

Meteoritical evidence for the timing of surface or near-surface liquid water on Mars

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There is widespread photogeological evidence for ubiquitous water flowing on the surface of Mars. Despite this observation, the absolute age of surface and near-surface water cannot be deduced from photogeology, because the uncertainty in the absolute calibration of the Martian crater flux results in uncertainties of ± 1.5 Ga in the middle period of Martian geologic history. Aqueous alteration of primary igneous minerals produces secondary minerals in Martian meteorites. Here we use the ages of secondary alteration minerals in Martian meteorites to obtain absolute ages when liquid water was at or near the surface of Mars. We find definitive evidence in Martian meteorites for aqueous alteration events at 3929 ± 37 Ma, 633 ± 23 Ma, and 0-170 Ma. These ages are based on absolute Rb-Sr and Pb-Pb ages of carbonates in ALH84001, Rb-Sr and K-Ar ages of iddingsite in two nakhlites, and the presence of secondary alteration products in several of the 170 Ma shergottites. These events appear to be of short duration, suggesting episodic rather than continuous aqueous alteration. Furthermore, the amount of secondary mineralization that is present in the meteorites appears to be decreasing with time. The 4500 Ma ALH84001 is made up of $\sim 1\%$ carbonates, the 1330 Ma nakhlites have obvious iddingsite alteration products that make up trace amounts of the meteorites, whereas some of the 170 Ma shergottites have vanishingly small amounts of various salts and clays. Although not definitive, this correlation is certainly consistent with the hypothesis that Mars has become dryer through time. The high $^{129}\text{Xe}/^{132}\text{Xe}$ ratio in the Martian atmosphere compared to Martian meteorites indicates fractionation of I from Xe within ~ 100 Ma after nucleosynthesis of ^{129}I . Such fractionation is difficult to achieve through magmatic processes. However, water very efficiently fractionates I from Xe, raising the intriguing possibility that Mars had a liquid water ocean within its first 100 Ma.

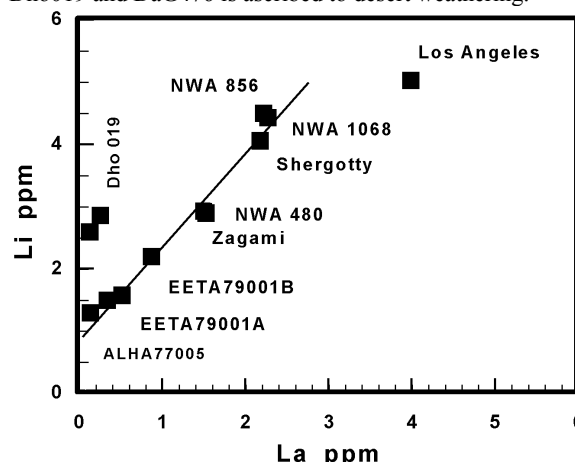
LI, CL, and BR in Martian (Shergottite) basalts: No evidence of water loss

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Shergotty and Zagami, Martian basalt meteorites (shergottites), are nearly anhydrous but may have crystallized from water-rich magmas. *McSween et al.* [2001] and *Lentz et al.* [2001] argued that decreasing abundances of Li and B, core-to-rim, in pyroxenes of Shergotty and Zagami reflect loss of an aqueous fluid from their parent magmas during crystallization. Losses of Li and B are inferred at 60-75% for Shergotty and $\sim 30\%$ for Zagami. The bulk compositions of Shergotty and Zagami should be similarly depleted in Li and B, and also be depleted in other elements that would be lost to an aqueous fluid, like Cl and Br. However, whole rock abundances of Li (Fig. 1), Cl, and Br in the shergottites show no evidence that Shergotty and Zagami were depleted (no analyses for B are available). Thus, core-to-rim decreases in Li and B in shergottite pyroxenes do not imply loss of a fluid phase, and must reflect other processes.

Fig. 1. Abundances of Li and La, both highly incompatible elements, in bulk shergottites. Nearly all fall on a single trajectory, suggesting that Shergotty and Zagami are not depleted in Li. Los Angeles is inhomogeneous. High Li in Dho019 and DaG476 is ascribed to desert weathering.



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Shock devolatilization of terrestrial impactites: Loss of fluid inclusions due to impact processing

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While impacts provided the flux of materials needed for planetary accretion, shock processing may have significantly reduced the volatile content of early planetismals. Fluid inclusions, which are abundant in terrestrial rocks, have only been observed in a few meteorites. In the past, the apparent lack of fluid inclusions has been interpreted as a lack of fluids on the parent body. However, recent experiments demonstrate that low to moderate shock pressures can effectively erase any evidence of fluid inclusions (Elwood Madden et al 2004).

This research investigates the effects of impact processing on fluids trapped in planetary materials by examining fluid inclusions in terrestrial impactites. Samples of crystalline basement rocks (granitic rocks and gneisses that experienced varying degrees of shock metamorphism) were collected from the Ries Crater and sedimentary rocks (Coconino Sandstone) were collected from Meteor Crater. Each lithology was then analyzed to determine its degree of shock-metamorphism and the percentage of quartz grains with fluid inclusions.

In both the crystalline basement and sedimentary rocks, fluid inclusions were abundant in quartz grains within samples that contained no shock features. Rocks containing planar fractures also contained fluid inclusions. Fluid inclusions were not observed, however, in samples with shock lamellae and diaplectic impact glass or in samples of partially melted Ries Crater crystalline basement rocks. However, fluid inclusions were observed within quartz grains entrained in glass in melted samples of Coconino Sandstone.

The correlation between shock and loss of fluid inclusions, plus examples of planar fractures offsetting solid inclusions, indicate volatiles trapped in fluid inclusions were lost from the rocks as a result of moderate shock deformation. This suggests that impact processing may lead to the loss of fluid inclusions and devolatilization of planetary materials.

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Oceanic temperatures recorded by the isotopic compositions of Precambrian cherts?

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"The world's oldest sedimentary rocks are cherts" [1]. As discovered by Knauth and Lowe [2] the least metamorphosed Precambrian cherts exhibit a regular increase in their $\delta^{18}\text{O}$ since 3.5 Gyr. that they attributed to the progressive cooling of the oceans.

Likely Precambrian cherts formed by the direct precipitation from seawater of amorphous silica, later transformed in micro quartz during sedimentary burial. As attested by the wide range of $\delta^{18}\text{O}$ for a given geological formation, the original isotopic signature of the amorphous silica may not be preserved during this transformation. Indeed, several isotopic exchange processes can modify the $\delta^{18}\text{O}$ of silica after its oceanic precipitation.

Since it is firmly established that all exchanges yield a decrease in $\delta^{18}\text{O}$, it has been proposed that the highest $\delta^{18}\text{O}$ values can be used as a proxy for oceanic temperatures. However it cannot be ruled out that cumulative post-depositional isotopic effects have progressively erased the original isotopic compositions of the cherts. Accordingly, the thermometric validity of oxygen isotopes in Precambrian cherts is considered by many workers as an open issue.

Cherts are made of silicon and oxygen (SiO_2). If an oxygen isotopic exchange took place between chert and water during diagenesis, its counter part for silicon isotopes can be evaluated. To try to make progress in this debate, we have measured the $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ at a micrometer scale with the 1270 Ion-microprobe in some of the Precambrian cherts having the highest known $\delta^{18}\text{O}$. We will show that (i) $\delta^{30}\text{Si}$ correlates with the highest $\delta^{18}\text{O}$ and that (ii) this correlation can be used to discuss the paleotemperatures of the archaic oceans.

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***In situ* use of microwaves to determine remotely the water content of minerals**

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The rovers Spirit and Opportunity are equipped with instruments to determine the chemistry of the minerals found on Mars. An emphasis has been placed on trying to correctly identify water-bearing minerals. While the Alpha-Particle-X-Ray spectrometer is used to determine elemental chemistry of minerals it cannot detect hydrogen. It also cannot determine the structure the minerals. These two drawbacks inhibit the direct determination of water in the samples. We propose to expose minerals to a microwave source and measure their heat gain as a method to determine if they contain water. A small microwave source and pyrometer could be included on future missions to determine if minerals contain water. To test this method we used a commercial microwave oven (2.4 GHz and 1000 Watts) and pyrometer to determine heating trends of several rock-forming minerals.

Minerals with higher amounts of water and/or hydroxide content should heat more than those with less amounts of water when exposed to microwaves over the same period of time. Minerals showed different heating patterns based on their water and or hydroxide content. Minerals that contained no water or hydroxide in their structure (i.e. quartz, calcite, anhydrite) showed little temperature increase with microwave heating. Clay minerals and zeolites showed a general increase in temperature with time. Borate minerals showed patterns of heating with time based on the amount of water and/or hydroxide contained in their structure.

Generally, minerals showed heating trends based on their water and/or hydroxide content: minerals with little or no water heated less over time, while minerals containing abundant water heated more over time. There were exceptions to the hypothesis, which indicate that other bonds may be microwave active. More experiments and a better theoretical understanding of the interactions of microwaves with minerals are needed before this method could be used to remotely determine water content. However the method shows promise as a means to determine the water content of rock-forming minerals, and possibly, by changing the frequency of the microwaves, to determine other chemical constituents of minerals.

Solute geochemical mass balance and forest biomass in small Appalachian Blue Ridge watersheds

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Weathering rates of rock-forming silicate minerals in natural forested catchments of the US Department of Agriculture - Forest Service Coweeta Hydrologic Laboratory (North Carolina, USA) are calculated using a system of geochemical mass-balance equations to calculate mineral weathering rates from solute fluxes. The equations are constructed and constrained by petrologic, mineralogic, hydrologic, botanical, and aqueous geochemical data. The number of mineral-weathering rates that can be determined is limited by the number of elements for which solute mass-balance equations can be written. Where simplifying assumptions can reduce the number of mineral reactions that need to be considered to a number less than the number of mass-balance equations, the rate of element transfer into or out of biomass can be solved as one of the unknowns. Uptake of major cations by aggrading forest vegetation can act as an intracatchment sink for at least some mineral-derived elements, producing mineral weathering rates higher than would be estimated from solute fluxes alone.

Biomass has the least influence on weathering rates of minerals whose rate is determined by the mass balance for botanically unimportant elements (e.g., sodic plagioclase). The largest biotic effects on weathering rates are for minerals that supply important nutrients to the forest biomass (e.g., biotite mica). Six of seven Coweeta control watersheds aggraded deciduous forest biomass during the solute-flux period-of-record. In the best-constrained, the annual increment of biomass uptake of Ca and Mg equalled the rate of atmospheric deposition of these nutrients. Forest demand for K exceeded atmospheric inputs and required uptake of K released by mineral weathering. The seventh Coweeta control watershed lost biomass and nutrients due to natural infestation by defoliating organisms and consequent decay of defoliation products, which acted as a non-mineral source of alkalis and alkaline earths to streams. The magnitude of the biotic effect on silicate weathering rates in Coweeta control watersheds depends on the history of natural disturbance of the forest ecosystem in each individual control watershed, and the botanical significance of specific elements in the mass-balance equations from which weathering rates of specific minerals are calculated.

Solute behavior in agricultural vs forested watersheds during storm events: Implications for DOC sources

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Background

Two paired watersheds were monitored during storm events to use perturbations in solute concentrations to help understand the source of dissolved organic carbon (DOC) to the stream system. To test the effect of land use, one watershed is forested and the other is under cultivation, primarily for corn. The two Southeast Pennsylvania watersheds have similar characteristics of slope, aspect, and bedrock geology.

Results and Discussion

Streamwater chemistry evolves in the agricultural watershed following hysteresis loops according to the contributions of endmember water sources, most likely defined as throughfall, shallow soil water, and groundwater. During the rising limb of the hydrograph, the sequence of solute concentration maxima is (from earliest to latest arrival): potassium, turbidity, DOC, iron and manganese. At the peak of the hydrograph, minima of sodium, silica and conductivity are observed. On the falling limb, potassium and turbidity return to pre-event conditions followed by sodium, and silica. After the event, DOC remains lower than pre-event concentrations for at least several days. Potassium, turbidity, DOC, iron, and manganese all follow clockwise hysteresis loops, while conductivity, sodium, silica, and calcium follow counterclockwise loops. The forested watershed stream pattern is similar, though solutes follow more similar pathways on the rising and falling limbs of the hydrograph, creating narrower hysteresis loops. The forested watershed also takes longer to return to pre-event chemical conditions.

Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge: Solving more equations in more unknowns through incorporation of rare earth elements

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Watershed solute-based geochemical mass balance methods are considered the most accurate means of quantifying elemental transfers and weathering rates at the Earth's surface. However, such calculations often suffer from the limitation that the number of unknowns exceeds the number of mass-balance equations, either yielding a system of equations that cannot be solved mathematically, or requiring less-realistic approximations to solve for a reduced number of unknowns.

New solute-based mass balance calculations for low-order watersheds at the Coweeta Hydrologic Laboratory, western North Carolina, include solute fluxes of rare earth elements (REE), yielding enough equations to calculate eight unknowns (rates of primary mineral weathering and secondary mineral formation). Weathering of garnet and accessory allanite are the major contributors of REE to Coweeta stream waters. Inclusion of REE in Coweeta watershed mass balance calculations yields mineral weathering rates that are more geochemically reasonable (e.g., garnet weathering rates are up to approximately 90% slower) than previous studies.

Use of REE in watershed solute mass balances is in its infancy. Stream REE fluxes are from one-time samples that have been converted to approximate long-term fluxes using stream SiO₂ chemistry. Also, no data have been collected on REE in precipitation. Despite these potential limitations, sensitivity analysis of the new mass balance results, and the more geochemically reasonable results, encourage further work to overcome these limitations.

Exploring the effects of urban and agricultural land use on surface water quality

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Approach

This research is based on the hypothesis that the influences of land use on water quality are unique and can be quantified. In this study we investigate the influence of urban land use on nutrient cycles and trace elements and attempt to validate the applicability of previously developed biogeochemical fingerprints. (Wayland, et al., 2003)

Samples were analyzed for nutrients, major ions, and trace metals. Sites were selected representing surface watersheds with a variety of dominant and mixed land use types. Factor and cluster analysis were used to investigate the processes controlling the effects of land use on river chemistry.

Discussion of Results

Biogeochemical fingerprints of land use were referenced to the natural environment aiding in the identification of the unique contributions of urban and agricultural land uses to surface water chemistry. Similar biogeochemical fingerprints are found between the two watersheds (Urb: Na, K, Cl / Ag: Ca, Mg) and additional correlations were found for nutrients (Ag: N & Urb: N, P) and for selected trace metals (Urb: Rb, Mo, Mn, Sr and Ba / Ag: U).

Conclusions

The higher correlations of urban than agricultural land uses with nutrients were not expected and may reflect the effects of fertilization and wastewater or the season the samples were taken. More study in different geologic and urban settings is needed to help quantify these fingerprints. These studies could lead to a rapid assessment tool for the quality and sources for degradation of urban environments.

Reference

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The coprostanol/sterol ratio as indicator of organic matter provenance in soils and rivers

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This study presents the potentiality of organic markers to trace the impact of pig slurry in soils and rivers after their land disposal as organic amendment.

As described by Gruau and Jardé (abstract in this session), the analysis of long term records of dissolved organic matter (DOM) in four watersheds in western France shows divergent trends which cannot be explained by global changes solely. One alternative explanation could be that long-term record of DOM in rivers are controlled by human activities, and notably by agricultural practices. In order to test this hypothesis, a molecular analysis has been developed. This methodology is based on the molecular markers concept. Potential sources of organic matter have been studied and molecular markers or specific distributions have been evidenced. In this study we focused on the analysis of pig slurries because of the importance of pig production in the studied region. Each animal species is characterised by one specific sterol profile. The analysis of pig slurry evidenced the presence of coprostanol (5β -cholestan- 3β -ol or 5β) as a specific marker, originating from the bio-hydrogenation of cholesterol in their gut by anaerobic bacteria, and by the presence of C_{29} -sterol. The difference with other animal or human wastes has been evidenced by comparison with cow and poultry manures and human wastes. Two ratios have been used in order to differentiate pig slurry from the others: $5\beta/C_{27}$ and C_{29}/C_{27} -sterols. Moreover, different amended soils with pig slurry have been analysed in order to test the preservation of this potential molecular marker. The presence of coprostanol has been evidenced in amended soils, even in the deepest layers (40-60 cm). The validation of the ability of this compound to be a molecular marker of pig slurry made, our analysis has been centered on DOM of the four watersheds with divergent evolutions. The results show a systematic relation between the C_{29}/C_{27} and $5\beta/C_{27}$ ratios and the type of animal breeding in each watershed. This study allows us to evidence the impact of animal breeding activities in DOM of the analysed rivers. Such a study supports the view that DOM export by rivers is not solely under the control of global, climatic parameters, but also under the control of local land-use factors.

Human impacts on boron geochemistry of the Seine River, France

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Boron concentrations and isotopic compositions have been measured in the dissolved load of the Seine basin rivers, France. Hydrology and chemistry of the Seine River and its tributaries are highly influenced by human activities as the anthropogenic pressure on the Seine catchment is one of the highest in Europe. The samples were collected between 1994 and 1996 during various hydrological regimes, complemented by a time-series of the Seine River in Paris for one year. In particular, the decennial flood event of winter 1994 was sampled. Boron appears to be conservative in rivers and not influenced by riverine processes such as adsorption onto suspended matter and/or consumption by micro-organisms. To a first order, the origin of the dissolved boron can be traced using boron isotopes in spite of the complexity of the Seine river system and boron is a suitable tracer of contamination in rivers. The total dissolved boron of the Seine River at Paris can be explained by the contribution from three distinct components: Urban effluents constitute 65 % of the boron discharge measured in the Seine River whereas agriculture-affected waters contribute to less than 10 % with a more marked influence during high water discharges. Rainwater contribution is important (25 % mean) and can reach 30 % of dissolved boron during high flood events.

Boise Valley groundwater geochemistry – Origin, infiltration rate and transport characteristics

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Ground water/ aquifer interrelationships and estimates of vertical infiltration rates and horizontal flow rates are estimated. Groundwater chemistry of the Boise Valley aquifer is apparently inverted from what is commonly found in most large intermontane groundwater basins with highly dilute groundwater at depth. Highly dilute groundwater underlies higher TDS groundwater in the aquifer.

The Boise aquifer has a complex geohydrologic history that includes elevated concentrations of microbially generated carbon dioxide gas originating from a buried lacustrine sedimentary sequence. Thermal ground water is present at depth and also occurs along the faulted northern boundary of the basin where it interacts with natural surface water recharge from the Boise River. Large scale historical flood irrigation has created an upper alluvial groundwater system with a considerably different groundwater chemistry than the deeper ground water aquifer recharges.

Groundwater geochemistry indicates that the oxidized shallow alluvial groundwater is moving into previously reduced deeper sections of the alluvial aquifer creating an intermediate-depth oxidizing portion of the alluvial aquifer. The vertical infiltration rate of the upper aquifer, is estimated from nitrate concentrations and tritium activities sampled from water wells of various depths.

Calculated groundwater ages based on carbon-14 isotopes support the geohydrologic interpretations based on the groundwater chemistry. Remarkably, the deep ground water chemistry has almost the same chemistry as that of the natural recharge water (Boise River) even though it has moved miles horizontally through the Boise aquifer through thousands to tens of thousands of years of contact time with the aquifer mineralogy.

Geochemical indicators of natural and anthropogenic water inputs to a lake in a mixed land use watershed

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The geochemical compositions of lake waters and source water inputs are investigated to examine human impacts on the biogeochemical cycling of phosphorus in a lake and to evaluate the utility of selected chemical species as indicators of specific source types. The project is conducted in the Table Rock Lake watershed (4020 square miles) on the Missouri-Arkansas border. The lake is an 43,000 acre reservoir with a watershed that includes a diversity of land uses and an array of potentially significant phosphorus sources, which include point sources and non-point sources such as decentralized wastewater treatment systems, confined animal feeding operations, poultry litter applied to farm fields, and storm water runoff.

The project involves a coordinated plan of sampling and analysis of potential sources and lake water at sites that have been impacted by particular types of sources (source-rich surface waters). Identification of lake sampling locations was performed using geospatial data analysis techniques to relate land use patterns and other surface characteristics with areas of potentially high densities of source types. Sampling and on-site analyses were performed once per season to assess effects of seasonal variation in source loadings and lake dynamics. Samples were analyzed for dissolved and total phosphorus, a suite of anions (Br^- , Cl^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}), major elements (Ca, Mg, K, Na), and trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Sr, U, V, Zn). Evaluation of the large dataset looks for patterns of dissolved species that are unique to specific source types. Multivariate statistical analysis methods, including principal component analysis, are used to identify factors that are characteristic of both natural and anthropogenic inputs. Using a web-based geographic information system (GIS), the analytical results of the present study were integrated with measurements by other groups and additional geospatial data on the watershed (e.g., land use, size and locations of permitted discharges) and made available to other parties interested in Table Rock Lake water quality.

Understanding radioactive disequilibrium in river-borne material: Dependence on colloid/particle size

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Recent studies have used U-series isotopes in river-borne material to investigate the conditions and timescale of erosion at the basin scale (e.g. Vigier et al., 2001; Dosseto et al., submitted). Because U is more soluble than Th and ²³⁴U can be preferentially ejected from the solid, ²³⁴U excess over ²³⁸U, (²³⁴U/²³⁸U) > 1, and ²³⁸U excess over ²³⁰Th, (²³⁰Th/²³⁸U) < 1, are expected in the nominally “dissolved” phase (<0.2 or 0.45 µm) and the opposite in suspended particles. However, in some cases, opposite trends have been observed (e.g. Porcelli et al., 2001). To better understand the size dependency of radioactive disequilibrium in river-borne material, U-series isotopes have been measured for different colloid/particle sizes in waters from the Murray River Basin, SE Australia. Preliminary results show that all fractions <1 µm have (²³⁴U/²³⁸U) > 1 and (²³⁰Th/²³⁸U) < 1, the extent of disequilibrium decreasing with increasing colloid/particle size. Douglas et al. (1999) have shown that the composition of colloidal matter (<1 µm) in these rivers is controlled by mixing between detrital silicate and organic material. The increasing proportion of detrital silicate may be responsible for the decrease in disequilibrium. Hence, the “true” dissolved phase (free of detrital silicate) is probably characterized by a higher disequilibrium than that observed in the nominally “dissolved” phase. This observation may have implications for the lack of complementary nature between nominally “dissolved” phase and suspended particle compositions, currently used to discuss the steady-state nature of erosion in large drainage basins (Vigier et al., 2001; Dosseto et al., submitted).

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Diel cycles in stable isotopes of dissolved O₂ and dissolved inorganic carbon in the Big Hole River, Montana

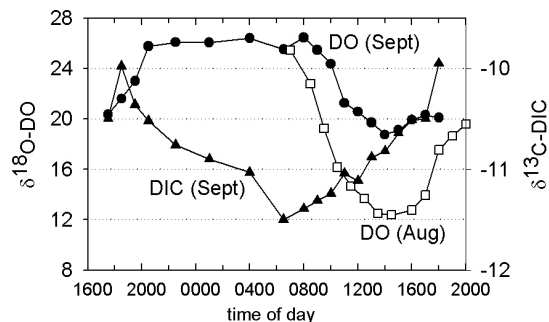
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Large diel changes in the isotopic composition of dissolved oxygen ($\delta^{18}\text{O}$ -DO) and dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) were measured in the Big Hole River, SW Montana. $\delta^{18}\text{O}$ -DO showed a diel range of 14‰ in August 2004, and 8‰ in September 2004. $\delta^{13}\text{C}$ -DIC showed a diel range of 1.4‰ in September 2004.



The results are explained by daytime photosynthesis with the net production of isotopically light O₂ and net consumption of isotopically light CO₂, and by night-time respiration which consumes isotopically light O₂ and produces isotopically light CO₂, together with gas transfer between the river and the atmosphere. Other measured river parameters (such as pH, DIC and DO concentrations) were consistent with this interpretation. The greater diel range of $\delta^{18}\text{O}$ -DO in August vs. September is consistent with a higher rate of biological productivity during August (warmer), and by the higher DO concentrations during September (cooler).

This study is one of the first to document diel changes in $\delta^{18}\text{O}$ -DO and $\delta^{13}\text{C}$ -DIC in a river, and is consistent with the preliminary data of Tobias and Bohlke (2004). The use of $\delta^{18}\text{O}$ -DO and $\delta^{13}\text{C}$ -DIC has potential to advance our understanding of the biological, chemical, and physical processes that take place in rivers and lakes.

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Ecohydrochemical studies in the Achankovil River basin, Western Ghats, South India

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Preliminary studies on the nutrient and water chemistry of the high altitude river basin with relatively homogeneous lithology with pristine ecosystem in Western Ghats region has been carried out. A time series survey has been carried out to understand the natural and anthropogenic hydro geochemical processes controlling the water chemistry in the Achankovil River of the Western Ghats. The water is neutral with pH and EC ranges from 6.32-7.56 and 24 – 54 $\mu\text{S}/\text{cm}$. Chloride and sodium are the dominant anion and cation in the water respectively. Correlation analysis of the chemical parameters of the water shows that some ions have additional sources such as sea spray, soil conditioners and evaporates. This study shows that the majority of carbonate is derived from carbonate weathering followed by silicate weathering. Cation concentrations show decreasing trend from upstream to downstream in contrast to the increasing trend in the major world rivers. Dissolved silica in premonsoon water is low. This is due to the silica uptake by diatoms. The Gibbs plot indicates that the river chemistry is dominated by rock weathering induced by precipitation. The partial pressure of CO_2 in water is high and is in equilibrium with the atmosphere. Thermodynamic plots show that dolomite, kaolinite, albite and chlorite are in equilibrium with the river water. The additional sources which influence the water chemistry are sea spray leaching of evaporates and anthropogenic inputs. Chemical weathering is predominant here compared to physical weathering. The annual discharge of the Achankovil River is $1.48 \text{ km}^3/\text{yr}$ and transports a significant amount of solute flux ($1389 \times 10^6 \text{ t/yr}$) and suspended flux ($27 \times 10^6 \text{ t/yr}$) to the Vemband estuarine lake. The overall material transport seems to be lower compared to the other Indian rivers nevertheless the solute loads are comparable to certain large rivers like Cauvery in the south India. The concentration of PO_4 , NO_3 and Carbon are very high due to the contribution from multiple sources. The solute flux including the nutrient flux is very high among the Western Ghats Rivers in comparison to its size, which will certainly supplement the productivity of the lake/estuary and the coastal waters. Since this study is restricted to limited period, long-term data procurement and analysis along with micro nutrients studies are needed, which are lacking in the present study, to gain insight into the material flux by this river into the Arabian Sea.

Key words: Achankovil River; Nutrient concentrations, seasonal variation; solute acquisition

Export of DOM by rivers: Assessing the relative effects of climate change and human activities using long-term records

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This study presents long-term records of dissolved organic matter (DOM) as indicated by oxydability measurements that were constructed for four watersheds in western France as back as 1979. Observations show contrasted evolutions with three watersheds exemplifying large increases in DOM concentrations over the period of study (a doubling of the concentration over a period of 25 years is observed in one case), while the fourth shows DOM concentrations that decrease with time. All watersheds show common inter-annual control on DOM concentration in response to a succession of dry and wet periods with a cyclicity of 5-7 years. The same cyclicity in DOM concentrations is apparent in the long term records of DOM for rivers located in northern England. The evidence support the view that this cyclicity is climatic in origin being likely a consequence of the North Atlantic Oscillation that controls the yearly amount of precipitation that falls over Western Europe.

As regards the significance of long-term trends, we note that the onset of DOM increase in those rivers showing positive long-term DOM trends is in phase with an increase in average annual temperature. This might suggest that the change in temperature is the key mechanism that causes these trends, suggesting that the climate is also the driving force of long-term DOM trends in river. However, such an hypothesis is faced with the problem of explaining why one of the studied watershed shows a divergent evolution, i.e. a long-term DOM decrease. Alternative explanations must thus be found. One such alternative explanation could include changes in land management and agricultural practices. A survey of agricultural practices in the four studied watersheds reveals that the watershed showing a long-term decrease of DOM is marked by massive spreading of pig manure, a process that does not occur in the other three watersheds. Spreading of pig manure may acidify watershed soils, thereby promoting the adsorption of organic matter on soil minerals which could ultimately limit the export of DOM by rivers. The evidence supports a view that DOM export by rivers is under the control of global, climatic factors mediated by local land-use factors which can cause divergent long-term evolutions in the DOM export capacity of rivers on relatively short spatial scale.

Chemical weathering and erosion in New Zealand monitored by bedload and suspended sediments

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Chemical and physical erosion processes have been investigated in a wide range of high sediment yielding rivers from New Zealand using major and trace element data from suspended sediments and fluvial bedload grain size fractions. Average fluvial particulate compositions from New Zealand are similar to estimates of average upper continental crust (UCC) composition. Recalculation of global fluvial elemental fluxes using average New Zealand suspended and bedload sediment compositions as a proxy for sediment derived from all high standing islands (HSIs, 30% of total) results in world average compositions that more closely resemble the UCC than previous estimates using major world rivers alone.

Weathering of the Southern Alps is strongly partitioned(?) between the chemical weathering of carbonates and physical weathering of silicates. The similarity of sediments from rivers draining both sides of the drainage divide indicates minimal climatic control on weathering intensity of fluvial sediments. Rather, bedload geochemistry is controlled primarily by mechanical attrition and hydrodynamic fractionation, both of which depend on sediment residence time within the fluvial system. Combined with suspended sediment data from rivers throughout New Zealand, these findings suggest that HSI fluvial sedimentary evolution is dominated by physical weathering processes and that several cycles of sedimentary recycling may occur without production of a silicate chemical weathering signature.

Impact of storm runoff from subtropical watersheds on coastal water quality and productivity

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Runoff from storms occurring in subtropical watersheds in Hawaii leads to sediment and freshwater pulses to coastal waters that rapidly affect water quality. This is particularly true in semi-enclosed embayments with relatively long residence times. The response of coastal waters to such inputs has often been evaluated by synoptic sampling that only provides snapshots of the evolution of these highly dynamic environments. In contrast, continuous in-situ measurements, when combined with synoptic sampling, are better able to reflect the short-term biogeochemical response of these systems. Our approach facilitates the characterization of impacts of storm runoff from watersheds on coastal waters and is better suited to evaluating overall ecosystem responses over extended periods of time following storm events.

In this presentation we discuss data from several extreme rain events during the winter seasons of 2003-2004 and 2004-2005 acquired by our Coral Reef Instrumented Monitoring Platform (CRIMP). We discuss the response of Kaneohe Bay to storm sediment and nutrient inputs, the relationships between physical, biological, and chemical processes in the watershed and the bay, and the evolution of the aquatic community structure during and following phytoplankton blooms.

Elevated DIN:DIP (25) in storm runoff changes significantly the proportion of dissolved nutrients available for biological uptake. Increases in Chl-a in the bay shortly after storms and changes in the plankton community structure reflect an evolving biological response stimulated by the inputs of excess nutrients.

An approach to interpreting contaminant deposition fluxes from dated sediment cores

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Background

Detailed interpretation of trends in particle-associated contaminant fluxes to sediment often requires modeling to resolve the effects of drainage basin holdup and post-depositional mixing. Modeling is especially necessary for constraining flux estimates for atmospherically deposited contaminants. We apply simple models of drainage basin holdup and post-depositional mixing to the interpretation of ¹³⁷Cs and other tracer profiles in dated cores collected from lakes and reservoirs in New York State.

Discussion of results

Dated cores collected from two New York City drinking water reservoirs are well described by a 3–4 year half-time of delayed delivery followed by simple, complete mixing of sediments to a fixed depth. Model results for the reservoir cores are consistent with delayed delivery of atmospheric ¹³⁷Cs indicated by historical measurements in reservoir-derived tapwater.

Modeling of a core collected from Central Park Lake, Manhattan, suggests that a substantial portion (ca. 40–85%) of recent contaminant flux is due to indirect inputs from the drainage basin, and cannot be attributed to direct atmospheric input.

Conclusions

A small set of simple models constrained by geochemical tracers can comprise a workable approach to the interpretation of local and regional atmospheric contaminant depositional fluxes from well-dated sediment cores. This is in contrast to recent efforts to model less-ideal cores using models which are markedly more complex and less constrained by geochemical evidence.

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Factors controlling tufa deposition at waterfall sites

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Study on calcite precipitation has major implications for both the hydrochemical evolution of river systems and the global carbon cycle. The precipitation of calcite generally requires the water to be 5 to 10 times supersaturation with respect to calcite, which is usually achieved by the removal of CO₂. Formation of waterfall tufa has been often simply described as the result of water turbulence in fast-flowing water. In this paper, the formation mechanisms of waterfall tufa are discussed and a series of laboratory experiments are designed to simulate the hydrological conditions at waterfall sites. The influences of the air-water interface, the water flow velocity and the solid-water interface on CO₂ outgassing and calcite precipitation are compared and evaluated quantitatively. The results show that the principal cause of waterfall tufa formation is the enhanced inorganic carbon dioxide outgassing resulted from the sudden hydrological changes occurring at waterfall sites, rather than organisms, evaporation or the solid-water interface. The air-water interface area and the water flow velocity are greatly increased at waterfall sites as a result of the “aeration effect”, “low pressure effect” and “jet-flow effect”, which greatly accelerate CO₂ outgassing. Inorganic CO₂ outgassing drives the waters to become highly supersaturated with respect to calcite, and consequently results in much calcite deposition. The solid-water interface is less important as the air-water interface in affecting calcite precipitation at waterfall sites. Field measurements showed that conductivity, Ca²⁺ and HCO₃⁻ concentrations along Tianhe Creek and Hot Creek decrease downstream while pH rises. Field observations also showed that tufa deposition occurred mainly at waterfall sites.

Soil contamination of heavy metals in Katedan industrial area, Hyderabad, Andhra Pradesh, India

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Studies on quantitative soil contamination due to heavy metals were carried out in Katedan Industrial Development Area, south of Hyderabad, Andhra Pradesh, India under the Indo-Norwegian Institutional Cooperation Programme. The geology of the study area consists of granites and pegmatite of Archaean age with residual soil from granite. The area falls under a semi-arid type of climate with average rainfall of 800 mm per year. The industrial area is having about 325 industries manufacturing batteries, chemicals and dealing with cloth dying, metal plating and edible oil production. Many industries discharge their effluents either on the open land, ditches or creeks. Solid waste from some of the industries is randomly dumped along roads contaminating the soil and water in the area.

Soil samples were collected during two hydrological cycles and were analyzed for major, minor and trace elements by XRF spectrometry. Comparing the results with the Soil Quality Guidelines (SQGL), it was observed that almost whole of the industrial area is heavily contaminated by high concentrations of lead, arsenic, chromium, copper, nickel and zinc. By and large, the residential area is not heavily contaminated except some of the pockets where high concentrations of Pb, As and Cr are observed. The pre and post monsoon studies indicate that As, Cd and Pb contaminants are more mobile and may reach the groundwater while the other contaminants seem to be more stable. The source of high concentrations of heavy metals like Cr, Cu, Pb etc seem to be anthropogenic and it is not possible to derive these concentrations from surrounding rocks which are predominantly granite.

Correlation diagram were plotted to find out the relationship between various trace metals. There is a well-defined relationship between As vs. Pb with extraordinary linear correlation.

Studies were carried out on surface water samples also, which indicate high concentration of toxic elements. Geochemical maps showing the distribution of many metals are prepared for the whole area and results will be presented in this paper.

Measurements of oxygen and hydrogen isotopes in the Skagway River catchment, Alaska

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This work investigated the seasonal variations in oxygen and hydrogen isotopes in the Skagway River, a medium-sized catchment (375 km²) fed by moderately high precipitation and glacial meltwater. Nearly weekly samples of river flow were gathered from August 2000 through November 2001 and again in the summers of 2002 and 2003. During the summer periods, samples of glacier ice, precipitation, and groundwater were also collected.

Riverwater showed the most depleted $\delta^{18}\text{O}$ near the river's mouth in early summer. Similar values were found in meltwaters sampled at the toe of Laughton Glacier. The precipitation samples were gathered from three sites of varying elevations: at sea level, at 825 meters, and at 1025 meters near the valley summit. The $\delta^{18}\text{O}$ values ranged from -8.2 ‰ at the lowest elevation site to -20.3 ‰ at the highest. Measured groundwater $\delta^{18}\text{O}$ value was -17.3 ‰, and the mean for surface glacier ice was -17.5 ‰.

The fractional components of water sources in the river were determined by using mass balance and by establishing isotopically derived endmembers of river baseflow and glacial meltwater. The baseflow $\delta^{18}\text{O}$ was computed from groundwater values taken by sampling a nearby well. Glacial runoff, measured in late June and early July at the toe of Laughton Glacier, yielded a mean meltwater value for $\delta^{18}\text{O}$ of -19.7 ‰. Rainfall contributions to the river have greatest influence in the fall, the typically rainy season, and during winter storms when temperatures are above freezing to allow for isotopically heavier rain, rather than snow, to fall. During these occasions, the riverwater may exhibit an isotopic signature more enriched than the groundwater endmember.

The δD values for a few of the river samples ranged from -125 ‰ to -137 ‰. A plot of these results and their corresponding $\delta^{18}\text{O}$ values, $\delta\text{D} = 7.7 \delta^{18}\text{O} + 4.9$ with $R^2 = 0.97$, shows a good fit with Craig's meteoric water line.

A 4 ‰ shift in $\delta^{18}\text{O}$ to more negative values occurred around mid-May. This shift corresponds with atmospheric temperature increases that result in lower $\delta^{18}\text{O}$ and δD from upper elevation snowpack and glacial melt becoming the major contributor to runoff. Isotopic analysis determined that up to 87 % of water in the riverbed during June is derived from glacial melt.

Riverine particulate organic carbon from the western Southern Alps, New Zealand

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The flux of particulate organic carbon (POC) from small mountainous rivers draining active orogens accounts for a large proportion of the global riverine POC flux [1]. Their importance in atmosphere-ocean carbon dynamics may be disproportionately large due to their high-sediment production, small storage potential and tendency to discharge sediment at extremely high concentrations [2]. It is therefore important to constrain the type and amount of carbon mobilised.

Suspended load, bedload and sediment samples from landslide debris fans were taken from catchments draining the rapidly eroding, densely vegetated western Southern Alps, New Zealand. The samples allow estimates of the POC yield and determination of the main sources of organic carbon (C_{org}) using C/N as a mixing proxy.

POC yield estimates range from $280\text{--}4600 \times 10^6 \text{ mol.yr}^{-1}$ – which are high globally and similar to previous estimates [1]. C_{org} decreases with increased suspended sediment concentration (SSC). At mean annual SSC C_{org} concentration $\sim 0.4\%$ and C/N ~ 13.5 , which is characteristic of the clay/silt fraction measured in landslide deposits. This may be the main POC source during mean flow and is related to breakdown and re-sorption of non-kerogen carbon onto mineral grains during soil processes (c.f. [3]). During higher flow events, when these rivers may transport the majority of their POC yields to the ocean, the source of carbon (and its C/N) may be significantly different.

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Geochemical evolution of Pleistocene glacial meltwaters within regional carbonate aquifer systems, Midcontinent, U.S.

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Pleistocene glacial meltwaters recharged regional aquifer systems along the margins of the Illinois, Michigan, and Appalachian basins, significantly suppressing freshwater-saline water mixing zones to great depths and reorganizing drinking water resources. Importantly, dilute water recharge into Silurian-Devonian carbonate aquifers migrated into overlying fractured, organic-rich shales and generated economic deposits of microbial gas. New elemental and isotope analyses of Sil.-Dev. groundwaters and overlying glacial drift, along the margins of the three basins, were integrated with previously published data on basinal fluids to investigate the impact of Pleistocene glaciation on regional-scale groundwater flow and geochemical evolution of glacial meltwaters within confined aquifers.

Groundwaters in the recharge areas of the glacial drift and carbonate aquifers are predominately Ca-Mg-HCO₃ waters with $\delta^{18}\text{O}$ and δD values within the range of modern precipitation (-11.0 to -4.5‰), and have $\delta^{13}\text{C}$ values of DIC consistent with open system carbonate mineral dissolution ($\sim -12.5\text{‰}$). Groundwaters in confined aquifers, beneath lake-bed clays and Upper Dev. black shales, have relatively low $\delta^{18}\text{O}$ and δD values (-18 to -11‰), within the estimated range of Pleistocene glacial meltwater (-25 to -11‰), and have low activities of ^{14}C ($<8\text{pmc}$). Since the Late Pleistocene, these glacial meltwaters have been extensively altered by water-rock interactions, biogeochemical processes, and mixing with Na-Ca-Cl brines. Confined groundwaters have high $\delta^{13}\text{C}_{\text{DIC}}$ values (-10 to -2‰), and elevated Sr/Ca and Mg/Ca ratios, indicating they evolved via incongruent dissolution of carbonate minerals and anhydrite under closed system conditions. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}_{\text{SO}_4}$ values are within the range of Sil.-Dev. carbonates and evaporites. Glacial meltwaters have been preserved at relatively shallow depths along the basin margins and have not been flushed out by more recent recharge, illustrating the importance of ice-induced hydraulic loading on deep circulation of meteoric waters, and the relatively long residence times of drinking water resources.

High concentrations of uranium and thorium in residual soils of Wailpalli watershed, Nalgonda district, Andhra Pradesh, India

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Environmental studies were carried out in Wailpalli watershed of Nalgonda district to find out the radiogenic elemental concentrations in soils and rocks of the area. The geology of the area comprises of Granites ranging from granodiorite to Granite, mafic dolerite dykes and pegmatite veins. These granites are of 2400 million years of age, they belong to Hyderabad granites. The granites contain quartz, orthoclase, microcline, hornblende etc., as major mineral phases and the accessory minerals are magnetite, zircon, allanite, fluorapatite and epidote etc. The concentration of radioactive elements is dependent on the presence of some of the above accessory phases.

Wailpalli watershed is located in between the latitudes 17°20'' to 17°40'', longitudes 78°48'' to 79°00'' comprising an area of 150 sq.km. Granite exposures are mostly found in western part of watershed. 600 soil samples and 195 fresh granite samples were collected covering the entire watershed and were analysed for their U & Th content by X-ray fluorescence spectrometer. The analytical data show very high concentration of U and Th. 85% of the soil samples and 80% of the rock samples show uranium above normal levels of 1 to 4.5 ppm (in residual soils and granites IAEA, 1988) and 85% of thorium concentrations in rock and soil are above the normal levels of 1 to 15 ppm (in residual soils and granites). The results demonstrate the high concentrations of U & Th in the residual soils, which are derived geogenically from the granitic rocks. Most of the area in Wailpalli watershed is under active irrigation and these radioactive elements may enter the food chain of the human beings and may be hazardous to human health.

Identifying sources of total dissolved solids (TDS) in the Pecos River, USA

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The Pecos is one saline river in the desert southwest. The causes of the high salinity ($>10000 \text{ mg L}^{-1}$) need to be determined. Analysis of hydrological and chemical variables indicates that relationship between ion flux (L_i) and stream discharge (Q) can be best described by a log-linear function, $\log L_i = a + b \log Q$ (YUAN and MIYAMOTO, 2004). Here we use the USGS daily flow and major ion concentration records from 11 gauging stations along the river spanning 1959-2002 to estimate mean TDS load and therefore TDS concentration (Figure 1). The stream discharge is an arithmetic average of continuous daily flow, whilst the TDS is a weighted average of inferred daily TDS. Flowpath from the upper basin downward is indicated by solid arrows. This analysis suggests that the TDS of the Pecos is controlled by salt pick-up or dissolution, evaporative concentration and / or crystallization, and dilution. Salt dissolution occurs mainly in the upper basin, whereas the dilution occurs in the lower end of the basin. The evaporative concentration is the dominant process for the increasing TDS in the middle portion of the basin. River water seeps into underground between Brantley and Malaga and back to surface between Malaga and Pierce Canyon Crossing. The losses of flow and salts upstream are offset by the gains downstream in a long run (i.e., 44 years).

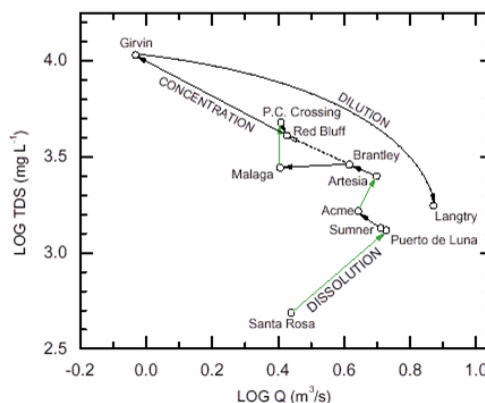


Figure 1 Logarithmic graph of stream discharge (Q) vs. TDS.

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The existence and mobility of hydronium ion in the structure of jarosite

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Jarosite is a common mineral of acid mine drainage systems. The most common end-members are jarosite *s.s.* ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), and hydronium jarosite ($(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$). Despite its ubiquitous presence as a component of the jarosite solid solution, the properties of hydronium jarosite are not known well. In particular, the question of the existence of the hydronium ion in this structure has not been resolved yet.

The structure of jarosite is built by triangular sheets of octahedra $\text{Fe}(\text{OH})_6$, decorated by sulfate tetrahedra. The Fe^{3+} sites are partially (5-15 %) vacant. The monovalent cations reside in cavities between the sheets.

We have investigated a series of jarosite samples and their deuterated analogs by ^2H magic-angle spinning nuclear magnetic resonance (MAS NMR) and quasi-elastic neutron scattering (QENS) on ^1H atoms.

^2H MAS NMR results clearly distinguish hydroxyls (OD) in the structure from scarce OD_2 groups bound to iron and abundant OD_n ($n = 2$ or 3) groups not bound to iron. The δ_{iso} values for these three sites are ≈ 0 , ≈ 70 , and ≈ 260 ppm, respectively. The OD_2 groups bound to iron correspond to water molecules that coordinate vacant sites in the structure. The OD_n groups are either OD_2 or OD_3 molecules in the cavities. Integration of the intensities of the peaks suggests that $n = 3$, i.e., the cavity is occupied by a D_3O^+ group. The shape of the NMR spectra indicates that the D_3O^+ deuterons are highly mobile and tumble in their cavities.

QENS spectra show that the hydrogen in the sample is in motion already at ~ 17 K. The quasi-elastic line is broadened when compared to the vanadium standard. The spectra collected at 50, 120, 170, 220, and 300 K show further broadening of the quasi-elastic line. Separation of the signal due to rotation and possible translation of the hydrogen atoms in the QENS spectra is now in progress.

Jarosites in acid mine drainage environments: Formation, mineralogy, stability

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Jarosites form a subgroup of the alunite supergroup of minerals, and have a general formula of $\text{AB}_3(\text{TO}_4)_2(\text{OH})_6$, where A represents cations with a coordination number greater than or equal to 9 (K^+ , Na^+ , NH_4^+ , H_3O^+ , Ag^+ , Ti^+ , Pb^{2+}), B represents cation sites with octahedral coordination (mainly Fe^{3+} , but also Cu^{2+}), and T represents cations with tetrahedral coordination (SO_4 , AsO_4) (Jambor 1999). Jarosites are commonly found in ferric-rich, acidic ($\text{pH} < 3$), oxic, acid mine drainage (AMD) environments, where they are important stores of SO_4 and of potentially toxic elements such as Pb and As.

In AMD environments such as the Río Tinto, Spain, and the Mathiatis mine, Cyprus, plumbojarosite [$\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$] and jarosite itself [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] are common, and form as a result of the decomposition of pyrite or precipitation of sulphate-rich, ferric solutions. Batch experiments and computational modelling, carried out to investigate the stability of jarosite, plumbojarosite and beudantite [$\text{PbFe}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})_6$] under acidic ($\text{pH} 2$) and alkaline ($\text{pH} 8$) conditions, have shown that these minerals all dissolve incongruently. The $\text{pH} 2$ dissolution of jarosite yields excess K and SO_4 relative to Fe in solution, which may be related to selective dissolution of the A- (K) and T- (SO_4) sites, since Fe is located deep within the T-O-T jarosite structure. Of the $\text{pH} 2$ dissolutions, only that of beudantite yields a secondary, Fe hydroxide-like phase.

The alkaline ($\text{pH} 8$) dissolutions all yield secondary phases: jarosite yields goethite, plumbojarosite and beudantite yield Fe hydroxide, and beudantite also yields PbSO_4 . There is evidence for some co-precipitation and resorption of the Pb and As in and onto the newly-formed phases, suggesting that the remainder of these potentially toxic elements may be released back to AMD waters.

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The attenuation of Ni, Zn, Cu, by secondary Fe phases from surface and ground water of two sulfide mine tailings deposits

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Secondary Fe phases, which could attenuate Cu, Zn, and Ni, formed in samples of unacidified filtered surface and ground water from two deposits of sulfide mine tailings at Thompson and Leaf Rapids, Manitoba. The precipitates were separated from the solutions by filtration, and analyzed by XRD, SEM and EMPA. Phases of different crystallinity were separated by selective dissolution with 0.2 M ammonium oxalate solution at pH 3.

An assemblage of goethite and schwertmannite precipitated from initially anoxic ground water with a pH of 5.7-6.2, whereas jarosite and/or schwertmannite were identified in acidic oxygenated (pH = 2.7-3.2) surface water. This difference in mineralogy is attributed to the redox and acidity conditions. In the surface water, activities of SO_4^{2-} and H^+ control the proportions of minerals in the assemblage and the composition of schwertmannite.

More Cu, Zn, and Ni were precipitated from the ground water than from surface waters due to the higher initial content of Fe and higher pH of ground water. The concentrations of the metals were not significantly changed in the surface water because of limited sorption of cations at low pH.

The affinity of the metals to the precipitate rather than the solution is in the order $\text{Cu} > \text{Zn} > \text{Ni}$. Sequential extraction indicated that Ni and Zn accumulate in poorly crystalline schwertmannite, while Cu concentrates in crystalline phases (goethite and jarosite). However, schwertmannite, as the principal phase in most of the precipitates, contains a significant proportion of Cu. During the recrystallization of metastable schwertmannite to goethite, the metals could be redistributed and released back into the mine water.

Mineralogical controls on acid-mine drainage from waste piles in the Vermont copper belt

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Secondary minerals sequester metals, sulfate, and acidity and complicate interpretations of static tests used to predict acid-mine drainage (AMD). The role of these minerals is evaluated in historic mine waste piles from pre-1958 copper mining of pyrrhotite-rich, Besshi-type massive sulfide deposits in Orange Co., VT, where waste piles in headwaters areas contaminate streams. Composites of <2 mm material from mine-waste pile surfaces were analyzed for mineralogy (semi-quantitative phase analysis using Rietveld refinement on a full XRD profile), acid-base accounting (ABA), chemistry, and leach studies. Waste piles are strongly acid-generating with paste- and leachate pH <3 and net neutralization potentials (NNP) of -14 kg CaCO_3/t or less. The inherent acidity of the deeply weathered mine waste is due to jarosite (4 to 40 wt.%), salts (tr to 2 wt.%, including melanterite, rozenite, copiapite, and halotrichite), and sulfides (<1 to 6 wt.%, mainly pyrrhotite, with minor pyrite, chalcopyrite, and sphalerite). Efflorescent sulfate salts that form locally and intermittently on wastes incorporate Cu and Co. Total S concentrations in wastes range from 1 to 5 wt. %. Sulfate S, and consequently NNP values, vary with HCl concentration and boiling time used for sulfate S determination because of the refractory nature of the jarosite (Vos and O'Hearn, 2001). Any calcite present in the waste was consumed to form gypsum (<0.1 to 1 wt.%). Goethite (10 to 17 wt.%) and silicates (quartz, micas, chlorite, feldspars) provide little neutralization, although biotite reacts to provide K for jarosite. Washing the waste with deionized water (20:1 water:rock) dissolved salts immediately and lowered solution pH to <3.5. After repeated washes, pH stabilized at or above 3.8. Evaporated wash solutions precipitated Fe sulfate salts. Surface runoff composition, simulated by leaching wastes with synthetic rain, approximates measured surface-water chemistry for Cu, Zn, and Cd, which commonly exceeds EPA acute aquatic toxicity standards. Salts, though volumetrically minor, contribute to AMD even after 50+ years of wet/dry cycling of waste piles.

Reference

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Use of a mine-tailing line as a geochemical reactor for treating acid-rock drainage: Bingham Canyon (USA)

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Kennecott Utah Copper Corporation (KUCC) manages $6.8\text{E}+07\text{ m}^3$ of low-pH, high-sulfate, high-metal groundwater in the Jordan Valley (Utah, USA), using the active tailing disposal system as a "geochemical reactor". KUCC evaluated the chemistry and mineralogy of tailing and pipeline scales, conducted laboratory-scale water-rock experiments, monitored the aqueous chemistry of source waters and the chemistry of both solutions and solids throughout the tailing system, and used thermodynamic calculations to shed light on specific mechanisms of reactions observed during experiments and monitoring.

At acidic flows of up to $22\text{ m}^3\cdot\text{s}^{-1}$, the tailing system acts as a nearly ideal plug reactor, with no measurable dispersion in parameters over a 25 km reach and maintains the discharge pH at a value ≥ 6.7 . Reaction of low-pH waters with the acid-neutralization capacity (ANC) of the tailing precipitates Fe- and Al- hydroxides and gypsum and removes trace metals by sorption at rates ranging from 60% for Mn to $> 99\%$ for Al, Cu, Fe and Zn. Because of the very high flux of alkaline tailing, the design-basis flows of acidic water do not deplete the ANC of tailing within the analytical precision of the measurements. By maintaining pH above 6.6, KUCC can meet all regulatory discharge limits.

Thermodynamic data for hydrated ferric sulfates and application to secondary minerals at Iron Mountain, California

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Acid mine drainage (AMD) is a serious environmental problem at many sites. AMD is produced by weathering of pyrite and other sulfides and is rich in Fe^{2+} , Fe^{3+} , Al^{3+} , SO_4^{2-} , and other constituents. Precipitation of secondary minerals from AMD can be caused by several processes including evaporation, oxidation of Fe^{2+} , mixing, neutralization, and change in temperature. Common secondary minerals include hydrated metal oxides and sulfates. The objective of the present study is to determine the thermodynamic properties and stability ranges of selected ferric sulfates by calorimetric experiments. Synthetic ferricopiapite, rhomboclase, and $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$ were prepared and used for the experiments along with a natural, Al-bearing coquimbite specimen from Iron Mountain, Calif.

The enthalpy of formation (ΔH°_f) of ferricopiapite, coquimbite, rhomboclase, and $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$ was determined by acid-solution calorimetry in 5 N HCl. An appropriate thermochemical cycle was employed for each studied phase. The reference phases were MgO, α -MgSO₄, γ -FeOOH, and H₂O. The ΔH°_f values are (kJ/mol) are -4115.8 ± 4.1 [$\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$], -12045.1 ± 9.2 (ferricopiapite), -5698.7 ± 3.4 (coquimbite), and -3201.1 ± 2.6 (rhomboclase). Standard entropy of these phases was estimated by considering solid-state reactions among the studied ferric sulfates and phases whose entropy has been measured. The estimated values are 488.2 ± 1.3 [$\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$], 1449.2 ± 5.0 (ferricopiapite), 641.0 ± 2.2 (coquimbite), and 380.1 ± 1.4 (rhomboclase).

Field relations among copiapite-group minerals, coquimbite, rhomboclase, and other secondary Fe-sulfate minerals at Iron Mountain will be discussed in light of available thermodynamic data.

Dehydration and rehydration of melanterite with significant copper content

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Melanterite (Fe,Cu)SO₄·7H₂O with more than a few atomic % copper dehydrates to siderotil (Fe,Cu)SO₄·5H₂O while melanterite with no copper dehydrates to rozenite FeSO₄·4H₂O. The field of stability of non-substituted melanterite is known (Chou *et al.* 2002). The present study investigates the humidity and temperatures where copper-substituted melanterite is in equilibrium with siderotil.

The dehydration and hydration of a copper-bearing melanterite was studied under controlled temperature and relative humidity in a chamber constructed to fit on a Philips X'pert Pro diffractometer. The boundary between the field of stability of the 7-hydrate(melanterite) and the 5-hydrate(siderotil) was explored by adjusting the relative humidity and temperature in the chamber during the diffraction experiment.

It was discovered that the relative humidity and temperature conditions where Cu-containing melanterite is in equilibrium with siderotil are the same, within experimental error, as the conditions where Cu-free melanterite coexists with rozenite.

Investigation of the factors which control the rate of dehydration shows the rate to be strongly dependent on temperature. It was also observed that at a given temperature, the rate of dehydration depends on the difference of the relative humidity of the atmosphere from the relative humidity where the two hydration states are in equilibrium.

The formation of a sulfate with the rozenite structure from copper-containing melanterite occurred when the melanterite sample was dried very quickly at high temperature. Rozenite was also observed to form from copper-containing melanterite during intense grinding. If this copper-containing rozenite is exposed to high humidity conditions, siderotil is the first higher hydrate to form followed soon after by melanterite.

Theories regarding the mechanisms of dehydration and hydration of these sulfates are discussed based on these observations

Reference

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Arsenic distribution in the Sansu Tailings Dam, AngloGold Ashanti gold mine, Obuasi, Ghana

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Gold recovery from ores containing arsenopyrite releases significant amounts of arsenic into the environment. The AngloGold Ashanti gold mine at Obuasi in Ghana is the second largest in Africa and the largest in Ghana. The tailings from processing of ore that contains up to 1% As at this mine is stored in the Sansu tailings dam.

Arsenic distribution in the tailings dam and downstream waters are studied by means of laboratory and field experiments. Total, soluble and labile arsenic measurements in pore waters and sediments were determined. Arsenic speciation of pore waters was carried out in the field using an acetate form of analytical grade AG1-X8 anion exchange resin. Arsenic (III) concentrations are between 48 to 84% of the total arsenic. Pond water arsenic measures between 2 ppm and 33 ppm. Labile arsenic concentration in the sediment samples are between 56 to 270 ppm. Seepage pond arsenic values were between 4-25 ppm.

The arsenic concentrations with depth in the dam vary with dissolved oxygen content, pH and Eh of the pore waters. The dam has different chemical conditions. Where pyrite oxidation generates relatively low pH pore waters As concentration is high and sediment As is low. The carbonates and secondary minerals (illite and kaolinite) in the dam consume the acid and increase the pH to near neutral. Arsenic is mobilized under these conditions.

In case of spill from this tailings enough As will be released that can kill fishes in the downstream waters and wildlife

Arsenopyrite weathering in tungsten mine tailings: A TEM analysis

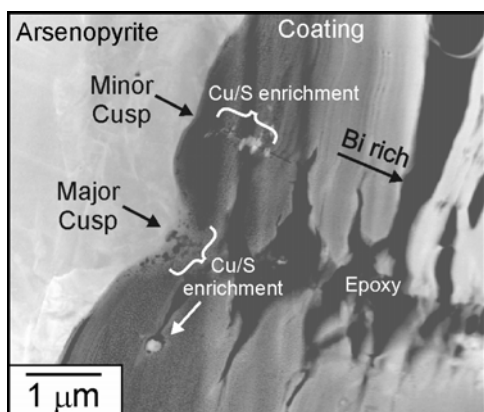
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The Mount Pleasant tungsten mine is located approximately 60 km south of Fredericton, NB, Canada. The tailings that resulted from a two-year mining operation have been exposed to oxidizing conditions since 1997. Consistent with the oxidation of sulfide-bearing minerals, the pore water in the oxidation zone is characterized by a relatively low pH and elevated SO_4 , As and metal concentrations compared to the pore water at depth. Of particular environmental concern are the elevated As concentrations, which reach a maximum of 7.1 mg/L in the oxidation zone.

Samples from two oxidized arsenopyrite (FeAsS) grains were obtained for Transmission Electron Microscopy (TEM) analysis. Energy dispersive X-ray spectroscopy analyses collected in scanning TEM mode suggest that the bulk secondary mineral is similar in composition to scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), a common arsenopyrite oxidation product (Fig. 1). Variable amounts of Ca, Si and Bi occur throughout the coating. Several distinct secondary-mineral inclusions, including wulfenite and copper sulfides, are found embedded within the bulk secondary coating. A Cu- and S-rich layer occurs along the perimeter of the arsenopyrite and ranges in thickness from approximately 50 nm to 500 nm. The Cu sulfide coating is thickest where the perimeter of the arsenopyrite grain forms discrete cusps. It is probable that aqueous Cu interacts with S from arsenopyrite leading to the precipitation of Cu sulfide at the interface. Variability in the rate of Cu sulfide accumulation at the interface may cause spatial variations in the diffusion rates for O_2 , S, Fe and As during weathering. This variability could result in non-uniform oxidation of arsenopyrite and the consequent formation of the prominent cusp features.

Figure 1: A dark-field STEM image of an oxidized arsenopyrite grain.



Anthropogenic heavy metal discrimination in stream sediments around an abandoned zinc smelter by using isotope tracers

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This study focused a small catchment close to a previous-abandoned zinc smelter. Water and sediments were sampled at the main watercourse of a stream and two tributaries. Water pH value, DO, EC were immediately measured in the field. Filtered water was used to analyze metal concentrations. Sediments were determined both metal concentration and their chemical forms, and lead and sulphur isotope compositions. Air-dried sediment particulates were fixed, imaged and analyzed on SEM-EDX.

Stream water pH values were usually higher than 7, and increased downstream. DO and EC fluctuated greatly with a decreasing tendency downstream. Pb, Zn and Cd concentrations in stream water usually fell downstream, highest metal concentrations were observed in the intersection sample. Similar fluctuation of heavy metal concentrations in stream sediments was discovered, highest metal concentrations were found in the most upstream sample, the Pb, Zn and Cd concentrations were as high as 21850, 28175 and 82 mg/kg, respectively. Pb and Zn were mainly bound to iron and manganese oxides in stream sediments; both correlation analysis and SEM-EDX observation testified the retain of Pb and Zn on iron hydroxides. Higher bioavailability of Cd than Pb and Zn was found.

In stream sediments, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios varied from 18.491 to 18.748, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios from 15.631 to 15.835, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios from 38.929 to 39.461. As shown in $^{208}\text{Pb}/^{206}\text{Pb} \times ^{206}\text{Pb}/^{207}\text{Pb}$ diagram, sediment samples plotted in a good agreement with mine ore samples, this indicated heavy metals in stream sediments were originated from mine ores. Considering the existence of ancient zinc smelters, it is reasonable to judge that anthropogenic activities brought great heavy metal accumulations in the small catchment. Sulphur isotope compositions further confirmed this relation.

Acknowledgements

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Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream

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Substantial diel (24-hour) cycles in dissolved (0.1- μm filtration) metal concentrations were observed during summer low flow, winter low flow, and snowmelt runoff in Prickly Pear Creek in southwestern Montana. The stream was alkaline (pH of 7.65-9.06), and dissolved metal concentrations were relatively low (1.8-7.1 $\mu\text{g/L}$ for As, 18-57 $\mu\text{g/L}$ for Mn, and 12-123 $\mu\text{g/L}$ for Zn). The metals are derived from abandoned mine lands in the stream's headwaters; As also is derived from geothermal sources. During seven diel sampling episodes, each lasting 34-61.5 hours, concentrations of dissolved Mn and Zn increased from minimum values in the afternoon to maximum values shortly after sunrise. The timing of diel cycles of dissolved As concentrations exhibited the inverse pattern. The magnitude of concentration increases during individual 24-hour periods ranged from 17-152% for Mn and 70-500% for Zn, and correlated positively with the magnitude of diel increases of pH and temperature, indicating that geochemical processes involving reactive inorganic and organic surfaces on and in the streambed probably control these diel metal cycles. Diel increases of As concentrations (17-55%) were proportionally smaller and less variable among the seasonal sampling episodes than for Mn and Zn, and they correlated poorly with diel increases of pH and temperature. Streamflow among the seven sampling episodes ranged from 0.35-3.3 m^3/s . The timing of minimum and maximum values of diel streamflow cycles was inconsistent among sampling episodes and had little relation to the timing of metal concentration cycles, indicating that hydrological processes are not a primary control of diel metal cycles. Diel cycles of dissolved metal concentrations may occur at any time of year and during various hydrologic conditions in all streams with dissolved metals and neutral to alkaline pH.

Causes of diel cycling of Zn in streams with near-neutral pH draining abandoned mine lands

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Many mining-impacted streams in western Montana with pH near or above neutrality display large (up to 500%) diel cycles in dissolved Zn concentrations (Nimick et al, 2003). The streams in question typically contain boulders coated with a thin biofilm, as well as black mineral crusts composed of hydrous Mn-Zn oxides (HMZO), some of which have the approximate stoichiometry of hetaerolite ($\text{Mn}_2\text{ZnO}_4 \cdot x\text{H}_2\text{O}$). Laboratory experiments simulating diel behavior in High Ore Creek (one of the Montana streams with particularly high Zn concentration) show that the Zn cycles are not caused by 24-h changes in streamflow or hyporheic exchange, but rather to reversible in-stream processes that are driven by the solar cycle. Photosynthetic consumption of CO_2 causes pH to rise during the day, at the same time that water temperature (T) increases. This process reverses at night, as pH and temperature drop. The dissolved Zn concentration of water equilibrated with HMZO is highly sensitive to small changes in both pH and T, increasing an order of magnitude for each unit decrease in pH, and decreasing 2.4-fold for an increase in T from 5 to 20°C. The response of dissolved Zn concentration to changes in either pH or T is rapid and reversible.

The field and laboratory observations are best explained by sorption of Zn^{2+} onto HMZO surfaces. From the T-dependence of residual Zn concentrations in solution, an approximate adsorption enthalpy of -51 kJ/mol was obtained, which is within the range of enthalpy values reported in the literature for sorption of divalent metal cations onto hydrous metal oxides (Trividi and Axe, 2001). Using the derived pH- and T-dependencies from the experiments, good agreement is shown between predicted and observed diel Zn concentration cycles for several historical data sets collected from High Ore Creek. As well, an empirical distribution coefficient has been derived that relates the dissolved Zn/Mn ratio of creek water to the Zn/Mn ratio of mineral crusts forming in several streams – including High Ore Creek – near the Basin Superfund area of Montana.

References

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Seasonal mineralogical transformations influence heavy metals release from mine-impacted Coeur d'Alene River (ID) wetlands

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The Coeur d'Alene (CDA) mining district in the Idaho panhandle is a major region of historical and contemporary mining of Ag, Au, Cd, Cu, Pb and Zn. Over the last century, 70 million tons of mine tailings were discharged directly into the CDA River [1]. These discarded tailings proceeded downstream into a series of wetlands and lateral lakes along the CDA River floodplain, and consequently the sediments in the river and lateral areas contain elevated trace metal concentrations. Here, we examine the geochemical processes that control the distribution and release of arsenic, lead and cadmium within the CDA River and associated wetlands.

Chemical extractions, diffraction and X-ray absorption spectroscopy, were used to characterize sediment mineralogy and the mechanism of trace element retention. Heavy metals are often associated with iron (hydr)oxides, as expected due to the strong retention of these metals on iron (hydr)oxides. However, adsorption on such phases alone is not able to describe trace element concentrations; trace metal retention is dynamic and responds to changing environmental conditions [2, 3]. These fluctuations in trace metal retention involve redox processes and are likely driven by microbiological processes. Arsenic speciation fluctuates between As(III) vs. As(V), and also may be associated with sulfide minerals when sediments and soils are flooded. These seasonal fluctuations in trace element speciation may significantly alter pore water concentrations, and must be considered when evaluating the fate of these contaminants. Furthermore, the transitory and mixed phase associations of arsenic and other elements leads to conditions in which either oxidation and reduction may release trace elements into solution.

References

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The mineralogical facies developed within an Apatite II PRB for Pb, Cd and Zn acid mine drainage

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Apatite IITM, in a subsurface permeable reactive barrier, treated acid mine drainage containing elevated levels of Zn, Pb, Cd, SO₄ and NO₃. The special properties of Apatite IITM make it ideal for this application allowing it to immobilize 20% of its weight in metals. The PRB, operating since January 2001, is reducing Cd and Pb to below detection, Zn to near background (100 ppb), and SO₄ and NO₃ to below detection. Geochemical facies, evidenced by sphalerite, pyromorphite and chlorapatite, combined with variable redox conditions, dissolved oxygen, and biological activity, have developed, as predicted by MINTEQA2 and confirmed by solids analyses. The PRB, filled with 100 tons of Apatite IITM, has removed 10,000 lbs of Zn, Pb, and Cd, and should last for at least twelve more years.

Dissolved Metal Concentrations Entering and Exiting PRB

Date	Entering Barrier (ug/L;ppb)				Exiting Barrier (ug/L;ppb)			
	pH	Cd	Pb	Zn	pH	Cd	Pb	Zn
03/23/01	4.5	333	1,230	44,700	6.0	<2	<5	27
10/27/01	5.0	437	1,110	71,300	6.5	<2	<5	74
01/10/02	5.0	779	1,210	116,000	6.5	<2	<5	66
10/19/02	4.5	414	1,030	68,350	6.5	<2	<5	69
03/14/03	4.5	650	1,190	48,700	6.6	<1	<1	55
10/03/03	4.6	587	1,330	86,800	7.0	<2	<5	<5
03/30/04	5.2	404	497	64,500	6.9	<2	<5	95
06/09/04	4.9	436	658	68,000	6.9	<2	<5	34



Apatite IITM collected from the PRB after 3 years showing sphalerite on surface

The role of minerals in catalysing manganese removal from mine water

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Manganese is a common contaminant of mine and other waste waters, and is notoriously difficult to remove. Systems that effectively remove manganese from mine waters involve oxidising the soluble Mn II species using high pH substrates; to what degree the substrate type and *in situ* microbiological community have upon manganese removal is unclear. In this work, net-alkaline manganese contaminated mine water was treated with the pure minerals dolomite, calcite, magnesite and quartz, to investigate the relationship between the chemical composition and surface roughness of the mineral. In addition, we examined the development of the biofilm community that grew on the substrate surface.

Manganese was removed in all continuous-flow reactors over a 3-month period. SEM, XRD and TG-A were used to assess both the spatial distribution and composition of the precipitates that accumulated on the substrate surface. Mn oxyhydroxides were formed in all the reactor types, however Mn carbonates (kutnahorite) were identified in the quartz reactors and on the reactor plastics only. Mg-rich calcites were identified in the dolomite and magnesite reactors, suggesting that the Mg in these minerals inhibited Mn carbonate formation. Biofilm community development was monitored over time using DGGE. Profiles showed no change over time and no difference between substrate types, suggesting that the microbiological community in the reactors may not play an active role in Mn removal in these systems.

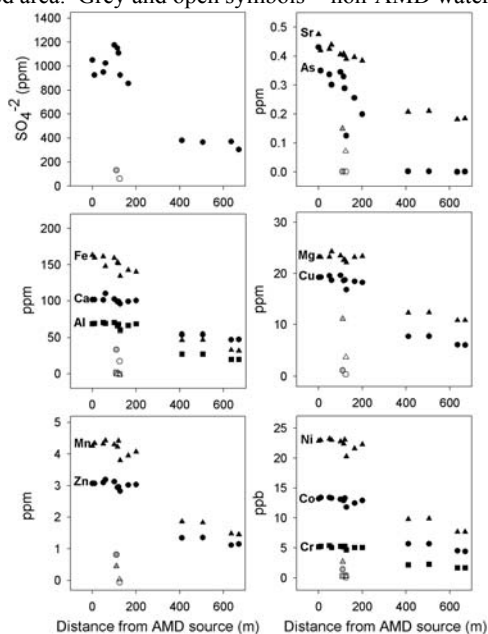
Water mixing and precipitation of arsenic-bearing iron sulfate in the Chinkuashih acid-mine-drainage area, northern Taiwan

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Acid mine drainage (AMD) coming out of a tailing site at Golden Falls is precipitating a mass of schwertmannite deposits along a stream in the Chinkuashih gold-copper mining area. Down stream water chemistry was measured by ICP-MS, ICP-OES, and an on-site photometer (Figure 1).

Figure 1. Compositional variations of stream waters in the studied area. Grey and open symbols = non-AMD waters.



The variations in the concentrations of Mg, Al, Co, Ni, Cu, Zn, Cr, Rb, and Sr and pH value suggest a water mixing ratio of approximately 2/3 between the AMD stream (pH = ~2.6) and the main stream (pH = ~6.0). On the other hand, arsenic and iron concentrations show significant decreases in addition to the mixing effect, concurrent with a decrease of pH values from 2.6 to 3.1. Transformation of schwertmannite to goethite with depths at Golden Falls do not seem to have a significant effect on the arsenic concentration in the AMD solution. The extra changes in As and Fe concentrations are attributed to precipitation of schwertmannite and imply an arsenate sorption process in schwertmannite.

The effect of arsenic on the nucleation and growth of schwertmannite: An in situ SAXS study

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The acid regimes of AMD are conducive to the formation of nano-sized schwertmannite, which plays a major role in the cycling of contaminants. However, the nucleation and growth kinetics of schwertmannite are poorly defined. The aims of this study were to characterise the sequestration of arsenic associated with nano sized schwertmannite *via* the *in situ* quantification of the formation mechanisms. Synchrotron-based time-resolved Small Angle X-ray Scattering (SAXS), interfaced with a rapid mixing stopped-flow cell, was used to investigate the nucleation and growth of schwertmannite nanoparticles from solution with varying concentrations of arsenate (0-2.5 mM). Experiments were performed on station 6.2m at the UK Synchrotron Radiation Source (SRS) and data analysis was performed using GNOM and DAMMIN. The rates and mechanisms of particle formation were studied and particle size, pair length distribution, and particle shape evolution were quantified. The results show that both the reaction induction times and the rate of schwertmannite nucleation are suppressed with increasing As-concentration. Shape analysis suggests particle growth by aggregation of sphere-like particles: a process that is suppressed by the presence of As.

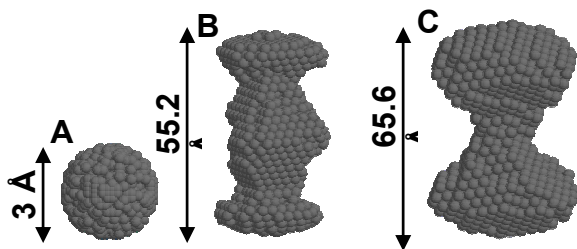


Figure 1. Average particle shape for a schwertmannite particle at A. 30 s B. 600 s (both 0 mM As), and C. with 2.5 mM As at 600 s.

Thermochemistry of arsenic minerals

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Introduction

Arsenic represents a major concern for drinking water supplies not only in USA (Ryker, 2003) but also in other countries around the world (Zhang, et al., 2002, Saha, 2003, Bundschuh, et al., 2004). Despite its high toxicity, the available thermodynamic data for arsenic containing minerals are scarce or not well determined (Nordstrom and Archer, 2003). Using these data, it is hard to model the behavior of arsenic in the environment.

The purpose of this research is to develop a technique to measure the enthalpies of formation of different arsenic containing minerals and review the available thermodynamic data in order to establish thermodynamically consistent datasets.

Analytical method

A custom built Tian-Calvet twin, high temperature calorimeter from Thermochemistry Facility, UC Davis will be used to carry out this research. The high-temperature oxide melt calorimetry will be used at 700 °C as is described by Navrotsky (1977, 1997), with sodium molybdate $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ as solvent.

Results

The research is in progress and the data will be reported.

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Mineralogical controls on mine drainage, Ervedosa mine, Northern Portugal

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At Ervedosa, tin-bearing quartz veins with cassiterite and sulphides cut Silurian schists and quartzites and a Sn-bearing muscovite granite. The veins were exploited at Ervedosa, so-called Tuela mine, for tin (Sn) and arsenic trioxide (As_2O_3), until 1969. The veins fill faults related to the Hercynian movements along a dextral N30°W shear zone and belong to three paragenetic stages separated by faulting. Euhedral to subhedral crystals of cassiterite are generally <10 mm across or associated in round masses with a diameter of 10 cm. The cassiterite shows alternating parallel darker and lighter zones and the darker zones show exsolved columbite, titanite, ixiolite, $\text{W} \geq \text{Ti}$ - ixiolite, niobian rutile and very rare wolframite and ilmenite. Arsenopyrite is the most abundant sulphide and has inclusions of pyrrhotite, bismuth, bismuthinite and matildite. It is replaced by pyrite, chalcopyrite, sphalerite and stannite.

At the tin-bearing quartz veins and their granite and schist walls, there are supergenic solid phases consisting mainly of hydrated sulphates of Al, Fe, Mg and Ca (alunogen, meta-alunogen, alunocopiapite, copiapite, halotrichite, fibroferrite, pickeringite and gypsum), while oxides, hydroxides, phosphates, arsenates and residual mineral phases (albite, muscovite and quartz) occur in mining tails.

The aim of this study is to compare the acid mine drainage (AMD) with the granitic rock drainage using data collected during winter. The waters at the mining site are toxic and affected by AMD (pH=3.1-3.5), with high conductivity (130-726 $\mu\text{S}/\text{cm}$) and significant metal concentrations ($\text{As}=3\text{--}8\mu\text{g}/\text{l}$, $\text{Cu}=410\text{--}415\mu\text{g}/\text{l}$, $\text{Zn}=1919\text{--}8370\mu\text{g}/\text{l}$, $\text{Fe}=922\text{--}11200\mu\text{g}/\text{l}$, $\text{Ni}=26\text{--}95\mu\text{g}/\text{l}$ and $\text{Co}=49\text{--}118\mu\text{g}/\text{l}$), while in the superficial granitic waters outside the mine influence the pH measured is close to neutral (pH=5.5-7), with low conductivity (28-35 $\mu\text{S}/\text{cm}$) and metal concentrations are lower ($\text{As}=0.3\text{--}3\mu\text{g}/\text{l}$, $\text{Cu}=7\text{--}22\mu\text{g}/\text{l}$, $\text{Zn}=108\text{--}147\mu\text{g}/\text{l}$, $\text{Fe}=50\text{--}411\mu\text{g}/\text{l}$, $\text{Ni}=6\text{--}9\mu\text{g}/\text{l}$ and $\text{Co}=0\text{--}3\mu\text{g}/\text{l}$). Waters associated with mineralised veins should not be used for human consumption and agriculture activities.

This research was carried out in the programme of Geosciences Centre, University of Coimbra.

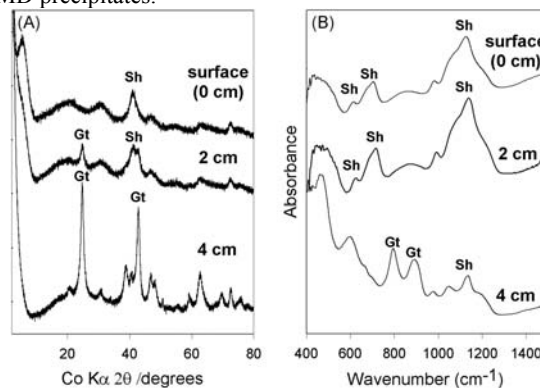
Formation and transformation of schwertmannite in acid-mine-drainage deposits of the Chinkuashih mining area, northern Taiwan

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Reddish yellow to reddish brown acid-mine-drainage (AMD, pH = 2.6–3.1) deposits of 20 to 30 cm in thickness occur at Golden Falls and its downstream riverbed in the Chinkuashih gold-copper mining area. Radiating aggregates of schwertmannite nanoparticles have an overall hedgehog morphology and form the principal constituent of the Golden Falls AMD deposit. Goethite starts to present at a depth of 2-3 cm and becomes increasingly abundant with depths, concomitant with a decrease of the schwertmannite content, as evidenced by XRD and IR analyses (Figure 1). The identification of schwertmannite and goethite has also been confirmed by our TEM results.

Figure 1. XRD patterns and IR spectra of the Golden Falls AMD precipitates.



The downstream riverbed rocks are coated by a thin layer of schwertmannite with a microstructure identical to that occurring at Golden Falls. Standardless EDS analyses suggest that the Golden Falls schwertmannite aggregates have iron/sulfur atomic ratios of 5-7 and invariably contain a small amount of arsenic content whereas those occurring in the downstream area do not have a recognizable arsenic constituent and are associated with a much lower arsenic concentration in the riverwater.

The combining effects of precipitation of schwertmannite and its transformation into goethite do not significantly change the pH values and elemental concentrations of the Chinkuashih AMD solution except those of Fe and As.

Baseline water quality at the Yanacocha Mine, Peru

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The Yanacocha Mine, located in the northern Peruvian Andes, is the largest gold mine in the world. The ore deposits occur in Tertiary dacite/andesite flow domes with extensive acid-sulfate alteration. Gold mineralization, accompanied by pyrite, enargite, and other copper sulfide minerals, resulted in elevated concentrations of As, Pb, Cu, Hg, Zn, and Mo in and around the orebodies. To define baseline water quality, water samples were collected from 20 stream locations unaffected by mining (13 mineralized, 7 unmineralized) over a 7-month period in 2002/03 that included portions of the rainy and dry seasons. Designations of mineralized and unmineralized were made using geologic maps, mineralogic information, and field observations. The baseline analysis included the influence of anthropogenic and natural impacts on water quality. Historical data collected by others, some of which covered periods before mining impacts began, were evaluated to determine pre- and post-mining-impact conditions. Data from the recent sampling and historical data were used to define baseline water quality. Even though mineralized streams had lower pH values, they generally did not contain elevated concentrations of toxic metals (e.g., Cd, Cu, Pb). However, examples of naturally elevated metals concentrations were found in all four basins (3 drain to the Amazon/Atlantic, 1 to the Pacific) in first-order streams, and some of these reaches would likely not have supported aquatic life before mining began. Concentration increases in SO₄, Ca, Cd, Cu, Pb, Zn, Fe, Al, and/or Mn and decreases in pH occurred in baseline streams in October-December, reflecting the first flush of metals and acidity from dried soils and salts with the onset of the rainy season. Results from the baseline analysis were used to discern the effects of mining on water quality at individual drainage and watershed scales.

Pre-mining ground-water quality at Molycorp's Questa molybdenum mine, Red River Valley, New Mexico

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Mineralized areas that host ore deposits, contain anomalously high concentrations of metals, sulfides, and sulfates. Prior to mining, weathering of minerals containing metal sulfides results in anomalously high concentrations of metals and sulfate in surface and ground waters. During remediation of mine-waste sites, the goal need not exceed pre-mining conditions.

The U.S. Geological Survey, in cooperation with the New Mexico Environment Department, is investigating the pre-mining ground-water quality at Molycorp's Questa molybdenum mine. The strategy uses a proximal analog, the Straight Creek catchment, which is underlain by hydrothermally altered andesitic and rhyolitic Tertiary volcanics similar to the mine site. Exposure of pyritized rock in the upper portions of the catchment produces acid rock drainage (pH 2.7-3.2) which infiltrates a colluvial debris fan and increases only slightly in pH (3.4-4.0). Infiltration of underlying bedrock produces ground waters of circumneutral pH (5.8-7.6). Both bedrock and debris-flow ground waters are Ca-SO₄ type, often at or near gypsum saturation because of the abundance of secondary gypsum. As ground water travels down the debris-flow aquifer the dominant trend is dilution. Modeling indicates aluminum is initially leached from kaolinite, chlorite, and albite under acid conditions but thereafter the Al concentration is controlled by pH. Evidence for precipitation of both aluminum and silica is apparent at pH= or >4. Trace elements are weathered from specific mineral sources: Zn and Cd from sphalerite, Pb from galena, Co and Ni from pyrite, pyrrhotite, and chlorite, Cu from chalcopyrite, F from fluorite, and Mn from rhodocrosite. From these results a mass-balance calculation has been made for the development and evolution of ground-water chemistry in this mineralized and rapidly weathered mountainous catchment. Hence, the underlying processes that give rise to the Straight Creek ground-water compositions have been determined from mineralogy and modeling.

The results from the analog study were further compared to ground-water quality from other wells in similar terrain of the Red River Valley. The data compares favorably and provides a basis for the range of ground-water chemistry that likely existed before mining began.

Rates of silicate dissolution in deep-sea sediments

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Ocean Drilling Project Site 984 in the North Atlantic is composed of high-porosity, uncemented, silicate-rich sediment derived primarily from Iceland. Geochemical profiles from Site 984, spanning approximately 2 million years of sediment accumulation, are modeled using a multi-component reactive transport model (Crunch) to determine in-situ rates of plagioclase dissolution and other diagenetic processes, including sulfate reduction and anaerobic methane oxidation. The dominant transport mechanisms in this system are molecular diffusion and burial. Thus many of the proposed mechanisms for the inhibition of dissolution in natural systems, such as hydrologic limitation of reactive surface area or variable fluid flow, are not present. The model also includes formulations for modeling the $^{234}\text{U}/^{238}\text{U}$ isotopic system. The $^{234}\text{U}/^{238}\text{U}$ in the pore water, sediment, and bulk calcite offers an additional constraint on the rate of plagioclase dissolution, and the rate and magnitude of calcite recrystallization. Many other factors that have been discussed as possible explanations for the discrepancy between laboratory and field rates, including the effect of solution saturation state (reaction affinity), Al-inhibition and the rates of transport relative to reaction, are also explicitly considered in the reactive transport formulation.

Plagioclase surface area was estimated at $3.0 \pm 0.6 \text{ m}^2/\text{g}$ based on geometric arguments and the depletion of $^{234}\text{U}/^{238}\text{U}$ in the solid sediment as a result of α -recoil of ^{234}Th . Using this surface area value for the reactive surface area, the modeling predicts a dissolution rate constant that is about 10^4 to 10^5 times smaller than the laboratory-measured value when a linear dependence of the rate on the reaction affinity is assumed. Alternative rate law formulations, including Al-inhibition and a nonlinear dependence on the undersaturation of the pore water with respect to plagioclase do not account for the slow rate because the pore fluid-plagioclase system is maintained strongly out of equilibrium by microbial processes and clay precipitation. The major element and isotopic models predict similar dissolution rate constants if additional lowering of the $^{234}\text{U}/^{238}\text{U}$ ratio is attributed to isotopic exchange via recrystallization of marine calcite. The results also highlight the important link between the biogeochemical and inorganic reaction pathways.

Length and time dependent properties at mineral-water interfaces

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Experimental observation of elementary step edge motion on mineral surfaces using *in-situ* Scanning Probe Microscopy (SPM) in aqueous solutions has enabled the calculation of specific properties relating to growth and dissolution at the atomic scale. In particular, the length dependent behavior of elementary steps may be directly linked to the dynamics of ion attachment and detachment from surface sites. Step speeds at very short step lengths ($< 300 \text{ nm}$) are generally found to increase with step length, but the observations are dependent on the experimental parameters chosen and thus, potentially biased. When these parameters were optimized, data scatter precluded quantitative comparison of different theoretical models in light of the experimental data. Analysis of experimental errors revealed that significant experimental bias in the determination of step edge properties such as the edge free energy and kinetics of kink propagation and nucleation are introduced if the instrument bandwidth is not appropriate for the specific dynamics of the step edge. In light of step growth models based on either equilibrium assumptions or non-equilibrium assumptions, these biases tend to favor one model over the other.

The time dependence of surface properties, characterized with SPM, reveals the response of surfaces to changing of solution variables such as pH and saturation state. These two variables, which probably are the most geochemically significant in terms of determining the kinetics of mineralization and dissolution in natural waters, influence both the kinetics at elementary step edges as well as mineral surface morphology. While step edges may respond relatively quickly to changes in conditions, the surface morphology often exhibits a history-dependence that may prevail for significantly longer time periods. This hysteresis has important implications in the modelling of mineral-water reactions.

Effect of solution saturation state on diopside dissolution

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Among all the physico-chemical variables that control mineral dissolution, the effect of solution saturation state has received the least attention. At present, two rate laws have received wide applicability. One rate law invokes etch pit nucleation at dislocations at a critical degree of undersaturation and the other is based on a cation exchange mechanism. In this study, the dissolution rate of diopside is measured as a function of temperature, pH, and solution saturation state using a flow-through reactor. Insights into the dissolution mechanism are gathered by imaging freshly cleaved diopside surfaces undergoing dissolution with hydrothermal Atomic Force Microscopy and Vertical Scanning Interferometry. At 150°C and pH 7.5, the dissolution rate is found to be congruent with respect to Ca, Mg, and Si. Dissolution rate continuously decreases, without reaching any apparent dissolution plateau, as solution conditions approach equilibrium. A generalized rate law for diopside dissolution will be presented.

Preliminary experimental results for ¹⁸O and ¹³C uptake in calcite and at 32°C and various precipitation rates

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Experimental studies have revealed that the growth rate of calcite affects the uptake of trace and minor elements into the crystal lattice [1-3]. The factor(s) responsible for this disequilibrium effect might also apply to stable isotope incorporation during calcite growth; however, this particular suggestion [4] has yet to be confirmed by experiment. Oxygen-18 and ¹³C contents of carbonates (expressed as ¹⁸O/¹⁶O and ¹³C/¹²C) are widely used in paleothermometry, yet it is clear from comparison of experimental results and marine samples that chemical (isotopic) equilibrium is not always maintained in nature. This observation underscores the importance of exploring possible effects of growth rate on isotopic fractionation, which is the focus of this study.

We controlled the rate of calcite precipitation by injecting solutions of CaCl₂ and Na₂CO₃ into a NaCl solution at different speeds using a syringe pump. Mass spectrometric analysis of the resulting samples revealed that δ¹⁸O dropped from -12 to -15‰ with increasing injection rate from 7.23·10⁻¹⁰ to 7.20·10⁻⁷ mol/min and remained constant over further increases in rate. Carbon-13 also decreased from -1.6 to -2.8‰ over a pumping rate increase from 7.23·10⁻¹⁰ to 7.20·10⁻⁷ mol/min, but returned to -1.6‰ at a pumping rate of 2.3·10⁻⁵ mol/min. These trends (decreasing δ¹⁸O and δ¹³C with increasing calcite growth rate) are not inconsistent with growth entrapment of an isotopically distinct near-surface region of the calcite crystals: if the rate of calcite growth exceeds a minimum value required to maintain equilibrium, then the crystal surface may be “captured” by the newly-formed lattice (4). Our results provide the first suggestive evidence that under equilibrium conditions ¹⁸O and ¹³C may be depleted in the near-surface region of calcite relative to the bulk crystal lattice. More work is required to confirm and evaluate this effect.

References

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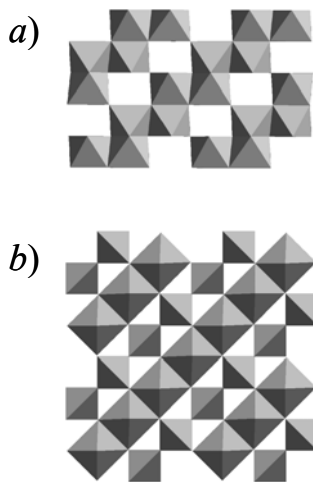
On charge transport in iron oxides

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Surfaces of iron oxide minerals are known participants or catalysts in a wide range of redox processes in natural environments. Examples include reductive dissolution of Fe^{III}-bearing oxides such as hematite by dissimilatory metal reducing bacteria, and the reduction of chromium or uranium by Fe^{II}-bearing oxides such as magnetite. A common aspect of these processes is the valence interconversion of structural iron through electron transfer. With progressive reduction of Fe^{III} or oxidation of Fe^{II} in the iron oxide surface, the lifetime of the electron transfer products becomes an important issue. Mounting experimental evidence suggests facile electron hopping through the solid outpaces surface transformation to more stable phases. This notion comes in contrast to the traditional view that electron transfer products are fixed in their initial location in the surface. Hence, the issue of electron mobility through the solid bears directly on the task of bridging time and length scales in these systems.

In this address, we will discuss what is currently known about electron mobilities in hematite and magnetite. We will also illustrate computational approaches for the transport of electrons through the lattices of hematite and magnetite, and present calculated rates of electron hopping. Rates for an electron or hole in hematite range from 10⁷-10¹⁰ s⁻¹ depending on crystallographic direction, whereas the rate for magnetite is 10¹¹ s⁻¹. These rates lead to electron mobilities in good agreement with experiment, both in terms of magnitude and directionality.



Zone views of the a) hematite structure down [110] and b) magnetite structure down [100].

The role of Si—O bonds in dissolution of silicate glasses: Inferences for rate-limiting step

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The dissolution kinetics of 5 chemically complex and 2 chemically simple borosilicate glass compositions (Na-B±Al-Si) were tested with a single-pass flow-through (SPFT) apparatus. The chemically complex glasses are representative of prospective vitreous waste forms and are characterized by relatively high molar Si/(Si+Al) and Na/(Al+B) ratios (>0.7 and >1.0, respectively). X-ray absorption spectroscopy (XAS) indicate that ratios of ^{iv}B to ⁱⁱⁱB vary between values of 40 to 55% for all specimens. MAS-NMR data yield ²⁹Si peak shift values that are virtually identical (-94 to -84 ppm), indicating a similar polymerization state for the glasses, despite differences in bulk chemistry. Forward rates of reaction are identical within error for all the samples tested (avg. log₁₀ rate = -1.9 g/m²·d at pH 9, T = 40°C). Compared to other borosilicate, synthetic silica, albite, jadeite, and nepheline, and natural basalt and rhyolite glasses, the forward rates of Na-B±Al-Si glasses are equal or only slightly (≤10X) faster, implying a similar rate-governing mechanism. In contrast, relatively de-polymerized soda-lime glasses dissolve at faster (>50X) rates. It appears, therefore, that glasses with similar polymerization states dissolve at like rates. Thus, these data support a model of transition-state theory (TST), in which rates are dependent only on the rate of the slowest elementary reaction, which is hydrolysis and rupture of Si—O bonds.

Barite dissolution: Computer simulations and experimental results

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A combination of Monte Carlo simulations and atomic force microscopy (AFM) studies explored barite dissolution kinetics at the molecular scale. This study shows that the barite (001) face undergoing dissolution develops two sets of oppositely-oriented triangular etch pits. The morphological evolution of the pits was successfully simulated using a kinetic model that incorporates the full 3-dimensional barite structure (Figure 1).

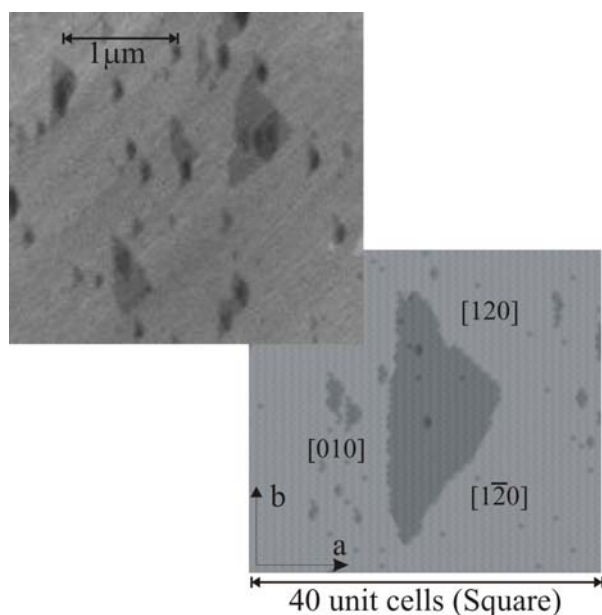


Figure 1. Top: AFM generated height map of the (001) barite surface after exposure to pure water for 37 minutes. Triangular shaped etch pits, one half unit cell deep, expand laterally as the crystal dissolves. Bottom: Monte Carlo simulation of the same crystal surface. The etch pits in the simulation are very similar to the real ones observed with AFM. The dimension of the simulated surface is 40x40 unit cells using crystallographic coordinates.

The relationship between cation/anion ratio, step velocities and bulk dissolution rate in calcite

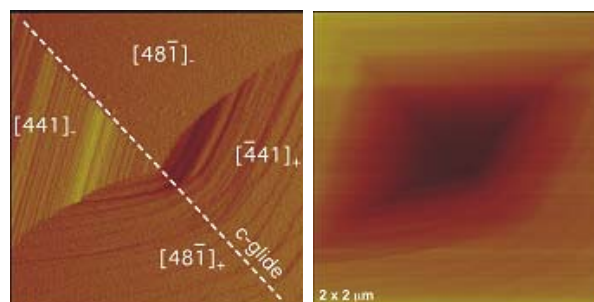
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A growing body of experimental data and theoretical arguments suggests that the ratio of mineral lattice ions in solution may exert a unique control on both dissolution and growth kinetics, and thus that the ion activity product does not offer a unique description of the rate. Zhang and Nancollas (1998) have demonstrated that the dissolution rate of a spiral dislocation in an AB crystal can be described as

$$R = -k_d \frac{(1-S) \ln S}{\sqrt{2-S}} q_d(r_i, S)$$

where r_i is proportional to the solution ratio of A and B ions, S is the saturation ratio, and q_d is a correction function describing the differences in kink nucleation and propagation



Dissolution spirals, AFM (L) and VSI (R) data.

rates between an AB and Kossel crystal lattice. We have used the native anisotropy of the calcite (104) surface as a means of exploring the sensitivity of step velocities (AFM) to changes in $\text{Ca}^{2+} / \text{CO}_3^{2-}$ ratio at various degrees of undersaturation. Our results confirm a strong sensitivity of the obtuse (+) step direction to changes in ionic ratio. From coupled experiments, we also discuss the relationship between ionic ratio and the overall dissolution rate (VSI). Our results imply considerable complexity in the relationship between solution composition, thermodynamic driving force, step-specific interaction, and dissolution rate. They also suggest variation in the rate as a function of the interaction between ionic ratio, saturation state, and impurity burden.

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Near-equilibrium albite dissolution kinetics

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Many kinetic processes of critical environmental importance occur close to thermodynamic equilibrium and derive their driving force from relatively small free energy differences.

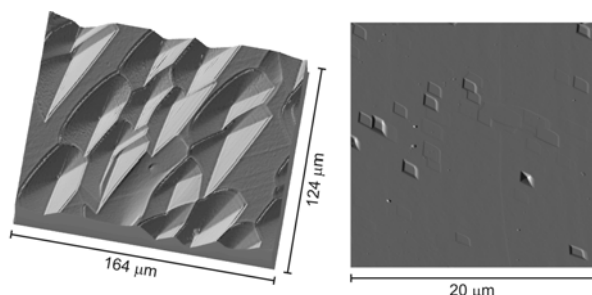


Figure: Left – 3D VSI map of treated albite (001) surface covered by coalescing, pyramidal etch pits. Right – AFM deflection map of untreated albite (001) surface dominated by smooth terraces containing flat-bottomed etch pits.

In order to generate a better understanding of the reaction kinetics of these systems we conducted dissolution experiments at pH 9 and 185°C. Combining vertical scanning interferometry (VSI) and atomic force microscopy (AFM) allowed us to identify the dissolution mechanisms and quantify the rates of albite single crystals over a range of Gibbs free energy. During our experiments both a “treated” (exhibiting etch pits) and “untreated” (pristine) crystal were dissolved simultaneously within the same reactor. We observed a difference of up to 100 times in dissolution rate between both samples. Examination of reacted crystals at the micron- and nanoscale revealed evidence of two different dissolution mechanisms dominating the dissolution of the different crystals (see Figure). The rate difference persists over a range of solution saturation state and indicates that the dissolution mechanisms obey different Gibbs free energy dependencies. As a consequence, a mineral’s history can have a major impact on its subsequent dissolution rate. With these results in mind, we examined existing kinetic datasets measured to determine the relationship between dissolution rate and Gibbs free energy. We suggest that existing discrepancies between experimental studies can be explained by differences in experimental methods. Finally, results from our albite dissolution study will be compared to similar experiments using single crystals of the other plagioclase endmember, i.e., anorthite and discussed within the context of an existing model for mineral/fluid interaction.

Feldspar dissolution rates and the Gibbs free energy of reaction

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This experimental study is an investigation of the relation between the dissolution rate of albite feldspar and the Gibbs free energy of reaction, ΔG_r . The experiments were carried out in a continuously stirred flow-through reactor at 150 °C and $\text{pH}_{(150^\circ)}$ 9.2. The dissolution rates R are based on steady-state Si and Al concentrations and sample mass loss. The overall relation between ΔG_r and R was determined over a free energy range of $-150 < \Delta G_r < -15 \text{ kJ mol}^{-1}$. The data define a highly non-linear, sigmoidal relation between R and ΔG_r that is characterized by 3 distinct free energy regions. The region furthest from equilibrium ($-150 < \Delta G_r < -70 \text{ kJ mol}^{-1}$) represents an extensive rate plateau. In the sigmoidal ‘transition equilibrium’ region ($-70 \leq \Delta G_r \leq -25 \text{ kJ mol}^{-1}$) the rates are strongly dependent on ΔG_r . Dissolution nearest equilibrium ($\Delta G_r > -25 \text{ kJ mol}^{-1}$) is characterized by a weak dependence of the rates on ΔG_r . The data have been fitted to a rate equation (adapted from Burch et al., 1993) that represents the sum of two parallel reactions. A comparison of the R - ΔG_r data with transition state theory (TST) reveals a complete incompatibility.

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Effect of Al/B ratio on the dissolution of nepheline glass, $\text{Na}_3(\text{Al}, \text{B})_{1-4}\text{Si}_4\text{O}_{16}$

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The release of alkalis from glass, via metal- H^+ counter diffusion, is widely recognized as an important mechanism in the initial stages of glass-water interactions. Our findings from experiments conducted with other borosilicate glass compositions suggest the alkali exchange (Na-IEX) mechanism may be more important than previously realized. To evaluate the factors that affect the Na-IEX mechanism, flow-through experiments were conducted as a function of pH at 40°C on four glass compositions along the nepheline-malinkoite join. The composition of each glass varied inversely in wt% of Al (5 to 20 wt%), and B (20 to 5 wt%) with Na (25 wt%) and Si (50 wt%) making up the remaining amount. The influence of glass structure on the glass corrosion rate was probed by magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy in which the local coordination environments of ^{27}Al , ^{11}B , and ^{29}Si for each glass composition were determined.

MAS-NMR spectra suggest changes in three- and four-fold coordinated B as the B/Al ratio was manipulated. Preliminary evaluation of the B local coordination, suggest that as the wt% of B increased from 5 to 20 wt%, the relative concentration of tetrahedrally coordinated B also increased, although more data is needed. Unlike B which has two coordinations, Al and Si are only tetrahedrally coordinated.

Results from the flow-through experiments showed a typical matrix dissolution rate increase with an increase in pH for all glass compositions. In contrast to matrix dissolution, as pH decreases the mechanism of Na-IEX becomes more important. In other words, as matrix dissolution decreases and the concentration of H^+ increases the influence of Na-IEX on glass dissolution increases.

The results obtained in this study emphasize the importance of glass structure on the mechanism of alkali-ion exchange.

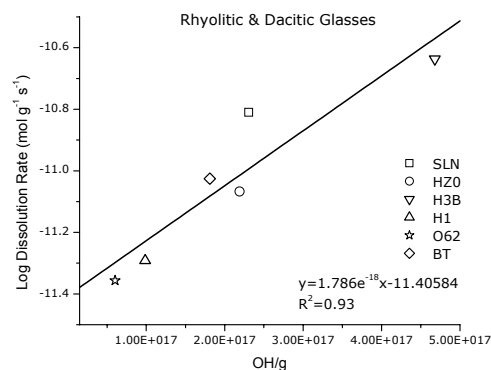
Dissolution rate dependence on reactive surface sites

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Dissolution rates are known to be dependent upon bulk mineral composition (e.g. cation species), but very little information is available regarding the molecular level surface composition and how it affects dissolution rates. A critical element for understanding the mechanisms and kinetics of adsorption and dissolution of natural minerals is their surface chemistry. To that end, we have used solid state nuclear magnetic resonance (NMR) to quantify the reactive site density on a suite of rhyolitic, dacitic, and basaltic glasses [1].



The above graph depicts surface hydroxyl groups per gram as measured by ^{19}F NMR correlated to dissolution rates normalized to mass, rather than BET or geometric surface area. Surface modification with a molecular probe containing fluorine generates a large NMR signal, allowing very low surface area materials to be examined (<1 m²/g). Although our molecular probe method cannot currently distinguish between aluminols and silanols we are investigating new NMR methodologies capable of targeting and quantifying specific surface hydroxyl species.

Reference

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Kinetics of oxygen isotope exchange between water and minerals from Mesozoic A-type granites in China

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Post-magmatic water-rock interaction is a common phenomenon for intrusives, but its timescale is variable from pluton to pluton depending on temperature and water origin. By means of the conventional BrF_5 method and the laser fluorination technique, O isotope analyses were carried out for whole-rocks and mineral separates from three A-type plutons at Nianzishan, Shanhaiguan and Suzhou in eastern China. The results show that, despite a relatively limited $\delta^{18}\text{O}$ range of 3.10 to 5.39‰ for zircon, the granites exhibit variable $\delta^{18}\text{O}$ values of -2.4 to 9.2‰ for whole-rock, 0.0 to 9.2‰ for quartz, -3.8 to 7.3‰ for alkali feldspar, -14.1 to 4.5‰ for magnetite, and -5.8 to 6.8‰ for biotite. Most of the samples exhibit apparent equilibrium fractionations between quartz and zircon, yielding temperatures of 800 to 1000°C that are unreasonably higher than the closure temperatures of O diffusion in quartz during granite cooling. In contrast, fractionations between alkali feldspar, biotite and quartz are significantly deviated from equilibrium values, indicating post-magmatic water-rock interaction at medium to low temperatures.

Quantitative simulation was carried out by using the kinetic model of O isotope exchange between multi-minerals and water. The initial $\delta^{18}\text{O}$ values of whole-rock and exotic fluid are estimated according to the O isotope compositions of zircon and modern meteoric water. The results obtain that the flow rate of fluid is about 10^{-15} to 3×10^{-14} mol/s, the timescale of water-rock interaction is about 0.3 to 3 Ma, and ratio of water to rock is about 0.11 to 1.02. Significant decrease in quartz $\delta^{18}\text{O}$ is ascribed to water-rock interaction of higher temperatures (~400°C) and longer duration (>1 Ma). The present study demonstrates that the A-type granites were not only crystallized from low- ^{18}O magma but also overprinted by meteoric-hydrothermal alteration. Because of significant differences in the rate of O isotope exchange by diffusion and surface reaction between granitic minerals and water, subsolidus alteration is readily distinguishable from such supersolidus reactions as crustal contamination, water-rock interaction and partial melting in the pattern of mineral-pair O isotope distributions.

Semantimetasomatism

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"When I use a word," Humpty Dumpty said, "it means just what I choose it to mean ..." Many geochemists use "metasomatism" in this way. Like dark energy and magic, the main evidence in support of trace element metasomatism is often that data don't conform to quantitative theory. In this talk I will expand on why this can be a problem, and suggest partial solutions.

"Metasomatism" refers to geochemical fractionation resulting from open-system interactions between a moving fluid or melt and an assemblage of minerals. Metasomatic processes involve *input* of fluid or melt, with or without output. They include hydrothermal alteration, flux melting, impregnation, assimilation, zone refining and chromatography. What is gained by calling all "metasomatic"? And, "equilibrium porous flow" (metasomatism) can be chemically identical to batch melting (not metasomatism). Similarly, melt extraction followed by "metasomatic enrichment" can look just like flux melting, Fluid fluxed, or melt fluxed? Supercritical goo? Who cares?

We can parse metasomatism into clearly defined processes. However, while causality may be clear in numerical or experimental models, "similarity" between rock data and models may not be unique. Many high temperature processes closely approximate grain scale equilibrium, but this is coupled with fractional distillation or other kinetic effects on a larger scale. Equilibrium is path independent and reversible, but disequilibrium is not. We can document "reaction progress" in the field or within samples, finding correlated chemical and spatial data. This reduces the number of models consistent with data. We can conceptually discriminate between processes in which fluid or melt mass increases, is constant, or decreases. Local effects may be identical, but their progressive evolution in time and space should be distinct. Multi-scale spatial studies will be increasingly valuable in studying melt transport in the mantle, for example.

Metasomatism above subduction zones is crucial for global geochemical cycles. Despite the recognition of supercritical melts in subduction zone conditions, we can document the "direction" of mass transfer in high P and UHP terranes, and interpret data within theoretical bounds defined by dilute aqueous fluids versus hydrous melts, just as we use fictive end-members, batch and fractional melting, as benchmarks in studying residual peridotites.

In summary, spatial studies will relate metasomatism to the geotherm, geochemical cycling, and geodynamics.

Regionally extensive light lithium in mantle lithosphere of far east Russia

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Lithium isotopes are increasingly employed to understand crustal recycling within the Earth, but the composition of lithium recycled from crust to mantle is uncertain. Because altered oceanic crust takes up isotopically heavy lithium from sea water, the subducted slab is generally expected to deliver heavy lithium to the mantle, yet, eclogites, considered analogs to subducted oceanic crust, have $\delta^7\text{Li}$ values that are generally lighter than MORB (down to -12‰). These light values may reflect loss of heavy lithium via low-T dehydration reactions in the down-going slab (Zack et al., 2003). Recently, Nishio et al. (2004) reported unusually low $\delta^7\text{Li}$ values for clinopyroxenes from mantle xenoliths from far east Russia and southern Japan. They interpreted these light values to reflect influx of lithium from a subducted slab and argued that acid leaching, applied to all samples, did not affect the lithium isotopic composition of the cpx. We have analysed cpx separates from well-characterized peridotite xenoliths from Far East Russia: six from the Tok volcanic field (400-1000 km to the north of the sites sampled by Nishio et al.) and one from the Barhatny volcano (near the Ennokentiev site of Nishio et al.). The xenoliths range from fertile to highly refractory in terms of modal and major element compositions (1.1 to 4 wt.% Al_2O_3), reflecting variable amounts of melt extraction at shallow levels (Ionov et al., 2005). All the xenoliths are metasomatised to various degrees (e.g., most are LREE-enriched). The cpx have variable, but mainly high lithium contents (ranging up to 16 ppm), and all show unusually light $\delta^7\text{Li}$ values (-6 to -14‰), irrespective of whether the minerals were mildly acid leached or simply washed in milli-Q water. Moreover, the enrichments in lithium and the low $\delta^7\text{Li}$ values do not appear to be correlated with Al contents, enrichments in highly incompatible trace elements or Sr and Nd isotope compositions. Although we cannot directly link the metasomatism of these samples with modern or ancient subduction zone fluids, a region of unusually low $\delta^7\text{Li}$ exists within the lithospheric mantle, stretching for over 1000 km, adjacent to the Pacific rim.

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Relics of subcontinental mantle in the Cape Verde oceanic lithosphere

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Mantle xenoliths from two Late Tertiary necks of Sal Island were investigated in order to define the petrological characteristics together with the compositional evolution of the Atlantic lithospheric mantle underneath Cape Verde Archipelago. They consist of mainly protogranular sp-bearing lherzolites and harzburgites. Whole rock and pyroxene trace element distribution, particularly HREE, suggest that compositional variation from lherzolites to harzburgites cannot be explained by a common progressive depletion process of a sp-bearing mantle peridotite. High Cr₂O₃, low CaO contents and upward-convex REE patterns in large protogranular clinopyroxenes ($La_N=3.6-5.3$; $Sm_N=8.3-12.8$; $Yb_N=2.4-4.8$), coupled with high Cr₂O₃ and low HREE contents in orthopyroxene, suggest in fact that lherzolites still preserve geochemical fingerprints consistent with a fertile gt-bearing stability field. By contrast the majority of Cape Verde harzburgites, are quite comparable to highly refractory mantle lithologies commonly observed in the Atlantic Ocean generated after extensive MORB extraction. This is also in agreement with the occurrence of Late Jurassic MORB in the islands of Maio and Santiago. On the other hand the abundant presence of lherzolites still recording equilibration in the garnet stability field suggests that a significant portion of Cape Verde lithospheric mantle was not formed at mid-ocean ridge, but most probably represent a portion of sublithospheric continental mantle incorporated in the newly-formed oceanic lithosphere. A few lherzolites and harzburgites show textural evidences of metasomatic enrichments. Metasomatic fluids react with the original paragenesis causing the formation of secondary minerals, such as clinopyroxenes after orthopyroxene and primary clinopyroxene destabilization and, in few cases, k-feldspar and K₂O-rich glass (K₂O up to 8.78wt%). These agents were reconstructed using major and trace element mass balance calculations between primary and secondary parageneses. The resulting compositions have geochemical features comparable to those of kimberlite (on dry basis, MgO:17-27 wt%; K₂O/Na₂O:1.6-3.2 molar; (K₂O+Na₂O)/Al₂O₃:1.1-3.0 molar; Rb:91-165 ppm; Zr:194-238ppm). These magmas may result from very low partial melting degree of deeper SCLM portions, left behind by drifting of the African Plate during the Central Atlantic opening.

Fluid-rock interaction in convergent margins: Evidence from stable isotopic studies of veins

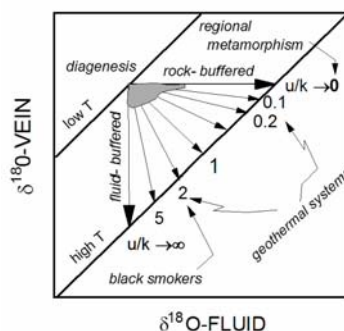
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Measurements of the oxygen isotope ratios of veins and their coexisting host rocks from the Lachlan Fold Belt (Australia), the Ouachita and Appalachian Orogens (United States), the Otago Schist (New Zealand) and the Oman Mountains constrain the styles of fluid-rock interaction in the crust at different levels during crustal convergence. The ratio of the fluid flux rate (u) to the isotopic exchange rate (k) is the dominant parameter effecting oxygen isotope distribution.

Modeling of the isotopic exchange shows that for many geologic environments the isotopic composition of the fluid reaches a quasi-steady state that can be approximated by a mixing equation of a rock-buffered fluid ($u/k \rightarrow 0$) and an externally derived fluid ($u/k \rightarrow \infty$); in a fluid + rock binary



system, any natural system generates a spectrum of fluid compositions that range from fluid-buffered to rock-buffered. The primary controls on this critical u/k ratio are permeability (for u) and temperature (for k). Mechanical limits

on permeability at depth permit the preservation of surface-derived isotopic heterogeneities to significant depths and for geologically extensive time scales. When $u/k \ll 1$, the fluid isotopic composition is buffered by the local host rocks on time scales of thousands of years while mineral heterogeneities will persist for millions of years. Secondary phases grown in the presence of this rock-buffered fluid will reflect isotopic equilibrium with the local fluid environment and exhibit non-equilibrium fractionations with the remaining partially-exchanged phases. The time scales for this style of fluid-rock interaction are comparable to the time scales for metamorphism in convergent margin settings.

Jadeitite: A record of metasomatism at various depths in Guatemalan subduction zones

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Jadeitites crystallize from hydrous subduction-related fluids in serpentinizing peridotite. The strike-slip Motagua Fault in Guatemala has brought jadeitites to the surface several times. Along the north side of that fault we studied 8 jadeitite locales along 65 km of E-W strike, and on the south side 3 locales along 15 km. We identified at least 4 distinct PTx settings for jadeitite.

Jadeitites north of the fault are all quite similar, light colored and altered by late-stage fluids. The presence or absence of potassic phases may be a further subdivision. A modest jadeite (Jd) – omphacite (Omph) gap and zoisite suggest 300-400°C. Absence of quartz (Qtz) and common albite (Ab), mica, and late analcime (Anl) suggests P = 6-10 kb. Albitites are common, implying further fluid crystallization at lower P and higher a_{SiO_2} . The associated rocks are garnet-zoisite-amphibole (with some retrograde eclogite) and omphacite-taramite metabasites. The southern jadeitites are subdivided as follows:

1- San Jose jadeitites are green to blue-green with late omphacite veins and little alteration. A larger Jd – Omph gap and lawsonite suggest 300-400°C, and higher P as indicated by Qtz at P = 12-20 kb. Lawsonite eclogites (P = 20-25 kbar, T = 350-450°C) occur with these jadeitites.

2- La Ceiba jadeitites are moderate to intense dark green, occasionally lavender, with veins of quartz, diopside, cymrite, and vesuvianite. A large Jd – Omph gap suggests 300-400°C and, as indicated by Qtz ± Ab, P = 10-14 kb. These coexist with omphacite-glaucophane blueschists.

3- La Ensenada jadeitites are whitish with green, blue, orange, and mauve. A large Jd – Omph gap and pumpellyite suggests <200~300°C at lower P=6-9 kb as indicated by primary Ab and secondary Anl. These are very low in iron and coexist with pure clinochlore and magnetite, which all suggest ferrous iron removal by a fluid. These are found with lawsonite-glaucophane blueschists and chloritite.

These four types of Guatemalan jadeitite record differences in fluid composition, crystallization T and P, and a variety of sodic metasomatic processes.

The origin of replacement dolomite, Dolomites, northern Italy: Part 1

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Massive dolomite typically forms at depth and elevated T through replacement of limestone by its reaction with flowing dolomitizing fluid. Details of the physical mechanisms of flow, and the chemical reactions remain unresolved. Our integrated mapping, stable isotope, and major- and trace-element study of the Triassic Latemar buildup addresses these issues. The Latemar is an ideal study area because dolomitization was arrested with both dolomite and unreacted limestone well-exposed in 3D. Boundaries between the dolomitized and undolomitized regions are sharp (usually <10 cm wide) and are easily mapped because of a color difference between limestone and dolomite. The distribution of dolomite was mapped on buildup- to m-scales to define the flow channels of dolomitizing fluid. Dolomite at lower elevations occurs as brecciated columns or vertical sheets; at higher elevations dolomite occurs mainly as horizontal, bedding-parallel sheets and tubes, and less commonly as vertical breccia pipes and sheets parallel to fractures and margins of dikes. The distribution of dolomite images an orthogonal lattice of interconnected vertical and bedding-parallel flow channels. The $^{87}\text{Sr}/^{86}\text{Sr}$ of Latemar dolomite is 0.7076-0.7079 and fluid inclusions in dolomite have salinities 3.6-5.1 wt % NaCl equivalent [1], implying seawater or seawater-derived fluid was the agent of dolomitization. Dolomite has $\delta^{18}\text{O} = 21.5\text{-}27.4\text{‰}$ (VSMOW), corresponding to T = 52-88°C (assuming equilibration with fluid of $\delta^{18}\text{O} = 0$). Calcite in limestone has $\delta^{18}\text{O} = 23.3\text{-}28.4\text{‰}$, corresponding to T = 25-52°C. Dolomite has $\delta^{13}\text{C} = +1.9$ to $+4.4\text{‰}$ (VPDB), and calcite has $\delta^{13}\text{C} = +1.1$ to $+4.0\text{‰}$. Calcite in limestones has average $X_{\text{Ca}} = 0.987$, $X_{\text{Mg}} = 0.013$, and $X_{\text{Fe}} < 0.001$ (microprobe analysis). Typical dolomite has $X_{\text{Ca}} = 0.537$, $X_{\text{Mg}} = 0.457$, and $X_{\text{Fe}} = 0.006$, although dolomite that occurs in high-T regions is more enriched in Fe: $X_{\text{Ca}} = 0.520$, $X_{\text{Mg}} = 0.464$, and $X_{\text{Fe}} = 0.016$. The presence of Fe in dolomite, as well as Mn- and Zn-enrichment from preliminary LA-ICPMS data, indicates that Triassic seawater alone was not the dolomitizing fluid. We suggest a mixture of Triassic seawater and hydrothermal fluid produced by the reaction of seawater with hot, mafic rocks of the adjacent Predazzo volcanic-intrusive complex that was active during dolomitization.

Reference

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The origin of replacement dolomite, Dolomites, northern Italy: Part 2

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Analysis of the spatial distribution of elements, isotopes, and heat with transport theory leads to insights into the flow system that produced dolomite (Dol) in the Latemar buildup. From Part 1, Dol typically replaced calcite (Cal) in limestone by $2\text{Cal} + 0.89\text{Mg}^{2+} + 0.01\text{Fe}^{2+} = \text{Dol} + 0.90\text{Ca}^{2+}$. Constraints (Part 1) of a dolomitizing fluid with seawater-like salinity, $\text{Ca/Mg} < 0.75$ (for dolomitization at $\approx 75^\circ\text{C}$), and significant Fe, Mn, and Zn point to fluid similar in chemistry and T to modern diffuse effluent. The development of Dol over a distance ≈ 1 km along the inferred flow path then requires, by mass balance of Ca and Mg, a time-integrated fluid flux (q) $\approx 10^8 \text{ cm}^3 \text{ fluid/cm}^2 \text{ rock}$. Given the composition and amount of fluid, spatial distributions of isotope compositions were computed from the advection-diffusion equation. Carbonate rock is predicted to have equilibrated with respect to ^{18}O - ^{16}O , ^{87}Sr - ^{86}Sr , and ^{13}C - ^{12}C exchange with dolomitizing fluid over distances 850x, 24x, and 0.11x the extent of dolomitization along the flow path. Near Dol-limestone interfaces, $\delta^{13}\text{C}_{\text{Dol}}$ thus is simply inherited from the limestone parent (confirmed by data in Part 1) while $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Dol}}$ and $\delta^{18}\text{O}_{\text{Dol}}$ correspond to equilibration with the dolomitizing fluid. Measured $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Dol}}$ is evidence for a Middle Triassic seawater-derived fluid and $\delta^{18}\text{O}_{\text{Dol}}$ records the T of dolomitization (Part 1). The elevated T recorded by $\delta^{18}\text{O}_{\text{Cal}}$ (Part 1), indicates that physical limits of the flow channels extended into limestone adjacent to Dol and that flow in the limestone occurred at lower T. Ranges in $\delta^{18}\text{O}_{\text{Dol}}$ within individual outcrops almost as large as for all analyzed samples is qualitative evidence that fluid flow occurred in multiple pulses of limited spatial extent and at variable T. Profiles in $\delta^{18}\text{O}_{\text{Dol}}$ across some vertical flow channels record steep gradients in $T \approx 10\text{--}25^\circ\text{C/m}$. Quantitative analysis of the T profiles with the heat equation suggests that individual flow pulses had $q \approx 2 \cdot 10^5 \text{ cm}^3/\text{cm}^2$ and a duration of ≈ 0.5 y. Dolomitization in the area was accomplished by ≈ 500 flow pulses over a total duration of flow and reaction only ≈ 300 y. The occurrence of 10-15% porosity in many Dol samples confirms that most (but not all) Dol replaced Cal at constant C rather than at constant volume. Replacement at constant volume does not make geochemical sense because even $q \approx 10^8 \text{ cm}^3 \text{ fluid/cm}^2 \text{ rock}$ is inadequate to transport the necessary amount of dissolved C.

Geochemistry, mineralogy, and chronology of K-metasomatism of volcanic rocks near Socorro, New Mexico, USA

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Potassium metasomatism, thought to be caused by deep circulation of alkaline-saline brines, affects an area of roughly 1000 km² near Socorro, New Mexico, increasing the K₂O content of local volcanic rocks by up to 10 wt.%. Petrographic and microbeam analyses indicate that during the chemical changes associated with metasomatism, Na-rich phases, primarily plagioclase, are dissolved and replaced by secondary mineral phases, mainly adularia and clay minerals. Bulk geochemical analyses of altered rocks compared to fresh rocks demonstrate consistent chemical patterns, including enrichments of K₂O, Fe₂O₃, As, Rb, Pb, Sb, Ba, and Cs and depletions of MgO, CaO, Na₂O, Eu and Sr. Analyses of alteration phases hand-picked from relict plagioclase grains provide the clearest picture of the chemical processes that occur during alteration, and allow quantitative correlations between the presence of alteration phases and the abundance of elements such as K₂O, Rb, CaO, Na₂O, Eu and Sr. This analysis also suggests that variations of elements such as As, Pb, Sb, Ba, and Cs are related to hydrothermal alteration, either overprinting, or overprinted by, potassic metasomatism. A final chemical signature observed in hand-picked alteration mineral suites is that the REE content of samples from a low-REE rock unit increase during metasomatism, whereas there is a significant decrease in samples from a unit with higher initial REE contents, suggesting that the variation in REE contents may be related to equilibration between the rocks and the metasomatizing fluid. Results suggest that the enrichment of REE may be roughly related to the abundance of metasomatism-derived clay minerals in the sample.

The chronology of metasomatism determined by $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of hand-picked secondary potassium feldspar, indicates that metasomatic alteration began at around 15 Ma, and continued to around 7 Ma. The areas that show the most intense effects of alteration yield the youngest ages, suggesting that this may represent the deepest, most central and longest-lived part of the playa system. The age range determined here is consistent with inferred timing of playa deposition from independent geological evidence.

The behavior of chlorine and $\delta^{37}\text{Cl}$ during the oceanic crust alteration

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The oceanic crust (OC) is a vector of chemical exchanges between the surface and the Earth's interior. Hydrothermal circulation in the ocean's floor is the major control of chemical compositions of both seawater (SW) derived fluids and crust (before subduction). In order to bring new constraints on the OC alteration, chlorine stable isotope composition ($\delta^{37}\text{Cl}$) was determined in both high (HTF) and low (LTF) temperature fluids, at ridge axis and off-axis, respectively, and in fresh and altered basalts.

Worldwide HTF ($T > 230^\circ\text{C}$) have a large range of chlorinity (250 to 821 mM), but show very constant $\delta^{37}\text{Cl}$, indistinguishable from the SW $\delta^{37}\text{Cl}$ (0.0‰). This $\delta^{37}\text{Cl}$ homogeneity suggests that the phase separation process, responsible for chlorinity variation at HT, does not fractionate Cl isotopes [1]. In contrast, despite very small variations of chlorinity ($550 \pm 6\text{ mM}$), LTF ($T \leq 60^\circ\text{C}$) show $\delta^{37}\text{Cl} = -0.71 \pm 0.67\text{‰}$ (1σ). Moreover, $\delta^{37}\text{Cl}$ values show positive covariations with $\delta^{18}\text{O}$ (mainly modified by water-rock interactions) suggesting that a single process leads to a depletion in ^{37}Cl of the interacting fluids.

Basalts, both fresh and altered at LT, are also depleted in ^{37}Cl relative to SW ($-2.0 < \delta^{37}\text{Cl} < -0.2\text{‰}$ and $-2.8 < \delta^{37}\text{Cl} < -0.5\text{‰}$, respectively). Cl of the reacting fluids has precipitated in the pores of the altered basalts upon drying. It was recovered by leaching as described in [2]. These residual salts, representative of the reacting fluids ($-5.1 < \delta^{37}\text{Cl} < 0.0\text{‰}$), have higher $\delta^{37}\text{Cl}$ than the associated whole rock, implying that $\Delta^{37}\text{Cl}_{\text{R-F}} < 0$. This contrasts with prior assumptions [3-4], and with classical fractionation laws predicting a ^{37}Cl enrichment of the solid phase.

Interaction of SW ($\delta^{37}\text{Cl} = 0\text{‰}$) with fresh OC ($\delta^{37}\text{Cl} < 0\text{‰}$) produces fluids and rocks with $\delta^{37}\text{Cl} \leq 0\text{‰}$. These data expose a mass balance problem.

The metasomatic history of the lithospheric mantle beneath NE Spain

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The spinel peridotite suite at Olot, is remarkably bi-modal consisting of very fertile protogranular lherzolites, sometimes bearing texturally equilibrated pargasite amphibole (3 samples out of 60), and very refractory harzburgites showing secondary recrystallization textures. Bulk rock REE systematics are widely variable: lherzolites display flat or depleted LREE patterns (HREE concentration up to $2.7 \times \text{Ch}$; $\text{La}_\text{N}/\text{Yb}_\text{N}$ down to 0.42); harzburgites are extremely depleted in HREE (down to $0.21 \times \text{Ch}$) displaying at the same time high LREE/HREE ratios ($\text{La}_\text{N}/\text{Yb}_\text{N} = 12.3\text{--}17.2$); this LREE enrichment is coupled with relative enrichment in Th, U, Nb and Ta. In situ LA-ICP-MS analysis of clinopyroxene highlights LREE depleted compositions with a slight spike at Eu in anhydrous lherzolites (HREE up to $13 \times \text{Ch}$, $\text{La}_\text{N}/\text{Yb}_\text{N}$ down to 0.3, and $\text{Eu}^* = 1.2\text{--}1.5$); the presence of LREE depletion ($\text{La}_\text{N}/\text{Yb}_\text{N}$ down to 0.2) coupled with a Eu positive anomaly (Eu^* up to 1.7) also characterize the clinopyroxenes of two amphib-bearing lherzolites. In these samples the clinopyroxene composition mimics, at slightly lower concentration, that of the coexisting amphiboles. The constituent clinopyroxenes of harzburgites display totally different REE distributions, characterised by remarkable HREE depletion (down to $0.4 \times \text{Ch}$) and ubiquitous M/LREE enrichment. In these harzburgites, $\text{Nd}_\text{N}/\text{Yb}_\text{N}$ (up to $20.7 \times \text{Ch}$) is generally higher than $\text{La}_\text{N}/\text{Yb}_\text{N}$ (up to $12 \times \text{Ch}$) giving rise to upward convex patterns. Geochemical features of the harzburgites indicate that the mantle section sampled beneath this area suffered major episodes of melt extraction followed by metasomatic processes - triggered by highly alkaline melts - that induced cryptic enrichments. Lherzolites, on the other hand, possibly indicate modal re-fertilization by pervasive impregnation of subalkaline (LREE-depleted) melts.

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Metasomatic processes of Paleozoic lithospheric mantle of Scotland Terranes

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Mantle melting events occurring intermittently from the late Carboniferous to mid-Permian in northern and north-western Scotland relate to lithospheric extension, generated small volumes of silica-deficient basic magmas, which in some case, contain peridotitic xenoliths. The present work concerns mantle peridotites from several localities of the Northern Highlands Terrane (Rinibar, Orkney- and Streap Com'laidh) of Midland Valley Terrane (Rudduns Point). A comparison with rare peridotite xenoliths from Hebridean Terrane, Grampian Highland Terrane and Southern Uplands Terrane which also experienced variable metasomatic enrichment is also put forward, with the aim of studying the evolutionary history of Scottish lithospheric mantle and highlighting the metasomatic agents which affected this portion of mantle during Paleozoic. Attention was mainly focussed on major and trace element contents of minerals, namely clinopyroxenes. In the Northern Highland Terrane, clinopyroxenes from Streap Com'laidh have less LREE-enriched and present less pronounced Ti and Zr anomalies (La/YbN 2.8-4.5; Zr* 0.42-0.57; Ti* 0.57-0.62) than clinopyroxenes from Rinibar. Clinopyroxenes from Rinibar have been variably enriched in LREE, with La/YbN ratios ranging from 2.7 to 32.2. Remarkable Ti and Zr negative anomalies, although to variable extent, are noticed (Zr* 0.10 - 0.86; Ti* 0.07 - 0.28). Phlogopite is present, and can account for the pronounced Ti negative anomaly in some clinopyroxenes. Two different enrichment styles can be identified in the Orkney's lithospheric mantle: one presenting LREE-enrichment and remarkable Zr (and Hf) and Ti negative anomalies, the other with LREE-depletion (compared to MREE) and less pronounced Ti (and Zr) negative anomalies, associated with the presence of high-TiO₂ phlogopite. The two kinds of clinopyroxenes compare well with clinopyroxenes related to carbonatite and kimberlite metasomatism respectively. A progressive enrichment processes may also be envisaged between clinopyroxenes in xenoliths from Midland Valley Terrane, and those from Hebridean Craton.

REE distribution in granites from the Crown Jewel gold skarn deposit: A LA-ICP-MS study

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Garnets from the Crown Jewel Au-skarn deposit, north-central Washington, range in composition from Adr₃₀Gr₇₀ to almost pure andradite (Adr_{>99}). Fe-rich garnets are isotropic whereas Al-rich garnets significantly deviate from cubic symmetry and are anisotropic, often showing sectorial dodecahedral twinning.

In situ LA-ICP-MS analyses of those garnets reveal a positive correlation of ΣREE^{3+} (<1-47 ppm) with Al content (0-2.6 a.p.u.f.), and consequently with their grossular component. REE patterns for Al-rich garnets show HREE-enrichment and LREE-depletion, and weak positive and negative Eu anomalies. Fe-rich garnets (Adr_{>90}) have much lower ΣREE and exhibit LREE-enriched and HREE-depleted patterns, with a strong positive Eu anomaly. Presence of magnetite, implying a reduced environment with $f\text{O}_2$ below the HM buffer, indicates that Eu is present as Eu²⁺, which in part explains its different behaviour from the other REEs and the consequent Eu/Eu* anomalies. Incorporation of REE into garnet is partially controlled by its crystal chemistry. REE³⁺ follow a coupled, YAG-type substitution mechanism ($[\text{X}^{2+}]_{-1}^{\text{VIII}}[\text{REE}^{3+}]_{+1}^{\text{VIII}}[\text{Si}^{4+}]_{-1}^{\text{IV}}[\text{Z}^{3+}]_{+1}^{\text{IV}}$), while Eu²⁺ substitutes for X²⁺ cations. Thermodynamic data (e.g., Hmixture) suggests preferential incorporation of HREE in grossular and LREE in andradite.

Textural evidence, optical characteristics and major and trace element geochemistry, show that variations observed in the Crown Jewel garnets are largely controlled by external factors (fluid composition, W/R ratios, mineral growth kinetics, and diffusive vs. advective metasomatism). The data are consistent with Al-rich garnets being formed by diffusive metasomatism, under low W/R ratios, and in equilibrium with metasomatic fluids whose composition is locally buffered by the host rocks. On the other hand, Fe-rich garnets grow rapidly by advective metasomatism, under relatively high W/R ratios, and in equilibrium with a magmatic-derived fluid, consistent with an increase in porosity by fracturing.

Geochemistry and petrogenesis of a South African diamondiferous eclogite

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A recently collected diamond-bearing eclogite from the Roberts Victor Mine of South Africa was studied for its major and trace element chemistry and mineral compositions, to gain insight into the relationships between eclogite and diamond petrogenesis. The relatively magnesian basaltic bulk composition of this xenolith is characteristic of other Roberts Victor eclogites. Its high Na₂O in garnet and K₂O in clinopyroxene puts this eclogite in the Group I classification group of McCandless and Gurney (1989), in common with most diamondiferous eclogites. Garnet-clinopyroxene Fe-Mg exchange thermometry yields an estimate of 1114°C at 30 kbars, also similar to estimates from other Roberts Victor Group I eclogites.

However, in contrast to most Group I eclogites, the reconstructed bulk rock rare earth element pattern of this rock (determined by ion probe analysis of unaltered garnet and clinopyroxene) is light rare earth depleted, with a positive europium anomaly, indicative of a plagioclase-rich cumulate gabbroic protolith metamorphosed to eclogite facies during emplacement into the lithosphere. In this regard, and in its textural character, (MacGregor and Manton, 1986) the xenolith is more similar to Group II eclogites. This contrast in classification may point to diamond growth during metasomatic re-enrichment of an originally depleted cumulate rock matrix, and emphasizes the diversity of protoliths in which diamonds may form through metasomatic processes.

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Tracing metasomatic agents by noble gas isotopes

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Elemental and isotopic compositions of noble gases trapped in ultramafic rocks provide valuable information regarding the processes that affected the terrestrial mantle. Here I present some of such examples we found in fresh suites of xenoliths from SE Australia (e.g., Matsumoto et al., 2000) and in orogenic peridotites from Horoman (Matsumoto et al., 2001) and from Finero complexes (Matsumoto et al., 2005, submitted) with a particular emphasis on mantle metasomatism.

Based on analyses on above mentioned suites of rocks, we identified at least four kinds of characteristic noble gas components:

- (1) A MORB-type isotopic component
- (2) A Plume-like component
- (3) A hybrid component with mantle-He and air-Ar
- (4) A highly radiogenic component

Irrespective of their isotope signatures, these components are preserved in fluid inclusions without being significantly disturbed by ingrowths of radio- and nucleogenic noble gas isotopes. Therefore, these noble gas signatures should reflect those of mantle domains from which respective metasomatic agents had been derived. A MORB-like component is the most widespread in variably metasomatised mantle xenoliths from SE Australia, whereas the plume-like neon is rare and only found in metasomatic apatite, indicating an involvement of mantle plume to this particular metasomatic event (e.g., Matsumoto et al., 1997 and 2004). A Hybrid of mantle-He and air-Ar can be regarded as a signature characteristic of the subduction zone settings, and is often found in orogenic lherzolites. We also found that this component is highly concentrated in thin apatite-rich layer of Finero lherzolite that hosts LREE-enrichment. This can be taken as rather direct evidence for metasomatic introduction of incompatible elements and noble gases with the same agent. Also, it is possible to identify more than two different noble gas components coexist in a single specimen, suggesting multiple episodes of metasomatism. These demonstrate the usefulness of noble gas isotopes to constrain tectonic setting of the metasomatism and source of its agent.

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Effects of K-metasomatism on the REE compositions of Precambrian Aravalli paleosols, Northwestern India

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Metamorphosed and metasomatised Precambrian paleosols occur at the base of the Paleoproterozoic Aravalli Supergroup, NW India. These paleosols have developed on granitic, gneissic and amphibolitic parent rocks constituting the 3.3 to 2.5 Ga basement gneissic complex. The paleosols have probably developed between 2.5 and 2.2 Ga. Based on detailed studies, it has been proposed that these rocks have witnessed a complex evolutionary history of metamorphism followed by metasomatism [1].

Rb-Sr isotopic analysis on wholerock and mineral separate samples have been carried out to delineate the timing of alkali metasomatism and to assess its effects on rare earth element (REE) and Th, U elemental compositions. The Rb-Sr isotopic data of paleosol samples yielded an age of 1399 ± 26 Ma with a very high Sr_i of 0.75145 ± 0.00063 . The $^{87}Sr/^{86}Sr$ data show a good correlation with $1/Sr$ values indicating that the observed straight line between Rb-Sr isotope compositions may be a result of mixing. However, the overlying metasomatically altered basaltic rocks also yielded Rb-Sr age of 1397 ± 53 Ma, indicating that the age obtained on paleosols may represent the timing of alkali metasomatism. Several Precambrian paleosols have also yielded Rb-Sr ages younger than their stratigraphic ages emphasizing the usefulness of paleosols as indicators of timing of alkali metasomatism [2].

Importantly, it has been noticed that Th, U and REE contents of the Aravalli paleosols are correlated with $^{87}Sr/^{86}Sr$ ratios indicating that they might have mobilized during alkali metasomatism. However, the Ce and Eu anomalies, which are more important for assessing the redox state of the Precambrian atmosphere appears to have been not correlated with the Sr isotope ratios.

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A synthesis of diamond and inclusion trace element studies

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We have performed in-situ trace element analysis of inclusions in diamond and of their diamond host by Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS). Impurities in the diamond host are attributed to sub-microscopic quenched melt inclusions which represent a metasomatic melt or a melt produced during mantle metasomatism. The trace element compositions of inclusions often indicate complex histories, this is difficult to reconcile with a syngenetic origin for diamond inclusions; therefore several workers prefer protogenetic growth.

We use partition coefficients to calculate the composition of melt in equilibrium with the crystalline inclusions and compare this to the analysed melt composition. If the inclusions are syngenetic, then the calculated and measured melt composition should lie along a fractionation trend. If the inclusions are protogenetic, then the diamond growth event will be one of a number of geochemical events affecting the included mineral. In either case, this data provides important information about the diamond growth event.

Traverses are used to look for distinct geochemical events and fractionation trends during diamond growth, with reference to the lattice-bound nitrogen concentration and aggregation state. This work forms a link between established inclusion studies and exciting new data from LA-ICP-MS fingerprinting of diamonds by provenance and paragenesis.

The behavior of boron in hydrothermal alterations of granites

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Boron contents and B-isotopic compositions are measured on fresh and altered granite samples from the Qitianling granite and related hydrothermal tin deposit in South China. The fresh granite has the highest boron content (36.62ppm) and the highest $\delta^{11}\text{B}$ value (-10.9‰). The granites near the tin ore veins were slightly altered and have lower boron contents (12.12 to 24.77ppm) and lower isotopic compositions (-15.6 to -13.4‰). The completely chloritized granites sampled from the tin veins have the lowest boron isotopic compositions (-27.3 to -21.9‰). B/Be and $\delta^{11}\text{B}$ values of granites decrease with increasing degrees of hydrothermal alteration. Boron isotopic variations are consistent with those of oxygen isotopes. The fresh granites have the highest oxygen isotopic composition ($\delta^{18}\text{O}$ =10.5‰). The most altered granites have the lowest oxygen isotopic composition (5.4 to 6.6‰). The oxygen isotopic variations of granites are the result of fluid-rock interactions. The colinearity of isotope ratios of B and O of granites indicated that the fractionation of boron isotope is also the result of fluid-rock interactions. These data indicate that the heavier isotope, ^{11}B is preferentially lost to hydrous fluids from altered granites during the fluid-rock interactions. It may be explained by coordination-dependent fractionation of trace B between tetrahedral sites in silicate and trigonal sites in hydrothermal fluids. This study identifies for the first time that boron isotope is an excellent tracer for hydrothermal alterations of granites and may be used as a useful exploration guide for mineralization. Future studies of the boron isotopic fractionations between main rock-forming minerals and hydrothermal fluids are needed in order to understand this tracer better.

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Molecular characterization of natural organic matter using non-discriminating flash pyrolysis

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A substantial fraction of natural organic matter (NOM) consists of complex mixtures of macromolecular compounds. Consequently, high-molecular-weight fragments liberated during the pyrolysis of NOM often carry the most significant structural information. Their diagnostic value, however, is commonly limited by the preferential transfer of lower-boiling pyrolysis products to the GC column.

Non-discriminating pyrolysis is an upcoming technique [1] that minimizes transfer losses of fragments such as long-chain alkanes and alkylated aromatics. In addition, the novel technique allows a range of sample sizes from less than a microgram for bacterial biomass up to 15 mg for the study of samples of low organic carbon content, such as soils and sediments (0.1-1.0% C), which eliminates pretreatment requirements. In this study, non-discriminating pyrolysis-GC/MS performed on a wide range of NOM sources allowed the observation of large molecular fragments, enabling a better understanding of the overall macromolecular structure of the NOM present. When comparing the results obtained with non-discriminating pyrolysis to those obtained by conventional Curie-point pyrolysis for Tertiary sandy aquifer sediments [2], the significance of macromolecular structures within NOM was stressed in the former technique by the strong presence of various polyaromatic and long-chain aliphatic compounds that were underexposed by the latter technique. Overall, non-discriminating pyrolysis promises to be a useful tool for the characterization of the macromolecular part of NOM.

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Mass spectrometric investigation of thioarsenate formation in waters

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Introduction

Arsenic (As) mobilization in ground water aquifers has been linked to reducing geochemical conditions. Recent studies have suggested that As may form soluble sulfur species in sulfidic waters, but no spectrometric proof of this hypothesis has been produced at ambient As concentrations.

Methods

The four thioarsenates mono-, di-, tri- and tetrathioarsenate were synthesized in solution following previously published procedures. All members of the homologue series were characterized mass spectroscopically (MS) using electrospray ionization (ESI) with either quadrupole-quadrupole or quadrupole-time-of-flight MS detection in the negative ion mode. Fragmentation patterns of major ions were obtained by collision-induced dissociation. Geochemical model experiments were conducted by mixing 10 mg/L arsenite or arsenate with equimolar amounts of sulfide or elemental sulfur in deionized water in an inert atmosphere, and withdrawing sub-samples at certain time intervals. These model samples were either analyzed by ESI-MS directly, or subjected to analysis by anion exchange chromatography-inductively-coupled plasma-MS (AEC-ICP-MS).

Results

All members of the homologue series (including arsenate itself) show the same general types of major ions in ESI-MS: the molecular ion in the form $H_2AsO_xS_{4-x}^-$ ($x = 0-4$), fragments where this molecular ion loses H_2O or H_2S (where possible), and clusters of the molecular ion with Na^+ and/or H_2O . Although certain fragments of different thioarsenates are either identical or have the same nominal mass, the molecular ions are characteristic of each compound and are not overlapped by fragments from other As species.

Of the four possible combinations of As and S species, only the reaction of arsenite and sulfide yielded thioarsenates fast; within 24 h reaction time, significant amounts of these species were observed. Although this reaction would be expected to yield thioarsenites, (AEC)-ESI-MS proves unequivocally that thioarsenates are the only reaction products. We will attempt to provide a geochemical explanation for this apparent contradiction.

Geometric constraints of *in situ* synchrotron micro-XANES determinations of oxidation state

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Many different microanalytical techniques are being applied to the study of multivalent cations: optical, IR, XANES, SEM/TEM, EELS, ELNES, auger, EPMS, micro-Mössbauer, etc. A fundamental constraint on interpretation of such spectra is the fact that minerals studied in thin section are generally randomly oriented. The pleochroism that is well-known in minerals at optical wavelengths also occurs throughout the EM spectrum. In X-ray spectra, the intensities of closely-spaced peaks in the pre-edge and main-edge regions of vary with crystal orientation, producing a “color” change that is characteristic of all types of polarized energy spectroscopy.

Systematic orientation studies in thin section and on oriented single grains reveal a range of uncertainty in oxidation state measurements that may be directly related to lattice geometry. Thus, oriented samples must be used to obtain truly quantitative spectroscopic results, whether in thin section or grain mount. Failure to consider orientation effects leads to false optimism about the relative precision of relevant techniques.

A marriage of traditional universal stage techniques (or electron backscatter selected area diffraction, its modern equivalent) with X-ray microanalytical tools provide solutions to orientation-related problems. Such combined studies are essential to full characterization of micrometer-sized extraterrestrial returned samples.

Transmission and fluorescence mode microXAS analysis of oriented mineral grains

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Using a 20x30 µm beam size, transmission and fluorescence mode Fe K α X-ray absorption spectra were acquired on identical spots on each of a suite of optically biaxial mineral grains oriented with their optical directions (i.e, X, Y, and Z) in the plane of the beam polarization. Mineral samples were selected to represent varying Fe contents, bulk compositions, grain sizes, and crystal systems. This method allows comparison of the relative effects of 1) differential x-ray absorption as a function of orientation (“x-ray pleochroism”), 2) self-absorption phenomena relating to Fe abundance, and 3) sample thickness. Results show significant variation in peak intensities as a function of orientation, suggesting that interpretations of valence state or coordination number based upon XAS of grains in thin sections or as single crystals require knowledge of the lattice orientation of each mineral for optimal results.

Fluorescence mode spectroscopy is more flexible in terms of sample preparation, but transmission mode spectra can be acquired more quickly, making them optimal for studies where high count rates are needed. Transmission mode spectra can only be acquired on thin samples for which the 1/e sampling depth allows the beam to pass, but the optimal thickness for most minerals is comparable to the standard 30 µm thickness already widely in use, so this constraint does not pose a significant problem. Fluorescence mode measurements have the advantage of being able to work on any sample bigger than the focussed X-ray beam and thick enough to fluoresce Fe atoms (even in very low Fe samples), making them more conducive to the study of minerals in thin section. Both methods require control of grain orientation for optimum results. Accordingly, novel procedures for orienting mineral grains and preparing them for analysis are being developed.

Apatite from Durango (Mexico) – A potential standard for *in situ* trace element analysis of phosphates

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The trace element geochemistry of phosphates (e.g. apatite, monazite, and xenotime) determined *in situ* by modern microanalytical techniques (such like SIMS and LA-ICP-MS) is increasingly used for petrogenetic purposes. For example, the trace element signature of phosphates has been employed as a monitor of granite petrogenesis (including changes in porosity and permeability during crystallization), as an indicator for mineral exploration, and for geothermometric and geochronologic purposes. Therefore, the availability of a matrix-matched phosphate standard is highly desirable.

Apatite from Cerro de Mercado, Durango, Mexico, is widely used as an electron microprobe (EMPA) reference standard. A large body of major element data exists demonstrating sufficient homogeneity (1 to 5% RSD) at the 10 µm level. The Durango apatite might therefore have considerable potential as a suitable standard for trace element microanalysis of phosphates.

We will present the results of a detailed geochemical study that investigated the trace element homogeneity of a euhedral, highly transparent, and inclusion-free Durango apatite crystal. After crushing, an aliquot of this crystal has been analysed for the bulk trace element content by solution ICP-MS. The remaining splits have been analysed by various microanalytical techniques (EMPA, LA-ICP-MS, and SIMS) for their trace element homogeneity. Our results indicate that the investigated crystals are sufficiently homogeneous (2 to 8% RSD) on a 20 to 40 µm scale. Therefore, after careful geochemical characterization, individual gem-quality crystals of the Durango apatite might be useful as a much-needed standard for microanalysis of phosphates.

High-precision Sr, Nd, Pb and Hf isotopic characterization of USGS reference materials by MC-ICPMS and TIMS

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The Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia has undertaken a systematic analysis of the isotopic compositions (Nd, Sr, Hf, Pb) and concentrations of a broad compositional range of United States Geological Survey reference materials, including basalt (BCR-1, 2; BHVO-1, 2; BIR-1), dunite (DNC-1), andesite (AGV-1, 2), rhyolite (RGM-1, 2), syenite (STM-1, 2) and granite (G-2). USGS reference materials are geochemically well-characterized for trace and major element concentrations, but there is neither a systematic methodology nor a database for radiogenic isotopic analyses, even for the most widely used ones, such as BCR-1 or BHVO. The instrumentation at PCIGR, which includes a Nu MC-ICPMS, a Triton TIMS, and an Element2 HR-ICPMS, permits a rigorous assessment and comparison of precision and accuracy in isotopic analyses.

For each of the reference materials 5 to 10 complete replicate analyses provide very coherent isotopic results, all below 60 ppm (2SD) for Sr, Nd and Hf (27, 24 and 58 ppm respectively). The MC-ICPMS and TIMS Nd isotopic results agree for all composition types to better than 15 ppm. For Pb, the reproducibility is not as good. A careful sequential leaching experiment of three first and second generation reference materials (BCR-1&2, BHVO-1&2, AGV-1&2) indicates that the inhomogeneity in Pb isotopic compositions, and concentrations (as measured by both HR-ICPMS and isotope dilution), can be directly related to contamination by steel (mortar/pestle) used to process the materials. Contamination also accounts for the high concentration in some specific trace elements in various USGS reference materials.

Preparation of Korean granite reference material (KG1): Its homogeneity, major and rare earth element composition

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Reference materials play an important role in supporting measurements in the geological sciences. Particularly, granite reference material is very important in measuring chemical composition of crustal rocks. Since 1990, the Korea Institute of Geoscience and Mineral Resources (KIGAM) has prepared thirty six geochemical reference materials for the determination of major, minor (including rare earth elements). In this paper, we report mineralogy, homogeneity and chemical composition of a Korean granite reference material KG1. The KG1 is Cretaceous biotite granite, which occurs at Sokrisan area, the middle part of Korean peninsula. The granite consists of quartz, K-feldspar, plagioclase and biotite with accessory minerals such as chlorite, sphene, zircon and magnetite. A 500kg sample of starting material was collected from active granite quarry. In this paper, thirty eight major, minor and trace elements are presented to support future collaborative analysis. Particularly, 30 splits were selected at random, and analyzed in 5 samples by XRF in the Geochemical Analysis Center of KIGAM. We also measured intensity 5 times in a sample for homogeneity test. The homogeneity tests showed that all elements studied can be considered to be homogeneously distributed in 95% confidence. Following data compilation (Table 1), outlier rejection, and statistical analysis, proposed and indicative total element concentrations are reported for twenty five elements.

Table 1. Homogeneity test data

Element	XRF CPS Mean value (n=800)	Std. deviation
SiO ₂	128,011	470
Al ₂ O ₃	17,298	60
Fe ₂ O ₃	39,897	181
CaO	4,235	14
MgO	50	1
K ₂ O	50,764	124
Na ₂ O	619	12
TiO ₂	1,661	8
MnO	1,352	36
P ₂ O ₅	89	3

SMOW-scale for isotopic ratios of NBS-28 quartz and some other reference silicate minerals

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NBS-28 quartz is often used as a reference for reporting oxygen isotopic composition of silicates and oxides. Its oxygen isotopic ratio has been assigned to 9.58‰ with respect to VSMOW based on the compilation of literature values [1]. However, individually reported values range from 8.8 to 10.0‰. This variability arises from different ways of fluorination using conventional or laser heating method with BrF₅, ClF₃ or F₂ as a fluorination reagent. The choice of gas (CO₂ or O₂) for mass spectrometric measurement may also contribute to the variability. The VSMOW-SLAP scaling of the measured $\delta^{18}\text{O}$ values needs to be applied [1]. If oxygen isotopic ratio of CO₂ recovered from NBS-28 quartz is compared with that of CO₂ in equilibrium with VSMOW, the choice of variously reported fractionation factors between CO₂ and H₂O [2] affects the $\delta^{18}\text{O}$ value.

To minimize such potential uncertainties described above, we directly compared oxygen isotopic ratios of O₂, liberated from silicate minerals using a laser fluorination technique with BrF₅ as a reagent, with those of O₂ from VSMOW prepared using the same fluorination line after minor modification for water. The VSMOW-SLAP scaling was also taken into account. $\delta^{18}\text{O}$ values of NBS-28 quartz, NBS-30 biotite, UWG2 garnet [3] were 9.30‰ (n=13), 5.01‰ (n=7), and 5.72‰ (n=50), respectively. $\delta^{18}\text{O}$ values close to 9.3‰ have been obtained for NBS-28 quartz by those who used O₂ as an analytical gas. $\delta^{17}\text{O}$ values were also measured. The analytical precision was better than 0.1‰ for both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. The results plot on the terrestrial fractionation line defined as $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ [4].

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Standardless XRF analysis for LOI-rich rock samples by scatter fundamental parameter method

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X-ray fluorescence (XRF) spectrometry has been used for bulk rock analysis instead of AA and ICP due to easy sample preparation and the high precision capabilities. In addition, XRF is used as a screening tool prior to other analysis methods such as ICP-MS. In some cases it is difficult to prepare calibration samples because of availability. In this case a standardless analysis would be performed using a Fundamental Parameter (FP) routine. However, since the analysis results are usually calculated as a total concentration of 100% (normalized), components that are not analyzed, such as loss on ignition (LOI), would increase the analysis error. Therefore, it is necessary to obtain the values of these missing components for an accurate analysis.

In order to accurately analyze LOI-rich samples without the pre-determination of an LOI content, scatter lines derived from the characteristic lines of the x-ray tube have been used. This estimation of the LOI content in standardless analysis has been combined with a fundamental parameter (FP) method.

Using the Scatter FP Method in standardless analysis by XRF, it is possible to carry out accurate screening even for LOI-rich samples such as dolomite, limestone, clay and soil.

Table

NIST 88b Dolomitic Limestone		
Analysis result by non-standard FP method for dolomite (mass%)		
Element	Std. Value	Scatter FP
Mg	12.7	12.0
Al	0.18	0.34
Si	0.53	0.64
K	0.09	0.10
Ca	21.4	22
Mn	0.012	0.0139
Fe	0.19	0.21

Total sample evaporation of ng-sized Li samples using the Finnigan TRITON thermal ionization mass spectrometer in static mode

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Lithium isotope analysis using TIMS is very challenging and time-consuming. Although the TIMS technique is extremely sensitive, sample preparation and sample heat up are critical to the stability of the mass bias during the run and even more with respect to the attainable external reproducibility.

A completely different approach involves the total evaporation technique, in which the sample is completely evaporated during the run and the isotopic ratio is taken from the integral of both intensities accumulated during the whole run. In theory this should avoid problems with time-dependent mass fractionation. Previous TIMS instruments had a limited parallel mass range so that the measurement of Li isotopes had to be done by single collector peak jumping measurements. This was one of the reasons why the total evaporation method gave limited reproducibility. However, the multicollector of the Finnigan TRITON instrument has up to 17% mass range, enabling the parallel detection of both Li isotopes. In this study we will show the potential of the total evaporation method for Li isotope ratio measurements with respect to sample throughput and achievable external precision.

ELEMENT XR: Increased linear dynamic detection range sector field ICP-MS for geological applications

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With the Finnigan ELEMENT XR, Thermo Electron has introduced a new instrument specifically tailored for demanding geochemical applications. The detection system introduced in the ELEMENT XR consists of a dual mode, discrete dynode detector and a single faraday detector. This unique detection system provides the user with a linear dynamic range of over 12 orders of magnitude. This detection range allows the measurement of count rates from the very low 'background noise' of 0.2 cps to a maximum of more than 10^{12} cps. With the very high elemental sensitivities achievable with the ELEMENT XR ($\sim 2 \cdot 10^6$ cps per ng/g of a mid mass element, e.g. ^{59}Co), this count range corresponds to a measurable concentration range of sub fg/g (ppq) to over a 0.1% in solution mode.

With this extreme detectable range complimentary analysis techniques (e.g. AAS or ICP-AES) for the determination of major matrix elements can be replaced with a single instrument. Possible applications include:

- Determination of majors, traces and ultra-traces in survey analyses
- Use of the matrix element in laser ablation analysis:
 - Na in fluid inclusions.
 - Al in melt inclusions.
 - Ca in bone / corals / fish otoliths etc.
 - C in diamond analyses
- Concentration determination in minerals by laser ablation.
- Elemental ratios by laser ablation (e.g. Ca / Sr etc).

Mineral identification in basalts using automated mass spectral data analysis

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A newly developed technology, a Laser-Based Optical and Chemical Imager (LOCI) was used to analyze basalt samples collected from Idaho and from Hawaii [1-3]. Spatially-correlated spectra were obtained using a 2-dimensional raster protocol that used hundreds of individual laser-desorption mass spectrometric analyses to characterize $\sim 1 \text{ mm}^2$ of the heterogeneous surface. An automatic Fuzzy Logic Inference Engine (FLIE) was developed and used to identify mineral phases within the basalt geomatrices. The rule base in the FLIE is based on mineral standards and separates. Identifications are made on the basis of the major elements and the relative abundances found in standards and separates (e.g., plagioclase, olivine, augite). A statistical rule base generator (SRBG) was developed for *a priori* analyses and for situations in which mineral separates are not available. The rule bases in the SRBG are generated and unknowns identified by statistical pattern analysis of the LOCI mass spectra. Comparison of the standard-based and pattern-analysis approach showed a consistency among mineral identifications. When comparing the Idaho and Hawaii basalts it was found that the relative concentrations of individual mineral types varied. The two independent methods consistently show that the major minerals in Idaho basalts are olivine, augite and some Ti-enriched minerals such as ilmenite, while Hawaii basalts consist mainly of olivine.

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$\delta^{13}\text{C}$ of carbon dioxide in ancient air from ice core samples

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The concentration and stable carbon isotope composition ($\delta^{13}\text{CO}_2$) of carbon dioxide (CO_2) trapped in ancient ice are essential for the reconstruction of the paleo record of greenhouse gases, the study of the global carbon cycle, and the prediction of the future climatic evolution.

At present, high-resolution ice core $\delta^{13}\text{CO}_2$ data for larger time spans are scarce. New analytical methods are being developed with the objective to increase the time resolution (smaller sample size), to improve the accuracy of the measurements, and, particularly in clathrate ice, to optimize the extraction efficiency. The recent analytical improvements include different continuous flow setups (LGGE, University of Bern) and off-line extraction by sublimation (AWI). Thus obtained higher sensitivity to changes in the $\delta^{13}\text{CO}_2$ record is important in view of the small variations of few tens of a per mill observed in previous studies.

The ongoing measurements are performed primarily on ice from two Antarctic drilling sites, the EPICA Dome Concordia (EDC) and Dronning Maud Land (EDML). We will present the status of $\delta^{13}\text{CO}_2$ and associated CO_2 concentrations data from ice cores with a focus on the Holocene and the recent glacial–interglacial transitions, and discuss the available constraints that they provide on the global carbon system and its past variations.

The influence of extracellular enzyme and protein to organic matter degradation in Lake Erhai sediments

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Organic matter, extracellular enzyme and dissolved organic carbon (DOC), protein were determined in sediments and pore waters of Lake Erhai respectively. Lake Erhai is located in the northern Dali city of Yunnan Province. It is 42 km in length and 8.4 km in maximum width. The lake surface is about 1974 m above mean sea level and water area is 249.8 km².

Organic matter contents decrease with depth and reach relative low level in 6 cm. DOC concentration was downward from suspend layer to 5 cm. Lowest concentration was appeared from 5 cm to 8 cm in sediment pore waters. Organic matter was mainly degraded within 6 cm of upper layer sediments of Lake Erhai. The degradation of organic matter constitutes was influenced by extracellular enzymes. Activities of both α -glucosidase and β -glucosidase are highest in suspend layer. It indicates starch and cellulose etc was hydrolyzed largely. Enzyme activities decrease gradually with the sediment depth. Protein is a part of organic matter and easy to be decomposed. Protein contents decrease to a low level in 7 cm depth in pore water of sediments. Organic matter and protein have the same vertical variation trends in Lake Erhai sediments. Protein as a important constitute influence the variation of organic matter.

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Fe isotope geochemistry in coastal dune pore waters and associated seeps

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The biogeochemical reduction and oxidation of Fe-oxide minerals in Pleistocene and Holocene dune sheets of the Oregon (USA) coast play a important role in the hydrology and geotechnical stability of these sediments/soils. Understanding the processes that control the precipitation of iron-cemented horizons within these soils/sediments, as well as their subsequent dissolution and further transportation of soluble iron to coastal beach seep pools, is key to characterizing these systems.

We have measured the dissolved constituents present in pore waters collected from wells along a transect of the dunal soils. Additionally, we have used iron isotope fractionation to trace the movement of Fe through the different ecological pools within the coastal dunes. Our results are compared to current models of Fe cycling and isotope fractionation in nature (Johnson et al. 2004; Bullen et al. 2001).

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Microbial oxidation of arsenite in geothermal waters

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The release of arsenic from natural sources is recognized as a worldwide problem affecting subsurface drinking water aquifers in many regions. The predominant forms of arsenic in aqueous environments are arsenate and arsenite, with arsenite being more toxic and more mobile than arsenate. A variety of microorganisms have been found to oxidize arsenite or reduce arsenate, yet the biogeochemical cycling of arsenic is not well understood, particularly in geothermal environments where arsenite is often a common constituent of geothermal fluids. Although several recent studies described As(III) oxidation in acidic geothermal springs [1, 2], none have described As(III) oxidation in neutral geothermal springs (pH range 6.5-8). Microbial arsenite oxidation was investigated in geothermal springs within the Alvord Basin, OR, USA. Arsenic concentrations within the hot springs ranged in concentration from 1-6 mg/L [3]. The water/sediment interface of outflow channels from several springs with a source temperature of 80-90°C were analyzed for changes in temperature and As(III) concentrations as a function of distance from the source. Several springs exhibited a decrease in As(III) within a few meters of the source and one spring was further studied because As(III) concentrations decreased within the first 250cm. Samples were collected and used for culture enrichments of As(III) oxidizers and As(V) reducers. Several As(III) oxidizing microorganisms were obtained in pure culture and further characterized. Samples were also collected for analysis of microbial populations using molecular methods to discern the prevalence of the isolated As(III) oxidizers within the zones exhibiting decreased As(III) concentrations.

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Relationship between sediment and lavers isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and recent decline of biological productivity in Ariake Sea, Japan

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Possible cause for the decline of biological productivity in Ariake Sea was investigated using $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of a 50-cm long sediment core and harvested lavers. The overall analytical precision was $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ values and less than $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$ values. The core sample was categorized in three parts from the top toward the deep.

- I. 1986-2002, $\delta^{15}\text{N}$ of sediment showed increasing tendency (0.03‰ per year), which was accompanied by decrease in laver production.
- II. 1970-1985, $\delta^{15}\text{N}$ of sediment was relatively constant at $6.8 \pm 0.1\text{‰}$.
- III. 1950-1970, $\delta^{15}\text{N}$ fluctuated significantly.

The above vertical change could be related to decadal change in number of dam construction that might interrupt terrestrial nitrogen input to the Ariake Sea. Nitrogen depression tendency was also indicated by temporary change in $\delta^{15}\text{N}$ of edible lavers (*nori*) during *in situ* cultivation period.

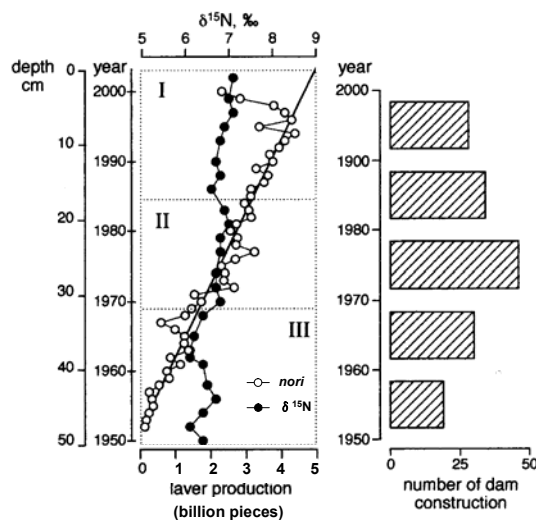


Figure 1 $\delta^{15}\text{N}$ of dated core sediment and annual *nori* production in Ariake Sea, and number of dam construction around Kyushu Island.