Growth rate effect on fractionation of elements and Li isotopes during calcite and aragonite growth

RINAT GABITOV
Department of Earth and Space Sciences, University of California, Los Angeles, Los Angeles CA 90095-1567 (gabitr@ucla.edu)

The interest in microscale distributions of elements and isotopes in calcium carbonate has increased in recent decades due to problems emerging from diverse disciplines such as paleoclimatology, paleoceanography, biomineralization, and geochemical cycling at the Earth’s surface. Naturally occurring and synthetic calcium carbonates are, in many cases, heterogeneous in trace or minor elements and stable isotopes. Often these variations cannot be explained by temperature variability or composition of the growth medium thus suggesting nonequilibrium crystal growth. Such disequilibrium is especially significant during growth of carbonate minerals under ambient conditions.

An experimental approach was employed to study the effects of mineral growth rate on the fractionation of $^{7}$Li/$^{6}$Li, Li/Ca, Mg/Ca, Sr/Ca, and U/Ca between Ca carbonates and fluid at 25°C. This work is unique because it evaluates linear mineral growth rates ($V$=distance/time), rather than bulk mass precipitation rates, through introducing chemical spikes as time markers during the experiment, and analyzing experimental carbonates in situ by secondary ion mass spectrometry (SIMS) and electron microprobe (EMP).

EMP data from this work show that partition coefficients of Sr between calcite and fluid ($K_{d}^{Sr}$=[Sr/Ca]mineral/[Sr/Ca]fluid) increase with $V$, extending the existed $K_{d}^{Sr}$-$V$ trend to the faster growth region [1, 2, 3]. $K_{d}^{Mg}$ and $K_{d}^{U}$ in aragonite increase with increasing of the growth rate of spherulite (hemispherical bundles of thin aragonite crystals) [4]. In contrast to calcite, $K_{d}^{Sr}$ in aragonite does not show significant correlation with $V$. The recent SIMS data on Li/Ca suggest that Li behaves similarly to Mg during aragonite growth. $^{7}$Li/$^{6}$Li yielded single sample variability that exceed those between two aragonite samples precipitated at different rates. Additional $^{7}$Li/$^{6}$Li, Li/Ca, and Li/Mg data will be presented.


Quantifying boron in natural type IIb blue diamonds

E. GAILLOU1*, D. ROST2, J.E. POST1 AND J.E. BUTLER3
1Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560, USA (gailloue@si.edu, postj@si.edu)
2The University of Manchester, SEAES, Oxford Rd., Manchester, M13 9PL, UK (detlef.rost@manchester.ac.uk)
3US Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, USA (james.butler@nrl.navy.mil)

Natural, type IIb blue diamonds are known to get their color from B impurities. Although many studies have reported B concentrations for laboratory doped diamonds (up to 1000 ppm; [1]), only a few values have been determined for natural diamonds. It is generally accepted, however, that the B concentration in natural diamonds is ~1 ppm [e.g. 2], which is a detection limit difficult to achieve for most analytical methods. More commonly, spectroscopic methods are used [3, 4] to obtain estimations of only the B that is not compensated in the structure by N. The goal of this study was to develop a direct and quasi non destructive method to measure total B concentration in what are typically high value blue diamonds, even in the most precious ones, such as the Hope diamond. For that purpose, B-implanted diamond standards were created, and several measurements on each of 8 natural, type IIb diamonds were acquired with a Time-of-Flight SIMS. Because of the high sensitivity of this method, a volume of sample only 50 x 50 µm wide and few nm deep was consumed for each analysis. The total B concentrations vary from 0.07 (±0.02) to 8.4 (±1.2) atomic ppm over all of the samples, and also appears to be heterogeneous within individual samples. These B values will be presented, and compared to results obtained by FTIR (i.e. total versus non-compensated B) and phosphorescence spectroscopy.

The origin of coloration in garnets: An optical spectroscopic study

L. GALOISY1*, J. FENEVROL2, A. JUHIN1, A. KIRATISIN3, G. GIULIANI2 AND G. CALAS1

1Institut de Minéralogie et de Physique des Milieux Condensés, Université Paris 6, Université Paris 7, IPGP, CNRS, 140, rue de Lourmel, 75015 Paris, France
(*)correspondence: galoisy@impmc.jussieu.fr)
2Centre de Recherches Pétrographiques et Géochimiques, CNRS, BP 20, 54501 Vandoeuvre lès Nancy, France. feneyrol@crpg.cnrs-nancy.fr)
3General Science Dept. Faculty of Sciences, Srinakharinwirot University, Sukhumvit 23, Wattana, Bangkok 10110, Thailand (amonmat@swu.ac.th)

Minor and trace elements provide important information about the formation conditions of minerals, although their location within the mineral structure has been often debated [1]. In addition, transition elements impart minerals and gems characteristic colors. A broad range of coloration in the same mineral group may arise from ions retaining the same oxidation state and substituted site, but experiencing variations in crystal field intensity. The recent evidence of a structural relaxation around octahedral Cr 3+ substituted in garnets and spinels demonstrates the role played by mineral chemistry in defining the actual crystal field responsible for the green or red color in these mineral groups [2, 3].

The color of garnets has been investigated in samples from Thailand and East Africa, the composition and homogeneity of which have been determined using electron microprobe analysis. The origin of color will be discussed at the light of optical spectroscopic data in the UV-visible-near IR range. The comparison with other Cr-containing minerals indicates the importance of the contribution of additional absorption bands arising from various transition elements (V 3+, Mn 2+, Fe 2+ and Fe 3+). By assigning the respective transitions observed, we will discuss the oxidation state, coordination number and relative concentration of these transition elements as a function of sample origin.


Geochemical and hydrocarbon generation differences of source rocks in diverse depositional settings in Biyang depression, Central China

H.J. GAN1,2, H. WANG1,2 AND J. CHEN3

1Faculty of Earth Resources, China University of Geosciences, Wuhan, 430074, China
(*correspondence: hjgan@cug.edu.cn)
2Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, China University of Geosciences, Wuhan 430074, China
3Jiangcheng College, China University of Geosciences, Wuhan, 430200, China

Biyang depression is a typical of terrestrial rifted basin with small area and extraordinarily rich reserves located in Zaoxiang Basin, Central China. The main hydrocarbon source rocks in the depression occur in the third member of Hetaoyuan Formation. The lithology of hydrocarbon source rocks in the lower member of the formation is mudstone and the Upper member contains abundant dolomitic mudstone. Based on the data of seismic, well logging, the previous geochemical results and experimental data, three styles of sedimentary facies in the member were recognized including fan-delta, braided-river delta and lacustrine facies in the deep zone of the depression. The content of Total Organic Carbon (TOC) in Lower member is lower than that of Upper member. Further researches showed that the higher content of TOC was distributed in the predelta and the distributed trends of TOC controlled by the sedimentary facies and the transported direction of provenance.

Two types of hydrocarbon source rock samples covered the mudstone and dolomitic mudstone were pyrolysed in open system under heating (300-700°C) conditions, and chemical compositions of its generated was measured online with a Rock-Eval Pyrolysis Instrument. A kinetic model for kerogen pyrolysis was established and extrapolated to the geological conditions. The kinetic parameter of petroleum generation shows that the activation energy of mudstone was lower than that of dolomitic mudstone, the generation time of mudstone is earlier than that of dolomitic mudstone in the same geological conditions. But when the two types of mudstone with similar content of TOC, the potential of hydrocarbon generation of dolomitic mudstone is better than that of mudstone. This new data has important information to revaluate the potential of hydrocarbon source rock and instruct the farther petroleum prospecting in the depression.
Nitrogen sources for new production in the NE Arabian Sea during winter

NAVEEN GANDHI¹, R.RAMESH¹, S. PRAKASH² AND S. KUMAR³

¹Physical Research Laboratory, Ahmedabad-9, INDIA
²Indian National Centre for Ocean Information Services, Hyderabad-55, INDIA
³Environmental Science Research Centre, St. Francis Xavier University, Nova Scotia, Canada

New productivity measurements using the 15N tracer technique were conducted in the north-eastern (NE) Arabian Sea during five expeditions from 2003 to 2007 in winter. Entrainment of NO₃⁻ which supports the observed nitrogen uptake has been quantified. Deepening of mixed layer below 100 m (from its inter-monsoon value between 30-40 m) transferred often more than 100 mmol N-NO₃⁻ m⁻² into the surface layers from below. The observed winter blooms in the region are supported by such input and are sustained for more than a month, as is also observed in satellite imagery. Higher new production and f-ratios have been found in late winter, whereas transport of NO₃⁻ is maximum in early winter. In general, new production and f-ratios vary progressively during winter.

Rethinking the organic sea spray function

BRETT GANTT AND NICHOLAS MESKHIDZE⁸

Department of Marine, Earth, and Atmospheric Science, North Carolina State University, Raleigh, NC 27695
⁸correspondence: nmeskhidze@ncsu.edu, bdgantt@ncsu.edu

As the study of climate change progresses, a need to separate the effects of natural and anthropogenic processes becomes essential in order to correctly forecast the future climate. Marine aerosols are particularly important as they contribute considerably to the global aerosol load, are emitted from a large area of the Earth’s surface, and can affect reflective properties and lifetime of marine stratiform clouds.

The marine primary organic aerosol emission function is explored using aerosol chemical composition observations from coastal stations in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and satellite-derived ocean and meteorological parameters. Multivariable regression analysis showed that the surface wind speed and dissolved organic carbon concentration are likely to be the key variables in determining the organic mass fraction of sea spray aerosols. Application of this new formulation to sea spray aerosols with aerodynamic diameter less than 2.5 µm gives an average marine primary organic emission of ~20.6 Tg C yr⁻¹. Low winds and high dissolved organic carbon concentrations (as opposed to productivity) enhance the organic fraction of sea spray in our formulation, resulting in relatively high emissions rates over ocean gyres (Figure 1). These results suggest widespread emissions of primary organic matter from the oceans that could potentially influence marine aerosol number/chemical composition and the microphysical properties of marine clouds, thus having a sizable impact on atmospheric radiative forcing and climate.

Figure 1: Predicted annual average marine primary organic emission rate in ng m⁻² s⁻¹.
Study of hydrogeochemical conditions of in situ leach uranium mining in the Shihongtan deposit

B. GAO*, H. ZENG AND Z.X. SUN

Laboratory of National Defence Key Discipline of Radioactive Geology and Exploration Techniques (East China Institute of Technology), Fuzhou, Jiangxi 344000, China (*correspondence: bgao@ecit.edu.cn)

In situ leaching (ISL) mining is in use commercially and offers many cost and environmental advantages in uranium extraction. The Shihongtan uranium deposit is one of the biggest sandstone-type uranium deposits in China, but the pilot acid and alkaline ISL mining of the deposit failed due to serious chemical plugging.

The water chemistry of groundwater in the ore-containing aquifer is given in Table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>21</td>
<td>2033</td>
<td>752</td>
<td>365</td>
<td>481</td>
<td>3150</td>
<td>3370</td>
</tr>
</tbody>
</table>

Table 1: Hydrochemistry of groundwater in the deposit (Concentrations in mg/L)

The groundwater is quite saline with TDS higher than 10 g/L. Geochemical simulations using PHREEQC show that the saturation index of CaSO₄ and CaCO₃ is higher than 0 in natural conditions. Gypsum will precipitate during the sulphuric acid leaching and calcite will be precipitate with the alkaline leaching. Both gypsum and calcite can cause plugging of pores of the host rock and result in failure of ISL mining.

The hydrogeochemical studies imply that sulphuric acid leaching or alkaline leaching is not suitable for the mining of the deposit. Therefore, ameliorating the hydrochemical conditions for uranium leaching is necessary. A new technique so called groundwater dilution-based with little reagent ISL uranium mining technology with four key techniques including dilution, oxidation, adding NH₄HCO₃ and acidification is proposed. The chemical plugging problem is solved by the new technology and the ISL mining in the high salinity groundwater area becomes feasible.

The study was supported by the projects of the National Natural Science Foundation of China (No. 40872165) and Science bureau of Jiangxi Province (No.2009AF00100).

Microgeochemistry of rutile and zircon in eclogites from the CCSD main hole: Implications for the fluid activity and thermo-history of the UHP metamorphism

CHANGGUI GAO¹*, YONGSHENG LIU¹² AND KEQING ZONG¹

¹State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, China (*correspondence: gaochanggui_1214@163.com)
²State Key Laboratory of Continental Dynamics, Northwest University, Xi’an 710068, China

Watson et al. [1] and Zack et al. [2] and Tomkins et al. [3] reported different temperature calculation by the Ti-in-zircon and Zr-in-rutile geothermometers. When we use these geothermometers to estimate the temperature evolution of UHP metamorphism at Dabie-Sulu eclogite, some special problems come out.

Both single spot and profile analyses of large matrix rutiles (> 60 µm) generally demonstrate core-rim variability of Pb, Sr, Zr and U. Estimated temperatures within the cores of matrix rutiles correlate positively with grain diameter. This suggests that the Zr content in rutiles is not only dependent on temperature and pressure, but is also affected by fluid activity and Zr diffusion. Estimated temperatures within the cores of matrix rutiles merely represent lower limits of the peak ultra-high pressure metamorphic temperatures.

Combined with Th/U and Ce/Lu ratios, rare earth element (REE) patterns and ²⁰⁶Pb/²³⁰U ages, Ti-in zircon geothermometers can be used to distinguish the thermal evolution of eclogites during the UHP metamorphism. (1) the inherited zircons record their crystallizing temperatures at the end stage of the original magma; and (2) metamorphic zircons may record both prograde and post-peak metamorphic temperature evolutions; (3) the traditional peak metamorphic zircons are probably not products of the peak UHP metamorphism, but instead crystallized during the post-peak metamorphism and record metamorphic temperatures subsequent to the pressure decrease. The much higher temperatures recorded by rutiles in samples adjacent to the ultramafic rocks and by zircons indicate that there may have been a locally short-lived heating event.

Formation and evolution of Hailaer basin, NE China: Constraints from zircon U-Pb geochronology of Mesozoic volcanic rocks

F.H. GAO, L. ZHAO AND Y.L. ZHANG

College of Earth Sciences, Jilin University, Changchun 130061, China (gaofh@jlu.edu.cn, zhaolei8502@126.com, zhangyl@jlu.edu.cn)

The Hailaer basin is located in the Ergun massif of the central Asian Orogenic belt between the North China Craton and the Siberian Craton. The Mesozoic strata including the Nantun Formation and Xing’anling Group contain a voluminous volcanic rocks in this basin. The formation timing of the strata and evolution of the basin are controversial issues due to lack of precise dating data. The volcanic rocks of the Nantun Formation are composed mainly of rhyolite whereas the Xing’anling Group consists chiefly of andesite and rhyolite. Six zircons from rhyolitic volcanic rocks in the Nantun Formation and Xing’anling Group display typical oscillatory zoning and have high Th/U ratios (0.50-2.44), suggesting their magmatic origin. LA-ICP-MS zircon U-Pb dating results indicate that weighted mean 206Pb/238U ages of zircons from six rhyolites in the Nantun Formation and Xing’anling Group range from 120Ma to 127Ma, representing the formation timing of the volcanic rocks, i.e. early Cretaceous. These early Cretaceous volcanic rocks chemically show bimodal volcanism. Combined with the existence of contemporaneous bimodal magmatism in the central Asian Orogenic belt [1], it is suggested that they formed under an extensional environment, which is corresponding for the faulting during the basin formation. Combined with the spatial variations of chemical compositions of the Early Cretaceous volcanic rocks in northeastern China [2], we conclude that the early Cretaceous volcanism in the Hailaer basin should be related to the subduction of the Paleo-pacific plate beneath the Eurasian continent.

This research was financially supported by research grant from the Natural Science Foundation of China (grant No. 90814003).


Mid-Eocene (42-44 Ma) melting of overthickened crustal materials in the Himalayan collisional belt

LI-E GAO*, LINGSEN ZENG1 AND KEJIA XIE3

1Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037 (*correspondence: liegao09@gmail.com)
2Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085

Within the Himalayan collisional belt, granotoids occur along two sub-parallel belts, the North Himalayan Gneiss Dome (NHGD) and the High Himalayan Crystalline Belt (HHC). In the Yardoi area of NHGD, a new type, two-mica granites occur in the core of the Yardoi gneiss dome (YGD), the Dala and Quedang plutons from north to south, and extends at least 50 km long. These granites have similar mineral composition, elemental and radiogenic isotope geochemistry, and age of formation [1, 2, 3]. SHRIMP zircon U/Pb dating indicates that the two-mica granites from the core of YGD and the Quedang formed at 42.6±1.1 Ma and 42.8±0.6 Ma, respectively, similar to those from the Dala pluton [4, 5]. These two-mica granites have (1) high SiO2 (>68 wt%), Al2O3 (>15 wt%), and A/CKN (>1.0); (2) relatively high Sr and LREE, but low Y (<10 ppm) and Yb (<1 ppm); (3) high Sr/Y (>40 and up to 250) and La/Yb (>30); (4) very weak or no Eu anomalies; and (5) low initial Sr (87Sr/86Sr (i)<0.7120) and unradiogenic Nd (69Nd (i)=-8.9~15.0) isotopic compositions, similar to those in the amphibolite but significantly different from those in the metapelite and granitic gneiss. Two-mica granites from the Yardoi area are of Na-rich peraluminous granite and have an adakite-like geochemistry. Such features are distinct from those in the younger leucogranites along the HHC as well as in the NHGD, and require melting of source consisting dominantly of amphibolite at overthickened conditions. This is also supported by the presence of amphibolites with similar Sr and Nd isotope compositions, and similar ages of metamorphism. Similar two-mica granites also occur in the other NHGD gneiss domes and along the HHC belt, implying that Mid-Eocene melting of overthickened crustal materials was widespread and the Tethyan Himalaya might have reached similar to or even higher elevations than the present-day High Himalaya.

Influence of water on D/H ratios of n-alkanes from hydrous pyrolysis of source rocks with kerogen types I, II, IIS and III

L. GAO1*, A. SCHIMMELMANN1, A.L. SESSIONS2, Y. WANG3 AND M. MASTALERZ4

1Department of Geological Sciences, Indiana University, Bloomington, IN, 47405-1405, USA
(*correspondence: lingao@indiana.edu)
2Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA
(als@gps.caltech.edu)
3Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA (ywang1@ciw.edu)
4Indiana Geological Survey, Indiana University, Bloomington, IN 47405-2208, USA (mmastale@indiana.edu)

Compound-specific D/H ratios of n-alkanes in soils and immature source rocks can be used to help constrain paleoenvironmental and paleoclimatic conditions. With increasing thermal maturity, however, the isotopic composition of primary biogenic n-alkanes can be altered both by isotopic exchange and the production of thermogenic n-alkanes via cracking of sedimentary organic matter. To investigate these effects, hydrous pyrolysis and supercritical heating experiments exposed four different immature source rocks with kerogen types I, II, IIS, and III to waters with differing D/H ratios at temperatures from 310 to 381°C for 12 to 144 hours. n-Alkanes from the artificially generated oils and waxes were extracted, purified, and measured to evaluate (i) the hydrogen isotopic influence of water hydrogen during cracking, and (ii) limits to the utility of n-alkane D/H ratios in petroleums and mature source rocks for paleoenvironmental studies. The use of differing D/H ratio waters helps us to distinguish between effects related to isotopic exchange versus those due to production of new n-alkanes.

The isotopic influence of water hydrogen on n-alkanes after heating source rocks to 330°C for 72 h decreased in the order of kerogen types IIS > II > I, similar to earlier findings on D/H of kerogens and bulk oils from the same source rocks. In general, longer-chain n-alkanes were more D-enriched than shorter-chain n-alkanes, but the relationship was not linear and featured many exceptions. With all other hydrous pyrolysis conditions being constant, longer heating resulted in increased n-alkane production and enhanced isotopic influence of water hydrogen. Similar effects were observed when reaction temperatures were raised from 310 to 381°C.

LA-ICP-MS U-Pb zircon geochronology and geochemistry of Hongliugou granite in the north Altyn Fault and its geological significance, China

XIAO-FENG GAO*, PEI-XI XIAO, LEI GUO, ZENG-CHAN DONG AND REN-GANG XI

Xi’an Center of Geological Survey (Xi’an Institute of Geology and Mineral Resource), CGS, Xi’an, Shaanxi 710054, China (*correspondence: xfgao2000@163.com)

Hongliugou granite pluton is located in the western segment of Hongliugo-Lapeiquan subduction collision complex zone in northern Altyn Tagh Mountains. The Hongliugou granite body is mainly made up of granite belonging to high-Na and calc-alkaline with SiO2 = 72.88% ~ 74.36%, Al2O3 = 12.71% ~ 14.34%, TiO2 = 0.20% ~ 0.25%, Na2O = 4.46% ~ 5.12%, K2O = 0.40% ~ 1.18%, CaO = 2.50% ~ 3.99% and A/CNK = 0.81-1.07. The LA-ICP-MS U-Pb age of zircons from granite is 512.2 ± 1.5Ma (MSWD = 0.77), which is the intrusive age of granitic magma (Figure 1). The characteristics of the granite are low contents of REE, strongly enriched and high-fractionated LREE (La/Srn = 5.19 ~ 6.44), relatively low-fractionated HREE (Gd/Ybnc = 1.12 ~ 1.30), slightly Eu negative anomalies, and Nb, Ta, P and Ti negative anomalies and Th, U and Yb positive anomalies. Furthermore, the granite samples are located at volcanic arc granite area (VAG) in trace discrimination diagram. All above indicate that the Hongliugou intrusions were formed in island arcs settings on the subduction zone, implying that the ocean-continent subduction took place in the area of Hongliugou-Lapeiquan during the middle Cambrian.

Figure 1: U-Pb concordia diagram of zircons of Hongliugou granite

This study was supported by the China Geological Survey project No. 1212010911025.
Multiphase solid inclusions in UHP eclogite from the Dabie orogen: Constraints on the nature of metamorphic fluid/melt during continental subduction-zone metamorphism

XIAO-YING GAO AND YONG-FEI ZHENG
School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China (gaoying@ustc.edu.cn)

There is growing evidence that multiphase solid (MS) inclusions preserved in UHP metamorphic minerals, such as garnet and omphacite, can derive from the trapped melts. This provides insights into the nature and composition of melt phases during subduction-zone metamorphism. Some MS inclusions may contain evidence for the existence of supercritical fluid in addition to hydrous silicate melts, enabling to recognize the mobility of trace elements in metamorphic fluid/melt.

Several types of MS inclusions were identified in garnet from UHP eclogite in association with UHP paragneiss at Shuanghe in the Dabie orogen, China. Chemical composition of the inclusions ranges from pure K-feldspar to pure quartz, with predominance of intermediate compositions composed of K-feldspar + quartz ± silicate (albite, plagioclase, or epidote) ± barite. Typical MS inclusions are usually surrounded with radial cracks in the garnet. LA-ICPMS in situ analyses of the MS inclusions and host garnet indicate strong enrichment of LILE, LREE and HFSE in the inclusions relative to the garnet, with significantly negative Ce anomalies in the inclusions. Barite shows significant heterogeneities in major element composition with total contents of only 50 to 70%, a negative correlation between BaO and SO₃ contents, and highly variable SiO₂ contents of 0.32 to 25.85% that are positively correlated with the BaO and SO₃ contents. These suggest the presence of microvoids and microcrystalline quartz in the barite and thus the occurrence of mixed silicate-sulfate melts in the UHP eclogite.

An integrated study of petrology, mineral chemistry and trace element geochemistry of the MS inclusions suggests that partial melting in the eclogite took place at the initial stage of exhumation but still in the coesite stability field. The partial melting was trigged by influx of aqueous fluid due to phengite decomposition. This results in the coexistence of hydrous silicate melts and aqueous fluids in the garnet under UHP conditions. Along with the consistent enrichment of LILE, REE and HFSE in the inclusions, the involved fluid is suggested to become supercritical at the peak UHP phase.

Bicarbonate competition in the desorption of arsenic species from sediments

X.B. GAO1,2, Q.H. HU2,*, Y.X. WANG1 AND X.G. LIU1
1School of Environmental Studies and MOE Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074 P. R. China (Xubo.gao.cug@gmail.com, YX.Wang@cug.edu.cn, Xgliu@cug.edu.cn)
2Department of Earth and Environmental Science, The University of Texas at Arlington, Arlington, TX 76010 (*correspondence: maxhu@uta.edu)

Release of arsenic from the sediments into groundwater may contribute to the elevation of arsenic content in groundwater, especially in the areas with abnormal high arsenic contents in the sediment, such as Bengal Delta (India), Inner Mongolia and Datong (northern China). This work studied the effect of bicarbonate on the desorption of four main arsenic species [As (III), As (V), DMA and MMA] in natural sediment samples (Faridspur surface soil from Bangladesh and sediment core samples DY 12 from Datong Basin) [1]. The desorption rate of four arsenic species was investigated while the bicarbonate concentration loading increased from 100 to 1, 500 mg/L in batch experiments. Bicarbonate concentration of 500 mg/L was selected in the column test based on field measurements of bicarbonate concentration in Datong Basin [2, 3]. The results indicate that even a low loading of bicarbonate of 100 mg/L can cause a relatively high release of total arsenic (about 10 µg/L) from sediments. Difference in the desorption extent of four arsenic species is also observed in the study.

Tracking CO₂ migration through a sandstone aquifer using Sr isotopes: Chimayó, New Mexico, USA

J.B. GARDINER¹,²*, B.W. STEWART¹,², R.C. CAPO¹,², J.A. HAKALA² and E.H. KEATING³

¹Dept. of Geology and Planetary Science, University of Pittsburgh, Pittsburgh PA 15260
 (*correspondence: jbg10@pitt.edu, bstewart@pitt.edu, rcapo@pitt.edu)
²National Energy Technology Lab, 626 Cochran’s Mill Rd., Pittsburgh, PA 15236 (jacqueline.hakala@netl.doe.gov)
³Earth & Environmental Sciences, Los Alamos National Labo, Los Alamos, NM 87545 (ekeating@lanl.gov)

The feasibility of storing CO₂ in geologic formations relies on our ability to understand the effects of high-CO₂ fluids on the storage formation and on impermeable seal rocks. Natural analogue sites provide an opportunity to observe effects of upwelling CO₂ on aquifer geochemistry. Wells in Chimayó, NM tap groundwater from the Upper Oligocene to Miocene Tesuque Formation of the Santa Fe Group, which is cut by faults that act as conduits for deeply sourced CO₂. Waters in the region can have elevated levels of dissolved CO₂, including a geysering well with 1.8 g/L CO₂.

Strontium isotope signatures of Chimayó well waters were used to track brine migration and quantify water-rock interactions. ⁸⁷Sr/⁸⁶Sr ratios range from 0.7176 for CO₂-charged brackish water (TDS up to 7,000 mg/L) to 0.7098 for low-TDS groundwater. Sr isotope compositions of sequentially extracted ammonium acetate and acetic acid leachates of unconsolidated and cemented Tesuque Formation lithosome samples indicate that most low-CO₂ Chimayó water chemistry can be explained by interaction with lithosome minerals. However, one high-PCO₂ well water has an ⁸⁷Sr/⁸⁶Sr of 0.7154, significantly higher than the lithosome leachates. Sr isotope mixing models indicate admixing of up to 5% of CO₂-charged brine, which could have migrated into the aquifer along the nearby Roberts Fault.

Two wells <150 m apart, located northwest of this fault, have similar ⁸⁷Sr/⁸⁶Sr ratios of 0.70979±2, significantly lower than the CO₂-brine value. However, these wells have very different CO₂ concentrations (0.3 vs. 1.3 g/L) and alkaline earth contents (0.8 vs. 45 ppm Ca). This suggests that a CO₂-resistant barrier divides the lithologically distinct unit tapped by these wells; leakage of CO₂ into one side could result in increased dissolution of carbonate cement. Strontium isotopes demonstrate that the influx of CO₂ into the aquifer in this case must have been completely decoupled from the deeper saline carrier waters observed at other sites.

Molecular simulations of the role of bridging oxygen on wet porous silica surfaces on proton transport

STEPHEN H. GAROFALINI* AND GLENN LOCKWOOD

Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ, 08855
 (*correspondence: shg@rutgers.edu)

Electrochemical studies have shown enhanced proton transport in mesoporous silica containing water. Achieving an accurate description of proton transport in such atomistically large and structurally complex systems requires application of dissociative potentials in molecular simulations. A dissociative water potential that matches many bulk water properties was applied to nanoconfined water, reproducing the change in thermal expansion of water confined in nanopores of silica, enabling a molecular explanation of the mechanism. The dissociative chemisorption of the water molecules on the silica surface show hydroxilation consistent with experiment and the enhancement of hydronium formation at these surfaces, similar to ab-initio molecular dynamics simulations. In addition to the formation of surface silanol (SiOH) sites, where protons are strongly bound, the simulations also show the location of weakly binding proton adsorption sites on the silica surface that contribute to enhanced proton transport beyond that observed in the nanoconfined water phase alone. These sites are on bridging oxygen (BO) with a Si-O-Si bond angle in the range similar to that obtained in molecular orbital (MO) calculations, providing an explanation of increased proton transport observed experimentally. Figure 1 shows the BO energy and the concentration of H on BO (BOH) vs Si-O-Si bond angle on silica surface exposed to water, with an energy minimum at angles similar to MO calculations at a maximum concentration of sites.
High-pressure hydrofracturing during deserpentinization

C.J. GARRIDO1*, J.A. Padrón-Navarta2, A. TOMMASI3, V. LÓPEZ SÁNCHEZ-VIZCAÍNO1,4, M.T. GÓMEZ-PUGNAIRE1,2, A. JABALOY5 AND A. VAUCHEZ3

1Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC & UGR, Facultad de Ciencias. 18002 Granada, Spain
2Dep. Mineralogía y Petrología, Universidad de Granada, Facultad de Ciencias, 18002 Granada, Spain
3Géosciences Montpellier, CNRS & Université Montpellier 2, F-34095 Montpellier cedex5, France
4Dep. Geología, Universidad de Jaén, Escuela Pol. Sup., Alfonso X, 23700, Linares, Spain
5Departamento de Geodinámica, Universidad de Granada, 18002 Granada, Spain

Volatile released from the dehydration reactions have to migrate across a relatively cold (<750°C), peridotite-layer above the incoming slab in subduction zones. To unravel the mechanisms allowing for this initial stage of fluid transport, we performed a detailed field and microstructural study of prograde peridotites in the Cerro del Almirez ultramafic massif (Betic Cordillera, Spain), produced during the HP antigorite breakdown (1.6-1.9 GPa & ~680°C) [1-2]. The metamorphic texture is partially obliterated by grain-size reduction zones (GSRZ), a few mm to meters wide, which form roughly planar conjugate structures characterized by (1) sharp, irregular shapes and abrupt terminations contacts with undeformed metaperidotite, (2) an important reduction of the olivine grain size (60-250 µm), and (3) decrease in the opx modal amount. Analysis of olivine crystal-preferred orientations in GSRZ shows similar patterns, but a higher dispersion than in neighboring metaperidotite. We propose that hydrofracturing is the main mechanism accounting for GSRZ supporting the substantial reduction of the opx modal content. Development of the GSRZ network was probably linked to the fluid release during atg-dehydration allowing for the formation of high permeability channelways for overpressured fluids. HP hydrofracturing may be an essential mechanism in the first stages of fluid flow through the coldest parts of top-slab mantle in subduction zones. The near-lithostatic pressure associated with this process produces transient low seismic velocities similar to those associated with episodic tremor and slip attenuation zones.


Monitoring of deep processes – The important part for understanding of a process of origin of hydrocarbons

NAKIP S. GATIATULLIN1 AND IRINA.N. PLOTNIKOVA2*

1Tatarstan Exploration Department TatNeft Petroleum Company, Kazan
2Kazan State University, Kazan (*correspondence: irena-2005@rambler.ru.)

The problem of an origin of oil should dare on the basis of complex use of geological, geochemical and geophysical data. Undoubtedly process of synthesis of oil is connected with deep processes which can be shown in a sedimentary cover in the form of modern geodynamic activity. Today, due to the use of up-to-date and high-precision exploration techniques including space geology, detailed seismic studies, geophysical dynamics studies, ultradeep drilling, geodesic instrumental surveys, etc. it has been found that active endogenous processes take place in the areas that were previously considered to be geodynamically inert, such as ancient platforms or shields.

The half-century history of petroleum production in the eastern portion of the East-European Platform provides strong evidence that the location of oil fields is closely related to the crystalline basement structure primarily, as a factor that governs the formation of the sedimentary cover structure and that the fault-and-block tectonics plays a leading role in these processes. A network of geo-observatories, as a multipurpose structure, could provide data on the deep strata of the Earth’s crust to be used both in fundamental studies and in applied research. The high-priority problems to be solved by geo-observatories are: 1). Petrographic, mineralogical and geochemical monitoring of the compositional evolution of loosely aggregated zones and their features. 2). Dynamic studies of physical fields in the deep strata of the Earth’s crust by conducting systematic measurements of various parameters. 3). Conducting periodic seismic-acoustic studies of the borehole environment. 4). Dynamic studies of the fluid regime in flow areas. 5). Analysis of seismic conditions in deep zones penetrated by boreholes. 6). Complex analysis and prediction of the hydrocarbon fluid regime in deep zones of the crystalline basement. Geo-observatories based on ultradeep wells have been created in many parts of the world including Russia (Kola Ultradeep Well SG-3), Germany (KTW ultradeep well) and Sweden (Silian well). Today, the Republic of Tatarstan offers adequate conditions for the development of regional geo-observatories.

A network of downhole geo-observatories can be created on the basis of the existing deep wells, among which the Novo-Yelkhovo-20009 well, that has reached a depth of 5881 m, plays the most important role. The creation of geo-observatories will require the use of the infrastructure in the Tatarstan's oil regions including power supply; traffic network; transport TRUNCATED.
The OIB signature in Central America: Old lithospheric and young asthenospheric mantle reservoirs

E. Gazel1*, M. Feigenson2, M.J. Carr2 and K. Hoernle3

1Lamont-Doherty Earth Observatory Columbia University, 61 Rt. 9W, Palisades, NY 10964
(*correspondence: egazel@ldeo.columbia.edu)
2Dept. of Earth and Planetary Sciences, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854-8066 USA
3IFM-GEOMAR Wischhofstr. 1-3 D-24148 Kiel, Germany

Although most Central American magmas have a depleted MORB-source mantle (fluxed by subduction-derived fluids), magmas in southern Central America have isotopic and trace element compositions with a Galapagos affinity. How Galapagos-influenced signature was introduced into the Central American mantle is at the heart of conflicting theories [e.g. 1, 2, 3]. Our new data for Costa Rica suggest that this signature has a relatively recent origin (~6 Ma) [4, 5]. REE inverse modelling [6] results indicate that garnet is not present in the distal back-arc region. In contrast, adakites from Central America, as well as volcanic front lavas and alkaline lavas from central Costa Rica (Fig. 1) and Panama, require garnet in the source. Garnet-present sources (<6 Ma) close to the volcanic front in Costa Rica and Panama suggest that the Galapagos-related reservoir can be either asthenospheric or recycled (subducting Galapagos tracks). The garnet-free source (>12 Ma) in the distal back-arc suggests that there is another enriched reservoir stored in the lithosphere, predating any recent subduction-generated or asthenospheric flow enrichment.

Minerals under attack: From ions to eukaryotes

S.A. Gazze12*, L. Saccone1, K.V. Ragnarsson2 and T.J. McMaster1

1H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK
(*correspondence: andrea.gazze@bristol.ac.uk)
2Institute of Earth Sciences, School of Engineering and Natural Sciences, University of Iceland, 101Reykjavik, Iceland

Atomic Force Microscopy (AFM) was used to visualize the effects of a wide range of weathering agents, from protons to filamentous fungi, on phyllosilicates. The effects of protons and oxalate on the basal and \{hk0\} surfaces of these minerals have been followed in real-time. On biotite, weathering process consisted in the retreat of \{hk0\} surfaces and in the formation of etch-pits on basal surface. For the first time, we have been able to follow the dynamics of the formation of etch-pits which consisted in a progressive removal of the first tetrahedral layer, followed by the octahedral and then the second tetrahedral sheet. The removal of the first tetrahedral layer takes place through the detachments of building blocks, suggesting that some Si-O-Si bonds are not broken. The presence of the underlying octahedral layers also implies that even if some cations could have been removed, this layer is relatively intact before the removal of the first tetrahedral sheet.

AFM have been also used to extensively characterize an ectomycorrhizal fungus, Paxillus involutus, colonizing mineral surfaces. Basal surfaces of both biotite and chlorite present channels created by the fungus. High-resolution imaging allowed us to detect channels that are only one basal layer deep (1.5 nm) and to identify non-mineral material, probably of fungal origin, associated with the channels. The latter often presented lateral, smaller channels. While the central part of hypha could be involved in the formation of the main channels, the lateral channels could participate to their enlargement.

Here we show how the direct visualization of mineral surfaces during weathering processes is fundamental in order to interpret the possible mechanisms involved in the process, both at atomic (protons on surface) and multicellular (fungi on surface) levels.
Molecular H₂O in microporous silicates: Thermodynamic and H-bonding behavior of confined H₂O

C.A. Geiger1*, E. Dachs1, M.C. Dalconi2 and G. Artioli2

1Universität Salzburg, A-5020 Salzburg, Austria
(*correspondence: chg@min.uni-kiel.de)
2Università degli Studi di Padova, I-35137 Padova, Italy

H₂O-bearing minerals provide an excellent starting point to investigate how the H₂O molecule interacts with natural crystalline materials. Many types of minerals contain H₂O and they interact with it in various ways. One general group of minerals, namely microporous silicates, offer the possibility to investigate the nature of hydrogen bonding and thermodynamic behavior, especially heat capacity, C_p, of confined H₂O at a relatively simple, yet fundamental level.

The microporous silicates armenite, BaCa₂Al₆Si₉O₃₀·2H₂O, and epididymite, Na₂Be₂Si₆O₁₅·H₂O, and their dehydrated analogs were studied by relaxation calorimetry between 5 and 300 K to determine the C_p behavior of their confined H₂O. DTA/TG measurements, FTIR spectroscopy, electron microprobe analysis and powder Rietveld refinements were undertaken to characterize the phases and the local environment around the H₂O molecule. The X-ray diffraction data show that armenite and its dehydrated analog have similar structures, whereas in the case of epididymite there are structural differences between the natural and dehydrated phases. The standard entropy for armenite is S° = 795.7 ± 6.2 J/(mol·K) and its dehydrated analog is S° = 737.0 ± 6.2 J/(mol·K). For epididymite S° = 425.7 ± 4.1 J/(mol·K) was obtained and its dehydrated analog has S° = 372.5 ± 5.0 J/mol·K. The entropy of dehydration at 298 K is 319.1 J/mol·K and 135.7 J/mol·K for armenite and epididymite, respectively. Of the three different H₂O phases ice, liquid water and steam, the C_p behavior of confined H₂O in both armenite and epididymite is most similar to that of ice.

Hydrogen-bonding behavior and its relation to the entropy of confined H₂O at 298 K was analyzed for various microporous silicates. The entropy of confined H₂O increases approximately linearly with increasing average wavenumber of the OH stretching vibrations. The interpretation is that decreased hydrogen-bonding strength between a H₂O molecule and the silicate framework, as well weak ion-dipole interactions and extra framework cations, results in increased entropy of H₂O. This results in larger amplitude external H₂O vibrations, especially the translations of the molecule, and they contribute most strongly to the entropy of confined H₂O at 298 K.

Stability analysis of a horizontal coalbed methane borehole in the San Juan Basin, USA

T. Gentzis*

Core Laboratories, 6316 Windfern Road, Houston, TX 77040, USA (*correspondence: thomas.gentzis@corelab.com)

Borehole stability analysis was conducted using STABView and FLAC geomechanical modeling for a horizontal coalbed methane well planned to be drilled in the San Juan Basin. The objective was to determine whether the coal seam at 3000 ft depth would yield under certain drilling and production conditions. Triaxial cell tests using 1-inch diameter core plugs were performed to construct the Mohr-Coulomb and Hoek-Brown failure envelopes. A reduction of the peak coal strength by approximately 30% was needed to correct the scale-dependent strength to a value believed to be representative of the a 4.75-inch diameter horizontal borehole. No yielding was predicted at underbalanced and overbalanced drilling conditions when the uncorrected M-C and H-B lab strength data were used in the models. A 30% reduction in peak strength predicted no yielding during overbalanced drilling, and only minor yielding during underbalanced drilling and during production. The maximum extend of the yielded zone at bottom-hole pressure of 100 psi predicted by STABView was 37% over gauge. FLAC simulations gave directionally similar but slightly more conservative results compared to SATView. A reasonable amount of yielding and subsequent detachment of the coal is expected along the horizontal well at the highest drawdown pressures. Stability analysis showed that drilling a horizontal well in Coal A in the location under study in an overbalanced mode would be possible. Drilling the same coal seam underbalanced will produce a rim of yielded coal but no catastrophic failure, provided that the coal seam is not highly fractured naturally.
Precise Re-Os age with exceptionally high $^{187}$Re/$^{188}$Os for black shales heralds Permo-Triassic extinction, Norwegian shelf and East Greenland

S. GEORGIEV$^{1,2}$, H. STEIN$^{1,2}$, J. HANNAH$^{1,2}$, B. BINGEN$^{1,2}$, G. XU$^{1,2}$ AND S. PIASECKI$^3$

$^1$Geological Survey of Norway, 7491 Trondheim, Norway
$^2$AIRIE, Colorado State Univ., Fort Collins, CO, USA
$^3$Geological Survey of Denmark and Greenland (GEUS)

The Permian-Triassic transition coincides with the largest mass extinction in Earth history. Understanding the causes that led to this biotic catastrophe requires detailed examination of bio/chemo stratigraphic changes pinned in absolute time. Here we report Re-Os data for well-defined black shale horizons in Upper Permian successions from the Mid-Norwegian shelf and East Greenland. These data provide (1) high-precision depositional ages; (2) constraints on the initial Os isotope ratio for Late Permian seawater; and (3) geochemical evidence for extraordinary paleoenvironmental conditions at the onset of the Permo-Triassic extinction.

A drill core penetrating a turbidite succession offshore mid-Norway provides three intervals of organic-rich shale. These intervals yield precise and indiscernable Re-Os isochrons at 252 Ma with MSWDs $\sim 1$. Accompanying well-determined initial $^{187}$Os/$^{188}$Os ratios of $\sim 0.6$ are distinctly less than Middle Triassic seawater [1]. Re concentrations increase dramatically upsection, whereas common Os concentrations vary little, resulting in a systematic increase of $^{187}$Re/$^{188}$Os approaching the Permian-Triassic boundary. Most of the shales have extraordinarily high $^{187}$Re/$^{188}$Os (ca. 2000 to 6000), compared to $^{187}$Re/$^{188}$Os ratios typical of black shales (ca. 1 to 600, and rarely $>1300$).

The second studied section from the Ravnefjeld black shales in East Greenland (drill core 303102) yields an identical age of $\sim 252$ Ma and also has exceptionally high $^{187}$Re/$^{188}$Os, affirming the proposed correlation between the shale intervals, now on both sides of the Norwegian Sea. These new data place a precise time pin in both sections and record catastrophic changes approaching the Permian-Triassic boundary. Experimental work suggests that high $^{187}$Re/$^{188}$Os in shales is achieved only under highly reducing conditions [2]. Thus, the remarkably high $^{187}$Re/$^{188}$Os ratios may indicate an unprecedented degree of basin anoxia.

Support: Petromaks (NFR 180015/S30), Statoil, Eni-Norge.


Identification of metacinnabar in mixed mercury, sulfide, and dissolved organic matter solutions through chromatographic concentration and EXAFS

CHASE GERBIG$^5$, JOSEPH RYAN$^1$, GEORGE AIKEN$^2$, CHRISTOPHER KIM$^3$, JOHN STEGEMEIER$^1$ AND JOHN MOREAU$^4$

$^1$University of Colorado at Boulder, Boulder, CO 80309, USA
$^2$United States Geological Society, Boulder, CO 80303, USA
$^3$Chapman University, Orange, CA 92866, USA
$^4$The University of Melbourne, Parkville, VIC 3010, Australia

Mercury speciation in environmental systems that contain mixtures of mercury, sulfide, and dissolved organic matter (DOM) has important ecological and human health ramifications. We have identified evidence of colloidal metacinnabar using synthetic systems with 10 or 50 mg L$^{-1}$ DOM, 100 µM total sulfide, and a range of mercury concentrations (350 pM to 1.4 µM). Solutions were run through a column of C$_18$ resin to concentrate hydrophobic mercury species in preparation for X-ray spectroscopy. Extended X-ray absorption fine structure (EXAFS) spectroscopy of the mercury on the resin indicates a mercury–sulfur bond distance of 2.52 Å, with approximately three sulfur atoms coordinating the mercury atom. The coordination number is lower than expected, but the Hg-S bond distance is consistent with metacinnabar. The bond distance does not match the sulfide-free mercury-DOM model that was also determined. These results are the first direct evidence of the presence of metacinnabar in systems that contain dissolved organic matter, sulfide, and relatively low mercury concentrations.
Experimental investigations on TSR in a mineral buffered system with fixed H\(_2\) and H\(_2\)S fugacities

S. GERMEROTT\(^1\)*, C. OSTERTAG-HENNING\(^2\) and H. BEHRENS\(^3\)

\(^1\)Institute of Mineralogy, Leibniz Univ. of Hanover, Germany
\(^2\)Federal Institute for Geosciences and Natural Resources, Hanover, Germany
\(^3\)Siberian Federal University, 660025 Krasnoyarsk, Russia

The importance of thermochemical sulfate reduction (TSR) has been recognized for petroleum reservoirs, e.g. the formation of sour gas provinces [1] or natural dry gas [1], as well as for sulfide ore deposits [2]. In spite of this importance, the process is not well understood and the extrapolation of many experimental results to natural systems is often questionable because key chemical variables, e.g. the H\(_2\) fugacity (fH\(_2\)), were not controlled at geologically reasonable values [3].

In this study experiments with synthetic n-octane, Na\(_2\)SO\(_4\) and H\(_2\)O as reactants were conducted in gold capsules at 300 and 350\(^\circ\)C, 350 bar for 24 to 336 h in order to elucidate fundamental mechanisms of TSR. Furthermore, the influence of elemental sulfur on the reaction rates and progress was investigated. The pyrite-phyrrhotite-magnetite (PPM) mineral assemblage was used to control the chemical environment, with respect to fH\(_2\) and fH\(_2\)S, at geologically reasonable values during the experiments. Gaseous and highly volatile organic compounds were measured by gas chromatography.

CO\(_2\) data, the C\(_1\)/CO\(_2\) ratio and the C\(_3\) to C\(_5\) distribution were used to identify TSR. Regarding the experiments with a run duration of 168 h, the experiment with n-octane, Na\(_2\)SO\(_4\) and H\(_2\)O at 300 \(^\circ\)C did not show evidence for TSR, whereas the same assemblage at 350 \(^\circ\)C clearly showed the effect of TSR. At both temperatures, the addition of elemental sulfur led to an enhanced oxidation of the hydrocarbons, which is clearly visible by significantly increased CO\(_2\) values and the formation of organosulfur compounds.

The results of this study are discussed with regard to possible reaction mechanisms and are compared to data provided by Seewald [3] who investigated the stability of different hydrocarbons in the PPM-water system.


Variability of Nd and Sr isotopes in alkaline rocks of the Polar Siberia: A consequence of plume-lithosphere matter mixing

I.F. GERTNER\(^1\)*, V.V. VRUBLEVSKY\(^1\), A.M. SAZONOV\(^2\), T.S. KRASNOVA\(^1\) and E.A. ZVYAGINA\(^2\)

\(^1\)Tomsk State University, Lenin avenu 36, 634050 Tomsk, Russia
\(^2\)Siberian Federal University, 660025 Krasnoyarsk, Russia

The Maymecha River basin in the Polar Siberia is a unique area where numerous alkaline ultramafic massifs are spatially and temporally confirmed to the flood tholeitic and alkaline volcanism. Their forming is usually connected with a rifting breakup of Siberian craton by a global action of Asian superplume at 250 \(\pm\) 3 Ma. Arndt et al. [1] proposed two plumbing systems to explain geochemical and isotopic features of rocks in this province. Our new and early-published data [1, 2] allow us to suggest any model of magmatism based on different degrees of mantle-crust interaction during the plume uplift.

The volcanic and plutonic sequences are characterized by the wide rock variety from tholeitic to alkaline series. The role of alkaline and ultramafic units is successively increasing in the upper (for the cross section) and central (to the Guli giant pluton) parts of the Maymecha region corresponding to the geophysical model of plume system uplift in lithosphere. The \(\varepsilon\)Nd vs \(\varepsilon\)Sr plot for the bulk rock composition demonstrates a tendency to increase \(\varepsilon\)Nd and to decrease \(\varepsilon\)Sr values from the bottom to up volcanic section and towards the Guli centre with a shorting of differentiation between isotopic parameters of tholeitic and alkaline rocks. The full coincidence of rocks compositions is corresponding to \(\varepsilon\)Nd (+5) and \(\varepsilon\)Sr (–15) values and is responsible to that of initial plume source type of PREMA. The obtained variation of Nd and Sr isotopic data in studied rocks can be explained by different degrees of lower (LC) or upper (UC) crust matter participation in the melting of plume with the proportion between LC and UC from 1:1 to 1:10. In this case we don’t need to assume few mantle sources for tholeitic and alkaline magmas so their isotopic parameters show a successive change of values according to their spatial position. It is more accompanied with a model of thermal interaction between hot mantle plume and continental crust of the Siberian craton.

The study was funded by RFBR (pr. 10-05-00377) and Ministry of Education and Science of Russia.

Advanced argillic alteration in Tarom zone, Central Alborz, Iran

A. GHASEMI1 AND B. TAGHIPOUR2

1Academic Center for Education, Culture and Research (ACECR), Esfahan University of Technology Branch, Esfahan, Iran (A_ghasemi@acecr.ac.ir)
2Department of earth sciences, faculty of sciences, Shiraz University, Shiraz, Iran (taghipour@shirazu.ac.ir)

Tarom area is a part of Central Alborz in north of Iran. Hydrothermal alteration processes are extensively took place on Eocene volcanic and pyroclastics rocks. Existence of deep fracturing and subvolcanic intrusions are enhanced extend hydrothermal alteration zones.

The following alteration zones are determined: propilitic, argillic, advanced argillic and sillicic. There are outcropped and widespread in different size and limit. Formation of siliceous sinter, silicified tuffs with preserved primary sedimentary layering including pure mineralized alunite patches are most outstanding. Quartz, sussoritic plagioclase, chlorite, sericite and alunite are main mineral constituents in the volcanics. On the basis of geochemical data volcanic rocks are rhyolite, dacite, andesite, andesitic-basalt and basalt in composition. Acid-sulfate zone is the most type of alteration in Tarom area and alunite is an index mineral of this zone.

In the past 40 years stable isotopes have been used extensively in the recognition and discrimination of various hydrothermal systems. As a result oxygen and sulfur isotope systematics from sulfur-bearing minerals in many ore deposits is well documented [1, 2]. In the present study the focus is on stable isotope geochemistry to determine various epithermal environments in Tarom area. Results of 18O, D and 34S stable isotope geochemistry on altered minerals (muscovite, kaolinite and alunite), revealed that advanced argillic alteration fluids are magmatic in origin.


Modeling of Index ratios and prioritization of the data mine

R. GHAVAMI-RIABI*, H. ALIZADE AND T. ASLAMKISH

Mining Dept., Shahrood Univ. of Tech.
(*correspondence: rghavami2@yahoo.com)

Modeling of the index ratios prioritization of data mine

In order to discriminate the high prioritization data for follow up exploration program, the modelling of the index ratios might be used as a method [1, 2]. Different common and advance statistical methods are used to identify the best index ratios. The threshold values for the ratio that separates the high potential areas must be determine based on the data modelling.

In a gold mineralized area, shear zone type, two ratios of Au/W and Au/Bi was modelled by the prob-plot software for separation of the anomalous values of these ratios [1]. The comparison of each ratio with Au values was led to a better understanding from the high potential values. The modelling of the data was also separated the anomalous trend from the background trend. Based on the two threshold values for each ratio, the first (mineralized areas) and second (geochemical halos) prioritize data were discriminated from the background values (Fig. 1).

Figure 1: High prioritized data related to the Au mineralization

Conclusion

Modeling of the indexes ratios is more confidential for prioritization of the high potential area.

Effects of arsenic-bearing deposits on groundwater resources along Zagros Orogen in Iran
Fereydon Ghazban* and Mojtaba Ardestani
Faculty of Environment, University of Tehran, Iran (*corresponding author: fghazban@yahoo.ca)

Recently, there has been an increasing concern over the toxicity of arsenic and its health effect caused by exposure to high levels in the geochemical environment. The risk to human health as a result of arsenic poisoning has been recognized in many countries including Iran. The common symptom of chronic arsenic poisoning including: hyperpigmentation, keratosi have been observed in many areas.

The source of arsenic is geochemical in nature, locked in many minerals, including Fe-oxides and sulfides. The main cause of elevated arsenic concentrations in many regions is Iran seems to be oxidation of sulfides from mining activity resulting in contamination of groundwater with subsequent detrimental health effects. The concentrations of arsenic reach levels of 100–1000 ppb in wells in mineralized areas.

The regions along in the NW to SE Iran have been the subject of arsenic poisoning. The arsenic contamination covers areas along the Zagros Orogen including; the Sanandaj-Sirjan tectonic zone and metallogenic setting of the Tertiary Urumieh-Dokhtar magmatic belt and its ore deposits, including porphyry copper and skarn deposits.

The ore deposits and metal producing mines in the district contain excessive amounts of arsenic and groundwater resources in these regions appear to contain very high levels of arsenic in the water. The arseniferous groundwater belts are mainly located in the Zagros Orogen.

Occurrences of mineralization tend to give rise to high concentrations of arsenic. Increased amounts of arsenic may be released into the groundwater over metalliferous mineralization because of the increased solubility of many ore minerals. Arsenic in the groundwater is quantitatively related to the release of arsenic that absorbed on the surface reactive Fe-oxides and hydroxides. Lowering the water table and allows the penetration of oxygen which oxidizes the sulfides and releases the arsenic into water.

LEPR 2.0
M.S. Ghiorso
OFM Research Inc., 7336 24th Ave NE, Seattle, WA 98115, USA (ghiorso@ofm-research.org)

LEPR (the Library of Experimental Phase Relations; [1]) is a web-portal (lepr.ofm-research.org) and search engine to a database of published experimental phase equilibrium data that documents liquid-fluid-solid phase relations in magmatic systems. In addition to information on the major element chemical compositions (including reported uncertainties) of all documented experimental run products, LEPR makes accessible data on run parameters (e.g. temperature, pressure, redox state) and experimental conditions (e.g. duration of the experiment, analysis procedures, experimental apparatus). LEPR is interoperable with the rock composition databases (NAVDAT, GEOROC, PetDB) of EarthChem [2], which permits cross-database searches to be performed that link experimental results to naturally occurring rocks.

In LEPR 2.0, the web-portal has been upgraded to allow privileged users to input their own experimental data or to augment the archive with additional published material. Unpublished user data are maintained as private sources that are only accessible to the user who entered these data (the data owner). In addition to providing a structured environment for storage of unpublished experimental data, the owner may edit, search, and analyze these data using LEPR interface tools; once data are published, it is a simple matter to move them into the public LEPR data archive. The goal is to provide a simple to use data storage and manipulation environment that will encourage experimentalists to use LEPR to maintain data prior to publication and make them cognizant of data and metadata standards. This workflow simplifies transfer of these data to the public archive once they are published.

User interface search tools in LEPR 2.0 have been upgraded and augmented to include filtering on derived compositional quantities such as CIPW normative components in both bulk and liquid compositions, common compositional indices (e.g. Mg # and alkali index), and cation concentration per formula unit in mineral run products. These upgrades have necessitated a major revision of the relational database schema. In addition, an extensive user-configurable plotting facility has been created and the search interface has been improved to streamline user interaction. An on-line help facility and tutorials are available.

**Structure and reactivity of hydrated goethite (100) interface and Arsenic sorption: CTR and RAXR study**

SANJIT K. GHOSE1, GLENN A. WAYCHUNAS2, PETER J. ENG3 AND THOMAS P. TRAINOR4

1NSLS II, Brookhaven National Laboratory, Upton, NY 11973, USA (*correspondence: sghose@bnl.gov)
2Earth Sciences Division, LBNL, Berkeley, CA 94720 USA (GAWaychunas@lbnl.gov)
3GSECARS, University of Chicago, Chicago, IL 60637 USA (eng@cars.uchicago.edu)
4Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, AK 99775 (fftpt@uaf.edu)

Goethite (α-FeOOH), an abundant and highly reactive iron oxyhydroxide mineral phase found in soils and sediments, plays an important role in many natural processes. The reactivity of the goethite surface depends on the types of exposed surface functional groups which are a function of the structure and composition of the bulk material, the orientation of the exposed surface, and the chemical history of the surface, along with the interfacial water/ionic species. Hence determination of the molecular structure of the hydrated goethite interface and the precise mode of binding of sorbed species is critical to developing a fundamental understanding of the chemical reactions that control the fate of contaminants in natural aquatic systems. We used crystal truncation rod (CTR) diffraction to investigate the interface structure of the hydrated goethite (100) surface under environmentally relevant conditions [1]. The interface was found to be terminated by a relaxed double hydroxyl layer over which two ordered water layers occur with specific hydrogen bonding to the hydroxyl layers. These results give new fundamental information on water and hydroxyl structure at a geochemical interface, and indicate how sorption processes might be affected by functional group and water structure variations. We further examined arsenate sorption on the goethite (100) surface using both CTR and Resonance Anomalous X-ray Reflectivity (RAXR) methods, which we will compliment and add to the structural analysis. Preliminary results will be presented on the structural analysis of arsenate sorption on goethite (100) surfaces. Arsenate sorption on goethite has particular relevance to many contamination sites including Taiwan and Bangladesh.

Rapid transformation of P across a podzol chronosequence in Northern Sweden

REINER GIESLER
Climate Impacts Research Centre, Department of Ecology and Environmental Science, Umeå University, 981 07 Abisko, Sweden (reiner.giesler@emg.umu.se)

Biological activity can accelerate soil processes and can thus have profound effects on weathering and the transformation of phosphorus (P). Here we show that the transformation of P is closely linked to soil development across an about 9000 years old soil chronosequence formed through glacial rebound. Easily weathered forms of P such as apatite are rapidly lost from the surface mineral horizon (within < 500 yrs) and these changes are coinciding with succession changes in the plant and microbial community structure. Long-term changes in P pools are, however, also dependent landscape topography. For instance, across a boreal landscape gradient, P concentrations increased dramatically in the surface soil of toe slope areas and decreased plant and microbial P availability [1, 2]. These differences are probably established already at early stages of soil formation.

Also environmental disturbances, such as wildfires can have profound effects on the distribution of P. In the absence of wildfires organic P will build-up at the surface of the mineral soil whereas regular wildfires promote losses of P [3]. Despite large differences in fire frequency (40 to 5, 300 yrs since last fire) only small differences in the distribution of P forms in the surface soil were found in a wildfire chronosequence [3]. Possible adaptations to temporal and spatial variations in the P distribution will be discussed further.


Changes in microbial community structure and activity during amendment with long-term electron donor sources for bioreduction of groundwater contaminants

T.M. GHIHRING1, C.W. SCHADT1*, G. ZHANG1, Z. YANG1, S. CARROLL1, K. LOWE1, T.L. MEILHORN1, P. JARDINE1, D. WATSON1, S.C. BROOKS1, W. WU1, J.E. KOSTKA1, W. OVERHOLT1, S.J. GREEN3, J. ZHOU4, P. ZHANG4 AND J. VON NOSTRAND4

1Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 (*correspondence: schadtcw@ornl.gov)
2Stanford University, Stanford, CA 94305
3Florida State University, Tallahassee, FL 32306
4University of Oklahoma, Norman, OK 73019

Long-term maintenance of reduced zones is considered a primary impediment to a biostimulation approach to uranium-contaminated groundwater remediation. Here we present an experiment exploring the use of slow-release substrates (SRS) to achieve longer periods of sustained U bioimmobilization. Objectives included tracking microbial populations as the subsurface manipulation zone transitioned through reduction and re-oxidation phases, correlating microbial and geochemical observations, and thereby improving predictions of the long-term effectiveness of remediation activities. SRS, consisting mainly of emulsified vegetable oil, was injected into a contaminant plume which was sampled for over 12 months. Prokaryotic communities were characterized using 16S rRNA gene pyrosequencing, and functional gene microarray and qPCR analyses.

The subsurface amendment of SRS resulted in sequential reduction of nitrate, Mn (IV), Fe (III), and sulfate over the first 20 d; soluble U concentrations decreased by >80% for up to 4 mo. and remained at <50% of original levels after >365 d. After 4 mo. gradual rebound of soluble sulfate, U, and nitrate in groundwater was observed. Members of the Anaerosinus and Desulforegula genera were identify as key taxa for performing initial oil degradation (triglyceride hydrolysis and long-chain fatty acid-oxidition, respectively) and providing a sustained source of labile electron donors (e.g. propionate, acetate, H2). Sulfate (Desulfuregula, Desulfovibrio) and iron (Geobacter) reducers predominated and presumably acted syntrophically to achieve long-term U reduction. H2-oxidizing, CO2-reducing methanogenic archaea flourished after other electron donors and acceptors were largely depleted, suggesting that reduced zones persisted during the overall subsurface re-oxidation.
Observing iron redox dynamics at the nanosecond scale with time-resolved X-ray spectroscopy

BENJAMIN GILBERT1, JORDAN KATZ1, HENGZHONG ZHANG2, JILL BANFIELD1,2, ROGER FALCONE1,3 AND GLENN WAYCHUNAS1

1Lawrence Berkeley National Laboratory (bgilbert@lbl.gov)
2Department of Earth & Planetary Sciences, University of California Berkeley, Berkeley, CA 94720
3Department of Physics, University of California Berkeley, Berkeley, CA 94720.

Redox processes at the surfaces of minerals drive crucial (bio)geochemical cycles. However, electron transport steps, structural rearrangement, and the formation of transition state complexes often occur too quickly for straightforward identification. Progress towards understanding rapid reaction steps will be aided by ultrafast X-ray science, an emerging field that will transform our understanding of molecular-scale processes in diverse disciplines, including geochemistry. This field requires the development of the technology and methodology to capture the molecular-scale steps in reactions of importance to environmental redox cycles.

Our work is focused on the reductive dissolution of iron oxide and oxyhydroxides, a central process in the biogeochemical cycling of iron. In this system, interfacial electron transfer leads to the formation of structural ferrous iron that may be released into solution or further react with adsorbed ions. We will describe the first ultrafast X-ray absorption studies of interfacial electron transfer to two crystal phases of iron oxide – ferrihydrite and maghemite. We have demonstrated that the binding of photoactive dye molecules to iron oxide nanoparticles permits reduction of Fe (III) in the oxide to be initiated by optical excitation of the dye. Iron redox dynamics were followed by time-resolved X-ray absorption spectroscopy (TR-XAS) at the Fe K-edge, using the pump-probe approach to observe the rate of formation and evolution of ferrous iron. Transient XAS spectroscopy at specific timepoints after electron transfer provide insight into the electronic structure and coordination of the transient Fe (II) species. This work represents the first studies of the nanosecond dynamics and eventual fate of ferrous iron sites formed in an iron oxide.

The development of a nickel sulphide standard for the in situ analysis of platinum group elements and gold by Laser Ablation ICP-MS

S.E. GILBERT1*, L. DANYUSHEVSKY1, P. ROBINSON1, C. WOHLGEMUTH-ÜBERWASSER2, M. NORMAN3, J. HANLEY4 AND N. PEARSON5

1CODES, University of Tasmania, Hobart, 7001, Australia (*correspondence: sgilbert@utas.edu.au)
2University of Bonn, Bonn, 53115, Germany
3ANU, Canberra, ACT, 0200, Australia
4St. Mary’s University, Halifax, NS, B3H3C3, Canada
5GEMOC, Macquarie University, NSW, 2109, Australia

A new LA-ICPMS SRM has been developed, which contains the platinum group elements and Au. The standard NiS3 was made from high purity Ni and S powders which were spiked with a solution containing Ru, Rh, Pd, Os, Ir, Pt and Au, aiming at a concentration of ~25 ppm for each element in the SRM. The mix was dried at 105 °C and subsequently fused with Na2CO3 at 1000 °C for 1.75 hours, yielding a 5 g NiS button. The button was cut, and a polished portion was examined by optical microscope and electron microprobe and determined to be a single phase nickel sulphide (Ni3S2). Quantification was performed on four, 100 mg powdered portions of the button, which were digested in aqua regia. To retain Os in solution, the portions were digested in closed vessels and the acid was not evaporated. Solutions were then diluted to 1000x immediately prior to analysis on an Agilent 7700x ICP-MS. Matrix effects were corrected for by analysing a pure pyrite sample solution spiked with similar amounts of PGEs and Au. The concentrations of the PGEs and Au were determined to be 21-24 ppm. Homogeneity of NiS3 was assessed on 15 randomly selected, 100 micron diameter LA-ICP-MS spot analyses with a New Wave UP213, yielding 1 sigma %RSDs of <4 % for Ru, Os and Ir; <8 % for Rh and Pt and ~15 % for Pd and Au. NiS3 has also been assessed against a number of other PGE and Au SRMs including 8b [1], PGE-A [2], Lombard meteorite and Po41 [3]. The analyses of these SRMs have been compared and the problems with internal consistency of the reference values will also be discussed.

Biogenic methane potential for Surat Basin, Queensland coal seams

P.C. GILCREASE1*, S.L. PAPENDICK1, K.R. DOWNS1, P. MASSAROTTO2 AND S.D. GOLDING3

1Chemical & Biological Engineering, South Dakota School of Mines & Technology, Rapid City, SD 57701, USA  
2Chemical Engineering, University of Queensland, St. Lucia, QLD 4067, Australia  
3Earth Sciences, University of Queensland, St. Lucia, QLD 4072, Australia

Real-time Biogenic Methane Potential

Produced water samples collected from Surat Basin coal seams in eastern Queensland, Australia were shown to contain viable microbial consortia. Consortia from all eight of the wells sampled demonstrated the ability to produce new methane when native Wallon coal was provided as the sole organic carbon source. Methane generation rates of up to 0.9 m^3/tonne/day were observed, with overall yields up to 6 m^3/tonne coal. In comparison, total methane reserves for the Surat Basin are typically 4 to 8 m^3/tonne. These rates are comparable to the 0.1-0.5 m^3 methane/tonne/day observed for Powder River Basin enrichment cultures [1]. This is the first direct evidence of real-time biogenic coal-to-methane potential for an Australian coal seam sample; Li et al. [2] found that Archaea were rare or absent in samples taken from the Sydney, Surat and Port Phillip Basins. Midgley et al. [3] detected methanogens in a Gippsland Basin sample, but the consortia did not produce methane from a non-native coal.

Pathway and Bioavailability Results

Six of the eight Surat Basin water samples tested positive for biomethane production when H_2-CO_2 was provided as the sole methanogenic substrate. An active H_2-CO_2 pathway could be promising for the conversion of sequestered CO_2, if an in situ source of reduced hydrogen is present in excess. In an initial laboratory study, biomethane production from a Wallon coal was not enhanced when the bicarbonate concentration in the medium was doubled.

It is anticipated that the low surface area/solubility of coals may limit their biological conversion to methane. When a Zonyl FSN-100 surfactant was added to a Wallon coal culture, the initial methane production rate increased by 240%, and the final methane yield increased by 180% in comparison to a no surfactant control.


He and Ne as tracers of natural CO_2 migration from a deep reservoir

STUART GILFILLAN1*, MARK WILKINSON, R. STUART HASZELDINE, STEPHEN NELSON2 AND ROBERT POREDA3

1Scottish Centre for Carbon Storage, University of Edinburgh, UK (*correspondence: stuart.gilfillan@ed.ac.uk)  
2Department of Geological Sciences, Brigham Young University, Utah, USA  
3Department of Earth and Environmental Sciences, University of Rochester, New York, USA

Capture and geological storage of CO_2 is emerging as an attractive means of economically abating anthropogenic CO_2 emissions from large point sources. However, for the technology to be universally deployed it is imperative that a reliable method to assess the integrity of a storage site for both safety and regulation compliance exists. Hence, the ability to track, and identify the origin of, any CO_2 seepage measured at the near-surface and ground surface is critical.

As an analogue for post-emplacement seepage, this presentation will examine natural CO_2 rich springs and groundwater wells in the vicinity of the St. Johns Dome CO_2 reservoir, located on the southern tip of the Colorado Plateau on the border of Arizona and New Mexico. Extensive travertine deposits in the vicinity of St. Johns document a long history of the migration of CO_2 rich fluids to the surface. Whilst travertine formation appears to be insignificant at present, there is strong evidence of the migration of CO_2 rich fluids to the surface as shown by high levels of HCO_3^- in the surface spring waters.

 Noble gases are conservative tracers within the subsurface, and combined with carbon stable isotopes, have proved to be extremely useful in determining both the origin of CO_2 and how the CO_2 is stored within natural CO_2 reservoirs from around the world including St. Johns Dome [1, 2]. This presentation will compare measurements of the dissolved 3He/4He, CO_2/3He, 3He, 4He and 20Ne concentrations from surface spring and groundwater well waters with those from the deep CO_2 reservoir. We show that a component of the helium fingerprint observed in the gaseous CO_2 contained in the St. Johns reservoir can be traced in waters from both the groundwater wells and the springs emerging at the surface above the reservoir. Our results show that CO_2 can be traced from source to surface using noble gases and illustrates that this technique could be used to identify CO_2 migration from engineered storage sites.

From sea to lake, the geochemical history of Lake Champlain, North America

W.P. GILHOOLY III1*, A. ROBINSON1, T.W. LYONS1, P. MANLEY2, T. CRONIN3, T. MANLEY2 AND C. KELLEY4
1Dept. of Earth Sciences, Univ. of California, Riverside, Riverside, CA 92521, USA
(*correspondence: williamburg@ucr.edu)
2Dept. of Geology, Middlebury College, Middlebury, VT 05753, USA (manley@middlebury.edu)
3USGS, Reston, VA 20192, USA (tcronin@usgs.gov)
4Dept. of Geological Sciences, Univ. of Missouri-Columbia, Columbia, MO 65211, USA (kelleyc@missouri.edu)

The Lake Champlain region (NY and VT) experienced a transition from freshwater to marine to freshwater deposition as a consequence of post-glacial sea level rise and isostacy. Here we focus on the marine stage known as the Champlain Sea as it developed into the modern freshwater Lake Champlain approximately 9 kyr ago. The marine-lake transition offers the unique constraint of two well-established endmember environments that include modern marine conditions (with sulfate of known concentration and isotopic composition) and a large (1100 km²) freshwater lake. These transitions yielded juxtapositions of chemical conditions that could favor biological hotspots associated with sulfate reduction and methanogenesis. Collectively, these gradients provide an ideal opportunity to define and refine geochemical proxies for marine and nonmarine conditions, including the complications and novel chemical fingerprints of secondary overprints associated with dramatic variations in depositional conditions.

Several lines of evidence support the transition from marine to freshwater deposition. Coupled with changes in physical properties and microfossil abundances are pronounced geochemical constraints, including a shift from a carbonate-rich marine stage to a carbonate-lean lacustrine stage and a prominent maximum in pyrite concentration at the depositional contact. The chemical record within the environmental switch has the potential for an interesting biogeochemical interface between methane charged lake sediment ([CH₄] upwards of 1.5 mM) overlying marine porewater sulfate. We continue to explore the signals of redox sensitive metals (e.g. Mo and Fe) coupled with provenance indicators (Al/Ti) to fully develop and refine geochemical indices of marine/nonmarine deposition.

Spectro-microscopy of carbonaceous particulates

MARY K. GILLES, 1* R.C. MOFFET,2 AND A. LASKIN3
1Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 2-315, Berkeley Ca, 94705 (*correspondence: mkgilles@lbl.gov)
2Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 2-319 Berkeley Ca, 94705 (rmoffet@lbl.gov)
3William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, MSIN K8-88, Richland, Wa 99352 (Alexander.Laskin@pnl.gov)

Combining multiple spectro-microscopic techniques can provide detailed information on morphology, elemental analysis, and chemical bonding. We combine complementary spectro-microscopic techniques such as scanning transmission X-ray microscopy, capable of performing near edge X-ray fine structure micro-spectroscopy, (STXM/NEXAFS), and computer controlled scanning electron microscopy coupled with an energy dispersive X-ray analyzer (CCSEM/EDX). Results are presented on the chemical analysis of individual atmospheric aerosol particles collected at urban and rural sampling sites during the Mexico City MILAGRO 2006 field study. Physical and chemical transformations of particles aged in the outflow from Mexico City were investigated. Our results show that as the aerosol plume evolves from the city center, the organic mass per particle increases and the fraction of carbon-carbon double bonds, associated mostly with elemental carbon, decreases. At the city center the most prevalent aerosol types had substantial inorganic phases containing S, N, O and K and were coated with organic material. As the aerosols travelled further from the city center, the fraction of homogenously mixed organic particles increased. These observations demonstrate the unique evolution of physicochemical mixing state and organic bonding in individual particles as they age in a photochemically active environment.

These complementary methods also provide chemical speciation on metals in sub-micron particles and serve as a further example of the strength of combining multiple micro-spectroscopic methods when examining environmental samples.

Atmospheric evolution of terrestrial planets constrained by isotopic data: The effects of degassing on Mars

C. Gillmann1*, P. Lognonne3, E. Chassefiere2 and M. Moreira3

1IPGP, GSP, UMR 7154, 94100, Saint Maur des Fossés, France (*correspondence: gillmann@ipgp.fr)
2CNRS/INSU, LATMOS-IPSL, UPMC Univ. Paris 06, 75005 Paris, France (eric.chassefiere@aero.jussieu.fr)
3IPGP, 75252 Paris cedex 05, France

In order to study the long term evolution of the surface condition of terrestrial planets we need to understand the interactions between inner mechanics and atmospheric history. Here we propose an example of such interaction leading to scenarios for the evolution of the Martian atmosphere we constrain with isotopic ratio data for noble gases.

We model the past state of the Martian atmosphere with a balance between atmospheric loss through escape by non-thermal processes and volatile input by degassing through volcanism. CO2 is our main subject of study considering it represents the bulk of present and, probably, past atmosphere on Mars. The atmospheric escape model is based on the decreasing Extreme UV flux over the history of Mars and on Mars. The atmospheric escape model is based on the ASPERA instrument. Degassing is estimated from crust production rate models ([1][2][3]) and possible volatile contents of the melted material. It is also confronted to present day observation of the surface of Mars.

Our results show that an eruption rate of 0.01 km3/y would be needed for the atmospheric CO2 to be at equilibrium in the present-day situation. We also show that after the early heavy loss of primordial atmosphere during the first billion year, the atmospheric CO2 pressure variations are relatively small. It is highly unlikely Mars has supported a thick (~1 bar or more) atmosphere during the last few billion years. However periods of higher pressures (like three billion years ago) correspond to the occurrence of fluvial landforms [4]. We also suggest that the present-day Martian atmosphere is composed of a large part of volatiles of volcanic origin and is quite young with possible ages ranging from 1.25 to 1.75 billion years. We finally study the history of water and the evolution of isotopic ratios of C, N and Ar.


The sulfate-reducing bacterium Desulfovibrio desulfuricans ND132 as a model for understanding bacterial mercury methylation

C.C. Gilmour1*, D.A. Elias2, A. Kucken3, S.D. Brown2, A.V. Palumbo2 and J.D. Wall3,

1Smithsonian Environmental Research Center, Edgewater, MD 21037 USA (*correspondence gilmourc@si.edu)
2Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA
3University of Missouri, Department of Biochemistry, Columbia, MO 65211 USA

We propose the use of Desulfovibrio sp. ND132 as a model species for understanding the genetics and biochemistry of microbial Hg methylation. ND132 is a dissimilatory sulfate-reducing bacterium (DSRB) that exhibits exceptionally high rates of Hg methylation in culture, but is otherwise a characteristically typical Desulfovibrio strain. The full genome sequence of ND132 will be available soon. ND132 is very similar to other DSRB that are sequenced but do not methylate Hg, allowing comparison for potential methylation genes. Here, we describe the physiological characteristics of the strain, examine its MeHg production capability, and place the strain within the phylogeny of the Desulfovibriionales using 16S rRNA. We also examine Hg toxicity and the inducibility of MeHg production amongst the DSRB by comparing ND132 to non-methylating DSRB.

The optimal growth medium for Hg methylation is pyruvate/fumarate, which supports strong respiratory growth without sulfide production. At moderate Hg concentrations (10 ng/ml), and using TiNTA as a reductant, ND132 methylates about 30% of added HgCl2 during batch culture growth on 40 mM pyruvate/fumarate. Under constant culture conditions, MeHg production is an exponential function of Hg concentration, probably reflecting Hg partitioning between aqueous and solid phases. To help understand how Hg is taken up by this organism, we examined the influence of a variety of small thiol-bearing ligands, as well as select amino acids, on MeHg production amongst the DSRB by comparing ND132 to non-methylating DSRB.

To identify enzymes for the methylation activity, a genetic approach is being pursued. Conjugation from E. coli donors works well that allows the generation of a transposon library of random ND132 mutants. These mutants will be screened for affects on mercury methylation.
The effect of redox cycles on the partitioning of Fe, C, and P within soil systems

BRIAN R. GINN, CHRISTOF MEILE, MICHELLE M. SCHERER AND AARON THOMPSON

1311 Miller Plant Sciences Building, University of Georgia, Athens, GA 30602 (bginn3@gmail.com, AaronT@uga.edu)
2Marine Sciences Building University of Georgia, Athens, GA 30602 (cmeile@uga.edu)
34105 Seamans Center Iowa City, IA 52242, michelle-scherer@uiowa.edu

Developing a quantitative understanding of the coupled cycling of Fe, C, and P in soil systems can lead to better land management practices for both agriculture and forestry systems. The biogeochemical cycles of C and P are known to be coupled through sorption and co-precipitation of iron-oxide minerals, and through valence-state transitions of C and Fe. The reduction of iron-oxides to aqueous Fe(II) can lead to the release of sorbed phosphate and organic compounds which can then migrate to different reservoirs within the soil system. Re-oxidation of aqueous Fe(II) to insoluble iron-oxides may result in further repartitioning of the soil system as phosphate and organic carbon sorb onto the newly formed minerals. Thus, oscillating redox conditions promote dynamic redistribution of Fe, C, and P within the soil.

To quantify the importance of redox oscillation on Fe, C and P distribution, retention and – in the case of iron oxide – reactivity in soils, we have constructed controlled atmospheric chambers (CAC) that allow precise dynamic manipulation of soil redox conditions. These chambers are situated within an larger anoxic chamber allowing for the sample extraction under strict anoxic conditions. We exposed soils from a lowland site within the Luquillo National Forest, Puerto Rico, to redox oscillations of two frequencies for several months. We will present results from sequential extractions targeting different Fe, P and C pools, XRD and Mossbauer mineral composition data, and a preliminary model quantitatively describing reductive and oxidative iron cycling.

Chalcophile elements in peridotites as a proxy for sulfide mineralization during serpentinization

C. GIONFRIDDO, M. BIZIMIS, I. SEN AND V. SALTERS

1Dept. of Chemistry, Univ. of South Carolina, Columbia, SC 29208, USA (gionfrid@email.sc.edu)
2Dept. of Earth and Ocean Sciences, Univ. of South Carolina, Columbia, SC 29208, USA (mbizimis@geol.sc.edu)
3Dept. of Earth Sciences, Florida International Univ., Miami, FL, USA (isen001@fiu.edu)
4NHMFL and Dept. of Geological Sciences, Florida State Univ. Tallahassee, FL, USA (salters@magnet.fsu.edu)

Petrographic observations in serpentinized abyssal peridotites [1] show evidence for sulfide mobilization / recrystallization during hydrothermal alteration, while thermodynamic modelling suggests that sulfide, Fe-Ni-O-S, systematics may be a useful indicator of T, fO2, fS2 for hydrothermal systems [2]. Chalcophile element concentrations (e.g. Cu, Zn, Pb) in peridotites may then reflect the processes of sulfide precipitation / desulfurization during serpentinization. We present preliminary trace element data on bulk-rock serpentinized abyssal peridotite and fresh Hawaiian peridotites with a focus on chalchophile elements, to investigate the effects of sulfide precipitation in the mantle. Our results show that Cu concentrations in abyssal peridotites are extremely variable (x10), and extend to significantly higher concentrations than the Hawaiian peridotites. Copper, and to a lesser extent Zn, are entirely decoupled from any lithophile element (Ti, Zr, REE), indicators of melt depletion and refertilization in both the serpentinized and fresh peridotites. Petrographic and EPMA investigation showed a much greater modal abundance of sulfides in the abyssal vs. Hawaiian peridotites, with abyssal sulfides being dominantly petlandites with often Cu-rich lamellae. We suggest that the high Cu contents in abyssal peridotites likely result from sulfide precipitation during serpentinization, and bulk rock Cu contents may be a proxy for the abundance of chalcopyrite (CuFeS2) in peridotites.

Evidence for seismicity influencing deep sea primary productivity: A year-long study of microbial processes at the Juan de Fuca ridge using biological osmotic samplers

PETER GIRGUIS1, JULIE ROBIDART2, GEOFFREY WHEAT3 AND KIANA FRANK1

1Harvard University, 16 Divinity Avenue Room 3085, Cambridge, MA 02138
(*correspondence: correspondence: pgirguis@oeb.harvard.edu)
2University of California Santa Cruz, Ocean Sciences Department, 1156 High Street, Santa Cruz, CA 95064
3Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039

Hydrothermal vents host some of the most productive ecosystems on Earth. Hydrothermal fluid flow provides reductants to support chemoautotrophic activity, though the relationship between geochemical composition and microbial activity in these systems is poorly constrained. Moreover, the degree to which geological processes, e.g. seismicity, influence geochemistry are equally unconstrained. Here we present data from a unique assemblage of osmotically powered fluid samplers that collected co-registered fluid samples and preserved them in situ for microbial analyses (DNA and protein characterization), dissolved ion analyses (cations and anions), and volatile analyses (e.g. methane). The osmotic samplers were equipped with a temperature logger at a diffuse vent site at the Juan de Fuca ridge. The samplers collected nearly 300 samples over a one-year deployment. Changes in protein representation from select samples were analyzed via tandem mass spectrometry, while changes in microbial community diversity over time are currently being assessed via 454 pyrosequencing. Changes in protein expression during the last ninety days of deployment suggest a notable increase in chemoautotrophy, which correlated with seismic activity in the vent field. These data further suggest that geological processes may have pronounced impacts on microbial activity over short time scales in hydrothermal systems.

Novel, mat-forming *Thiomargarita* spp. thrive on a sulfidic fluid outflow at the Amon mud volcano (Eastern Mediterranean)

A.-C. GIRNTH1, S. GRÜNKE2*, A. LICHTSCHLAG1, J. FELDEN2, K. KNITTEL1, F. WENZHÖFER2, D. DE BEER3 AND A. BOETIUS2

1Max Planck Institute for Marine Microbiology, 28359 Bremen, Germany
2HGF-MPG Joint Research Group on Deep Sea Ecology and Technology, Alfred Wegener Institute for Polar and Marine Research, 27515 Bremerhaven, Germany
(*correspondence: sgruenke@mpi-bremen.de)

*Thiomargarita* spp. are giant, colorless sulfur bacteria which gain their energy from oxidizing sulfide or internally stored elemental sulfur with oxygen or nitrate. In this study, a dense population of single, spherical *Thiomargarita* cells thriving on a sulfidic mud outflow at the Amon mud volcano (Eastern Mediterranean) was investigated. Visual observations and in situ microprofiling during ROV dives indicated episodic coverage of the mat with briny fluids, creating non-steady state conditions. With an average diameter of $47 \pm 8$ µm, cells of the novel *Thiomargarita* spp. population were significantly smaller than previously observed cells of this genus. All cells showed a vacuolated phenotype. A retrieved 16S rRNA gene sequence clustered with other published *Thiomargarita* phylotypes. As *Thiomargarita* spp. possess an exceptional ability to survive temporal cut-off from their electron acceptors as well as high concentrations of oxygen and sulfide [1-3], they are able to populate dynamic habitats such as brine and mud flows. At the Amon mud volcano, brine supplies *Thiomargarita* cells with sulfide, but at the same time separates them from oxygenated bottom water. If anoxic conditions are resulting, *Thiomargarita* spp. could use their internally stored nitrate resource [3]. Once a brine flow has passed, *Thiomargarita* cells could oxidize residual sulfide in the upper sediment layers and internally stored elemental sulfur aerobically and replenish internal nitrate reservoirs [4].

The impact of climate and dam construction on silicon fluxes to the oceans

S.R. GISLASON1*, E.S. EIRIKSDOTTIR1, E.H. OELKERS2 and K. BURTON3

1Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland
(*correspondence: sigrg@raunvis.hi.is)
2LMTG-Université de Toulouse-CNRS-IRD-OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France
3Earth Sciences, Oxford University, Oxford UK

Silicate weathering rates are affected by lithology, climate and biota creating a dynamic link between weathering, climate and biology. Silica is transported to the oceans by rivers either as dissolved species or as suspended particles. Estimates suggest that some 26% of the global suspended material delivered to the oceans is trapped behind dams. Data from rivers in NE Iceland show clear evidence of increases in chemical and physical weathering accompanying increases in temperature and runoff over the past 40 years, and that the suspended material flux is much more dependent on discharge and therefore climate than the dissolved species [1, 2]. Recent dam construction on some of these rivers likely filters out the larger suspended load fraction changing the nature and chemistry of the metals transported to the ocean. Furthermore it can be predicted that, regulating the flow of the river systems with dams will alter the delivery of dissolved nutrients like silica to the coastal waters. The main flux of silica occurs during the spring and summer in pristine direct runoff rivers but late in the summer and early fall in glacial fed rivers. Spring fed rivers are more like regulated rivers, with even flux of silica throughout the year. The much needed flux of nutrients for algal blooms that normally occur during the spring and summer time at high latitudes, will most likely be partly shifted to the winter, and some of the silica can be sequestered by diatoms within the man made reservoirs. This project will document the natural elemental and isotopic variations in weathering fluxes accompanying seasonal changes in runoff prior to dam construction, and compare these with the present-day (post-dam) variations. These data will allow assessment of the impact of dam construction on chemical weathering in these rivers catchments and on the elemental and isotope composition of material delivered to the oceans.


Mineral sequestration of CO2 in basalt – The CarbFix project

S.R. GISLASON1*, D. WOLFF-BOENISCH1, A. STEFANSSON1, H. ALFREDSSON1, E.H. OELKERS2, E. GUNNLAUGSSON2, H. SIGURDARDOTTIR2, B. SIGFUSSON3, E.S.P. ARADOTTIR3, W.S. BROECKER4, J.M. MATTER4, M. STUTE4 and G. AXELSSON5

1Institute of Earth Sciences, University of Iceland, Askja, Sturlugata 7, 101 Reykjavik, Iceland
(*correspondence: sigrg@raunvis.hi.is)
2LMTG-Université de Toulouse-CNRS-IRD-OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France
3Reykjavik Energy, Baejarhalsi 1, 110 Reykjavik, Iceland
4Lamont-Doherty Earth Observatory, 61 Route 9W, Palisades, NY 10964, USA
5ISOR, Iceland GeoSurvey, Grensasvegur 9, 108 Reykjavik, Iceland

Carbonate minerals provide a long-lasting, thermodynamically stable, and environmentally benign carbon storage host. Mineral storage is in most cases the end product of geological storage of CO2. The relative amount of mineral storage and the rate of mineralization depend on the rock type and injection methods. Rates could be enhanced by injecting CO2 fully dissolved in water and/or by injection into silicate rocks rich in divalent metal cations such as basalts and ultramafic rocks. The CarbFix project [1] aims at mineral sequestration of carbon in southwest Iceland and will start injection in early 2010. Carbon dioxide will be fully dissolved in meteoric water and injected into basaltic rocks. The initial test injection will contain 0.07 kg/s of CO2 dissolved in 2 kg/s of water. The CO2 gas-water mixture will be pumped into the injection well, at 25 bar total pressure and 350 m depth. The pH of the water after dissolution at 25 bar in situ partial pressure of CO2 is estimated to be 3.7 and the dissolved inorganic carbon concentration (DIC) to be ~1 mol/kg. As the CO2 charged waters percolate through the rock the dissolution of mafic minerals and glass will consume the protons provided by the carbonic acid. As a result of these dissolution reactions, combined with dilution and dispersion the pH of the injected water will rise and alkalinity will increase. Concomitantly, the concentration of dissolved elements will increase and alteration minerals will form, resulting in mineral fixation of carbon. Conservative tracers and 14C labelled CO2 will be mixed into the injected gas and water stream to monitor the subsurface transport and to constrain the carbonate mass balance. If successful, the experiment will be up-scaled.

Microbial Nitrogen and Sulfur cycles at the Dune Field, White Sands National Monument (New Mexico)

M. GLAMOCLIIJA1, M.L. FOGEL1, A. KISH2 AND A. STEELE1

1Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA
2Institut de Génétique et Microbiologie, Paris, France

Sulfates, including gypsum, have been identified within dunes at the Olympia Undae and Meridiani Planum on Mars [e.g. 1, 3]. The origin of these deposits is still unknown, however, they were likely produced by a combination of hydrothermal processes and/or groundwater upwelling, and later weathered by eolian processes [3, 1]. The White Sands National Monument (WSNM) (New Mexico) contains one of the largest known gypsum dune fields on Earth and has been proposed as a geochemical analog to the gypsum rich dunes on Mars [4]. Our intention is to investigate the dune field (dune slopes and interdune areas) at the WSNM in order to detect different microbial habitats and to assess their ecological characteristics through identification of mineral assemblages, pigments, extractable nitrogen, and functional genes of the microbial communities.

The surfaces of the interdune areas show higher mineral diversity than the dunes. Additionally, most of the microbial mat was found ~ 1/3 cm beneath the surface at the interdune areas. Nitrogen concentrations from ammonium and nitrates indicate ongoing processes of nitrification in the surface layers of the interdune settings have the metabolic capacity to contribute to nitrogen cycling and the detected nitrification. The high groundwater table contributes to minor dissolution and re-precipitation of sulfates at the interdunes. Microbial consortia with andenosine-5'-phosphosulfate reductase enzyme (APS), genes characteristic for green non-sulfur bacteria (CFX) and purple phototrophic bacteria (pufM) detected in the surface layers of the interdune settings have the metabolic capacity to contribute to sulfur cycling through the reduction of sulfate, and the oxidation of sulfide to sulfur and then to sulfate.

Trace elements in sulfides from Precambrian stromatolites and banded iron-formations

S.E. GLASER*, E.D. SWANNER AND S.J. MOJZIS
Department of Geological Sciences, University of Colorado, Boulder, CO 80309 USA
(*correspondence: steven.e.glaser@colorado.edu)

The evolution of the mineral biogeochemical cycles of transition metals (e.g. Ni, Co) has been modulated both by their supply to the oceans, and the evolutionary innovations in microbial metabolisms that utilize (d) these metals through time. For example, ferro-ferric-oxide phases in banded iron-formations (BIFs) appear to record secular decreases in molar Ni/Fe – and thereby declines in aqueous Ni concentrations – beginning around 2.7 Ga [1]. Subsequent major drops in Ni/Fe are coincident with later pO2 rise recorded by multiple S isotopes at ca. 2.42 Ga [2, 3]. The Ni/Fe data have been used to support a model for severe limitation in aqueous Ni availability to co-factors of several metalloenzymes central to methanogenesis. Such a ‘Ni famine’ [1] could have curtailed microbial methane production to the Paleoproterozoic atmosphere and effectively cut off a key O2 sink. Although BIFs probably record ocean-scale trace metal contents, it is unclear what information they impart on the diversity of microbial communities that would have used Ni or Co and the changes to these communities with changing metal availability. It makes sense now to independently verify the BIF trace metal dataset derived from Fe-oxides [1] and extend such studies to metal sulfide minerals in BIFs as well as stromatolites in a more global sampling of the Precambrian oceans. If BIF sulfides faithfully record trace metal concentrations in the ancient seawater column, sulfides in stromatolites ought to capture information about the organisms within the microbial stromatolite-building community at time of sedimentation. Furthermore, unlike relatively deep-water sedimentary facies such as BIFs and black shales, stromatolites are (for the most part) considered to be shallow-water sedimentologic features. The ‘Ni famine’ hypothesis requires suppression of methane production at the global scale. We report our comparative trace metal analyses (Ni & Co vs. Fe) of stromatolitic and BIF sulfides as a means to test the ‘Ni famine’ hypothesis and to explore its effects to both shelf- and deep-marine environments in the Precambrian.


Low temperature S biomineralization at a supraglacial spring system in the Canadian High Arctic

DAMNHAIT GLEESON1,3, CHASE WILLIAMSON2, KATHERINE WRIGHT1, JOHN SPEAR2, ROBERT PAPPALARDO3, STEVE GRASBY4 AND ALEXIS TEMPLETON1*

1Dept. Geological Sciences, University of Colorado (*correspondence alexis.templeton@colorado.edu)
2Colorado School of Mines, Golden, CO, USA
3Jet Propulsion Laboratory, Pasadena, CA, USA
4Geological Survey of Canada, Calgary, Alberta, Canada

Elemental sulfur (S0) is deposited each summer onto the ice at Borup Fiord pass on Ellesmere Island in Canada, when high (millimolar) concentrations of aqueous H2S are discharged from a supraglacial spring system. The resulting sulfur deposits host abundant microbial communities that have been phylogenetically characterized by 16s rRNA sequencing. The clone libraries are dominated by $\delta$-proteobacteria, particularly Ralstonia sp., as well as several known sulfur-cycling microorganisms such as Thiomicrospira sp., and $\gamma$-proteobacteria such as Sulfuricurvales sp., and Sulfurovumales, sp. Cultivation experiments have also been conducted to isolate psychrophilic, chemolithoautotrophic sulfide oxidizing bacteria. Light, florescence and scanning electron microscopy of the mineral aggregates produced in laboratory cultivation experiments reveal abundant filaments and sheaths variably mineralized with extracellular sulfur as a function of time and environmental conditions. 16s rRNA analysis has been used to characterize the stable sulfur -biomineralizing consortia as well as isolates. We will also present a detailed characterization of the mineral products formed in laboratory biomineralization experiments, and relate our findings to potential biosignatures for microbial sulfur cycling in cold environments on Earth and other planetary systems.

Mechanistic organic geochemistry of carboxylic acids

C.R. GLEIN1*, I.R. GOULD2, L.B. WILLIAMS1, H.E. HARTNETT1,2 AND E.L. SHOCK1,2

1School of Earth & Space Exploration, Arizona State University, Tempe, AZ. (*correspondence: cglein@asu.edu)
2Dept. of Chemistry & Biochemistry, Arizona State University, Tempe, AZ.

Organic compounds containing the carboxyl group are present in many hydrothermal systems. In an effort to better understand carboxylic acid reactivity, geochemists have performed experiments in aqueous solutions at high temperatures and pressures, and in the presence of minerals [1]. These experiments revealed that decarboxylation (RCO2H $\rightarrow$ RH + CO2) is a major reaction pathway for carboxylic acids, and that minerals can have an unpredictable effect on the reactivity of carboxylic acids. Despite this progress, we currently lack a mechanistic framework that allows extrapolation of experimental snapshots to the vast range of organic structures and mineralogical environments that exist in natural systems.

This project seeks to elucidate mechanisms of decarboxylation in hydrothermal systems by applying tools of physical organic chemistry. We have performed gold capsule hydrothermal experiments using derivatives of phenylacetic acid (PAA) as mechanistic probes. By changing the identity or position of substituents attached to the ring of PAA, we gain information about mechanisms of decarboxylation through observations of both reaction rates and product distributions. This type of approach, while common in the field of organic chemistry, is rarely applied to geochemical problems.

Experiments with PAA in water at 300°C and 103 MPa gave toluene as the only detectable organic product, and an apparent first-order rate constant of 9.2x10-6 s-1. Decarboxylation of PAA is dramatically faster in water than in the gas phase, where a bond homolysis mechanism has been proposed [2]. An anionic mechanism for decarboxylation of PAA in the absence of minerals is supported by preliminary studies of kinetics and products of a PAA substituted with a strong electron-withdrawing group. In the presence of hematite, however, products indicate additional pathways, including oxidative decarboxylation and radical coupling. Experiments with other minerals are in progress.

Microbial methanogenesis from a consortium enriched from the Powder River Basin, WY

A.W. GLOSSNER1*, L. GALLAGHER2, L. LANDKAMER2, L. FIGUEROA2, J. MUNAKATA-MARR2 AND K. MANDERNACK1

1Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, USA (aglossne@mines.edu, kmandern@mines.edu)
2Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO 80401, USA (lgallagh@mines.edu, llandkam@mines.edu, lfiguero@mines.edu, junko@mines.edu)

Evidence for microbial methanogenesis from petroleum hydrocarbons in oil reservoirs [1, 2], organic-rich shale [3, 4], and coalbed reservoirs [5] is growing. The goal of this project is to better understand the factors controlling microbial methanogenesis from coal in order to potentially stimulate this process in situ. A methanogenic microbial consortium was enriched from coal collected during drilling of a coalbed methane well in the Powder River Basin, WY. The consortium produces methane under anaerobic conditions in inorganic nutrient medium with coal as the sole carbon source. This consortium has been characterized by phospholipid fatty acid (PLFA), phospholipid ether lipid (PLEL), and 16S rDNA sequencing. Stable carbon isotopic analysis of the microbial phospholipids is planned in order to determine the carbon sources and dominant pathway of methanogenesis used by this consortium. Experiments are ongoing to determine factors that may affect methanogenesis from coal, such as pH, organic carbon sources, and variable pCO2 in headspace gases.


Element cycling and the evolution of the Earth System

Y. GODDERIS1*, Y. DONNADIEU2, J.Z. WILLIAMS3, C. ROELANDT4, J. SCHOTT1, D. POLLARD1, R.T PIERREHUMBERT2 AND S. BRANTLEY3

1LMTG, CNRS-Université de Toulouse, France (godderris@lmtg.obs-mip.fr)
2LSCE, CNRS-CEA, Gif-sur-Yvette, France
3CEKA, PennState University, USA
4University of Bergen, Norway
5Dept. of Geophysical Science, U. of Chicago, USA

Since the early work by Walker and co-authors in 1981, continental weathering is thought to be a key process of the Earth system evolution at the geological timescales. By balancing the release of CO2 by the solid Earth outgassing through a climatic negative feedback loop, weathering of continental silicate rocks and sediments controls the long term relative stability of the climate at the multimillion year timescale. However, several recent field studies have shown the high sensitivity of the weathering processes to anthropogenic forcings (climate and land use change) at the decadal scale, for both small and continental-scale rivers. These rivers display up to a 30% increase in their alkalinity flux over the last four decades. This high sensitivity points at a possible rapid evolution of the chemical composition of the large rivers in response to human activities, impacting on the discharge of elements into the coastal area and eventually into the ocean. This observation challenges our ability to model the weathering reactions at the continental and global scale. Indeed, although a simplified description of the weathering can be generally assumed when worrying about the multimillion year evolution of the Earth (except for some rapid transitions), a process-based method is needed at the decadal to centenial scale. The climate, the lithology, the soil characteristics, the vegetation dynamics, the erosion processes must be accounted for at the highest spatial resolution possible. In this talk, we present an overview of the recent advances in the process-based modelling of the weathering processes from the geological down to the anthropic timescales. Through the coupling of numerical models of climate, vegetation dynamics, and weathering (based on kinetics laws derived from laboratory experiments), we explore the role of tectonics in the Earth climatic evolution, and of important thermodynamic and kinetic (like clay mineral stability and near-equilibrium rate laws) on the budget of monitored watersheds.
Sensitivity of the chemical weathering of the continents to environmental gradients

Y. GODDERIS1*, A. VIOLETTE1, E. BEAULIEU1, J.Z. WILLIAMS2, C. ROELANDT3, N. VIGIER3, J. SCHOTT1, D. POLLARD2, M.-C. PIERRET3 AND S. BRANTLEY2

1LMTG, CNRS-Université de Toulouse, France
(godderis@lmtg.obs-mip.fr)
2CEKA, PennState University, USA
3University of Bergen, Norway
4CRPG, Nancy, France
5CGS, Strasbourg, France

Chemical weathering of the continental surfaces is a key process of the biogeochemical global cycles, including the cycles of the main cations, carbon, nutrients, isotopes. Recent field studies have emphasized the high sensitivity of the weathering systems to the ongoing anthropogenic changes (land use and climate change). These observations challenge our ability to predict how continental weathering (and hence the chemical composition of the waters flowing on the continents) will evolve in the future. There are only two methods for exploring and understanding this sensitivity to the environmental gradients such as climatic changes, variability in the vegetation cover, physical erosion intensity: the pluri-decadal monitoring of watersheds, and numerical modelling. Numerical modelling is a powerful tool, but it must be mechanisms-based if we want to catch the dynamics of the weathering system and predicts its future evolution. Here we present recent advances in the modelling of weathering reactions in the critical zone and at the watershed scale for a large variety of environments: temperate area, humid equatorial environment, tropical zone. The mathematical expressions of the dissolution/precipitation reactions are based on laboratory kinetic laws, and the hydrological parameters (soil water content, water fluxes) are calculated by offline biospheric models. The output of the models is compared first to available data from monitored watersheds. Then the sensitivity to the vegetation cover and climatic change is explored. The models suggest that the sensitivity of the weathering system (soil+saprolite) to the presence of vegetation appears to be higher in warm humid environment where intense evapotranspiration eventually limits the soil drainage. This is confirmed by climate change sensitivity tests where drainage changes overwhelm the temperature rise and thus seem to control the weathering response.

The geochemistry of the Brent impact structure, Ontario, Canada

S. GODERIS1,2*, B. VLEMINCKX1, F.S. PAQUAY3, R. CHAKRABARTI4, V. RENSON1, V. DEBAILLE5, W. SLUYTS1, F. VANHAECKE2, J. SPRAY6, S.B. JACOBSEN4 AND PH. CLAEYS1

1ESS, VUB, B-1050 Brussels, BE
(*correspondence: stgoderi@vub.ac.be, phclaeys@vub.ac.be, vrenson@vub.ac.be)
2Dept. Anal. Chem., Univ. Gent, B-1050 Ghent, BE (frank.vanhaecke@UGent.be)
3Dept. Geology and Geophysics, Univ. of Hawaii, HI 96822–2225, USA (paquay@hawaii.edu)
4Dept. EPS, Harvard Univ., MA 02138, USA (chakrab@fas.harvard.edu, jacobsen@neodymium.harvard.edu)
5Dept. STE, ULB, B-1050 Brussels, BE (vdebaill@ulb.ac.be)
6Planetary and Space Science Centre, Univ. of New Brunswick, NB E3B 5A3, CA (jgs@unb.ca)

Thirteen impact melt samples and basal suevitic breccias from two drill cores of the 3.8 km diameter Brent impact structure have been analyzed for major and trace elements, including PGE. In selected samples, Os, Cr, W, Sr, and Pb isotope ratios were also measured. This multi-tool approach not only characterizes the projectile responsible for the formation of the structure, but also documents the distribution and nature of the meteoritic component(s) within. The Brent simple crater is an ideal case study: the target consists of mainly gneiss with minor alnoite dykes and the structure was extensively drilled beyond its lenticular melt sheet. Using a Ni-Cr correlation, the Brent structure was previously interpreted as formed by an ordinary chondrite (OC; type L or LL) [1]. Although the CI-normalized PGE concentrations of the melt rock show relatively flat patterns [2], the characteristic deviations from chondrite patterns could only be explained by fractionation of the meteoritic component(s) within. The Brent simple crater is an ideal case study: the target consists of mainly gneiss with minor alnoite dykes and the structure was extensively drilled beyond its lenticular melt sheet. Using a Ni-Cr correlation, the Brent structure was previously interpreted as formed by an ordinary chondrite (OC; type L or LL) [1]. Although the CI-normalized PGE concentrations of the melt rock show relatively flat patterns [2], the characteristic deviations from chondrite patterns could only be explained by fractionation of the meteoritic component. In recent years, a previously poorly constrained projectile type was characterized and proposed for the Rochechouart, Saiksjärvi, and Gardnos impact structures [3, 4]. The PGE pattern observed for Brent resembles that of IA and IIIC non-magmatic iron meteorites (NMI). The moderately siderophile element concentrations were affected by hydrothermal alteration, but the melt zone samples retain Ni/Cr ratios not only consistent with OC, but also with IA and IIIC NMI.

Buchite type glasses in the West Eifel Volcanic Field (Germany)
A. GOEPEL*, K. HEIDE, D. MERTEN AND G. BÜCHEL

Friedrich-Schiller-University Jena, Institute of Earth Sciences, Burgweg 11, D-07749 Jena, Germany
(*correspondence: andreas.goepel@uni-jena.de)

Sedimentary siliciclastic xenoliths from Devonian and Triassic source rocks, pyrometamorphically overprinted by cooling volcanic deposits, are common in numerous scoria cones in the West Eifel Volcanic Field (WVF). Some of these upper crustal rock fragments are affected by anatexis and high-temperature metamorphism leading to formation of pyrometamorphic glasses.

We have systematically mapped 71 phreatomagmatic scoria cones in the WVF and performed thermoanalytical and geochemical analyses on sampled glasses and xenoliths. The compilation of the results led to the development of a petrological model. According to the obtained p-T-X-conditions during formation these glasses can be classified as ‘buchites’. They have rhyolitic to trachytic compositions and their enrichment in the buchites. An increase of silica in chromophores like Cr, Cu, Fe, Mn, V) from the volcanic rocks and their enrichment in the buchites. An increase of silica in the buchites is due to its mobilization from the siliciclastic upper crust xenoliths.

Geoelectrochemical model of ore formation on the base experimental data
I.S. GOLDBERG

Level 2, 49-52 York Street, Sydney, NSW, 2000, Australia
(*correspondence: igoldberg@ionex.com.au)

Numerous self-potential (SP) anomalies are known to exist in upper continental and ocean crust [1]. SP anomalies represent both local and regional electric fields. The most widespread SP anomalies associated with hydrothermal and subsurface water flow (steaming potential) [2]. Under the influence of electric energy electrochemical processes are inevitable. These processes include: the extraction of elements from rocks, migration of charged particles in the domains of the poles and a concentration in these local areas. Existing geophysical data allow the quantitative estimation of redistribution of elements in the geoelectrochemical cell (system). For example, in the case of local electrical fields with sections of electrochemical cells, e.g. 100 km², a direct current of approximately 10³A is generated. According to Faraday’s Law, in a period of around 1 million years, approximately 10⁸ tones of substance should be transported within the geoelectrochemical system.

This electrochemical processes study was carried out during the development of the CHIM method between 1960 and 1990 [3]. Experimental data showed that under the impact of electrical energy, a selective release of ore elements from rock depending on the form of their occurrence from 20% or more took place, while the degree of release of macro-components did not exceed 0.4%. Such high degree of release of ore elements can be achieved in a period not exceeding 1 million years. According to experimental data on ion mobility, the scope of the migration of elements could be tens of kilometers. As a result geochemical systems with depletion and enrichment zones of ore elements can be formed. Such systems have to be characterized by ellipse-like structure, in accordance to the structure of electric fields.

Similar geochemical system patterns for mineral targeting of various types and structures have been established by geochemical researches [4, 5]. Good correlation exists between the dimension of the systems and the reserve of metals in mineral targeting [5]. Such systems are formed as open far from equilibrium (self-organized systems) and can be considered as ore-forming systems.

The subduction origin of mantle nitrogen

COLIN GOLDBLATT1 AND KEVIN ZANHLE2

1Space Science and Astrobiology Division, NASA Ames Research Center, MS 245-3, CA 94035 (colin.goldblatt@nasa.gov)
2Space Science and Astrobiology Division, NASA Ames Research Center, MS 245-3, CA 94035 (kevin.j.zahnle@nasa.gov)

Mantle nitrogen correlates strongly with radiogenic \(^{40}\text{Ar}\) but not primordial \(^{36}\text{Ar}\): \(N_2/^{40}\text{Ar} \approx 80\) over several orders of magnitude in concentration, whereas \(N_2/^{36}\text{Ar}\) varies by orders of magnitude. \(^{40}\text{Ar}\) is the decay product of \(^{40}\text{K}\), so with an estimate of the \(\text{K}\) content of the mantle one can calculate that the mantle nitrogen inventory is \(1.9^{+1.5}_{-1.2} \times 10^{20}\) mol \(N_2\) (\(5.4^{+1.5}_{-1.2} \times 10^{18}\) kg), equivalent to 1.4 times the present atmospheric nitrogen inventory.

A key point is that the lack of correlation between \(N\) and primordial \(^{36}\text{Ar}\) means that mantle \(N\) is not primordial. By contrast, the strong correlation with radiogenic \(^{40}\text{Ar}\) indicates that the main source of the mantle's nitrogen is \(\text{NH}_4^+\) substituted for \(\text{K}^+\). Because \(\text{K}\) is incompatible with the solid phase of the mantle and fractionates to crustal rocks, this implies that the mantle's \(N\) is from subducted crust. Consequently, a history of monotonic volatile depletion of the mantle can be excluded.

Presently, the net transfer of nitrogen to the mantle at subduction zones (input to the trench minus arc volcanic output) is \(3.3^{+0.8}_{-0.6} \times 10^8\) kg N yr\(^{-1}\). This flux was likely much larger in the past, when the deep ocean was anoxic and \(\text{NH}_4^+\) concentrations were much higher than today. \(\text{NH}_4^+\) incorporate into altered oceanic crust during early hydrothermal alteration, so much more would incorporate under the high \(\text{NH}_4^+\), high heat flow and fast spreading rate regime of the Archean. Also, less sedimentary \(\text{NH}_4^+\) be lost in diagenesis. Consequently, the atmosphere—mantle balance of nitrogen is likely to have changed over Earth history. An higher atmospheric nitrogen inventory would have enhanced greenhouse warming, contributing to the resolution of the Faint Young Sun paradox [1].

That the nitrogen in the mantle arrived by subduction, and therefore was once in the atmosphere is clear. When this transfer took place is not yet clear. Can noble gas systematics shed further light on this?


Single-particle characterization of Saharan dust events at an urban site in Freiburg, Germany

E. GOLDENBERG1*, R. GIÈRE1, B. GROBÉTY2, V. DIETZE3, P. STILLE4, U. KAMINSKI AND C. NEURURER2

1Department of Geosciences, University of Freiburg, Albertistrasse 23b, D-79104 Freiburg, Germany (*correspondence: Ella.goldenberg@minpet.uni-freiburg.de, Reto.giere@minpet.uni-freiburg.de)
2Department of Geosciences, University Fribourg, Chemin du Musee 6, 1700 Fribourg, Switzerland
3German Meteorological Service, Air Quality Department, Stefan-Meier-Strasse 4, D-79104 Freiburg, Germany
4École et Observatoire des Sciences de la Terre, Université de Strasbourg, rue Blessig 1, 67084 Strasbourg, France

During 2008, Saharan dust reached southern Germany during several events, increasing significantly the weekly levels of particulate matter. The aim of this study was to characterize these dust events by using aerosol samples collected at an urban site in Freiburg, Germany. These samples were compared to non-event conditions at the same site. Using a standardized, rain-protected passive sampler (Sigma-2), airborne particles >2.5µm were collected on transparent adhesive collection plates. Computer-controlled single-particle optical microscopy (IAS) was used to determine size and optical density of individual particles, allowing for distinction between anthropogenic (opaque), geogenic (transparent mineral dust), and biogenic particles, as well as for calculation of mass concentrations. Additionally, chemical composition, geometry and morphology were determined using scanning electron microscopy (SEM), combined with energy-dispersive X-ray (EDX) and automated single-particle analysis (Genesis, EDAX). Particles were classified according to size and composition, whereby geogenic particles were further subdivided into several mineralogical groups. By combining IAS with SEM-EDX single-particle analysis there will be a high chance for a successful differentiation between particles of local origin and particles transported over long distances. This differentiation of the morphological and optical properties as well as chemical composition will be an improvement for a better distinction between Saharan and Non-Saharan dust events.
Chemical weathering in the Central and Coastal Ranges of Taiwan

S.T. GOldsmith1,2*, S.J. Kao3, A.E. Carey1,2, W.B. Lyons1,2, K Selveraj3, and T.Y. Lee3

1School of Earth Sciences, The Ohio State University, Columbus, OH 43210-1398, USA (*correspondence: goldsmith.35@buckeyemail.osu.edu)
2Byrd Polar Research Center, The Ohio State University, Columbus, OH 43210-1002, USA
3Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan

The uplifting weathering hypothesis suggests that the uplifting Himalaya and Qinghai-Tibet Plateau was responsible for large scale silicate weathering and the resultant drawdown of atmospheric CO2, and global climate cooling during the Cenozoic. Subsequent geochemical studies from streams in the Himalayas and Tibetan Plateau have shown a water signature dominated by carbonate weathering originating from both carbonate exposures and disseminated calcite. This is important as the weathering of carbonate results in no net CO2 drawdown from the atmosphere over time scales longer than a million years.

Herein we evaluate the stream water geochemistry in the rapidly uplifting Central and Coastal Ranges of Taiwan as an analogy to the early stage growth of the Himalayan Plateau. Carbonate weathering supplies a significant portion of the total cation yields while silicate weathering plays a lesser role. However, absolute silicate weathering rates are so high that they fall at the upper end of those previously determined from sedimentary and metamorphic terrains of HSIs. Silicate and carbonate weathering yields exhibit varying relationships with basin average mean annual rainfall and average basin runoff, and annual suspended sediment loads. H2SO4 weathering, originating from the dissolution of pyrite, accounts for some of the total chemical weathering in these systems. After correction for H2SO4, calculated CO2 consumption from silicate weathering is highly elevated over world average values. While these CO2 fluxes presented herein should be taken with some caution as they do not account for weathering originating from metamorphic CO2, they still likely represent the upper limit for a non-volcanic active margin setting.

Modelling the terrestrial phosphorus cycle in the framework of an Earth System Model (ESM)

D.S. Goll1,2*, V. Brovkin2, B.R. Parida1,2, C.H. Reick2, and V. Gayler2

1International Research School on Earth System Modelling, D-20144 Hamburg, Germany (*correspondence: daniel.goll@zmmaw.de)
2Max-Planck-Institute for Meteorology, D-20144 Hamburg, Germany (victor.brovkin@zmmaw.de, bikash.parida@zmmaw.de, christian.reick@zmmaw.de, veronika.gayler@zmmaw.de)

Productivity of many terrestrial ecosystems is limited by nutrients, predominantly nitrogen (N) and phosphorus (P). The cycling of these elements is significantly altered by human activities. To estimate changes in land carbon (C) uptake in respect to P availability, the spatially explicit land surface model JSBACH, which already includes terrestrial C and N cycling, is extended by a model of the P cycle. The JSBACH model serves as a terrestrial component of the comprehensive Earth System Model (ESM) ECHAM5-MPIOM-JSBACH.

In the JSBACH model, the element cycles are driven by net primary productivity constrained by climate and atmospheric CO2 concentration. The P model consists of 8 organic pools and 3 inorganic pools. The nutrient cycles are coupled to the C cycle by use of fixed C:N:P ratios for biosphere compartments, except herbaceous litter and soil organic matter. It is assumed that under pre-industrial condition vegetation and soil microbes are optimally adapted with respect to the nutrient environment and therefore nutrient limitation does not occur. Changes in climate and atmospheric CO2 lead to disbalance of the P cycle and the plant productivity can become limited by P availability.

To evaluate the effect of nutrient limitation on future land C uptake, a set of simulation with the JSBACH model driven by ESM projections of climate and CO2 change in the 21st century was carried out. Model simulations were performed (i) without nutrient cycles, (ii) one nutrient cycle active (N or P), and (iii) both N and P cycles active. The simulation results suggest that nutrient limitation becomes visible in the beginning of the 21th century. In highly productive ecosystems, P limitation is more pronounced than N limitation, and therefore P has a stronger effect on land C uptake. Consequently accounting for P in the model leads to a less pronounced increase in soil C stocks than without P.
Mineralogy and magnetic fabric of Triassic Red Beds from the Conraria Formation, Central Portugal

C.R. Gomes¹, A. Dória², A. Rocha¹, L.G. Pereira¹
and H. Santi°Ovaiá²

¹CGUC, DCT, Universidade de Coimbra, Portugal
²Centro de Geologia da U. Porto, DGAOT, FCUP, R. Campo Alegre, 4169-007 Porto, Portugal

The Conraria Formation is the lower unit of the ‘Grupo de Silves’ (Silves Sandstones Group) of Upper Triassic age. It is the sum of two subunits which have mean thickness of 40 ± 5 m and 120 ± 15 m, respectively, in the Coimbra region. The main goal of this study is to quantify the magnetic fabric of the upper subunit of the Conraria Formation and to relate it to the magnetic mineralogy. Studies of Anisotropy of Magnetic Susceptibility (AMS) were carried out on 50 samples from 11 sites in order to characterise the magnetic fabric. The magnetic susceptibility of these samples is comprised between 40.6 and 329.7 x 10⁻⁶ SI (average 170.36 x 10⁻⁶ SI). Magnetic susceptibility is higher (292.83 and 329.68 x 10⁻⁶ SI) have always oblate, exceptionally the sites where the magnetic N197° trending magnetic lineations. The shape parameter is dipping magnetic foliations associated with subhorizontal anisotropy.

The specular hematite associated with calcite is responsible for the presence of calcium carbonates in country rocks that probably are the sources of Ca. The weathering of rock-forming minerals and ores caused the precipitation of secondary phases (halloysite, smectite, vermiculite, ferritungsitie and Fe sulphates).

Weathering and hydrochemistry associated with the old mine workings at Fonte Santa (NE of Portugal)

M.E.P. Gomes¹, I.M.H.R. Antunes², F.A.L. Pacheco¹, A.M.R. Neiva³ and P.B. Silva⁴

¹Department of Geology, UTAD, Apartado 1013, 5000-801 Vila Real, Portugal (mgomes@utad.pt, fpacheco@utad.pt)
²Polytechnic Institute of Castelo Branco, 6000-919 Castelo Branco, Portugal (imantunes@esa.ipcb.pt)
³Department of Earth Sciences, University of Coimbra, 3000-272 Coimbra, Portugal (neiva@dct.uc.pt)
⁴National Laboratory of Energy and Geology, LNEG, 4466-001 S. Mamede de Infesta, Portugal (paulo.braovo@ineti.pt)

The quartz veins from the Fonte Santa mine consist of scheelite, pyrite, pyrrhotite, sphalerite, chalcopyrite, arsenopyrite, galena, iron oxides, Al, Fe and Pb hydrated phosphates and Fe sulphates. Scheelite has a homogeneous composition, but their fractures are filled with stolzite and ferritungsitie. The area was mined for W between 1942 and 1982 and 2784 tonnes of tungsten were produced. Since then there has not been any development. Most waters from Fonte Santa are of mixed type, some are of Na-Mg and HCO₃⁻ type. They are poorly mineralized. However, most parameters and element contents show an increase from outside to inside the mine influence due to the effect of abandoned old mining activities. There is no significant acid drainage associated with the old mine workings, which can mainly be attributed to the presence of calcium carbonates in country rocks that probably neutralized the waters and decreased metal concentrations. The most acid waters with the highest SO₄²⁻ and metal contents are from the mine lagoons, which received waters from fine-grained tailings and waste rock. The environmental impact of the Fonte Santa mine area is essentially related to a flooding event that carried a suspended contaminated load, increasing the Fe and Al contents in natural stream waters inside the mine influence. Most waters associated with the mineralized veins and old mine activities have Fe and Mn concentrations that forbid their uses for human consumption and agriculture. Some waters present concentrations above parametric Portuguese values for other contaminants (SO₄²⁻, NO₃⁻, Mg, Zn, Al, Ni and Co) and must not be used for human consumption. The alteration of albite, chlorite and muscovite from country rock is responsible for Na, Mg and K contents in the waters, whereas the weathering of carbonates and scheelite are probably the sources of Ca. The weathering of rock-forming minerals and ores caused the precipitation of secondary phases (halloysite, smectite, vermiculite, ferritungsitie and Fe sulphates).

...
Growth and aggregation of ZnS nanoparticles during coprecipitation with aquatic humic substances

A. GONDIKAS¹, A. DEONARINE¹, H. HSU-KIM¹*, G.R. AIKEN², J.N. RYAN¹, A. MASON³ and M. AUFFAN⁴

¹Duke University, Civil & Environmental Engineering, Durham, NC 27713 USA
²U.S. Geological Survey, Boulder CO 80303 USA
³University of Colorado, Civil, Environmental and Architectural Engineering, Boulder, CO 80309 USA
⁴CEREGE, CNRS-Aix Marseille Université, Aix-en-Provence, France

Nanoparticulate metal sulfides such as ZnS are important for the speciation of pollutant metals in sediments, wastewater effluent, and other sulfidic environments. The aim of this work was to investigate how the composition of dissolved natural organic matter (NOM) influences colloidal stability as these nanoparticles precipitate in natural waters. In our previous work, we showed that for low molecular weight organics, surface association by thiol groups was important for stabilizing ZnS nanoparticles in water [1]. Humic substances, however, are complex macromolecules that can interact with surfaces through long-range interactions (e.g. electrostatic effects) that will influence overall nanoparticle stability. In this study, we compared NOM fractions that were isolated from several surface waters and represented a range of characteristics (molecular weight, type of carbon, sulfur content, etc.). Dynamic light scattering was employed to monitor the size of ZnS nanoparticles as they precipitated and aggregated over hours to days in solution containing dissolved NOM isolates. Overall, growth rates were slower as NOM concentration increased (from 1 to 10 mg-C/L) and faster as ionic strength increased (up to 0.1 M). For the same NOM concentration and ionic strength, particle growth rates varied for the different types of NOM isolates. Rates appeared to correlate with the molecular weight of the NOM ($R^2 = 0.7$), weakly correlate with aromatic C content ($R^2 = 0.45$), and poorly correlate with reduced-S content ($R^2 = 0.01$). We performed additional experiments with small angle X-ray scattering to elucidate the size and structure of ZnS aggregates that coprecipitated with humic and fulvic acids. Overall our results highlight the important molecular components of NOM that may be responsible for surface association with ZnS nanoparticles, and ultimately, colloidal stability and mobility.


The presence of molecular water in addition to structural hydroxyl in nominally anhydrous minerals from UHP metamorphic rocks

B. GONG, R.-X. CHEN and Y.-F. ZHENG

School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China (yfzheng@ustc.edu.cn)

Commonly the concentrations of structural hydroxyl in nominally anhydrous minerals (NAMs) have been determined by the FTIR method for UHP eclogites and mantle-derived xenoliths. The results have been used as a proxy for the concentration of water in the NAMs for the purpose of estimating water concentration in the mantle. However, significant amounts of the molecular water are also present in the NAMs as indicated by the occurrence of fluid microinclusions in NAMs. This is detected by the qualitative TEM observations and the quantitative FTIR and TC/EA-MS analyses of such NAMs as garnet, omphacite, rutile and quartz from UHP metamorphic eclogite and jadeite quartzite in the Dabie-Sulu orogenic belt, China.

While the TEM observations show different sizes of fluid microinclusions in the NAMs, the FTIR and TC/EA-MS analyses via stepwise heating gave water concentrations in the forms of total water, molecular water and structural hydroxyl, respectively. For UHP eclogite at Bixiling in the Dabie orogen, the results yield molecular water concentrations of 550 to 1755 ppm in omphacite and 240 to 710 ppm in garnet, and structural hydroxyl concentrations of 1240 to 2810 ppm $H_2O$ in omphacite and 280 to 745 ppm $H_2O$ in garnet. The TC/EA-MS online analysis also enables determination of mineral hydrogen isotope composition in addition to water concentration. The results are that the molecular water has $\delta D$ values of $-112$ to $-92\%$ for omphacite and $-98$ to $-94\%$ for garnet; the structural hydroxyl has $\delta D$ values of $-91$ to $-85\%$ for omphacite and $-87$ to $-72\%$ for garnet. Stepwise-heating TC/EA-MS analyses indicate that the molecular water are depleted in D relative to structural hydroxyl and has higher mobility than the structural hydroxyl in the NAMs. The low $\delta D$ values are consistent with incorporation of continental deglacial meltwater into eclogite protolith by high-T hydrothermal alteration. The meltwater $H$ isotope signature was preserved in the UHP minerals during the deep subduction of continental crust, with only limited activity of fluid within the UHP slab. Nevertheless, the fluid became active during exhumation due to a decrease in water solubility with pressure decrease. Therefore, exsolution of both structural hydroxyl and molecular water from the NAMs is the important source for retrograde fluid.
The model of the element geochemistry of metamorphic rock in early Precambrian period in Liaoning

LI GONG1, MA GUANG1*, HU SHUNTIAN2, HE SHIGEN2 AND GAO ERGEN2

1Henan Polytechnic University, Henan, 454001, China
(*)correspondence: maguang5678@163.com
2Institute of Disaster Prevention Science Technology, Beijing 101601, China (grg@fzxy.edu.cn)

The established geochemical model is based on the close relationship between the ore-forming and original ore-bearing rocks, the change characteristics of metallic materials or elements with the construction of space-time evolution of the original rock and the element abundances and concentration factor of metamorphic rock.

The element geochemical model is to express with the combination of simple style in accordance with its main elements (10^5 order of magnitude / 10^4 order of magnitude). The enrichment patterns of main element are composed of the elements of original concentration factor greater than one and the elements of the same order of magnitude arranged according to content decreasing order. Trace element enrichment patterns consist of the elements of the original concentration factor greater than one and elements of the same order of magnitude arranged according to concentration factor decreasing order.

The model will provides a new way of thinking in the search for buried ore bodies, summary the formation rule of deposits, metallogenic environments and ore-forming geological conditions, etc, and will become another new favorable means of tested on the known deposits and the exploration of unknown deposits.

This study is supported by the National Natural Science Foundation of China (Grant No: 40072032), Dr. Fund (No:648512) and Teacher Foundation of CEA (No: 20090112)


Hydroclimatic and geomorphic controls on particulate organic matter in small mountainous rivers

M.A. GONI1*, J.A. HATTEN1, R.A. WHEATCROFT1, J. BORGELOD2, G. PASTERNACK3, A. GRAY3 AND B. WATSON3

1College of Oceanic & Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA
(*correspondence: mgoni@coas.oregonstate.edu)
2Department of Oceanography, Humboldt State University, Arcata, CA 95521, USA
3Department of Land, Air, and Water Resources, University of California, Davis, Davis, CA 95616, USA

Small mountainous rivers (SMRS) are critical drivers for the erosion and transport of continental materials, including particulate organic matter (POM), to the ocean. Worldwide, SMRS are a highly heterogeneous, exhibiting marked tectonic, climatic and vegetation contrasts and highly variable discharges on event, seasonal and inter-annual scales. Here, we investigate changes in concentration and composition of POM as a function of discharge among US west coast SMRS with distinct hydroclimate, geomorphology and land use. Particulate samples collected at different discharges, including several flood events, were analyzed for elemental (C, N), isotopic ($\delta^{13}$C, $\delta^{15}$N, $\%^{14}$C), and biochemical compositions. These data are used to compare and contrast the provenance, age, and molecular make-up of materials transported by each river. We evaluate both the processes responsible for these contrasts and their impacts on the delivery and fate of terrigenous POM in the coastal ocean.

Figure 1: Location of SMRS studied and relationship between river discharge (Q) and concentration of suspended sediments (SS), POC and lignin products.
Thermogenic hydrocarbons in Fe-Mn nodules from the Gulf of Cadiz: A new tool for oil and gas exploration

F. J. GONZÁLEZ1*, L. SOMOZA1, T. TORRES2, J. E. ORTIZ2, R. LUNAR3, J. MARTÍNEZ-.FRÍAS4, T. MEDIALDEA5 AND R. LEÓN1,
1Geological Survey of Spain (IGME). Madrid, Spain
(*correspondence: fj.gonzalez@igme.es)
2Lab. Estratigrafía Biomolecular (LEB/UPM). Madrid, Spain
3Facultad de Ciencias Geológicas (UCM). Madrid, Spain
4Centro de Astrobiología (CAB/CSIC/INTA). Madrid, Spain

Ferromanganese nodules were firstly sampled during the Tasyo Project cruises from mud-carbonate mounds and mud volcanoes at the Guadalquivir Diapiric Ridge (Central eastern Atlantic). The metallogenetic study has revealed their genesis, linked to the anaerobic oxidation of hydrocarbons via biomineralization processes [1]. N-alkanes have been discovered in all the nodules, which were analyzed by Gas Chromatography, comprising a unimodal distribution maximizing at the n–C18 isomer with an important presence of n-C16 and n- C20. Pristane and phytane and/or crocetane (2, 6, 11, 15-tetrametilhexadecane) were detected in all the samples analysed. Isotopic values of δ13C for these compounds, measured by Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry, ranged between -20 and -37 per mil (vs. PDB). These values are supporting the idea of deep thermal maturation. Moreover, the carbon preference index (CPI) ranged from 0.66 to 1.15, which is also characteristic of mature samples. In the same way, polycyclic aromatic hydrocarbons as phenanthrene and anthracene, present in mature substances such as petroleum, have also been detected in the nodules.

We propose the use of these ferromanganese nodules as tools for reconstructing the fluid venting history in modern or ancient hydrocarbon-seeps from the Gulf of Cadiz. The nodules acted as ‘traps’ for fluids during their growth, remaining for long time when the fluids responsible of the mineralization have disappeared in the area. Therefore, they can be useful for seep detection. In addition, these nodules and their thermogenic hydrocarbons may be used as indicators to explore and define deep-seated reservoirs for oil and gas, giving important information on sub-seafloor fluids composition and migration patterns, geology and tectonic conditions.


The environmental aspect of mercury emission from coal fired-power plants – An example from Western Canada

F. GOODARZI AND H. SANEI

Environmental Study Group, 3303-33rd Street NW, Calgary, Alberta, Canada T2L1A7

The environmental aspects of coal from mining to emission from coal fired power plant is discussed and attempted is made to reduce mercury by selective mining of coal to reduce the part that includes high Hg. The nature of organic matter also studied in fly ash and it was found that the reactive carbon is able to capture Hg in tandem with other elements such as Cl and S reduce the emitted mercury.

The mercury in feed coals was reduced by 15-58% using selective mining as compared to routinely prepared feed coals and by eliminating the high Hg dirt bands (partings) from the coal seam (s) and the emitted mercury by 36-58% decrease in to total emitted Hg (g/h).
Mn/Cr systematics: A tool to discriminate the origin of primitive meteorites?

C. GÖPEL* AND J.-L. BIRCK
Lab. Géochimie et Cosmochimie, IPGP, 4 Place Jussieu, 75252 Paris Cedex 05, France

Until today no consensus on the classification of the Tafassasset meteorite has been obtained. It was suggested that it is: - an equilibrated CR chondrite, - a primitive achondrite and – that is has strong affinities with brachinites [1-3]. In order to lift this ambiguity and to better understand its origin, we performed a Mn/Cr isotope study of Tafassasset. For comparison we also analyzed Acapulco because only few Mn/Cr data are available on primitive achondrites.

**Tafassasset:** We analyzed Cr isotopes in separated minerals and in a bulk silicate fraction. The large comogenic excesses of $^{53}\text{Cr}$ and $^{54}\text{Cr}$ measured in the metal allow us to correct the other phases for potential cosmic ray effects. In the $^{53}\text{Cr}$ versus $^{55}\text{Mn}/^{53}\text{Cr}$ space chromite, olivine and bulk silicate define an isochrone with a slope corresponding to $^{53}\text{Mn}/^{55}\text{Mn} = 3.07 \times 10^{-6}$ and an origin at $^{53}\text{Cr} = 0.07$. All Tafassasset samples exhibit a clear excess of $^{54}\text{Cr}$: $1.37 \times 10^{-3}$. So far, carbonaceous chondrites represent the only meteorites that display such positive $^{54}\text{Cr}$ excesses; moreover this value measured for Tafassasset is in agreement with that published by [4] for Renazzo.

**Acapulco:** We analyzed Cr isotopes in separated minerals and in a bulk silicate fraction. Similar to Tafassasset, the metal phase also displays large cosmogenic effects in $^{53}\text{Cr}$ and $^{54}\text{Cr}$. Chromite, olivine and bulk silicate define an isochron in the $^{56}\text{Mn}/^{54}\text{Cr}$ versus $^{54}\text{Cr}$ diagram. Zipfel [5] in earlier Mn/Cr study on Acapulco showed that the initial $^{53}\text{Mn}/^{54}\text{Cr}$ ratio corresponds to $7.5 \times 10^{-7}$, our determination lies close to Zipfel’s value ($^{53}\text{Mn}/^{54}\text{Cr} = 1.038 \times 10^{-6}$). The Mn/Cr and U/Pb closure age of Acapulco are concordant. The initial $^{54}\text{Cr}$ (0.069) indicates that the evolution of the Acapulco source region occurred with an eucritic Mn/Cr ratio [6]. All Acapulco minerals display an identical $^{53}\text{Cr}/^{54}\text{Cr}$ deficit (~0.75 $\epsilon$). This value is in agreement with the specific ratio determined for HED meteorites and it establishes the close relationship of Acapulco with this group.

Our investigation shows that the $^{53}\text{Cr}$ and $^{54}\text{Cr}$ isotope systems represent an efficient tool to decipher the origin and classification of meteorites.


---

**Armalcolite (Mg,Fe)Ti₂O₅ in the Siberian platform floodbasalts**

M.P. GORA AND A.YA. SHEVKO
V. S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk 630090, Russia (gora@uggm.nsc.ru)

Armalcolite is a common mineral of the Moon basalts, whereas it is a rare mineral of the Earth rocks. It was described in lamproites, kimberlites, and some basic rocks with native iron association. We have found armalcolite in basalts of the Gudchikhinsky suite of the Norilsk Region, Siberian platform (T₁gd). These basalts are the result of early stage of trap magmatic events and are characterized by high concentration of both Ti and Fe. Armalcolite of the Gudchikhinsky basalts is Mg-poor and corresponds to ferropseudobrookite (Fe₂TiO₅) in composition, as the end member of armalcolite solid solution. This mineral contains (n=3, EPMS, wt.%): TiO₂-64.1-71.7, Al₂O₃-0.1-0.2, FeO-23.9-28.4, MnO-0.21-0.39, MgO-0.33-1.47, Cr₂O₃-0.04-0.5 [1]. Ferropseudobrookite forms the prismatic dendrite crystals for various types of basalts. This armalcolite has very complicated microstructure that can be observed only by scanning electron microscopy method. Fig. 1 shows this armalcolite (grey) overgrown with ilmenite (light grey).

**Figure 1:** BSE image of armalcolite dendrite crystal.

We believe that this microstructure may be interpreted as armalcolite interaction with surrounding melt resulting in forming of ilmenite. Dendrite habit of the armalcolite crystals indicates that the melt cooled rapidly, this in turn caused incomplete replacement of primary armalcolite by ilmenite. Thus this armalcolite crystallized from high-Ti melt under reduced conditions at temperatures above 1010°C, according to experimental study of the FeO-MgO-TiO₂ system [2].

Fungal growth on bare rock surfaces – Where does the carbon come from?

ANNA A. GORBUSHINA
Geosciences, Free Universiy & BAM, Berlin
(anna.gorbushina@bam.de)

Primary successions in terrestrial ecosystems usually involve microbial growth on bare rock surfaces. In these extremely stressed environments complex microbial communities must adapt to high solar irradiation, low water and nutrient availability, extremes of temperature as well as atmospheric composition. The term ‘Subaerial biofilm’ (SAB) has been used to describe microbial communities that develop on solid surfaces exposed to the atmosphere. SAB are ubiquitous, self-sufficient, miniature microbial ecosystems that are found on buildings, bare rocks in deserts, mountains, and at all latitudes where direct contact with the atmosphere and solar radiation occurs. SAB on exposed terrestrial surfaces are characterised by patchy growth that is dominated by associations of fungi, algae, cyanobacteria and heterotrophic bacteria. Although microbial members of rock-inhabiting communities vary, the presence of yeast-like micro-colonial fungi is common in SAB. Despite being ubiquitous, the role and symbiotic relations of heterotrophic micro-colonial fungi in natural and model SAB systems has not been thoroughly examined. To assess the importance of carbon inputs, we simulated growth of a single fungal micro-colony on a solid rock surface. Analysis of this model showed that the continued lack of organic nutrition is a major environmental factor in limiting growth of MCF on exposed rock surfaces. We suggest that fungi either use an atmospheric source of organic carbon which can be particulate and/or volatiles, or associate with phototrophic components of the subaerial microbial community. In a novel simulation laboratory approach we examine model bipartite biofilms (fungus/cyanobacterium) growing under different atmospheric CO₂ concentrations. The results will be discussed in the context of the terrestrial carbon cycle, climate change and establishment of SAB.

Electronic and biogeochemical properties of bacterial nanowires

Y. GORBY¹*, G. WANGER¹, T. YUZVINSKI², M. FIELDS³ AND M. EL-NAGGAR²

¹J. Craig Venter Institute, San Diego, CA 92121
(*correspondence: ygorby@jcvi.org, gwanger@jcvi.org)
²University of Southern California, Los Angeles, CA
(mnaggar@usc.edu, yuzvisnk@usc.edu)
³Montana State University, Bozeman, MT
(matthew.fields@erc.montana.edu)

Many organisms, including including dissimilatory bacteria such as Geobacter and Shewanella produce electrically conductive appendages called bacterial nanowires. Catalytic transformation of hydrous ferric oxide into nanocrystalline magnetite was reported over 5 years ago [1, 2]. Nanowires and partially characterized extracellular polymeric substances have also been implicated in the reductive transformation of dissolved uranium into nanoparticulate uraninite particles [3, 4]. For the past several years our collaborative team—with funding from the Air Force Office of Science, J. Craig Venter Institute, and the Legler Benbough Foundation—has developed and applied approaches for characterizing the molecular and electronic properties of bacterial nanowires using the metal reducing bacterium S. oneidensis as our model organism. Recent funding from the Department of Energy will be used to investigate the composition, conductivity and biogeochemical reactivity of nanowires from metal- and sulfate-reducing isolates from subsurface sediments from the Oak Ridge Field Research Center. This presentation provides an update on our current knowledge of electronic properties of nanowires and their role in reductive transformation of iron and uranium in subsurface sediments.

Overbank sediments used for regional geochemical mapping and research of environmental contamination

V. GORDANIC1*, V. SPASIC-JOKIC2, A. CIRIC3 AND D. JOVANOVIC3
1Geo-Science, Belgrade (gordanicv@gmail.com)
2Faculty of Technical Science (svesna@uns.ac.rs)
3Geological Institute of Serbia, Belgrade, Serbia (abciric@eunet.rs, dragan.jovanovic@gis.co.rs)

Samples of the sediments collected from the alluvial plains of Serbia were silts to gravelly-sands. Development of river bank profile depends on position of the flows and duration of sedimentation process. In the mountainous areas overbank sediments were less developed and coarser grained, while in the plain flows, they are fine grained and abundant. Containing geochemical inscription of the wider drainage area, they were used for Regional geochemical mapping of Serbia and for determination and analysis of anthropogenic influence on selected areas.

Variations of the chemical compositions in the river bank profile as the result of natural conditions and anthropogenic influence are very indicative and manifested in different concentrations of elements in the profile levels. We have chosen locations in the different parts of Serbia (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Pb</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nera River</td>
<td>A</td>
<td>8.9</td>
<td>95</td>
<td>185</td>
<td>98</td>
</tr>
<tr>
<td>OB</td>
<td>13.4</td>
<td>270</td>
<td>60</td>
<td>988</td>
<td>3.8</td>
</tr>
<tr>
<td>S</td>
<td>12.5</td>
<td>180</td>
<td>40</td>
<td>468</td>
<td>1.9</td>
</tr>
<tr>
<td>Borska River</td>
<td>A</td>
<td>15.0</td>
<td>19</td>
<td>500</td>
<td>58</td>
</tr>
<tr>
<td>OB</td>
<td>20.0</td>
<td>34</td>
<td>300</td>
<td>60</td>
<td>1.2</td>
</tr>
<tr>
<td>S</td>
<td>7.0</td>
<td>82</td>
<td>6222</td>
<td>75</td>
<td>0.8</td>
</tr>
<tr>
<td>Djetina River</td>
<td>A</td>
<td>-</td>
<td>30</td>
<td>125</td>
<td>159</td>
</tr>
<tr>
<td>OB</td>
<td>-</td>
<td>67</td>
<td>1873</td>
<td>1837</td>
<td>1.0</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>39</td>
<td>381</td>
<td>424</td>
<td>1.0</td>
</tr>
<tr>
<td>Kriva Reka River</td>
<td>A</td>
<td>40</td>
<td>714</td>
<td>58</td>
<td>1150</td>
</tr>
<tr>
<td>OB</td>
<td>45</td>
<td>377</td>
<td>56</td>
<td>1160</td>
<td>5.6</td>
</tr>
<tr>
<td>S</td>
<td>177</td>
<td>1580</td>
<td>428</td>
<td>38900</td>
<td>85.5</td>
</tr>
</tbody>
</table>

A=A-horizon.; OB=overbank sediments; S=stream sediments

Specific geochemical behavior of the oil as evidence of its abiotic origin

RIMMA.P. GOTTIKH1, BOGDAN.I. PISOTSKIY2 AND IRINA.N. PLOTNIKOVA3*
1VNIIGeoSystem, Moscow (rimgot@mail.ru)
2Institute of Problems of Oil and Gas, Moscow (pisotskiy@list.ru)
3Kazan State University, Kazan (*correspondence: irena-2005@rambler.ru)

Among the evidences of participation of deep fluids in formation of oil accumulations are the results of geochemical studies. The long-term study of micro-elemental composition of oil suggests the presence of a wide range of metals in oil. Both the presence and composition of these metals could not be related to rocks of the sedimentary cover. For example, sometimes the abundances of volatile chalcophile and dispersed elements characteristic of basal and ultrabasic rocks (Hg, Au, Ag, Cu, Re, Se, As, et al.) are ten to hundred times higher than the Earth’s crust Clarke values. Moreover, oil contains high-charge and high-ionic lithophilous elements (U, Th, REE, Zr, et al.) characteristic of alkaline and ultra-alkaline rock complexes. In addition platinoids, among which palladium is predominating, are found in oil. Palladium is commonly predominating over the total of Ru+Ir+Rh. Interrelation between these components is controlling the geochemical classification of oil provinces by platinum metal specialization. The presence of chromium, cuprum, nickel and cobalt in oil in addition to platinoids is indicator of the chemical and metallogeny features of platform hyperbasites. Of much importance is the presence of a sharply defined positive europium anomaly in hondrite-normalized distribution of rare elements in oil that is unusual for host rocks, formation water and organic material. Finally, the inconsistence of isotopic composition of neodymium and strontium enclosed by oil and the isotopic composition of bitumoids of probable oil source rocks is found. Presented are experimental data about the traces of migration of ascending fluids in the geological formations of oil areas and geochemical characterization of these fluids, produced by the analysis of mineral inclusions and differentiation products – bitumen. Discussed are possible sources and conditions controlling formation of such systems. Magmatic pulses on platforms created the multistage character of magmatism, both in time and in space, and the observed chemical differences. The intrusion of magmas and their stratification due to convection were followed by the final stage of the intrusion's development. This was accompanied by substantial losses of thermal energy and by the concentration of a major portion of the fluid and incoherent elements in the upper part of the magmatic chamber. The composition of separated magmatic fluids of the C-O-H-N-Cl-F-S-P system can vary depending on the chemistry and the stable depth of their sources. This mainly occurs due to the binding of hydroxyl in minerals of overlying rocks and the TRUNCATED
Kinetics of Cr(VI) reduction by pyrite surfaces at pH 4 to 9: Surface coverage and passivation effects

A.M. Graham AND E.J. Bouwer*
Johns Hopkins University, Department of Geography and Environmental Engineering, Baltimore, MD, USA 21218
(*correspondence: bouwer@jhu.edu)

Pyrite is a common constituent of modern anoxic sediments, and may contribute to redox transformations of a range of pollutants including Cr (VI). Previous studies of pyrite oxidation by Cr (VI) have focused primarily on acidic pH conditions [1, 2]; here we present a detailed investigation of the kinetics of Cr (VI) reduction by acid-washed pyrite surfaces over a range of pH (4.0 to 9.0) and surface coverage conditions.

Cr (VI) reduction occurred almost entirely via a surface-reaction pathway, and complete reduction of 7 to 120 μM Cr (VI) by 0.3 to 2.1 m²/L pyrite suspensions was observed for the pH range 4.0 to 9.0. Timescales for complete Cr (VI) reduction increased significantly with increasing initial Cr (VI) concentration. In general, rates of Cr (VI) reduction increased 5-15 times upon decreasing pH from 9.0 to 4.0, with the greatest pH effect occurring for the highest surface coverage conditions.

A complex dependence of the reaction rate on aqueous Cr (VI) concentration is attributed to a combination of surface-site saturation behavior and declining pyrite reactivity with accumulation of a Cr (III) (hydr)oxide product overlayer. X-ray photoelectron spectra of reacted pyrite surfaces confirmed the presence of a Cr (III) (hydr)oxide overlayer, the accumulation of which limits access of Cr (VI) to reactive surface sites and slows reaction progress. Available reductant (either Fe (II) or S²⁻) at the surface was insufficient for the complete Cr (VI) reduction observed, suggesting a role for cycling of Fe (II)/Fe (III) at the pyrite surface in regenerating reactive surface sites.

Results of this work indicate that pyrite will rapidly remove μM levels of Cr (VI) from polluted sediment porewaters or groundwaters at circumneutral pH, while surface site limitations or surface passivation will limit rates of Cr (VI) reduction for higher Cr (VI) loadings.


Biological and biochemical pathways of litter decomposition and soil carbon stabilization

A. Stuart Grandy* AND Kyle Wickings
Department of Crop and Soil Sciences, Michigan State University, East Lansing, MI 48824
(*correspondence: grandya1@msu.edu)

Current models predict that changes in plant litter chemistry during decomposition are primarily regulated by initial litter chemistry and the stage, or extent, of decomposition. Far less is known about the degree to which decomposer community structure and land use management regimes – including the conversion of grasslands to biofuel crop production – influence litter chemistry during decomposition. Given the recent agricultural intensification occurring globally, our objectives were: 1) to determine the potential effects of agricultural intensification on plant litter chemistry and decomposition rates; and 2) to investigate possible links between ecosystem management, litter chemistry and decomposition, and decomposer communities and activity. After one growing season, conventional-till litter decomposition rates were 20% greater than in old field communities and grass residue in both conventional- and no-till systems was enriched in total polysaccharides relative to the initial litter, while grass litter in old fields was enriched in nitrogen-bearing compounds and lipids. These differences corresponded with differences in decomposer communities. Our results show that agricultural intensification can increase litter decomposition rates, alter decomposer communities, and shift litter chemistry in ways that could have long-term effects on soil organic matter dynamics. We suggest that future efforts to predict soil C dynamics should consider that changes in litter chemistry during decomposition are not merely a function of initial litter quality, but are also strongly influenced by the specific metabolic capabilities of decomposer communities.
Aerosol samples were collected in Steubenville, OH where a mercury deposition hot spot [1] and an association between air pollution and mortality has been postulated [2]. The samples were collected over 26 consecutive days in summer 2004 using a ten stage MOUDI. The particulate from each size fraction was leached to provide a water soluble fraction (1 day leach) as well as a dilute acid extractable fraction (30 day leach) [3]. Metal concentrations in the extracts were then quantified using SF ICP-MS.

Event precipitation samples from this area indicate significant wet deposition contributions from coal combustion, iron/steel production, oil/incineration and crustal sources [1]. This study was designed to assess aerosols at this location from inhalation perspectives. When examined from a coupled size fractionation and solubility perspective, the elements from the aerosols clustered into six groupings. Water soluble elements mostly in the finer fractions included As, Cd, Rb, Ge, S, Se, and V; those requiring acidification to increase solubility included Cr, Cu, Mo, Sn and Pb. S and Se were key indicators for monitoring condensation processes in the fine fractions. Water soluble elements mostly in the coarser fractions included Ba, Ca, Mg, P, and Sr, whereas La, Ce and Ti required acidification to increase solubility. Some elements displayed a bimodal distribution with relatively equal contributions from the coarse and fine fractions. Of these elements Co, K, Mn, Na, and Zn were water soluble, whereas Al and Fe were acid extractable. Aerosols from both anthropogenic and natural sources are of concern from an inhalation perspective; and some of the elements predominantly in the water soluble fraction from this study include metals that are known to be cytokine–active [4] and have produced toxic responses in epidemiologic studies [5].

Submarine tholeiitic volcanism (ca. 3.6 to 4.9 Ma) West of Ka‘ena Ridge, Hawaiian Islands: Implications of low magma productivity in the evolution of the Hawaiian Plume

ANDREW R. GREENE¹, DOMINIQUE WEIS², MICHAEL O. GARCIA¹, MAIA KUGA³, GARRETT ITO¹ AND JOEL ROBINSON⁴

¹University of Hawaii at Manoa, Honolulu, HI, USA  
²University of British Columbia, Vancouver, BC, Canada  
³Ecole Normale Supérieure de Lyon, Lyon, France  
⁴Volcano Hazards Team, U.S.G. S., Menlo Park, CA, USA

The largest gap in volcanism in the Hawaiian Islands is between the islands of Kaua‘i and O‘ahu, where the volume of the islands is the smallest. Volcanic cones west of Ka‘ena Ridge are samples of the Hawaiian plume at a time of low magma productivity along axis of the Hawaiian chain. Ka‘ena Ridge is an elongate, relatively flat-topped submerged terrace 35-55 km wide that extends ~80 km from the western edge of O‘ahu. The volcanic cones west of Ka‘ena Ridge were sampled by Jason II from R/V Kilo Moana in 2007. The flat-topped and conical cones are <400 m high and <2 km in diameter at water depths ranging between ~2700 to 4300 m, and consist predominantly of pillowed flows and mounds. Ar-Ar ages of eight lavas are between 4.9 and 3.6 Ma; three additional K-Ar ages range from 4.7 to 4.3 Ma. These ages overlap with shield volcanism on Kaua‘i (5.1-4.1 Ma) and Wai‘anae volcano shield basalts (3.9-3.1 Ma) on O‘ahu. Half of the volcanic cones contain high-SiO₂ basalts (51.0-53.5 wt % SiO₂). Isotopic compositions of West Ka‘ena lavas diverge from the main Ko‘olau-Kea shield mixing trend in binary isotope diagrams and extend to lower 206Pb/204Pb and 208Pb/204Pb ratios than any Hawaiian tholeiitic lava. Several West Ka‘ena samples are similar to SiO₂-enriched, Loa-trend lavas of Ko‘olau Makapuu stage, Lāna‘i, and Kaho‘olawe, which are thought to be from an eclogite source. Our results demonstrate that Loa-type magmatism extends beyond Ko‘olau volcano. Loa-type volcanism persisted when there was not a dual chain of volcanoes or bilateral asymmetry in the Hawaiian plume. A correlation is apparent between magma productivity and isotopic compositions in the Hawaiian Islands. The temperature structure and distribution of heterogeneities in the plume, and position relative to the plume center, controls emergence of greater eclogitic component relative to peridotite.

Electrochemical processes in pressure solution

GEORGE W. GREENE, ¹ KAI KRISTIANSSEN, ² MARKUS VALTINER, ² JIM BOLES³ AND JACOB ISRAELACHVILI¹,²

¹Materials Department, University of California, Santa Barbara, CA 93106. USA  
²Department of Chemical Engineering, University of California, Santa Barbara, CA 93106. USA  
³Department of Earth Science, University of California, Santa Barbara, CA 93106. USA

Experiments were carried out using a recently developed in situ electrochemical cell in a Surface Forces Apparatus (SFA) to investigate the dissolution of silica surfaces in close proximity to muscovite mica as a function of both time and electrochemical potential. We have measured changes in the electrical potential difference between quartz and mica surfaces that correlate strongly with the changing quartz dissolution rate when surfaces are pressed together at relatively low pressures (2-3 atm) in acidic electrolyte solutions of 30 mM CaCl₂ at 25 °C. The origin of the electrical potential is interpreted as overlapping of the double layer of dissimilar surfaces when they are forced into close proximity. In addition, we have applied external electric fields across amorphous silica and mica surfaces and investigated its effect on the observed silica dissolution rate. We find that, depending upon the polarity and strength of the electric field, the rate of silica dissolution can be either enhanced or retarded suggesting the dissolution is driven, at least in part, by electrochemical reactions.
D/H of Lunar water: Implications for the origin of the Earth’s water

JAMES P. GREENWOOD1, SHOICHI ITOH2, NAOYA SAKAMOTO3, PAUL H. WARREN4, LAWRENCE A. TAYLOR5 AND HISAYOSHI YURIMOTO2,3
1Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA
2Natural History Sciences, Hokkaido University, Sapporo 060-0810 Japan
3Creative Research Initiative “Sousei”, Hokkaido University, Sapporo 060-0810 Japan
4Institute of Geophysics & Planetary Physics, University of California, Los Angeles CA 90095 USA
5Dept. of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996-1410 USA

We have used a new ion microprobe technique that combines quantitative spot analyses with semi-quantitative 2-D ion imaging to study H and D distributions in individual apatite grains {Ca5 (PO4)3 (F, Cl, OH)} in a range of lunar rocks collected during the Apollo program. We find the Moon has abundant water and a distinct range of D/H compared to known water sources in the solar system. Our results suggest a significant delivery of cometary water to the Earth-Moon system shortly after the giant impact. A 10% contribution of cometary water to the Earth’s oceans is indicated by our data.

Figure 1: δD vs. H2O (wt.%) of lunar apatite grains from mare basalts, highland alkali anorthosite clast (14305, 303) and two highlands breccias (14303, 94 and 12013, 148).

Seawater calcium isotope record over the Paleocene-Eocene Thermal Maximum

E.M. GRIFFITH1,2 AND A. PAYTAN1
1Institute of Marine Sciences, University of California, Santa Cruz, California, 95064 USA (apaytan@ucsc.edu)
2Department of Geology, Kent State University, Kent, Ohio 44242 USA (egriffi9@kent.edu)

Calcium carbonate (CaCO3) sedimentation in the ocean represents the largest calcium (Ca) and carbon (C) sink in the combined atmosphere, biosphere, and ocean system, thus connecting the global C and Ca cycles. The Ca isotope record over the Paleocene-Eocene Thermal Maximum (PETM) will be examined at high resolution (20ky) using coeval marine barite and bulk marine CaCO3 from ODP Leg 199, Site 1221C from 55.1 to 54.9 Ma. The marine barite Ca isotope record decreases briefly at the P-E boundary and then immediately increases in values to a maximum at the highest accumulation rates of CaCO3 in this core; and quickly returns to values near modern day seawater. This record will be compared to a bulk carbonate Ca isotope record from the same site.

Short term imbalances in marine Ca sources and sinks could have resulted from extreme shoaling of the CCD and may be reflected in seawater Ca concentrations and Ca isotopic composition. It has been shown that theoretically [1] in a ‘buffered’ ocean dominated by biogenic pelagic CaCO3 sedimentation, as long as the pelagic flux of CaCO3 (sink) remains greater than the riverine flux (source) of CO3^2-, the deep ocean CO3^2- concentration and thus CaCO3 saturation remains stable. Moreover, the global marine Ca cycle is likely stabilized (as is the case at the Eocene-Oligocene Transition [2]). However, during the PETM when the pelagic flux could have significantly decreased relative to the riverine flux, large changes in the marine Ca (and C) cycles could occur. A simple isotopic mass balance model is constructed to compare predicted and observed isotopic fluctuations over a range of potential scenarios.

Low $\delta^{18}$O(Zrc) in plagiogranites at Oman: Evidence for remelting

C.B. GRIMES$^{1,2,*}$, T. USHIKUBO$^2$ AND J.W. VALLEY$^2$

1Dept. of Geosciences, Mississippi State Univ., MS 39762
2WiscSIMS, Dept. of Geoscience, Univ. of Wisconsin, Madison, WI 53706 USA (cgrimes@geosci.msstate.edu)

Early, high temperature (T) infiltration of seawater may significantly impact late magmatic processes during growth of ocean crust. Magmatic $\delta^{18}$O from zircons in plagiogranites from northern Oman ophiolite (Stakes & Taylor 1992 JGR) provide new evidence for the role of seawater in formation of oceanic plagiogranite. Zircons were separated and imaged by SEM at WiscSIMS prior to analysis of $\delta^{18}$O and trace element (TE) using a Cameca 1280. Many zircons are oscillatory zoned (OZ) or contain OZ domains, but CL imaging also reveals late rims, and irregular/chaotic zoning sometimes associated with porous areas. Similar textures are reported in zircons from mid-ocean ridge (MOR) plagiogranite, and highlight potential concerns with geochemical analysis of whole crystals without prior imaging.

Igneous OZ zircons from Oman plagiogranites range in $\delta^{18}$O from 3.9-5.2‰ VSMOW, averaging 4.6 ± 0.6‰ (2SD). This average value is distinctly lower than the average determined on a large suite of zircons from 43 rock samples of slow-spreading ocean crust (5.2 ± 0.5‰; n=221; Grimes et al. 2010) and lower than $\delta^{18}$O of zircon in high-T equilibrium melt of Oman zircons and MOR plagiogranite zircons are equivalent, arguing against differences in magma source or crystallization T as a cause of lower $\delta^{18}$O for Oman zircons. Instead, the low $\delta^{18}$O (Zrc) can be explained by formation of the parent magmas by melting of a protolith altered at high T by a low $\delta^{18}$O fluid. The Oman ophiolite has been interpreted to represent ancient fast spreading ocean crust, formed either at a MOR or backarc spreading center. These new low $\delta^{18}$O (Zrc) data contrast with slow-spreading MOR zircons and could thus reflect 1) contrasting high T hydrothermal circulation systems at different spreading rates, with lower water/rock in slow spreading centers, or 2) melting of preexisting, hydrothermally altered crust in a backarc setting.

Single particle analysis of aerosols from El Chichón and Stromboli

B. GROBETY$^1,*$, M.F. MEIER$^1$, M. FIERZ$^2$, C. BOTTER$^1$ AND T. RICCI$^3$

1Dep. of Geosciences, Univ. of Fribourg, 1700 Fribourg, Switzerland (Correspondence: bernard.grobety@unifr.ch)
2Inst. Aerosol- and Sensortechnology, FH Nordwestschweiz, 5210 Windisch, Switzerland
3Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy

Particulate matter emission into the troposphere by continuous smaller eruptions and degassing of quiescent volcanoes has not been given the same attention as to stratospheric aerosols produced by large eruptions. The effect on the radiation budget of the volcanogenic tropospherical sulfur containing aerosols (sulfuric acid, sulfates) is, however, considered to be at least as high as the antropogenic contribution. Previous investigations on the mineralogy of the aerosols and the condensation processes were done mainly by remote sensing and on bulk aerosol samples. Computer controlled SEM and EDX allows to gather quantitative information on a single particle basis. In 2009, we collected aerosol samples on Stromboli, Italy, a volcano with continuous moderate eruptive activity, and El Chichón, Mexico, a quiescent volcano with fumarolic activity. The particles were collected actively onto Nuclepore filters and Transmission Electron Microscopy grids. At El Chichón the sampling devices, an active PM10 and a corrosion resistant electrostatic sampler, were located close to the fumaroles and on the crater rim. On Stromboli, samplers were placed on the crater rim and on three locations along the coast. Over 2000 particles per sample were analyzed. Particles from the steam dominated fumaroles at El Chichón consist mainly of sulfuric acid, silicates and minor alkali sulfates. The composition of the aerosol does not change in composition during transport to the crater rim 200m above. Total sulfuric acid and sulfate particle flux out of the crater is estimated at 0.1 kg s$^{-1}$. A different picture is seen at Stromboli. The aerosol at the crater rim is dominated by submicronic K and Na bearing sulfates, almost no sulfuric acid droplets were found. The sulfate fraction in the samples collected in the three other locations, however, consist of sulfuric acid and Mg or Ca-bearing sulfate phases, which are rare in the crater samples. The change in sulfate mineralogy from the top to the lower parts of the volcano is either due to the increased mixing between volcanic and sea aerosols, or may reflect a change in the chemistry (ph, F02) of the volcanic gas plume itself. The low concentration of sea salt particles in the latter speaks in favor of an evolution in plume chemistry.
Post-perovskite phase transition in compositions related to mantle rocks

B. GROCHOSLKI1*, S.-H. SHIM1
AND VITALI PRAKAPENKA2

1Department of Earth, Atmospheric, and Planetary Sciences.
Massachusetts Institute of Technology, Cambridge MA 02139 (*correspondence b.grocholski@gmail.com)
2GeoSoilEnviroCARS, University of Chicago, Chicago IL 60637

Studies have shown that the D” discontinuity is much more readily observed at high-velocity regions than low-velocity regions [1]. The variation has been attributed to the thermal response of the perovskite to post-perovskite (PPv) transition due to its positive Clapeyron slope. This assumes a narrow depth interval and a large Clapeyron slope for the PPv transition. However, our recent study on binary and ternary systems [2] showed that 10% Fe and 10% Al increase the thickness of the two-phase region to 400-600 km, making seismic detection of the PPv transition difficult. The buffering effects of ferropericlase (Fp) have been modelled [2], but not directly measured. We have determined the depth and thickness of the PPv transition in pyrolite and San Carlos olivine compositions up to 170 GPa and 3000 K in laser-heated diamond cell. Both compositions produce Fp in the lower mantle. While pyrolite contains Al, San Carlos olivine does not. Our measurements on a pyrolitic composition indicate the PPv transition begins at a depths 100±100 km below the core-mantle boundary (CMB) and has a wide two-phase region of 800±200 km. In contrast, the PPv transition in a San Carlos olivine composition occurs at a depth 100±100 km above the CMB with a two-phase region thinner than 100±100 km. These are in good agreement with our predictions in [2] that Al increases both depth and thickness of the PPv transition (as measured in pyrolite) while Fp (or high Mg/Si) decreases the thickness through buffering effect (as measured in San Carlos olivine). Harzburgite, existing in the subducting lithosphere, has much smaller amount of Al and higher Mg/Si ratio, making an ideal candidate rock for a sharp PPv transition. Therefore, the PPv transition may exist in harzburgite subducted into the deep mantle, while it does not exist in pyrolitic mantle.


Dispersed Fe/Mn ratios of lunar rocks: ALHA81005’s view from the Farside

JULIANE GROSS* AND ALLAN H. TREIMAN

Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058 (*correspondence: gross@lpi.usra.edu).

Lunar meteorites come from random sites on the Moon (including areas not visited by Apollo or Lunar missions) and therefore are crucial for understanding the development of the whole Moon. Their mineralogy and chemistry can also be used as ground truth for lunar remote sensing. We are re-investigating lunar meteorite ALHA81005 to help understand unsampled areas of the Moon, and enlarge our knowledge of lunar highland rock types, and place constraints on the Moon’s early history.

ALHA81005 is a lunar breccia from the farside [1], which contains a wide variety of rock and mineral fragments, most of which are granulites and anorthosites [2, 3]. While other rock types are rare, some mineral fragments must represent lithologies other than granulites and anorthosites. Using mineral compositions and elemental systematics (specifically Fe/Mn ratios) we can place constraints on the chemical variation and evolution of the lunar crust and mantle.

We have focused on the Fe/Mn ratio of lunar minerals because it does not vary much during basalt genesis & fractionation. Fe/Mn is used to categorize the basaltic source composition (i.e. mantle) which reflects the planet’s bulk composition, its oxidation state, extent and composition of its core and is used as a characteristic for particular planetary bodies, e.g. Moon versus Earth versus Mars [4-6]. However, lunar mafic minerals in fact have extensive variation in their Fe/Mn ratios. Karner [5] noted that olivines in high-Ti mare basalts have Fe/Mn ~ 87 (but with variation) and that low-Ti mare basalts had Fe/Mn ~ 115 (again with variation). In ALHA81005, olivines in anorthosites, granulites, basaltic clasts (low Ti and VLT) and isolated mineral fragments have Fe/Mn ~ 85-92 like high-Ti mare basalts [5] although they are not rich in Ti. The cause of these variations in Fe/Mn could suggest that the source regions of the samples (i.e. nearside vs. farside) have different compositions or oxidation states, and thus different geochemical histories.

The oxygen isotope record for the Phanerozoic

ETHAN L. GROSSMAN
Dept. of Geology and Geophysics, Texas A&M University, College Station, TX 77843 USA (e-grossman@tamu.edu)

Oxygen isotopic data for the Phanerozoic have been compiled to examine long-term trends in paleotemperature and seawater δ18O [1]. The δ18O record is based on calcium carbonate and phosphatic fossils and microfossils – foraminifera for the Cenozoic, belemnites and brachiopods for the Mesozoic, and brachiopods and conodonts for the Paleozoic. The data are derived from recent literature (e.g. [2]) and compilations by Zachos et al. [3] and Prokoph et al. [4]. To minimize the effects of diagenesis, this study has emphasized (1) sample-screening of Paleozoic brachiopods by petrographic examination of thin-sections, (2) samples from cratonic regions and localities with unusual fossil preservation, and (3) phosphatic fossils and microfossils.

Veizer et al. [5] observed a trend of increasing δ18O with decreasing age that they attributed to evolution of seawater δ18O. In this study, brachiopod values are low for some intervals in the Devonian, Silurian, and late Ordovician (2 Ma means as low as -5.6‰) that must be explained by warm temperatures (25-40°C assuming seawater δ18O of an ice-free modern world, -1‰), lower seawater δ18O (-3‰; either locally or globally), or sample alteration. Conodont δ18O values yield mean temperatures only as low as ~30°C and suggest alteration of the brachiopod signal or local environmental effects. For samples younger than Devonian, the δ18O records of carbonates and phosphates yield isotopic paleotemperatures consistent with the modern ocean with no evidence for long-term changes in seawater δ18O.

Some key features in the Phanerozoic δ18O record include latest Ordovician and late Silurian, Middle Devonian rise, mid-late Devonian decline, and early Carboniferous rise. Conodont δ18O values increase to a late Mississippian maximum that is not seen in brachiopod data. Jurassic and Early Cretaceous belemnites show a Toarcian decrease, a mid-late Devonian decline, and early Carboniferous rise. The Late Cretaceous and Cenozoic sea-surface record depends on whether “glassy” or less well-preserved planktonic foraminifera were analyzed. Some “glassy” foraminifera yield low (warm) values approaching those of some early Paleozoic brachiopods.

Multi-phase fluid flow simulations of Brothers volcano: Application of realistic constraints

G. GRUEN1*, T. DRIESNER1, C.E.J. DE RONDE2, AND C.A. HEINRICH3
1ETH Zurich, Department of Earth Sciences, 8092 Zurich, Switzerland (*correspondence: gruen@erdw.ethz.ch)
2GNS Science, Avalon, Lower Hutt 6315, New Zealand (cornel.deronde@gns.cri.nz)

Brothers volcano [1] is an active hydrothermal system located on the Kermadec intra-oceanic arc, northeast of New Zealand, and is one of the best studied submarine arc volcanoes on Earth. It provides insight into the complex subsea floor hydrology of a submarine volcano with evidence for different stages in its magmatic-hydrothermal evolution. Its edifice comprises an elongated caldera surrounding an asymmetrically centered cone. While hydrothermal venting at the NW caldera wall is focused, and which dates back to at least 1,200 years, hydrothermal discharge at the cone summit is diffuse and significantly younger. Recent studies of regional seismicity and local harmonic tremor at Brothers volcano [2] imply the existence of a hydrothermal fluid reservoir located underneath the area of the present cone.

We are computing multi-phase mass and heat transport with a process simulation scheme based on realistic fluid properties and correlations describing phase stability relations in the binary salt-water system [3]. Earlier results of generic fluid flow simulations showed that water depth, seafloor topography, crustal permeability and the relative contributions of seawater and magmatic fluids are first-order physical parameters controlling the style of hydrothermal venting.

In our more recent simulations, we use available data from Brothers volcano, including detailed bathymetry, physical and chemical measurements from different vent sites, and evidence for the size and location of the underlying magma chamber(s). The implementation of two distinct magmatic stages (pre-cone vs. post-cone) with different underlying magma chambers shows that the topography of the volcanic edifice, in combination with the location and size of the magma chamber, play an important role in the style and evolution of the hydrothermal system.

**Dating the depths of the Himalayan orogen**

D. GRUJIC1*, C. WARREN2 AND J.L. WOODEN3

1Department of Earth Sciences, Dalhousie University, Halifax, Canada (*correspondence: dgrujic@dal.ca)
2Earth and Environmental Sciences, The Open University, Milton Keynes, UK
3Department of Geological and Environmental Science, Stanford University, Stanford, USA

The formation of the Himalaya is currently explained by two contrasting tectonic models that differ in their predictions for the sequence of deformation along the main structures. Therefore PTxD data would provide crucial field tests of the tectonic hypotheses.

Mafic and pelitic granulites exposed in the eastern Himalaya preserve textural evidence for a precursor high-pressure metamorphic event, the precise conditions of which are generally unrecoverable due to the later high-temperature overprint. U–Pb zircon geochronological and trace element data suggest that zircons crystallized at 14–15 Ma, which is interpreted to indicate the timing of HP metamorphism due to the lack of negative Eu anomaly, the depleted heavy REE signature and the low temperatures of crystallization. U-Th-Pb Monazite ages indicate that the near peak T conditions were attained shortly after and much later than in the somewhat lower grade area underneath separated by a ductile shear zone. Ti-in-zircon and Zr-in-rutile geothermometry further help to establish links between accessory mineral crystallisation and metamorphism. Finally, crystallization ages of deformed leucogranites suggest concomitant shift of deformation along the roof normal geometry shear zone towards the interior of the orogen, consistent with the exhumation of the high-grade rocks.

We suggest that rocks in the metamorphic core of the Himalaya were buried to greater depths and subjected to greater temperatures than in the central parts of the orogen, and were exhumed rapidly during the later stages of orogenic evolution.

---

**Visualization and statistical methods for the interpretation of geochemical survey data**

E.C. GRUNSKY

Geological Survey of Canada, Natural Resources Canada, Ottawa, Ontario, CANADA K1A 0E8
(*correspondence: egrunsky@nrcan.gc.ca)

An overwhelming amount of geochemical survey data is now available from government around the globe. These geochemical surveys are derived from bedrock, soils, stream sediments, lake sediments, glacial till, regolith, laterite and a range of other less common materials. These surveys are highly variable in their spatial sample site density, heterogeneous mixture of media, choice of size fractions, methods of digestion and analytical instrumentation, which complicates the assembly of large regional-scale datasets. These assembled sets of data often contain thousands of observations with as many as 50 or more elements. Although the assembly of these data is a challenge, the resulting integrated datasets provide an opportunity to discover a range of geochemical processes that are associated with underlying geology, alteration, weathering, base- and precious metal mineralization and anthropogenic effects [1].

Modern methods of evaluating data include the application of multivariate data analysis and statistical techniques combined with geographical information systems. The use of these tools can significantly assist in the task of data interpretation and subsequent model building. Leveling techniques are often required during the assembly of regional geochemical datasets. Geochemical data require special handling when measures of association are required. Because geochemical data are compositional in nature (i.e. ppm, wt%), the application of statistical methods requires the use of logratios in order to eliminate the effect of closure.

Exploratory multivariate methods include: scatterplot matrices, adjustments for censored and missing data, identifying atypical observations, computing robust measures of association, principal component analysis, cluster analysis and knowledge based indices of geochemical processes. The separation of geochemical data into target and background sets forms the basis of a modeled approach for discriminating and classifying data and the subsequent identification and confirmation of geochemical processes.

Effect of natural humic substances on the dissolution and stability of reduced technetium and uranium

B. GU¹, W. DONG¹, W. LOU¹ and N.A. WALL²
¹Oak Ridge National Laboratory, TN (gub1@ornl.gov)
²Washington State University, TX (nawall@wsu.edu)

Reductive precipitation and immobilization of soluble technetium (as pertechnetate, Tc (VII)O₄⁻) and uranium (as uranyl, U (VI)O₂²⁺) to sparingly soluble Tc (IV) and U (IV) species have been proposed as one of the promising remediation technologies to sequester uranium and technetium in situ in the subsurface. However, the dissolution and long-term stability of Tc (IV) and U (IV) are poorly understood, particularly in the presence of natural and synthetic organic ligands, which are known to cause the complexation and mobilization of certain metal ions and radionuclides. In this study, the kinetics of both ligand-promoted and oxidative dissolution of Tc (IV) and U (IV) are determined, and their mobility is evaluated in the presence of naturally occurring humic substances and synthetic ethylenediaminetetraacetate (EDTA). We found that EDTA and the humic acid are among the most effective in promoting the ligand-induced dissolution of Tc (IV) and U (IV) by complexation. However, EDTA is found to suppress the oxidative dissolution of Tc (IV) and U (IV), whereas the humic acid enhances the oxidative dissolution due to its redox reactive functional properties. Furthermore, the oxidative dissolution is found to be much quicker than the ligand-promoted dissolution by humic substances. Evaluation of the dissolution and stability of reduced U (IV) in a contaminated sediment column confirms that both the synthetic and natural organic ligands can cause the mobilization of U (IV) although the dissolution rate appears to be relatively slow. Our results suggest that the presence of both synthetic and natural organic ligands, as commonly observed at many contaminated sites, can potentially impact the long-term stability and mobility of reduced Tc (IV) or U (IV).

Spectroscopic and DFT studies of pentachlorophenol reactions on Fe(III)-montmorillonite clay surfaces

C. GU¹, C. LIU¹, C.T. JOHNSTON², B.J. TEPPEN¹*, H. Li¹ and S.A. BOYD¹*
¹Department of Crop and Soil Sciences, Michigan State University, East Lansing, MI 48824
(*correspondence: boyds@msu.edu, teppen@msu.edu )
²Crop, Soil and Environmental Sciences, Purdue University, 915 W. State Street, West Lafayette, IN 47907

In situ FTIR methods and DFT cluster model calculations have been used to investigate the formation of octachlorodibenzodioxin (OCDD) from pentachlorophenol (PCP) on Fe (III) saturated smectite clay, which has been observed under environmentally relevant conditions [1]. The clay-facilitated single electron transfer from PCP to Fe (III) as the crucial step of the reaction pathway was proposed and examined by the combined techniques.

Figure 1: Comparison of calculated infrared spectra of PCP/Fe (OH)₂(OH₆)²⁺ with experimental spectra. The calculated peak intensities and binding energies of PCP/Fe (OH)₂(OH₆)²⁺ are linearly related to the number of coordination H₂O.

The formation of PCP radical cations on the clay surface as the reaction-initiating step is strongly supported by this combined spectroscopic and theoretical study. DFT calculations of PCP/Fe (OH)₂(OH₆)²⁺ reproduce observed FTIR vibrational features, and demonstrate that they are a direct result of single electron transfer from PCP to Fe (III).

The relationship between gold mineralization and hydrocarbon accumulation in the Youjiang basin, South China

X.X. GU1, Y.M. ZHANG1, B.H. LI2 AND S.Y. DONG2

1State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, P.R. China (xuexiang_gu@163.com)
2College of Earth Sciences, Chengdu University of Technology, Chengdu 610059, P.R. China (libaohua@cdut.edu.cn)

The Youjiang basin in South China lies along the southwestern margin of the Yangtze craton and developed upon a lower Paleozoic basement. It is characterized by containing many sedimentary-rock hosted, disseminated Au deposits of the Carlin-type. Meanwhile, the basin is also well-known as an important host to abundant fossil oil reservoirs and has attracted wide attentions of petroleum geologists. The gold deposits spatially show close association with paleo-petroleum reservoirs, suggesting a genetic linkage between Au mineralization and hydrocarbon accumulation.

The fluid forming paleo-petroleum reservoirs is characterized by a low temperature (typically between 90~160°C) and a low salinity (mostly below 6 wt % NaCl), with main components of hydrocarbon, CO2, and H2O. The ore-forming fluid of gold deposits has a medium to low temperature (typically between 150 to 250°C) and a low salinity (0.4~6.7 wt % NaCl) and is composed mainly of H2O and CO2 and subordinately of hydrocarbon. The spatially close association of paleo-hydrocarbon reservoirs and gold deposits, the contemporaneous activity of reservoir fluid (240~185 Ma) and ore-forming fluid (270~170 Ma), and the intimate relationship in reservoir and ore genesis suggest that both the paleo-oil reservoirs and the gold deposits are products of organic ore-forming basinal fluids. During the late Caledonian to the middle Indosinian, the sedimentation of deep-water, organic- and metal-rich mudstone, siltstone, and micrite in the basin laid a material base for the formation of hydrocarbon reservoirs and Au deposits. The activation of organic ore-bearing basinal fluids during the late Hercynian to early Indosinian was responsible for both gold and petroleum accumulation. Extensive tectonic uplift and denudation during the middle and late Yanshanian have greatly reworked and destructed the deposits and reservoirs.

The research was funded by the National Natural Science Foundation of China under grants of 40772060 and 40930423.

Chemical and isotopic properties of airborne particles in urban and rural environments of the Rhine valley

F. GUÉGUEN1,2, P. STILLE1, V. DIETZE3, M. MILLET2 and R. GIÉRÉ4

1Laboratoire d’Hydrologie et de Géochimie de Strasbourg (UMR7517 CNRS-Université de Strasbourg), rue Blessig 1, 67084 Strasbourg, France (pstille@illite.u-strasbg.fr)
2Equipe de Physico-Chimie de l’Atmosphère, Laboratoire Matériaux, Surfaces et Procédé pour Catalyse (UMR7515 CNRS-Université de Strasbourg, 1 rue Blessig, 67084 Strasbourg, France
3German Meteorological Service, Air Quality Department, Stefan-Meier-Strasse 4, 79104 Freiburg, Germany
4Department of Geosciences, University of Freiburg, Albertstrasse 23b, 79104 Freiburg, Germany

A passive ‘Sigma-2’ device has been used for sampling and chemical/isotope analysis of airborne particles (<100µm); collection time was four weeks. Automated light- or electron-optical analysis of the sampling substrates collected during 1 week in urban and 2 weeks in rural environments provides mass-concentration and mass-deposition rates (MDR). MDR in rural environments are on average 5 times lower (2mg/m2/d) than those in cities (9mg/m2/d). They appear to be strongly controlled by traffic and industrial emissions and, therefore, depend on sampling locality and wind direction. MDR are positively correlated with those deduced from total mass of trace element deposition.

The continental crust-normalized trace element data show distribution patterns very similar to those of tree barks collected at corresponding sampling sites. This confirms our suggestion that tree bark biomonitoring yields very reliable informations of atmospheric pollution (Lahd Geagea et al. 2008). The trace element distribution patterns of samples from rural and urban environments are similar, indicating that the dust traveling over long distances has taken up characteristic anthropogenic signatures. Only dust samples collected within a distance of 5 kilometers from industrial sources allow recognition of source characteristics like lanthanum enrichments typical for steel plant emissions (Lahd Geagea et al. 2008). Trace element deposition rates are highly variable and range between a few mg ha⁻¹y⁻¹ (e.g. U), g ha⁻¹y⁻¹ (e.g. Pb) and up to 15 kg ha⁻¹y⁻¹ (Ca in rural environments with agricultural activities). Pb isotope data allow to distinguish between traffic, industrial and baseline compositions. The industrial aerosols, however, are only distinguishable with help of Sr and Nd isotopes.
Produced water quality: Implications for treatment and beneficial use

K.L. GUERRA1* and K.G. DAHM2
1Bureau of Reclamation, Denver CO 80225-0007
(*correspondence: kguerra@usbr.gov)
2AQWATEC, Colorado School of Mines, Golden CO 80401
(kdahm@mymail.mines.edu)

Approximately 100 million gallons of produced water are generated per day in the Western US from oil and gas extraction. In many areas of the Western US, conventional water supplies are fully allocated and a need exists for additional water resources. Produced water, if it meets the necessary quality standards, has the potential to be used for stream flow augmentation, irrigation, live stock watering, municipal and industrial uses, recreation, and environmental restoration [1].

Produced Water Quality

Produced water TDS concentrations range from 1,000 mg/L to over 400,000 mg/L. Sodium chloride and sodium bicarbonate are the dominant salts in produced water [2]. Minor ions in produced water may also be problematic for treatment and beneficial use.

Treatment and Beneficial use of Produced Water

Desalination will often be required to reduce the total dissolved solids concentration of produced waters to meet beneficial use requirements (Figure 1).

Figure 1: TDS range for oil and gas produced water and beneficial use.


Mineral control on organic carbon and nitrogen biogeochemistry

GEORG GUGGENBERGER1, ROBERT MIKUTTA1, OLIVER A. CHADWICK2, JON CHOROVER3, KLAUS KAISER4, MARC G. KRAMER5 and ANTJE VOLLMER6
1Inst Soil Sci, Leibniz Univ Hannover, D-30060 Hannover
(*correspondence: guggenberger@ilfbk.uni-hannover.de)
2Dept Geogr, Univ California, Santa Barbara, CA 93106, USA
(oc@geog.ucsb.edu)
3Dept Soil Water & Environm Sci, Tucson, AZ 85721, USA
(chorover@cal.arizona.edu)
4Soil Sci, MLU Halle-Wittenberg, D-06099 Halle
(klaus.kaiser@landw.uni-halle.de)
5Earth Planet Sci, Univ California, Santa Cruz, CA 95064
(mkramer@es.ucsc.edu)
6BESSY II, Albert-Einstein-Str. 15, D-12489 Berlin
(antje.vollmer@bessy.de)

The mechanisms involved in interactions of organic carbon (OC) and nitrogen (ON) with minerals still remain poorly understood. Using density fractionation together with biomarker and spectroscopic methods, we studied the role of minerals on the composition and dynamics of mineral-associated OC and ON along the Hawaiian basaltic weathering gradient.

Mineral-organic associations (MOAs) at the youngest 0.3-kyr site were mainly composed of primary minerals with small amounts of attached OM, the 20–400-kyr sites with prevailing poorly crystalline (PC) minerals had larger sorbed OM concentrations, which dropped towards the oldest sites (1400 and 4100 kyr) comprising crystalline secondary minerals [1]. At the 0.3-kyr site, compounds linked to microbial activity, i.e. peptides/proteins and carbohydrates were enriched in sorbed OM. Lignin phenols preferentially accumulated as PC minerals form due to their larger affinity towards variable-charge mineral surfaces. Likewise, acidic peptide/protein structures were more effectively retained by PC minerals [2]. The D/L ratio of lysine revealed an active cycling of the peptidic ON fraction in biologically active topsoil MOAs. In the subsoil, 14C and D/L signature indicated a longer turnover of proteinous components strongly bound to minerals [2]. Hence, stabilization of OC and ON not only depends on the mineral composition but also on the location of MOAs in the soil profile.

Our results call for a pedogenic approach in assessing the biogeochemistry of mineral-associated OC and ON.

Application of the modified-BCR sequential extraction procedure to the assessment of the anthropogenic pollution in contaminated soils from the city of Huelva (SW Spain)

M.T. GUILLÉN*, J. DELGADO, J.M. NIETO AND M.A. CARABALLO

Department of Geology, University of Huelva. Avda. Fuerzas Armadas s/n, 21071 Huelva, Spain (marco.guillen@dgeo.uhu.es)

Modified-BCR sequential extraction procedure has been successfully employed in the last decades to study metal distribution in samples affected by different anthropogenic activities and considered potentially toxic to human health. [1], [2]. Soil samples from the municipal district of Huelva were analyzed with this procedure to establish As, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn distribution in 5 selected soil phases (interchangeable ions, metals bound to carbonates, metals bound to Fe and Mn oxides and residual fraction). In addition to the modified-BCR the samples were studied by X-ray diffraction to determine its mineralogical composition and a total digestion were performed to know the bulk chemistry of the samples. Bulk chemistry analyses of the samples affected by industrial activity showed a significant As, Cd, Cu, Cr, Pb and Zn concentration with maximun values of 2065 mg kg\(^{-1}\) of As, 18 mg kg\(^{-1}\) of Cd, 425 mg kg\(^{-1}\) of Cu, 112 mg kg\(^{-1}\) of Cr, 5469 mg kg\(^{-1}\) of Pb and 4707 mg kg\(^{-1}\) of Zn. Obtain values for the local baseline are: 63 mg kg\(^{-1}\) of As, 0.85 mg kg\(^{-1}\) of Cd, 392 mg kg\(^{-1}\) of Cu, 154 mg kg\(^{-1}\) of Pb, and 321 mg kg\(^{-1}\) of Zn. Fe, Mn and Ni concentrations are representative of the lithology of the area of study and do not imply any risk to the environment. Elements distribution in the different phases reveal greater mobility for Cd, Cu, Mn and Zn as they are released in the bioavailable phase of the sequential extraction (Step 1), showing them as a mayor risk to the human health. Although As, Cr and Pb showed high concentrations in the bulk chemistry analyses, they were only release in the sequential extraction after digestion of the residual phase (Step IV), and they do not represent great risk [3].


Pushing laser ablation ICP-MS to the limit: Speed, reproducibility and sensitivity

MARCEL GUILLONG* AND LEONID DANYUSHEVSKY
CODES, UTAS, Hobart TAS, 7001 Australia (*correspondence marcel.guillong@utas.edu.au)

Laser Ablation in combination with ICP-MS has become the leading method for trace element and isotope ratio analysis of solid samples. The ease of sample handling, high sample throughput, low limit of detection, high possible spatial resolution, and a wide range of elements that the technique can analyze, are the key figures of merit making this method versatile and popular.

This presentation shows recent results obtained using a commercially available laser ablation system (Resonetics M50) equipped with 193nm excimer laser and a constant volume equal geometry ablation cell [1]. Reproducibilities better 2% RSD for more the 100 individual spots covering the whole 25 cm\(^2\) of the cell can be achieved (Fig. 1). With such an excellent stability across the cell of both the ablation and aerosol transport characteristics, it becomes possible to investigate in detail the effects of a number of important analytical parameters such as optimum laser energy density, elemental fractionation, and fine-scale sample heterogeneity.

The laser ablation system can produce laser beam sizes between 5 and 380 micrometer and is able to change aerosol density, sensitivity and LOD’s within six orders of magnitude varying the repetition rates up to 100 Hz and energy densities up to 30 J/cm\(^2\). We will present the results of investigating the effect of plasma mass load using a quadrupole ICP-MS with an increased tolerance of changing matrices.

Figure 1: RSD of quantitative concentrations versus the average intensity of 116 spot analyses of NKT-1G.

Geochemistry and genesis of bedded siliceous rocks in Carboniferous in Jiangshan, Zhejiang, China

F. GUO1,2 *, F. LIU1, Z. HOU1,3 AND G. GUO2

1East China Institute of Technology, Fuzhou, Jiangxi 344000, China (*correspondence: fsguo@263.net )
2Key Laboratory of Nuclear Resources and Environment, Ministry of Education, Nanchang, Jiangxi 330013, China
3Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China

There is a peculiar type of bedded siliceous rock in the Outangdi Formation of the Late Carboniferous in Jiangshan, Zhejiang Province. The siliceous rocks which interbed with feldspathic quartz sandstone, siltstone and conglomerate, are characterized by white in color, light in weight, porous nature, and the residual bioclasts structure, with plenty of silicized calcareous biology. The study suggests that the siliceous rocks originated from bioclastic limestone through replacement, and the limestone was formed in subtidal shallow beach environment. The porosity of the rocks was made by corrosiveness, weathering and eluviating of bioclasts (such as encrinite caudex) and dolomite (or calcareous matter). The first author named this peculiar type of siliceous rock as 'silicized calc-bioclastic chert'.

The rocks are rich in silicon and calcium. The eigenvalues of petrochemistry support the derivation of silicon from normal groundwater, instead of typical hydrothermal or volcanic activities. Rare earth element contents of the rocks are lower total, flat pattern curves, positive anomaly of thorium. The character of lower total REE is similar to that of limestone, showing the inheritance relationship between the two kinds of rocks. The values of silicon and oxygen isotope are lower, and their variation ranges are similiar to those of quartz formed by diagensis, which demonstrates that the siliceous rocks are of metasomatic genesis in the early diagenetic processes.

Arsenic distribution in colloidal size fractions of high As groundwaters in the Hetao basin, Inner Mongolia

H.M. GUO*, B. ZHANG AND Y. ZHANG

School of Water Resources and Environment, China University of Geosciences, Beijing 100083, China (*correspondence: hmguo@cugb.edu.cn)

It is a very important issue whether As can be transported as organic colloids, or not in real groundwater, which is still not established [1, 2, 4]. Eight high As groundwater samples were in situ ultrafiltered with N2 as the protect gas in the Hetao basin, Inner Mongolia. Five successive filtration steps with the nominal size cutoffs 0.45 µm, 100 kDa, 30 kDa, 10 kDa and 5 kDa were used to distinguish between colloids with different size fractions.

Concentrations of As, Fe, DOC vary in fractions ‘< 0.45 µm’, with the ranges from 40 to 1020 µg/L, 0.06 to 0.95 mg/L, and 17.52 to 46.34 mg/L, respectively. Concentrations of Ca, Mg, Na, K, Ba, Sr are not affected by ultrafiltration, while those of As, Fe, Al, Si, DOC, Mn, Mo, U and V show variable through successive filtrations. Results show that the portions of As in the dissolved size fraction smaller than 5 kDa are dependent on the mol ratio of dissolved Fe to dissolved organic carbon (Fe/C). About 90% As remains in the dissolved fractions for the samples with the Fe/C > 0.009, while around 60% with Fe/C < 0.001. About 15-40% was retained in the ultrafilters and removed for the groundwater samples having the Fe/C between 0.001 and 0.009. Experimental study also showed that As distribution depended on Fe/C ratios [2]. The majority of removed As was observed in the filters with molecular weight of 5-30 kDa. The retained As is believed to be bound to organic colloidal particles [3], especially low molecular organic matters. Since As would interact with organic matter molecules through ternary As-Fe-DOM bridging complexes [2], Fe controls the distribution of As among the size fractions, especially for the samples with Fe/C ratios < 0.009.

Natural Science Foundation of China (Nos. 40872160, 40710104037 and 40572145)
Biomarker study of depositional environment during the formation of organic rich source rocks of Nenjiang Formation, Songliao Basin of China

JIANGTAO GUO$^{1,2}$, ZHIGUANG SONG$^1$ AND LI WANG$^{1,2}$

$^1$SKLOG, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou, 510640 China (*correspondence: guojt@gig.ac.cn)
$^2$Graduate University of Chinese Academy of Science, Beijing, 100049

Depositional environment study of the organic rich petroleum source rocks in Songliao Basin of China has long been a major concern for the understanding of the massive lacustrine petroleum source rock formation. The previous understanding of the organic rich source rocks were deposited under fresh to brackish water condition has been challenged as there were suggestion that marine incursions may have significant influence on the formation of massive lacustrine source rock in Songliao Basin. This study aimed to use the source and environmental specific biomarkers as major approaches and to reconstruct detailed depositional condition in the duration of the massive lacustrine source rocks formation. By careful analyses of biomarkers in the core sedimentary samples from the continuous drilling hole in the Songliao Basin, a number of source and environmental specific biomarkers were detected. These source and environmental specific biomarkers include gammacerane, pristane, phytane, 4-methyl steranes, dinosteranes, benzohopanes and a number of aryl isoprenoids as well as isorenieratane. The occurrence and distributions of these biomarkers on the profile strongly suggest that a stratified water column were permanently existed during the deposition of organic rich source rocks. This water stratification was characterized by both oxygen depletion in the bottom water which even extended into the photo zone of upper water column and a higher salinity of bottom water column than that of upper layer water.

This study is supported by State ‘973’ Project (2006CB701404).

Multiple growth of titanite in response to lower crustal thickening and recycling

J.L. GUO$^1$, S. GAO$^{1,2,*}$, W.L. XU$^3$, Z.C. HU$^1$, H.L. YUAN$^2$, Y.S. LIU$^3$ AND K.Q. ZONG$^1$

$^1$State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China (*correspondence: sgaot@263.net)
$^2$State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi’an 710069, China
$^3$School of Earth Sciences, Jilin University, Changchun 130061, China

Titanites from eclogitic xenoliths in the Xu-Huai region of the North China craton were determined in situ for U-Pb age using LA-ICP-MS. They can be divided into primary and secondary, exsolution-free and -rich types. They are depleted in HREE, indicative of equilibrium with garnet. In an amphibole-bearing garnetite, eight large primary titanites give three major concordant age peaks at 230 Ma, 214 Ma and 203 Ma, which correspond to the core-to-rim age variations. In a garnet clinopyroxenite, small titanites yield one major concordant age peak at 157 Ma and two minor peaks at 203 Ma and 134 Ma. In another garnet clinopyroxenite, exsolution-free and -rich titanites yield indistinguishable lower intercept ages of ~160 Ma.

Previous studies show that Triassic collision of the Yangtze craton beneath the North China craton formed the Dabie-Sulu ultrahigh-pressure metamorphic belt and the Xu-Huai eclogitic xenoliths, which foundered in Jurassic [1, 2]. The above core-to-rim age zonation well corresponds to the ages of peak eclogite-facies metamorphism and exhumation of the Dabie-Sulu belt. The ~160 Ma and ~134 Ma ages agree with the thermal-magmatic activities caused by the proposed Jurassic delamination [1] and the magmatic zircon age of the host porphyry [3], respectively. Thus, the titanites record a complete history of eclogitic xenoliths from formation to destruction and later entrapment. This cannot be resolved by zircron from the same suite of xenoliths, which are small and rare and have very low U-Th concentrations with large analytical uncertainties in age dating.

Partitioning and transformation of phosphorus between dissolved, colloidal and particulate phases in the Bay of Saint Louis

LAODONG GUO1* AND PENG LIN2

1Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529, USA  (*correspondence: laodong.guo@usm.edu)
2Department of Oceanography, Xiamen University, Xiamen 361005, China

Field studies and laboratory mixing experiments were conducted to examine the dynamic partitioning and transformation between organic and inorganic P in dissolved, colloidal and particulate phases and key processes and mechanisms that control their distribution, variation and mixing behavior in the Bay of Saint Louis estuary in the northern Gulf of Mexico. A highly dynamic variability in P concentration and a non-conservative mixing behavior was observed within the estuary for all P species: dissolved inorganic P (DIP), dissolved organic P (DOP), particulate inorganic P (PIP) and particulate organic P (POP). The concentration of total dissolved P (TDP) first increased with increasing salinity, but decreased with increasing salinity in the lower estuary (S >21). In contrast, the concentration of total particulate P (TPP) decreased in general with increasing salinity with an elevated concentration in coastal waters. DOP was the dominant species in the TDP pool in both lower salinity (S<10) and higher salinity (S>25) regions, while DIP was the dominant species in mid-salinity regions (S of 10–20) comprising up to 75% of the TDP. Results of short-term laboratory mixing experiments resembled those of field observations in the distribution, variation, partitioning, and mixing behavior of P species, suggesting that physico-chemical processes are the predominant control on the biogeochemical cycling of P in the Bay of Saint Louis estuary. The partitioning coefficient of P between dissolved and particulate phases ranged from 4.0 to 5.5 (in terms of logKd), indicating its particle reactive nature and potential control of soluble P concentration by TPP. Within the DIP pool, colloidal inorganic P decreased rapidly from ~60% near the river mouth to negligible in waters of salinity >18. Colloidal organic P was more abundant, decreasing from over 90% of the DOP pool at low salinity stations to <30% at middle salinity stations but increasing again to over 80% at coastal stations, further indicating dynamic partitioning, transformation and source change within the estuary.

U-Pb zircon ages and Hf isotopic compositions of the magmatic and metamorphic rocks from Nyingchi group in Eastern Himalayan syntaxis and their geological implications

LIANG GUO, HONG-FEI ZHANG*, WANG-CHUN XU AND ZHANG-LIANG SHI

State Key Laboratory of Geological Processes and Mineral Resources and Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, China  (*correspondence: hfzhang@cug.edu.cn)

Syn-collisional tectonothermal history of southern Lhasa terrane is critical to understand collisional process of India and Asian continents. In the eastern Himalayan syntaxis, the southern Lhasa terrane is mainly composed of middle-high-grade metamorphic rocks and anatectic rocks. This assemblage was termed as Nyingchi Group. Detrital zircons from a paragneiss of Nyingchi group yield U-Pb ages from 333 to 2965 Ma, with four major populations at 330-362 Ma, 440-625 Ma, 1057-1283 Ma, 1500-1850 Ma. Their εHf (t) values range from -28.9 to +3.6. A granodioritic orthogneiss has magma crystallization age of 84.3±0.6 Ma, with metamorphic ages of 64.5-56.0 Ma. This granodioritic orthogneiss is characterized by positive εHf (t) values of +7.4 to +10.7. Zircons from a gneissic leucogranite exhibit core-rim structures. The cores yield ages ranging from 347 to 2690 Ma, with age populations at 347-400 Ma, 450-650 Ma and 1000-1200 Ma. Their εHf (t) values range from -33.2 to +6.9, consistent with those of detrital zircons in the paragneiss, indicating that the protolith magma was derived from partial melting of the Nyingchi group. The zircon rims show that the protolith of the gneissic leucogranite crystallized at 64.9±1.4 Ma, but suffered subsequently metamorphisms at 55.4±1.0 and 41.4±2.3 Ma. Zircons from a diorite yield magma crystallization age of 63.1±0.5 Ma, with εHf (t) values of -8.3 to -2.7, indicating the diorite sourced from partial melting of ancient crustal materials.

These results indicate that the late Cretaceous magmatism in southern Lhasa resulted from the Neo-Tethys oceanic slab subduction towards the Asian plate and the early Paleocene magmatism resulted from partial melting of ancient crustal materials and anatexis of the Nyingchi Group. Meanwhile, the southern Lhasa terrane had experienced a protracted metamorphism from early Paleocene to Eocene. We suggest that the crustal melting, anatexis and metamorphism were related to crustal thickening of southern Lhasa terrane due to the collision between the India and Asian continents. This implies that the collision of India-Asian continent took place probably prior to 65 Ma.
Sulfur isotope fractionation during broadband low pressure SO₂ UV photolysis: Testing SO₂ self-shielding hypothesis in the laboratory

W. GUO1*, M.L. FOGEL1, H.D. ODURO2, J. FARQUHAR2 AND D. RUMBLE1

1Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA
(*correspondence: wfguo@ciw.edu)
2Department of Geology, University of Maryland, College Park, MD 20742, USA

Non-mass dependent sulfur isotope fractionations associated with SO₂ UV photochemistry are widely accepted as the cause of the anomalous sulfur isotope signals observed in Archean sulfides and sulfates [1], but the exact mechanism of this fractionation process is uncertain. Several hypotheses have been proposed to explain these fractionations, including SO₂ self-shielding, SO₂ photo-oxidation, SO₃ photolysis, SO photolysis and S₃ recombination reactions. Here, we present preliminary results from broadband low pressure SO₂ UV photolysis experiments and compare them with theoretical predictions from self-shielding calculations. Our goal is to evaluate whether SO₂ self-shielding fully explains the Archean signals [2], or if other reactions also participate.

Experiments were undertaken using a three–chamber cylindrical photocell, a 300W Deuterium lamp, and SO₂ gas pressures of 0.4- 1 torr. The SO₂ pressures are lower than the 10-900 torr used in prior studies [e.g. 1, 3, 4] and minimize contributions from reactions other than SO₂ photo-dissociation. Residual SO₂ in each chamber was collected after irradiation, and analyzed using a CF-IRMS (ThermoFinnigan Delta-V mass spectrometer coupled with a Gas Bench II) by simultaneous monitoring of ion beams with m/e of 48, 49, 50 and 64, 65, 66 which allows simultaneous determination of $\delta^{34}S$, $\delta^{33}S$, $\delta^{18}O$ and $\delta^{17}O$ of SO₂.

Both $\delta^{34}S$ and $\delta^{33}S$ of the residual SO₂ in all three chambers decreased after the irradiation with a Δ (Δ$^{34}S$)/ Δ (Δ$^{33}S$) slope of ~0.2. This slope broadly agrees with the theoretical predictions from self-shielding calculations based on published ultraviolet absorption cross sections of SO₂ [5]. Detailed comparison between experimental results from each chamber and predictions from the self-shielding calculations will be presented and discussed.


Assessment of factors responsible for climate change and human health

SAPANA GUPTA
Pt Ravishankar Shukla University, Raipur CG India

Weather and climate play important roles in determining patterns of air quality over multiple scales in time and space. Air quality is strongly dependent on weather and is therefore sensitive to climate change. There is growing recognition that development of optimal control strategies for key pollutants like fine particles now requires assessment of potential future climate conditions and their influence on the attainment of air quality objectives. Climate change induced by anthropogenic warming of the earth's atmosphere is a daunting problem. In addition, other air contaminants of relevance to human health, including smoke from wildfires and airborne pollens and molds, may be influenced by climate change. While further research is needed, climate change coupled with air pollutant exposures may have potentially serious adverse consequences for human health in urban and polluted regions. Climate change producing alterations in: food webs, lipid dynamics, ice and snow melt, and organic carbon cycling could result in increased PMs level in air. In this study, the focus is on the ways in which health-relevant measures of air quality, including particulate matter, and aeroallergens, may be affected by climate variability and change. The small but growing literature focusing on climate impacts on air quality, how these influences may play out in future decades, and the implications for human health is reviewed.. In the present study to find out the particulate dust in air, the sampling of particulate matters from different locations were carried out during December, 2006 - February, 2007 in Raipur city, one of the most industrialized parts of India, to characterize the ambient mass concentrations of coarse particulate matter (PM) and their sources. Techniques i.e. thermal method, proton induced X-ray emission spectrophotometry and ion chromatography was used for monitoring the species i.e. trace elements and water soluble ions, respectively and it is observed that the particulates are accompanied by high fractions trace elements (9.7%) and water soluble ions (15.5%), which play an important role in climate change.
Extreme silicate weathering rate in a tropical river, southwest coast of India

G.P. GURUMURTHY1*, K. BALAKRISHNA1, JEAN RIOTTE2,3, JEAN-JACQUES BRAUN2,3, STEPHANE AUDRY3 AND H.N. UDAYASHANKAR1

1Department of Civil Engineering, Manipal Institute of Technology, Manipal University, Manipal 576104 (*correspondence: gurumurthy.gp@manipal.edu)
2Indo-French Cell for Water Sciences, Indian Institute of Science, Bangalore 560 012
3Université de Toulouse, UPS (OMP), CNRS, IRD, LMTG, 14 Av Edouard Belin, F-31400 Toulouse, France

The rate of silicate weathering (SWR) and associated carbon dioxide consumption (CCR) of granite gneissic terrain of southwestern India is calculated, for the first time in a western flowing peninsular river, the Nethravati. Monthly samples (n=56) were collected from five fixed locations along the river Nethravati and its two tributaries over a period of twelve months. The total dissolved salts of the samples are in the range of 29 to 66 mg/l, with least values recorded during the months of peak discharge. Silicate weathering rate for the entire catchment is deduced by applying seawater correction using river chloride as a tracer. The SWR in the river Nethravati is estimated as 59.3 tons/km²/yr. Such value is higher by 3.5 times than those reported for granitic rocks, at Rio Icocos, Puerto Rico [1] and comparable to Jalisco Highlands, Mexico [2]. The CCR in the river Nethravati is also comparable to the rivers draining Deccan basaltics, located on the west coast of peninsular India [3]. Similarly, the CCR for river Nethravati is estimated as 11.6x10³ mol/km²/yr. The calculated molecular ratio (RE) from the river water dissolved compositions suggests both seasonal and spatial variability in the intensity of silicate weathering; gibbsite precipitation during high flow and at upper catchments and kaolinite precipitation during base flow and at lower catchments. High SWR in the study area is likely due to the extreme precipitation and runoff induced by the Western Ghats. The annual fluxes of total dissolved salts discharged in to the Arabian Sea from the river Nethravati is estimated as 5.48 x 10⁵ tons/yr, of which silicate derived cation flux amounts to 0.81x10⁵ tons/yr.


Calcium isotopes as tracers of high-pressure subduction-zone fluid-rock interaction

NIKOLAUS GUSSONE1, TIMM JOHN1, ANDREAS BEINLICH2 AND GRAY BEBOUT3

1Institut für Mineralogie, Corrensstr. 24, 48149 Münster, Germany (Nikolaus.Gussone@uni-muenster.de)
2Physics of Geological Processes (PGP), University of Oslo, 0316 Oslo, Norway
3Lehigh University, Bethlehem, PA 18015, USA

The formation of eclogite in subducting slabs has great geodynamic importance, as it causes changes in rheology and could contribute fluids and slab geochemical signatures to arc magma source regions. Nevertheless, well-preserved field occurrences that provide insights into the process of eclogite formation are rare. We investigated samples from the Tianshan mountains (China) that show a ‘frozen in’ example of eclogitization of upper oceanic crust. Our sample set consists of wall-rock blueschist cut by an eclogite vein (with a reaction envelope) representing a major fluid conduit of fluid release. Within the envelope, the degree of eclogitisation (and thus dehydration) increases towards the vein [1]. Calcium content increases also towards the vein, indicating that, during the fluid-mediated eclogitization, external Ca was introduced to the reacting wall-rock blueschist [1]. A Rb/Sr whole rock isochron reveals that the vein formed at the time of peak metamorphism and has since then remained undisturbed. Calcium isotope ratios of these rocks indicate mixing of two distinct Ca sources, the blueschist and an external fluid source, the latter of which is enriched in heavy Ca isotopes.

Our results demonstrate a great potential of Ca isotopes as tracers of fluid-rock interaction in the deeper parts of the subduction zones and the shallower parts of accretionary wedges [2].

Neutron diffraction studies of liquids at high pressure

M. GUTHRIE1*, M.G. TUCKER2, C.A. TULK3, A.F.M.D. SANTOS3 AND J. MOLAISON3

1EFree EFRC, Geophysical Laboratory, Carnegie Institution of Science, Washington, DC 20015, USA. (*correspondence: mguthrie@ciw.edu)
2ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK
3Neutron Scattering Science Division, ORNL, Oak Ridge, TN 37831, USA.

To date, the intrinsic strengths of neutron diffraction for non-crystalline structure have remained largely unexploited at high pressure. However, activity has been increasing over recent years, most notably at the PEARL diffractometer at ISIS spallation neutron source. These studies have included characterisations of amorphous ice [1, 2], liquid water [3] and silicate glasses [4]. Measurements of GeO2 have also been conducted at the ILL reactor source [5].

Two of us (MG & MGT) have been heavily involved in the PEARL developments, and are now working to achieve similar capabilities on the SNAP diffractometer at SNS, Oak Ridge. SNAP was originally conceived as a single-crystal instrument, but has already demonstrated an aptitude for non-crystalline measurents. In addition, SNAP provides access to low Q data not readily available on PEARL, and tests of its elliptical focusing guide have suggested that higher conditions of P and T may be achievable.

We will present a neutron diffraction study of deuterated ammonia-water (dihydrate) solutions up to their room temperature freezing pressure. The liquid structure under these conditions is relevant to the deep subterannean ocean believed to exist on Titan [6]. In the near future, we hope to extend these capabilities to high temperature, permitting measurements of liquid structure to substantially higher pressures.


The potential feasibility of chlorinic photosynthesis on extrasolar planets

JOHNSON R. HAAS

Department of Geosciences, Western Michigan University, Kalamazoo, MI 49008, USA (johnson.haas@wmich.edu)

The modern search for life-bearing exoplanets emphasizes the potential detection of O2 and O3 absorption spectra in exoplanetary atmospheres as ideal signatures of biology. However, oxygenic photosynthesis may not arise ubiquitously in exoplanetary biospheres. Alternative evolutionary paths may yield planetary atmospheres tinted with the waste products of other dominant metabolisms, including potentially exotic biochemistries. This paper defines chlorinic photosynthesis (CPS) as biologically-mediated halogenation of aqueous Cl coupled with assimilatory CO2 fixation. This hypothetical metabolism appears to be feasible both energetically and physically, and could potentially evolve under conditions approximating the terrestrial Paleoarchean. It is hypothesized that an exoplanetary biosphere in which chlorinic photosynthesis dominates primary production would tend to evolve a strongly oxidizing, halogen -enriched atmosphere over geologic time. Expectations of the chemical attributes of exoplanetary biospheres should include consideration of chlorinic environments in addition to oxic or methanic atmospheres. It is recommended that astronomical observations of exoplanetary outgoing thermal emission spectra consider signs of halogenated chemical species as likely indicators of the presence of a chlorinic biosphere. Planets favoring the evolution of CPS would probably receive equivalent or greater surface UV flux than is produced by the Sun, promoting stronger abiotic UV photo-oxidation of aqueous halides than occurred during Earth’s Archean eon, and imposing stronger selection pressures on endemic life to accommodate and utilize photolytic halogens. Ocean-bearing planets of stars with equivalent or greater bulk metallicities than the Sun should especially favor the evolution of chlorinic biospheres, because of the higher relative seawater abundances of Cl, Br and I that such planets would tend to host. Directed searches for chlorinic worlds should probably focus on A, F and G0-G2 spectral class stars having bulk metallicities of +0.0 Dex or greater.