mexico. The difference in the weathering pattern in the sediments of the river basin could be related to the changes in the climatic cycle in the region [1-2]. The results also clearly indicate that the decrease in rainfall events during the last three decades have affected the farming land and has resulted in deforestation and subsequently it has resulted in erosion of finer particles into the aquatic system. The analysis of major, trace elements and the calculated weathering pattern results suggest that the region is frequently vulnerable to erosion. The concentration and distribution pattern of the geochemical elements also indicate that the higher concentration of toxic elements is mainly anthropogenic, which can be related to the industrialization of the region.

Evidence for a manganous surface sea at 2.5 Ga

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The Transvaal Supergroup in South Africa hosts one of the most pristine Archean sedimentary successions known, with largely flat lying strata and sub-greenschist metamorphism [1]. The relevant section of this unit records an intertidal carbonate platform deepening upward to a basinal iron formation. The carbonates from the platform, especially the Lower Nauga formation, have relatively high Mn concentrations, but more limited Fe. We propose that this resulted from surface sea waters containing substantial Mn and a paucity of Fe, based on the ideal partitioning coefficients of Mn and Fe into calcite and dolomite lattices [2].

Fe speciation data from deep basin sediments indicate deposition under anoxic, ferruginous conditions, implying that the water column was stratified with manganous surface waters overlying ferruginous bottom waters. Surface sea waters could be devoid of Fe(II) for a number of reasons, including photic zone oxygen production, anoxicogenic phototrophic Fe(II) oxidation, or sulfide scavenging of Fe(II). Dissolved Mn(II) can persist through all of these scenarios; however, pervasive oxygenation could be expected to oxidize Mn as well. Had Mn been deposited as oxide, the $\delta^{13}$C-CO$_3$ should move to more negative values, reflecting the $\delta^{13}$C composition from the organic matter used during dissimilatory reduction. Platform carbonates of the Campbellrand Subgroup from the intertidal to the lagoonal to the shelf margin together with the roughly 600 m of elevated Mn:Fe ratios in the carbonates suggest a substantially thick anoxic surface layer above the more reducing (mostly ferruginous) deep basin.

Field evidence of Sr exchange between particulate material and seawater in estuaries

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The reactivity of riverine particulate material upon arrival in the ocean is an important consideration for global element cycles, as this flux dominates for the majority of elements [1]. A small amount of particulate dissolution in saline water would have a noticeable impact on land-to-ocean fluxes of key elements such as Ca, Mg and Sr. A recent study showed significant dissolution and/or exchange of strontium between riverine particulate material and seawater in laboratory conditions [2]. If replicated in the natural environment, the calculated Sr release upon arrival in estuarine waters would be of a similar order of magnitude to hydrothermal exchange at mid-ocean ridges. To date, no study has found evidence of Sr exchange in field studies, potentially because the concentrations of Sr in seawater are high and there is experimental evidence for contemporaneous precipitation of Sr-bearing phases [2].

This study focuses on the Borgarfjörður estuary in western Iceland. The basaltic lithology of the catchment and the shallow depth of the fjord make this site ideal for detecting any interaction between solid and liquid phases, as this should equate the most easily weathered material and the highest sediment to water ratio in the natural environment. Two independent field trips collected water, suspended material and bedload samples in transects along the fjord, and subsequently analyzed for major element concentrations and multiple isotopes (by LA-ICPMS respectively), reveal variations in hafnium isotopic analysis, of the same magmatic zircons (by SIMS during the late Eocene to late Oligocene (35 - 26 Ma). Oxygen and carbon isotope ratios of the same magmatic zircons (by SIMS and LA-ICPMS respectively), reveal variations in δ18O(VSMOW) of between 9.78 ± 0.21‰ and 3.59 ± 0.21‰ and in εH of between 10.4 ± 1.3 and -4.4 ± 0.8. This new data, when combined with the results of whole rock, major and trace element analysis, provides increased constraint on the amount of continental material being subducted to depth and recycled to the continental crust via arc magmatism during this key time in the evolution of the Andes.


Subduction erosion, magmatism and continental crust formation in the southern Central Andes

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Subduction zones, such as the Andean convergent margin, form large recycling systems and are the main producers of new continental crust. The subduction of continental material through either tectonic subduction erosion or sediment cycling is an important component when estimating the mass flux through an active margin over time. Subduction erosion in particular has been highlighted as an important process along certain parts of the Andean continental margin, especially to the west of the Central Andes [1, 2].

It has been suggested that the rate of subduction erosion along the north-central Andean margin has varied over time with constant, fast rates between 150 and 20 Ma and slower rates during the Neogene [3]. A near constant rate of subduction erosion between 150 and 20 Ma suggests a continuous supply of continental material into the subduction zone, during this time.

We have combined high resolution, U-Pb dating, isotopic geochemistry, and major and trace element analyses, from a suite of magmatic rocks sampled from the southern Central Andes (28° to 32°S), in order to investigate source contamination by subducted continental material between the late Cretaceous and the late Miocene.

The results of new, in-situ U-Pb dating of magmatic zircons by SIMS place further constraints on the presence of a widespread period of reduced arc magmatism in the southern Central Andes during the late Eocene to late Oligocene (35 - 26 Ma). Oxygen and hafnium isotopic analysis, of the same magmatic zircons (by SIMS and LA-ICPMS respectively), reveal variations in δ18O(VSMOW) of between 9.78 ± 0.21‰ and 3.59 ± 0.21‰ and in εH of between 10.4 ± 1.3 and -4.4 ± 0.8. This new data, when combined with the results of whole rock, major and trace element analysis, provides increased constraint on the amount of continental material being subducted to depth and recycled to the continental crust via arc magmatism during this key time in the evolution of the Andes.

Size-dependent surface charging of TiO$_2$ nanoparticles

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Metal oxide nanoparticles show variations in their structure relative to corresponding larger microparticles of the same material, often with new unexpected features occurring in the nanoscale size range. Generally, nanoparticles have increased roughness and curvature of the surface, large specific surface area and high abundance of active binding sites; thus are very reactive. The surface charge is highly affected by the surrounding media, which in turn affects the colloidal stability of nanoparticles.

This study focuses on the size-dependent surface charging of TiO$_2$ (anatase) nanoparticles. TiO$_2$ nanoparticles with well-defined particle sizes (<30 nm) and without any coatings or surfactants were synthesized using low-temperature hydrolysis of TiCl$_4$. Temperature during synthesis reaction, dialysis and storage was found to strongly influence the particle size and crystal structure, according to [1]. The nanoparticles were extensively characterized using several techniques and were found to have a sphere-like shape. In order to study the size-dependence on the pH$_{ZPC}$ (point of zero charge), potentiometric titrations were used to determine the surface charge of the TiO$_2$ nanoparticles at 25 °C, and at varying ionic strengths obtained with NaCl as background electrolyte. Further, zeta potential measurements were performed under similar conditions.

The experimentally determined size-dependent surface charging behavior of TiO$_2$ nanoparticles are compared with the corresponding surface charge densities calculated by classical surface complexation models, as well as by the Corrected Debye-Hückel (CDH) theory [2].


Biomineralization and fate of the Fe$^{II}$-Fe$^{III}$ hydroxy salt green rust vs. magnetite

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It is well known that iron oxide reduction by Shewanella spp. bacteria promotes the formation of Fe$^{III}$ bearing minerals, such as the mixed Fe$^{II}$-Fe$^{III}$ hydroxysalt green rusts (GRs), in anaerobic conditions. Although the microbial-promoted generation of GRs is widely demonstrated, the mechanisms and factors governing the GR formation as the main secondary iron mineral at the expense of other products in lab-scale investigations or environmental systems are largely unknown. As GR is an effective reductant for several contaminants the mechanism controlling the formation routes of GR merit investigation, from both the environmental and engineering points of view.

Some factors such as cellular material (i.e. autoclaved cells and/or bacterial polymers), synthetic anionic polymers or oxyanions have been identified to control the route of the GR mineralization as secondary mineral at the expense of other products such as magnetite.

The arrangement mode of the heterogeneous aggregates resulting from the interactions between bacterial cells, iron oxide particles and polymers was suggested to influence the routes of formation of secondary iron minerals by limiting the diffusion of reactive species and thus creating favorable microenvironment for GR formation. In these aggregates, the electron transfer from cells to iron oxides is supported by organic electron shuttles.

On the other hand, anionic polymers, colloidal and aqueous silicates were found to also influence the nature of the secondary iron minerals through the stabilization of the GR crystals.

These results indicate clearly that the bacterial cells drive indirectly the nature of the secondary Fe$^{III}$-bearing mineral. Moreover, they give new insights into the understanding of the mechanisms of « biogenic » mineral formation based on the electron transfers from bacteria towards iron oxides. Finally, this work contributes to our understanding of the processes leading to green rust formation in environmental systems, such as soils or aquatic systems biofilms, in which a very high cell density can be found at a micro-scale level, associated to exocellular polymers and natural silica mineral composites.
Soil vapour characterization and intrusion to indoor air: a reactive transport modelling approach

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Introduction

Vapour intrusion to indoor air often represents a significant exposure pathway for risk assessment at sites contaminated by volatile petroleum hydrocarbons. While the importance of biodegradation processes on the fate and transport of petroleum hydrocarbon vapours is well established [1; and references therein], fewer studies have investigated site specific factors such as source concentration and location with respect to the building, pressure conditions, and soil properties, all of which have been shown to impact the potential for vapour intrusion [e.g., 2-4]. In this numerical modelling study, site specific factors are evaluated using the multi-component reactive transport code MIN3P-DUSTY [5-6]. The model includes the key processes of hydrocarbon volatilization, gas- and aqueous-phase diffusion, gas-phase advection, aerobic biodegradation (using dual-Monod kinetics formulation) and sorption in a domain comprising the subsurface and the building foundation. Benzene and iso-octane are used as surrogates of the aromatic and aliphatic compounds of the gasoline vapours. Initially, a sub-model for transport through concrete and within foundations cracks was developed and benchmarked against an analytical solution. The model was calibrated based on a high quality data set for an unoccupied research house located above a petroleum hydrocarbon plume (located in North Battleford, Saskatchewan, Canada), and then used to predict the hydrocarbon vapour distribution for a range of observed and hypothetical conditions.

Results & Conclusion

For the observed site conditions, the calibrated model indicates soil vapour transport is dominated by diffusion and aerobic biodegradation, and that building pressures and soil gas advection have little influence on soil vapour concentrations. Comparison of wetter (spring) and drier (winter) conditions indicate that the vadose zone oxygen concentrations above the contamination source area are lower for wetter spring conditions because of the reduced diffusion through relatively wet surface soils. For most scenarios simulated, there is rapid attenuation of benzene within approximately 1 m of the source; however, less attenuation of iso-octane is predicted, consistent with site data. For a shallow NAPL scenario, a concrete foundation slab resulted in an oxygen shadow and increase in benzene and iso-octane concentrations below the building.

Clumped isotope Vs. fluid inclusion thermometry in crystals from Oman.

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Clumped isotopes are a new exciting tool in the domain of paleothermometry. The “clumped isotopes carbonate paleothermometer” has been tested and used as a new temperature proxy for paleoclimate studies during the last few years. Indeed, clumped isotopes (Δ47) appear to be a great proxy since they are based on the degree of association of 13C and 18O into the carbonate ions, a function of thermodynamics. Therefore, measuring Δ47 allows the determination of the formation temperature of the carbonate material independent of the isotopic composition of the precipitating fluid. Furthermore, unlike other proxies, Δ47 seems insensitive to potential “vital effects”.

However, there is still a lot to unravel in this field of geochemistry, and some improvement and development are necessary. Some processes, such as kinetic fractionation, need to be identified and better understood in order to apply this proxy in the most precise way possible. Studies need to include comparisons between clumped isotopes and other temperature proxies.

Here we intend to compare data from both fluid inclusions microthermometry and clumped isotopes measurements carried out on the same material. Our focus has been placed on calcite crystals sampled in the carbonate carapace of a salt dome at Jebel Madar, Oman, where preliminary data suggest a low temperature precipitation.

As carbonates are very reactive minerals, diageneis and metamorphism could re-order the isotope clumping configuration in the carbonate and the measurements would reflect the equilibrium temperature of recrystallisation. Hence, careful consideration needs to be given to sampling strategies. Calcite crystals were sampled in fractures showing multiple pulses of opening, and the crystals themselves show evidence for growth zoning and fracture healing. We focus our study on deciphering and understanding the processes and effects of diageneis on the reliability of the carbonate clumped isotope paleothermometer.

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References

Sources and processes identification for Zn cycling in the Seine river, France

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An accurate determination of the ecological status of the Seine River (flowing through greater Paris, France) is required as it is one of the most severely damaged European rivers. However, important evaluation limitation still exists, partly because the metal cycling in this system is not fully understood, with for instance half the Seine river Zn not having clearly identified sources[1]. Along with Zn isotopic measurements, this study proposes to use XAS (X-ray Absorption Spectroscopy) to determine precisely the speciation of Zn complexes, and thus to define the proportion of water mixing vs. processes for Zn transfer in the watershed. A geographical sampling transect has been performed downstream Paris, where the contamination is maximum – 5 samples from the Seine River and 3 tributaries.

Significant isotopic signature variations are observed, varying from δ66Zn = 0.04 to 0.14 ± 0.05‰ in the particulate phase, and from δ66Zn = -0.23 to 0.10 ± 0.06‰ for the dissolved phase. These results are in line with previous work by Chen et al.[2] on the Seine River, but as we focus on the most polluted downstream part of the river, the δ66Zn variation range in both dissolved and suspended loads is much narrower. The XAS analysis performed on the suspended load samples at the Zn K-edge confirmed however a real heterogeneity by showing different speciations with a major contribution of sulfides, iron oxides, amorphous silica and organic ligands.

The dissolved phase displays systematically lower isotopic signatures than the particulate phase, resulting from adsorption processes [3, 4]. A significant discrepancy was observed between summer and winter for the dissolved phase, with higher values in winter high-water stages, reflecting a bigger contribution of natural sources (δ66Zn is 0.88‰ for chalk [2]) than during summer low-water stages dominated by anthropogenic sources.

The regional major wastewater treatment plant (WWTP) in Achères (shortly after Paris) brings significantly heavier Zn to the Seine River particulate material. This change in δ66Zn follows a change in Zn speciation, with a strong decrease in sulfides contribution after Achères. This WWTP impacts both dissolved and particulate phases on concentration, speciation and isotopic signatures. Comparison with Chen et al.[2] indicates a significant variability of the WWTP Zn signal that needs further investigation.


Geochemical Assessment of the Metallogenic Potential of Proterozoic LIPs of Canada

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The lithogeochemistry of eight Proterozoic Large Igneous Provinces (LIPs) within Canada has been studied to determine the Ni-Cu-PGE prospectivity of these major magmatic events. Three of the LIPs discussed here, the 1.87 Ga Chukotat, 1.27 Ga Mackenzie and the 2.49-2.45 Ga Matachewan LIPs, host known magmatic Ni-Cu-PGE sulphide mineralisation; in addition, the 0.72 Ga Franklin LIP may be associated with the coeval and mineralised Doyven intrusion in Siberia and several Franklin-related Ni-Cu-PGE prospects are known within northern Canada. The other four LIPs, the 1.14 Ga Abitibi, 0.59 Ga Grenville, ~1.25 Ga Seal Lake and 1.24 Ga Sudbury (distinct from the Sudbury impact event) LIPs, have no known Ni-Cu-PGE mineralisation.

The mineralised Chukotat, Mackenzie and Matachewan LIPs are characterised by basaltic with Ti/V ratios below 50, Gd/Yb ratios close to primitive mantle values and variable La/Si ratios. The magmas that formed these LIPs assimilated significant amounts of crustal material and samples representing both chalcophile depleted and undepleted magmas are present within these LIPs. This suggests that the magmas that formed these LIPs were fertile and S-undersaturated when they left the mantle and subsequently underwent a S-saturation event, forming immiscible magmatic sulphides. The close relationship between chalcophile element depletion and crustal contamination evident in the geochemistry of these LIPs suggests that S-saturation was caused by assimilation of crustal material, most likely by assimilation of crustal sulphides. The magmatic sulphides produced during this event were presumably segregated from silicate magmas and were deposited in coegenetic mafic-ultramafic sills and intrusives associated with these LIPs.

The Grenville and part of the Franklin LIPs have similar magma source characteristics to LIPs with known Ni-Cu-PGE mineralisation. However, although magmas from both LIPs were fertile and assimilated crustal material, the Grenville LIP did not undergo a S-saturation event prior to emplacement, whereas the Franklin LIP may have; the timing and location of this S-saturation event may be a useful guide during exploration for Ni-Cu-PGE mineralisation. The Abitibi, Sudbury and Seal Lake LIPs are alkaline, dominated by alkali basalts and are characterised by high Gd/Yb ratios, a wide range in La/Si ratios and Ti/V ratios higher than 50. All samples from the Abitibi, Seal Lake and Sudbury LIPs are chalcophile element depleted, suggesting that these magmas left residual sulphide within the mantle during partial melting, and indicating that these LIPs are probably unprospective for Ni-Cu-PGE sulphide mineralisation.
Sulfate adsorption at buried mineral/solution interfaces probed via vibrational surface spectroscopy

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Introduction
Understanding the structure and energetics of adsorbed ions at the buried mineral/solution interface has great importance to the geochemical and atmospheric chemistry communities. Vibrational spectroscopy is a powerful tool for the study of mineral/solution interfaces as these techniques can be applied in situ, are sensitive to surface structures, and are generally non-destructive. Sulfate (SO\textsubscript{4}\textsuperscript{2-}) adsorption at buried mineral (fluorite, silica, hematite)/sulfate-solution interfaces was studied using either vibrational sum frequency generation spectroscopy (VSFG), which is inherently interface specific, or total internal reflection (TIR) Raman spectroscopy. Sulfate is a simple, inorganic anion whose behavior is important to understand as it is ubiquitous in the environment being the third most prevalent ionic species in seawater by weight [1].

Results and Conclusions
The use of VSFG and TIR-Raman allows for the spectral resolution of anion adsorption complex structure, i.e. inner-sphere versus outer-sphere adsorption, Figure 1, at the mineral surface. Utilizing VSFG the sulfate anion is observed to adsorb with a bidentate inner-sphere structure at the fluorite surface with a surface free energy of adsorption of -33 ± 2 kJ/mole for pH 7 solutions at 298 K. The use of TIR-Raman spectroscopy to examine sulfate behavior at silica and hematite surfaces, which feature differing surface charges at pH 7, allows for the direct observation of anion adsorption behavior as a function of the model oxide mineral surface charge.


Use of in vivo and in vitro assays for refining human health exposure assessment for As-contaminated soil

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Introduction
When quantifying exposure to arsenic (As) for human health risk assessment calculations, As bioavailability is assumed to be 100% which presumes that all of the As has been solubilised in the gastrointestinal tract and absorption into systemic circulation has occurred. In reality, a fraction of the soil-borne As may only be bioavailable and as such this assumption may overestimate the chemical daily intake thereby influencing risk assessment [1]. In order to refine risk calculations by adjusting the default bioavailability value, reliable assays are required that can quantitatively measure site specific bioavailability.

In this study, As bioaccessibility and As relative bioavailability was assessed in contaminated soils using a variety of in vitro and in vivo assays. In vitro results were compared to in vivo relative As bioavailability data (swine assay) to determined which methodologies have the potential to act as surrogates for in vivo assays.

Materials and Methods
Contaminated soils used in this study were collected from regional areas where the soil type, source of As and As-soil residence time varied. Arsenic bioaccessibility was determined using SBRC [2], IVG [3], PBET [1], DIN [4] and UBM [5] assays while in vivo As relative bioavailability was determined using a swine model according to Rees et al. [6].

Results and Conclusions
Comparison of in vitro and in vivo results demonstrated that the in vitro assay encompassing the SBRC gastric phase provided the best prediction of in vivo relative As bioavailability ($r^2 = 0.75$, Pearson correlation = 0.87). However, As relative bioavailability could also be predicted using gastric or intestinal phases of IVG, PBET, DIN and UBM assays but with varying degrees of confidence ($r^2 = 0.53-0.67$, Pearson correlation = 0.73-0.82).

Light is an active contributor to vital effect in coral skeleton proxies

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Biologists emphasize the Light Enhanced Calcification (LEC) for a long time, although the interaction between light and calcification in coral skeleton formation remains not understood. δ18O, Sr/Ca and Mg/Ca are regarded as temperature tracers. However, we have no information concerning potential light influence on proxies. Symbiotic colonies of the coral *Acropora* sp. were cultured, under constant conditions, in a factorial design of three temperatures (21, 25 and 28°C) and two light intensities (200 and 400 γmol photon m⁻² s⁻¹). Metabolic, growth and geochemical measurements (δ18O, δ13C, Sr/Ca and Mg/Ca) were conducted on 6 colony sets representing each environmental (light temperature) condition. The experiment intended firstly to identify the separated influences of temperature and light on metabolism and calcification rates and secondly to compare them with corresponding skeletal δ18O, δ13C, Sr/Ca and Mg/Ca variations. Metabolic parameters responded as biologists could expect: photosynthesis increased with temperature, being always higher at high light. When colony was maintained at low light zooxanthellae (coral symbionts) density was higher at 25 and 28°C than under high light, illustrating the coral capability of shadow-adaptation. Calcification rate was also positively correlated to temperature, the quantity of deposited aragonite being always higher under high light. In opposite, surface expansion (equivalent to linear extension) did not show straightforward behavior. In addition, mean (for each data set) photosynthetic activity was related to mean calcification rate following logarithmic relationship.

Proxy responses showed huge scattering especially under high light and high temperature, exceeding by several °C the value calculated by using conventional calibrations, thus compromising the robustness of commonly admitted temperature tracers. The average assessed by the 6 values of δ18O, δ13C, Sr/Ca and Mg/Ca measured on the 6 nubbins of each set were correlated to averaged calcification rates, following logarithmic relationship. Furthermore, they seemed to obey to the temperature-light synergy. In opposite, correlation between δ18O and calcification rate strongly depended on the light intensity, although δ18O seemed to the most relevant temperature tracer. Examination of isotopic micro-measurements confirmed that isotopic fractionation could differ following light intensity. By considering individual values measured on each colony developed under high light, we underlined that photosynthetic activity, covering the total measured amplitude, was strongly related to symbiotic algae density, regardless temperature value, such as individual proxy values showed strong correlation with calcification rate according to light intensity, regardless temperature value. We deduced that in these conditions the high scattering that we observed could be due to the light effect, at least under high light.

No coral proxy is dependent on the sole temperature and no temperature calibration could be regarded as a universal law.

Distribution of vanadium in a basaltic aquifer of Jeju Island, Korea: effects of geochemical reactions and hydrological mixing

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Hydrochemistry data (i.e., major cations and anions, and trace metals such as Fe, Mn, V, As, Mo and U) of 25 groundwater samples from the Gosan area at the southwestern part of Jeju volcanic island, South Korea, were examined to identify physico-chemical factors controlling the spatio-temporal distribution of vanadium in a basaltic aquifer. The study area is comprised of a wide coastal agricultural land with hills with moderate slopes in the northeast. Groundwater sampling was conducted in May 2009 and October 2010. Groundwater in the study area usually contains high concentrations of V with an average of 12.2 μg/L (max. 28.8 μg/L). Except for two samples that were influenced by seawater intrusion, as indicated by higher concentrations of Cl, Mg and SO4 and elevated δ13C, Sr/Ca and Mg/Ca variations (14.5–18.9 ‰), groundwater in the study area is clustered into two major hydrochemical types: 1) a Mg-Cl-N03 type and 2) a Na-HCO3 type. The latter type is characterized by higher pH values (8.2–8.9, avg 8.6), compared to water type 1 (pH: 6.9–8.3, avg 7.3). The concentrations of V are strongly correlated with pH (γ2 = 0.89) and are higher in the Na-HCO3 type water. In addition, positive correlations were observed between pH and Cl-normalized concentrations of Na (γ2 = 0.79), K (γ2 = 0.49), and HCO3 (γ2 = 0.64). These observations indicate that water-rock interactions during southwestward regional groundwater flow in the basaltic aquifer largely control the observed hydrochemical changes and increasing V concentrations. However, V concentrations also tend to decrease in samples with higher concentrations of NO3 characteristic for Mg-Cl-N03 type waters. Examination of relationships between concentrations and δ15N and δ34S values of nitrate in the study area revealed that nitrate is mainly derived from synthetic fertilizers (~3 to 4 % δ15N(NO3) applied to agricultural fields. During infiltration of rainwater into the aquifer, agricultural nitrate is locally attenuated by partial denitrification to low nitrate levels (~8 % δ15N(NO3)). These observations suggest that there are two major paths of groundwater recharge in the study area: 1) regional flow accompanying water-rock interactions with V leaching from basalts, and 2) local flow dominated by direct infiltration of rainwater through agricultural land, accompanied by nitrate loading. We suggest that V concentrations of groundwater will decrease with increasing nitrate concentrations at times of increased local recharge.