

## Lead, zinc and antimony leaching from glass-works fly ash in simple organic acids

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The release of hazardous elements from anomalous geomaterials represent risk for the environment. In our research, we focused on exogenic alteration of fly ash (FA) originating from glass-works in Svetla nad Sazavou (Czech Republic). This factory produces glass with high amounts of PbO. FA from electrostatic filter contains elevated concentrations of Pb, Zn and Sb. The main mineral phases of this material detected by X-ray diffraction are calcite CaCO<sub>3</sub> (79%), witherite BaCO<sub>3</sub> (10%), quartz SiO<sub>2</sub> (6%) and senarmontite Sb<sub>2</sub>O<sub>3</sub> (5%). Small amount of FA may be emitted from factory and can settle in the surrounding environment (soil).

Low-molecular-weight organic acids (citric, acetic and oxalic in concentration of 0.5 mmol/L), simulating soil-like environments and deionised water, were used to test possible mobilization of risk elements from the FA. The leaching experiments were carried out at liquid-to-solid (L/S) ratio of 10 (1 g of FA in 10 ml of leaching medium). The solutions were shaken in ten different times (0.5 to 1440 hours). Leachates were analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Lead, Zn and Sb exhibit different kinetic leaching curves corresponding to different behaviour of cations (Zn, Pb) and anion (Sb). The concentration of Zn in leachate initially increased, then rapidly decreased and subsequently very slowly increased. The Pb concentration increased rapidly at the beginning and then very slowly decreased due to possible sorption on present and newly formed phases. Concentration of Sb in leachate increased during all the experiment, which can be attributed to the slow dissolution of senarmontite. Large differences between four leaching solutions were not observed. The leaching is fastest in the citric acid solution. The initial pH were about 3.3–4.0 for organic acids and about 5.6 for deionised water). All the leachates reached the pH value about 10, which corresponds to the equilibrium with calcite present in the FA.

## Newly discovered MIL 090030, MIL 090032, and MIL 090136 nakhlites: Paired with MIL 03346?

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Here we present the petrology of newly discovered (2009-2010) meteorites: MIL 090030, MIL 090032 and MIL 090136 from Miller Range, Antarctica. Our aim is to test the hypothesis [1, 2] that these meteorites are paired with nakhlite MIL 03346, which underwent less equilibration and faster cooling than the other nakhlites, and so originate from the top of the nakhlite cumulate pile [3].

The mineralogy of these nakhlites is dominated by cumulus euhedral augite and less-abundant cumulus olivine. They also display a fine-grained albitic intercumulus matrix composition, which exhibits fayalite-magnetite filaments, and skeletal ilmenite. Pyroxene displays a 10 µm Fe-rich rim, suggesting re-equilibration with intercumulus matrix. Iddingsite has been observed, representing the aqueous alteration product of olivine. Pyroxene cores have a composition of Wo<sub>40</sub> and En<sub>36</sub>, and pyroxene rims have an average composition of Wo<sub>32-40</sub> and En<sub>8-12</sub>. Olivine has a composition of Fo<sub>35-42</sub>, and interstitial olivine has a composition >Fa<sub>90</sub>, which are similar to those of MIL 03346 [3].

Similarities in mineral compositions, abundances, and textures infer that these nakhlites are paired with MIL 03346. Major and trace elements combined with CSD analyses, will determine the location of these three nakhlites within the cumulate pile and further assess the possibility of a pairing with nakhlite MIL 03346. This enables the petrologic variability to be constrained within a much larger sample of MIL 03346.

- [1] Righter K. (2010) *Antarctic Meteorite Newsletter* **33**, 2.  
[2] Corrigan C. M. *et al.* (2001) *LPSC* **42**, #2657. [3] Day J. M. D. *et al.* (2005) *Met & Pl. Sc.* **41**, 581–606.

## 'Hidden' metals and minerals: How to detect nanocompounds

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Mining waste dumps provide materials suitable to investigate the fate of some metals and minerals during processing/alteration by meteoric waters. Such materials contain commonly all the minerals of the primary ores. It has been proven that, in addition, some minerals or compounds at nanometric scale can form within the waste dumps. Such minerals we can call 'hidden', as they escape the routine investigation by mineralogical methods. Their identification relies on structural techniques such as TEM/SAED, NGR (Mössbauer), XRD etc.

A waste dump in the Leaota Mts., South Carpathians, Romania, has been selected for detailed investigations. The material was produced by exploration of several types of ores, i.e. a combination of pentametallic ores (Ag-Co-Ni-Bi-U) and gold + Cu-Pb-Zn ores. Note that the waste dump is about 50-60 years old.

Attempts were made for the uptake of metals by using *Zea mays* and *Trifolium repens* planted on waste dump materials and neutral soils artificially enriched in metals (Au, U, Cu, As). Good results were obtained in both experiments. Significant enrichment factors of metals (plants vs. starting substratum) were obtained in both cases and both plants, plus surprisingly by analysing also *Alnus incana*, a spontaneously grown tree on the waste dump [2].

The 'hidden' compounds of nanometric size were identified in all the samples analysed: Au, Au-Ag alloys, Ag<sub>2</sub>CO<sub>3</sub> (probably the first occurrence under natural conditions), maghemite, wüstite, pseudobrookite, lavendulan, and an amorphous phase, on which the silver carbonate develops. Such nanocompounds are likely to facilitate the metals uptake by plants as the nano-sized compounds show a greater bioavailability as compared to the crystalline (larger size) equivalents [1, 3].

The search for nanocompounds in plants and a deeper investigation of the amorphous phase are in progress.

- [1] Hochella (2008) *Elements* **4**, 373–379. [2] Udubasa *et al.* (2010) *Rev. Roum. Geol./Rom. J. Geology*, **53–54** (in press). [3] Waychunas & Zhang (2008) *Elements* **4**, 381–387.

## Ultraviolet Spectra of <sup>32/33/34/36</sup>SO<sub>2</sub>; implications for the Archaean atmosphere

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Photodissociation of SO<sub>2</sub> is known to yield mass independent fractionation of sulfur isotopes (S-MIF). The MIF recorded in the Archaean sedimentary rocks can be an important tracer for the atmospheric chemistry at that time, though wavelength dependency of the MIF by SO<sub>2</sub> photolysis is still poorly understood. We newly determined the ultraviolet absorption cross sections of not only <sup>32</sup>SO<sub>2</sub>, <sup>33</sup>SO<sub>2</sub> and <sup>34</sup>SO<sub>2</sub> but also <sup>36</sup>SO<sub>2</sub> from 190 to 220 nm with a resolution of 4 cm<sup>-1</sup>. The spectra of the <sup>32</sup>S, <sup>33</sup>S and <sup>34</sup>S samples are in agreement with our previously published spectra [1]. The cross sections of the isotopically enriched species (>98% for all the four isotopologues) were corrected based on the isotopic composition of the samples used for the measurements. The absorption spectra show rich vibrational structure and the positions and widths of the peaks change with isotopic substitution in a complex fashion.

The results show that the mass independent fractionation observed during broadband photolysis is product of the change in the amount of red shifting of the heavier isotopologues as suggested by our previous analyses [1, 2].

We will discuss the implications for the chemical composition of the Archaean atmosphere and its evolution based on our calculated wavelength dependency of mass independent fractionation factors for <sup>33</sup>S and <sup>36</sup>S.

[1] Danielache *et al.* (2008) *J Geophys Res* **113**, D17314.

[2] Ueno *et al.* (2009) *PNAS* **106**, 14784–14789.

## A novel application of (U-Th)/He geochronology to constrain the age of small, young meteorite impact craters: A case study of Monturaqui crater, Chile

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Small and young impact structures have been commonly dated by methods such as thermoluminescence, <sup>14</sup>C, short-lived extinct radionuclide and cosmogenic techniques. However, (U-Th)/He dating is a low temperature radiometric technique that could potentially bridge the gap between the previously mentioned methods and common geochronological techniques employed on larger impact structures to yield precise impact formation ages. Here we report (U-Th)/He apatite and zircon single crystal ages from the small and young Monturaqui impact structure. The very small size of this crater will act as an ultimate test for the applicability of the low temperature (U-Th)/He technique for dating very small, young impact structures.

We selected two samples of impactite from the Monturaqui crater, representing different lateral sampling areas from the ejected material. A total of 10 zircons and 22 apatite grains were analyzed, and yielded a total of 10 successful zircon ages, and 12 successful apatite ages. The zircon (U-Th)/He ages range from 0.662 to 197.3 Ma and the apatite (U-Th)/He ages range from 0.616 to 61.5 Ma. This age fits well with the previous age range estimates for Monturaqui, and the range is interpreted to reflect a set of partially to completely reset (U-Th)/He ages, which yielded 2 reset apatite ages and 1 reset zircon age, which give a mean age of 663 ± 90 ka.

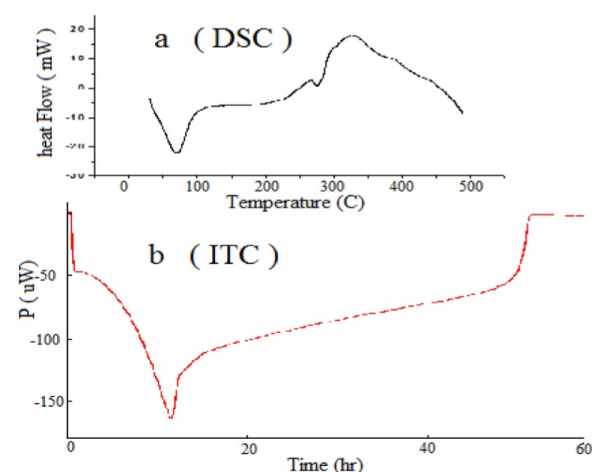
The results of this study show that the (U-Th)/He dating method has the potential to yield accurate ages for even very small impact structures, like Monturaqui: 663 ± 90 ka. Many of the grains are only partially reset, requiring analysis of a large number of grains to obtain an accurate age, similar to detrital dating studies.

## Calorimetry in soil sciences: An unique approach

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All physical, chemical and biological processes are accompanied by changes in energy which means, heat. This makes calorimetry one of the most suitable techniques to study all these process [1]. In Soil study, microorganism, microbial biomass and organic matter are the most important parameter of soil quality [2] and they could be evaluated, at the same time, using Calorimetry, more generally by ITC and DSC.



**Figure 1:** DSC (a) and ITC (b) curves of soil sample

In this study we have evaluated the use of Isothermal microcalorimetry (ITC) to study the effects of soil aging and influence of different experimental conditions on the glucose degradation of Brazilian soil. We also study the influence of the green house effect on the soil metabolism using ITC (Fig.1b). Differential Scanning Calorimetry used to study various properties (organic matter etc) of the soil under study (Fig.1a). [1] Barros, N.; Salgado, J. and Feijóo, S. (2007) *Thermochimica Acta* **58**, 11. [2] Sposito, G (1989), *The Chemistry of Soils.*, Oxford University Press, New York, pp, 43

## Oxygen and carbon isotope signatures of high-latitude Permian to Jurassic calcitic fossils from southern hemisphere

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Oxygen and carbon isotope values of calcitic fossils have been frequently used for characterization of palaeo-environments and for attempts to estimate temperature of past seawater. Fossil shell and skeletal remains of low-Mg-calcite are most suitable for this purpose because of their resistance to diagenesis and to resetting of their primary geochemical signals. Studies of samples from high palaeolatitudes are of particular interest of their potential to quantify past palaeotemperature gradients.

In the present study, brachiopods, bivalves and belemnites were sampled from Permian to Jurassic successions in New Zealand and New Caledonia that were deposited at palaeolatitudes higher than 60°S in marine forearc environments with sedimentation dominated by volcanogenic siliciclastics. The good temporal resolution, based on New Zealand stages, minimizes errors in stratigraphic correlation to low latitudes. The quality of samples was checked by scanning electron microscopy (SEM) with complementary trace element evaluation (ICP-OES) currently in progress. These screening techniques are used for evaluation of postdepositional alteration of samples as well as for detection of potential vital effects and ecological impacts.

A preliminary evaluation of about 1200  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values shows distinct temporal fluctuations based on the upper envelopes of the trends [cf. 1]. The overall carbon isotope trend is in good agreement with the low-latitude datasets, including its rapid increase of  $\sim 4\text{‰}$  during the early Late Triassic [2] that is therefore likely of global nature. The early and middle Permian and the late Jurassic high-latitude  $\delta^{18}\text{O}$  values are heavier if compared to their low-latitudes counterpart. The Triassic values, on the other hand, do not show any clear difference between high- and low-latitudes, indicating a diminished pole-to-equator sea surface temperature gradient at these times.

[1] Korte *et al.* (2008) *Palaeogeogr. Palaeocl.* **269**, 1–16.

[2] Korte *et al.* (2005) *Palaeogeogr. Palaeocl.* **226**, 287–306.

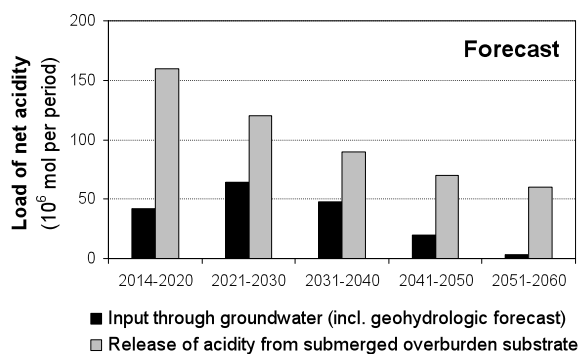
## Long-term forecast of acidity load from overburden substrate into a mining pit lake: An integrated approach

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Open-cast lignite mining in Germany left behind hundreds of lakes most of which are strongly acidic and do not meet water quality standards set for recreational use and water management purposes. To estimate future expenses and develop appropriate reclamation technologies, the authority in charge (LMBV) needs a reliable prediction of the lake water chemistry including the loads of acidity and alkalinity. By combining field and bench experiments with appropriate models, the most relevant physicochemical processes were identified and reliable data collected to determine crucial model parameters that enable a long-term forecast of net acidity load from the lake bed into the water of Lake Zwenkau, a pit lake of  $176 \cdot 10^6 \text{ m}^3$  currently being filled. The results demonstrate that the release of acidity is mainly by molecular diffusion of protons following ion exchange within the submerged overburden substrate ( $\sim 5 \text{ km}^2$ ). Similar release rates were found in both a 10-month field test and bench experiments under controlled conditions. While during the five-year period of lake filling the overburden substrate contributes by only ten percent to the overall load of net acidity, this source of acidity will dominate over other sources like groundwater recharge beyond the filling period.



Without technical treatments, the discharge of net alkalinity from natural groundwater may not balance the net acidity of the pit lake before the 2051-60 decade.

## Weathering effects on the mineralogical and geochemical composition of the New Caledonia ophiolite

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Since its complete obduction (at ~34 Ma), the New Caledonia ophiolite has experienced strong weathering due to tropical conditions. This alteration is expressed as laterization affecting the serpentinitized peridotites located at the upper part of the massif. This weathering does not macroscopically affect the serpentinites located in the lower part of the ophiolite, but previous studies showed that these serpentinites display anomalous chemical composition relative to the others (silica enrichment, strong Ce negative anomaly).

Our study focuses on the determination of the processes responsible of (a) the chemical variability of the serpentinites and (b) the formation of new mineral phases in the different parts of the ophiolitic sequence. First, mineral phases (including the polymorphs of serpentine) were identified by Raman spectrometry. Second, the relationship between mineral phases in finely-divided assemblages were characterized using an original method, based on micro-beam X-ray fluorescence mapping of cm-scale samples. Third, the chemical exchanges between the different parts of the ophiolitic sequence were estimated from the compositions of major elements and REE in serpentinites, peridotites and laterites.

Our results demonstrate that the chemical and mineralogical transformations of the basal serpentinite are directly linked to the laterization process occurring at the top of the ophiolite. Laterization leads to leaching of silica, magnesia (~80g/100g of protolith) and REE. Only the cerium, which is immobile in oxidizing conditions, remains immobile in the laterites. Leached elements are transported by percolation of meteoric fluids to the bottom of the ophiolitic sequence where they accumulate and precipitate by supersaturation. New phases such as magnesite and amorphous silica are formed. In the laterites located at the top of the sequence, the leaching process leads to the concentration of transition metals of economical interests such as iron and nickel.

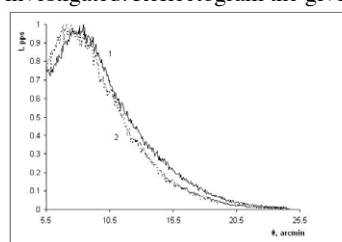
## Determining the porosity of analcime by X-ray reflectometry

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X-ray reflectometry represents the method of research based on measurement of reflective ability in x-ray range of lengths of waves and using the phenomenon of full external reflexion of X-rays. The given technique last years is used in chemistry, the physicist and materials technology for definition of physical and geometrical properties of surfaces, thin films and multilayered structures.

In the presented work as a method x-ray reflectometry porosity of a mineral - analcime  $\text{Na}_2 [\text{Al}_2\text{Si}_4\text{O}_{12}] (\text{H}_2\text{O})_2$  is investigated. Reflectogram the given mineral is on fig. 1.



On reflectogram we find a critical angle for each curve ( $\theta_{exp. cur.}$ ) which corresponds to a point with the intensity equal to half of the maximum size ( $I = 0.5$ ). From fig. it is

visible that a critical angle initial mineral:  $\theta_{exp. cur.} = 11, 9$  *argmin*. For this purpose, what to define porosity it would be necessary to know still a critical angle calculated theoretically under the formula of Frenelja  $\theta_{theor. cur.} = 13, 37$  *argmin*.

Knowing experimental and theoretical critical calculate angles porosity under the formula  $P = 1 - (\theta_{exp. cur.} / \theta_{theor. cur.})^2$  [1].

Porosity of the initial sample has made 21 % (an error of 1 %).

Let's consider reflectogram annealed analcime (a curve 2). In drawing distinctions of curves 1 and 2 are well visible. Annealing has led to displacement critical angle towards smaller corners ( $\theta_{exp. cur.} = 11, 5$  *argmin*). Porosity annealed a mineral has made 27 %.. Thus, annealed has led to porosity increase. At present while there is no strict explanation of this effect. It is possible to assume that during time annealed there was a partial phase transition in surface mineral areas. It can be assumed that during annealing occurred partial phase transition in the surface region of the mineral.

[1] A.A. Lomov, V.A. Bushuev, V.A. Karavansky. (2000) *Kristallografija* **45**(5), 915–920.

## Transboundary problems of water resources quality in the Selenga river basin

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The Selenga river basin occupies the territory of 447060 km<sup>2</sup> and it is divided by two countries – Russia and Mongolia. 67 % of territory is situated in Mongolia, 33 % - in Russia [1].

From 2007 to 2009 years the Baikal Institute of Nature Management together with Korea Environment Institute, Institute of Geocology of Mongolian Academy of Sciences have carry outed 3 scientific expeditions in the territory of Selenga river basin (in territory of Russia and Mongolia) within the scope of the International project 'Integrated water management model on the Selenge river basin' for social and economic information collection and water sampling.

We studied the identification of the general content of 15 microcomponents (Fe, Cu, Mn, Zn, As, Mo, Al, Pb, U, Cd, Ni, Co, Cr, Ag, Au) in 30 samples in water objects of the Selenga river basin: 16 from which are selected in territory of Mongolia, on river Selenga inflows – Orkhon, Tuul, Kharaa, 14 in Republic of Buryatia (Russian Federation) – in waters the river Selenga, and on its inflows – Uda, Dzhida, Modonkul.

The investigated waters of the Selenga river basin are alkaline and low-mineralized, concerning to hydracarbonate class of calcium group and have a favorable oxygen mode. Reduction of concentration of the main ions downstream the river is connected with effect of dilution by waters of inflows which have a smaller mineralization.

Results of researches of the Selenga river basin water quality have shown that the basic pollutants are metals: copper, iron, zinc, arsenic, aluminium, manganese, molybdenum, uranium.

Almost all water objects do not correspond to the requirements of water objects quality of fishery purpose (in Russia the rivers of fishery purpose have the highest standards on water quality, the river Selenga in the territory of Russia is the water object of fishery purpose). The Most polluted rivers are Tuul, Kharaa, Modonkul which basins are the most influenced by industrial regions, and also mining enterprises.

[1] *The Ecosystems of Selenga basin.*—Moscow, Nauka, 2005.

## Release mechanisms of Sr and Cs from the weathered Hanford sediments

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### Introduction

Various aspects of the acute effects of the released high level radioactive waste on sediments, including mineral weathering and contaminant transport have been extensively investigated at the Hanford Site. However, the long-term behavior of radionuclides in the contaminated sediment after the removal of the caustic source is not as well studied. Sediment pore water is expected to return to conditions of circumneutral pH and low ionic strength after long times, but the possibility exists that radioactive contaminants sequestered in the impacted sediments might be remobilized by the change in subsurface geochemical conditions.

### Results and Discussion

The leaching behavior and release mechanisms for Sr and Cs from the unsaturated columns packed with the two weathered Hanford sediments was modeled using the CrunchFlow code, which represented the reaction network as a combination of mineral dissolution/precipitation and ion exchange reactions. The leach tests were conducted using background Hanford pore water with focus on the first 200 pore volumes. The weathered sediments were prepared by reaction for 6 months with a synthetic Hanford tank waste leachate containing stable Sr and Cs ( $10^{-5}$  and  $10^{-3}$  molal representative of LOW- and HIGH-weathered sediments, respectively) as surrogates for <sup>90</sup>Sr and <sup>137</sup>Cs. The mineral composition of the weathered sediments shows that zeolite (chabazite-type) and feldspathoid (sodalite and cancrinite) are the major byproducts. However, the amount of secondary minerals in the sediments varied depending on the weathering conditions. Reactive transport modeling indicated that the leaching behavior of Cs was controlled by ion exchange, while Sr release was affected primarily by dissolution of the secondary minerals. The release of K, Al, and Si at later times in the leaching experiment using the HIGH-weathered sediment indicates additional dissolution of a more crystalline mineral (cancrinite-type). A two-site ion-exchange model successfully simulated the behavior of Cs release in the LOW-weathered sediment column. However, a three-site ion-exchange model was needed to describe Cs release in the HIGH-weathered sediment column.

## Petrological implications of temporal and spatial variations in magma chemistry of the Quaternary Tendurek shield volcano, Eastern Anatolian Collision Zone, Turkey

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The Quaternary Tendürek Volcano is one of the largest eruption centers of the Eastern Anatolia with a summit elevation of 3538 m and a footprint area of 650 km<sup>2</sup>. It is a shield volcano consisting of lavas ranging in composition from tephrites through benmoreites/phonolites to trachytes. The young volcanism of the region is thought to be related to the continent-continent collision taken place after the closure of the Neo-Tethys Ocean. The Tendürek volcano is of special importance, because it is one of the rare places in Eastern Anatolia where calc-alkaline and potassic alkaline volcanism coexisted.

Lavas of the Tendürek volcano are classified on the SiO<sub>2</sub> versus K<sub>2</sub>O diagram as medium K / high K and shoshonitic series. Medium to high potassic basalts, trachy-basalts, tephrites and basaltic-trachyandesites basically follow a partial melting trend on La vs. La/Yb diagram in contrast to the trachy-andesites, phonotephrites, tephriphonolites, phonolites, and trachytes of the shoshonitic series aligning along a fractional crystallization trend. The high-SiO<sub>2</sub> shoshonitic rocks (i.e. phonolites) uniformly contain lower concentrations of TiO<sub>2</sub> (0.52-1.17 %), MgO (0.46-1.05 %) and CaO (1.01-2.93 %) and high values of K<sub>2</sub>O (3.95-5.16 %). The high-SiO<sub>2</sub> phonolitic lavas have a more pronounced enrichment in incompatible elements, such as Rb, Th, La and Nb, in comparison to those in the other shoshonitic rocks. The aforementioned differences in the chemical compositions of these two groups of shoshonitic rocks may reflect variations in the fractional crystallization process which involved clinopyroxene and plagioclase during the petrogenesis of the potassic rocks.

## The global climate impact of civil aviation

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Aircraft emissions affect climate change through increasing carbon dioxide (CO<sub>2</sub>) but also a host of other short-lived non-CO<sub>2</sub> effects that are complex, involve impacts that are both warming and cooling and are unique to this sector. Previous assessments of aviation climatic impacts have used a segmented approach whereby each effect was calculated separately and the effects summed. Integrated approaches using newly available Earth System models that allow simulation of more realistic interactions between effects are now possible and give different results. Here, we apply the NASA GISS Earth System Model to reassess the net radiative forcing on 20- and 100-year timescales due to year 2006 emissions from civil aviation including the effects on ozone, methane, sulfate, black carbon, water vapor and CO<sub>2</sub>. A new hourly resolution aviation emissions inventory that was developed using the Federal Aviation Administration's Aviation Environmental Design Tool is applied. The model includes interactive tropospheric and stratospheric chemistry, full coupling between gas-phase chemistry and aerosols in the exhaust and background atmosphere. The sensitivity of the ozone climate impact to altitude of emission injection is examined for aircraft emissions and compared to other major anthropogenic surface sources of precursors. The climate impact of global desulfurization of jet fuel is examined. Global mean temperature response to aviation emissions is compared relative to the impacts of other major economic sectors.

## Metasedimentary rocks as indicators of crustal growth

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Results of Sm-Nd isotopic analyses and U-Pb dating on metasedimentary rocks of two main basement uplifts of western part of the Siberian Craton (illustrated by paragneisses of Angara-Kan granulite-gneiss block of the Yenisey Ridge and Irkut granulite-gneiss block of the Sharyzhalgai Uplift) were summarized to constrain provenance of metasediments, time of sedimentation and finally to determine stages of crustal growth.

Sm-Nd model ages of rocks under consideration ( $T_{Nd}(DM)=2.4-3.1$  Ga for the Sharyzhalgai Uplift and 2.4-2.8 Ga for Angara-Kan block) indicate presence of the Archean and Paleoproterozoic sources in the provenance [1, 2]. As regarding U-Pb data on zircons there are three detrital core age groups ( $\geq 2.7$ , 2.3, 1.95-2.0 Ga) in rocks of the Sharyzhalgai Uplift and cores varying in age from  $\sim 2.6$  to  $\sim 1.9$  Ga in rocks of the Angara-Kan block [3, 4]. The age of metamorphic rims of ca. 1.85-1.86 Ga in both cases determines the upper boundary of sedimentation and together with the youngest core ages brackets sedimentation time between 1.85 and 1.95 Ga for the Irkut block and 2.0-1.9 and 1.86 Ga for Angara-Kan block.

Potential source areas for ancient mainly Neoproterozoic material might be rocks of the exposed basement of south-west margin of the Siberian Craton. Presence of juvenile Paleoproterozoic crust in source area is indicated by minimal values of model Nd ages of paragneisses in common with prevail Paleoproterozoic detrital zircon cores. These Paleoproterozoic juvenile crustal sources may have been presented by buried basement of western part of the Craton, where model Nd ages of 2.3-2.4 Ga for granites and 2.8-3.4 Ga for gneisses were determined by Kovach *et al.* [5].

Finally, examined Sm-Nd and U-Pb isotopic data allow to identify derivation of detritus from buried and exposed basement of the Siberian Craton and determine the Archean and Paleoproterozoic stages of crustal growth within the Siberian Craton.

[1] Turkina & Urmantseva (2009) *Lithology & Mineral Resources* **44**(1), 43–57. [2] Nozhkin *et al.* (2008) *Dokl. Earth Sci.* **432A**(9), 1495–1500. [3] Urmantseva & Turkina (2009) *Acta Geol. Sinica* **83**(5), 875–883. [4] Urmantseva (2010) *IAGR Conf. Series* **9**, 18–19. [5] Kovach *et al.* (2000) *Petrology* **8**(4), 353–365.

## Nanoscale observations of dolomite dissolution

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The dissolution of carbonate minerals plays a fundamental role in a large spectrum of geological and biological processes as e.g. the global carbon cycle, and biomineralization. Moreover the understanding of carbonate dissolution is essential in the preservation of the Cultural Heritage and building stone. Among other carbonates, calcite ( $\text{CaCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ) dissolution has been thoroughly investigated over a range of environmental conditions and solution compositions. In contrast, there is a significant lack of understanding of the molecular-scale reaction mechanisms of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) [1]. In this work we present a systematic *in situ* Atomic Force Microscopy (AFM) study of dolomite dissolution in the pH range 3 to 10 aimed to unravel the nanoscale processes governing dolomite-fluid interactions. Dolomite dissolution under neutral to alkaline pH seems to be controlled by the removal of dolomite layers by spreading and coalescence of shallow etch pits, nucleated at point defects or in defect-free areas. Overall dolomite dissolution rate ( $R_{AFM}$ ) values were nearly pH-independent in the range 5 to 10 ( $7-9 \cdot 10^{-13}$  mol·cm<sup>-2</sup>·s<sup>-1</sup>), while a slight increase in  $R_{AFM}$  values was observed at pH < 5 ( $10-17 \cdot 10^{-13}$  mol·cm<sup>-2</sup>·s<sup>-1</sup>). At all pHs (and particularly at pH < 5) the formation of a Mg-rich surface precipitate (most probably nesquehonite) was detected. Our results suggest that the mechanism of dolomite dissolution inferred solely from measurements of the solution chemistry could be misestimated as a consequence of the precipitation of such a secondary phase, particularly at acidic pHs.

[1] Ruiz-Agudo *et al.* (2011) *Chem. Geol.* **281**, 364–371.



## Enhancing the bioavailability of subbituminous coal

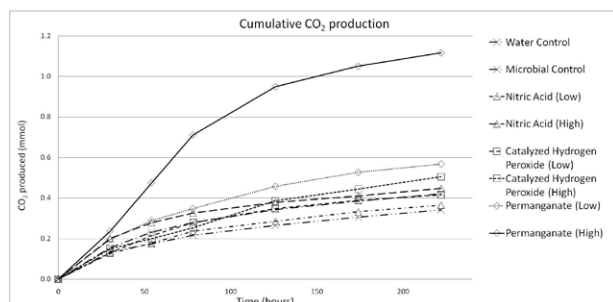
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Recent scientific discoveries suggest that much of the coal bed natural gas (CBNG) within the Powder River Basin, located in Wyoming and Montana, was generated by anaerobic microbial systems within the coal seams long after the initial process of coalification. This type of natural gas, referred to as secondary biogenic natural gas, relies on the active biological conversion of coal-derived constituents into methane. Secondary biogenic CBNG can also be found in numerous other coal fields located throughout the world. Interest in secondary biogenic natural gas has grown significantly in recent years with the realization of its vast potential and the significant benefits that this energy source has over fossil fuels.



**Figure 1:** Cumulative CO<sub>2</sub> production.

The aim of this study was to evaluate several conventional groundwater remediation technologies including *in situ* chemical oxidation with permanganate and catalyzed hydrogen peroxide, and acid treatments for enhancing the biodegradability of coal. Although dissolved organic carbon was increased with each method, only the permanganate treatment resulted in a significant increase in coal bioavailability (Figure 1).

## Enhanced shelf sediment weathering during glacial periods damps $p\text{CO}_2$ reduction: A negative feedback

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In the past 800 thousand years and before industrialization, the largest variations in atmospheric CO<sub>2</sub> concentration ( $p\text{CO}_2$ ) occurred in connection with the glacial cycles that characterized Earth's climate over this period [1]. The mechanisms responsible for the glacial-interglacial  $p\text{CO}_2$  changes have remained unresolved. One curious feature of at least the last four glacial-interglacial cycles is that  $p\text{CO}_2$  reached about the same upper limit of 280 ppm during peak interglacial periods and about the same lower limit of 180 ppm during peak glacial periods. Here, we show using a numerical model of earth system [2] that enhanced shelf sediment weathering during glacial sea-level low stand will tend to raise  $p\text{CO}_2$  and thus stabilize it from further reduction. This is contrary to the so-called shelf nutrient hypothesis [3], which proposed that increased weathering of nutrients (e.g. phosphate) would enhance the organic carbon pump of the ocean and thus reduce  $p\text{CO}_2$ . We demonstrate that weathering of exposed continental shelves would in fact raise  $p\text{CO}_2$  because not all nutrients from weathering will be utilized by biology but more importantly because the spatial distributions of carbon and phosphate from weathering become decoupled in such a way that carbon is preferentially stored in the upper ocean and phosphate in the deep ocean. An extension of this finding suggests that the preferential dissolution of phosphate in shelf sediments during interglacial high stand would tend to enhance biological production and thus stabilize  $p\text{CO}_2$  from further increase. The impact of sea level-driven continental shelf exposure and submersion on CO<sub>2</sub> is therefore a negative feedback that helps explain both the upper and lower limits of  $p\text{CO}_2$  over the Pleistocene.

[1] Luthi *et al.* (2008) *Nature* **453**, 379–382. [2] Matsumoto *et al.* (2008) *Geosci. Model Dev.* **1**, 1–15. [3] Broecker (1982) *Prog. Oceanog.* **11**, 151–197.

## Experimental and numerical investigations of the formation of felsic asteroidal crust

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Achondrites exhibit a diverse set of petrographical and geochemical features that individually reflect distinct environments during differentiation processes on their parent asteroids. Our study reports on experimental and numerical investigations that constrain the formation of felsic asteroidal crust recorded in paired achondrites GRA 06128 and GRA 06129 (GRAs).

GRAs are characterized by high abundances of sodic plagioclase, resulting in alkali-rich, felsic, whole-rock compositions. Geochemical studies suggest that the GRAs originate from a partial melt from a volatile-rich asteroid that did not segregate metallic core. We performed partial melting experiments on a synthetic, alkali-bearing, H-chondrite composition under a wide range of  $fO_2$  conditions (IW-1 to IW+2). The experiments suggest that  $fO_2$  conditions significantly influence the compositions of partial melts. Partial melts at IW-1 are distinctly enriched in  $SiO_2$  (up to 70 wt%) and depleted in FeO contents relative to those of >IW melts (~39-47 wt%  $SiO_2$ ). The silica-enriched, reduced (IW-1) melts are characterized by high alkali contents, resulting in silica-oversaturated compositions. In contrast, the silica-depleted, oxidized (>IW) melts, which are also enriched in alkali contents, have distinctly silica-undersaturated compositions. These experimental results suggest that alkali-rich, felsic, asteroidal crusts as represented by GRAs should originate from a low-degree ( $F = <15\%$ ,  $T = <1050\text{ °C}$ ), relatively reduced (~IW-1) partial melt from a parent body having near-chondritic compositions.

We also performed numerical simulations for the thermal evolution of a GRAs parent body by assuming  $^{26}Al$  and  $^{60}Fe$  with the CAI canonical values as dominant heat sources. The numerical investigations suggest that a GRAs parent body should have accreted 0.7-1.2 Myr after CAI and reached a size of 18-50 km in radius in order to satisfy both chronological and experimental constraints of GRAs. This implies that a planetesimal that possesses a felsic crust produced by low-degree partial melting would have intermediate characteristics regarding the size and/or timing of accretion between chondrite and highly differentiated achondrite parent bodies.

## Thermodynamic consequences of the injection of $CO_2$ - $H_2S$ gas mixtures in sulfur-rich hydrocarbon reservoirs

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Many petroleum basins around the world, among which the recently discovered giant oil and gas fields of the Northern Caspian Sea, are characterized by very high  $H_2S$  contents. In order to overcome the tremendous environmental challenge associated with the exploitation of these petroleum and natural gas reserves, the capture on the platforms and reinjection inside the reservoirs of  $CO_2$ - $H_2S$  gas mixtures has been proposed. If these gas mixtures are out of chemical equilibrium with the water-rock-gas-hydrocarbon systems at depth, predicting the occurrence of such reactions as the formation and destruction of organic sulfur compounds, or the precipitation of elemental sulfur in the reservoirs is of major importance for the oil industry.

Activity diagrams and temperature –  $\log f_{H_2S(r)}$  diagrams have been constructed to determine the relative stabilities of  $H_2S$ , hydrocarbons, organic sulfur compounds, and elemental sulfur at temperatures and pressures typical of petroleum reservoirs. The diagrams suggest that thiacycloalkanes and thiophenes may react with  $H_2S$  to produce hydrocarbons and elemental sulfur, while benzo- and dibenzothiophenes should not react with  $H_2S$  due to their higher stability.

Experiments have been conducted at 150°C and 500 bar in sealed autoclaves, in which various classes of organic sulfur compounds were reacted with  $H_2S$  in the presence of water. In accord with the thermodynamic predictions, thiacycloalkanes and thiophenes reacted with  $H_2S$ , while benzo- and dibenzothiophenes did not. Elemental sulfur was formed only in the reactions involving the thiophenes, which we interpret in terms of the potential for reduction (electron transfer) which is higher in the case of the thiophenes. In contrast, no hydrocarbons were detected at the end of the experiments. Dithiacycloalkanes were produced instead. Group additivity estimates of the thermodynamic properties of dithiacycloalkanes suggest that these compounds may be stable under the conditions of the experiments.

## Podiform chromitites from the Turkish ophiolites: An overview to the mineralogy of Platinum-group elements

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Podiform chromitites of Mesozoic ophiolites of the Western Mediterranean Tethys represent a major source of chromium, and are considered a potential target for platinum group elements (PGE) exploration. Turkey is one of the major chromite producers in the world, ranking 4<sup>th</sup> in exports. Most of the Turkish chromitites occur in the mantle tectonite unit of supra-subduction zone ophiolites. In this contribution we have summarized the results of investigation obtained on several Turkish Cr- and Al-rich podiform chromitites [Muğla (SW Turkey), Eskişehir, Bursa (NW Turkey), Kop Mountains (NE Turkey), Kahramanmaraş, Malatya, and Gaziantep (SE Turkey)] with special regard to their mineralogy of platinum group elements (PGE). About 450 PGM grains, generally less than 15 µm in size, have been identified in all the investigated chromitites. They occur in fresh (84%) and altered chromite crystals (6%), along cracks and fissures (8%) of the chromite and, rarely, in the silicate matrix (2%) generally composed of secondary silicates, such as chlorite and serpentine. The PGM form single phase crystals or they are part of polyphasic grains composed of other PGM, base metals sulphides and silicates. The PGM containing IPGE (Os, Ir, Ru) are the most abundant phases (96% of all PGM) compared to the PPGE (Rh, Pd, Pt) bearing PGM (4%). The IPGE bearing PGM are composed of laurite-erlichmanite serie (74%), native osmium (8%), unidentified Ru-Fe phases (6%), native iridium (4%), irarsite (3%), unidentified Ir phases (2%) and native ruthenium (1%). Very rare (up to 2%) kashinite, cuproiridsite, ruarsite, and unidentified Os phase have also been identified. A total of 20 grains of PPGE phases have been found in all the localities, and most of them are Pt-Fe alloys (40%), accompanied by platinum (20%), hollingworthite (20%) and unidentified Pt (10%), Rh (5%) and Pd (5%) phases. These results confirm a strong predominance of PGM containing IPGE over PPGE, as typical for mantle hosted ophiolitic chromitites.