

## Chemical and mineralogical composition of aerosol particles at Cape Verde

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The Saharan Mineral Dust Experiment II (SAMUM II) is dedicated to the understanding of the radiative effects of mineral dust. In January and February of 2008 a field campaign, focussed on investigation of aged Saharan dust and admixtures of biomass burning and marine aerosols, was conducted at the Island of Santiago, Cape Verde. Ground-based and airborne particle measurements and sampling were performed in the winter season, where mineral dust from the Western Sahara and biomass burning aerosol from the Sahel region are observed to occur.

The size-resolved particle aspect ratio and chemical composition is determined by individual particle analysis, performed by semi-automated energy dispersive X-ray microanalysis in a scanning electron microscope. Mineralogical bulk composition is analyzed by X-ray diffractometry.

First investigations of the collected samples confirm the presence of a mixture of sea salt, mineral dust, and anthropogenic material. A complex aerosol consisting of externally mixed particle types as well as internally mixed species – e. g., sea salt/mineral dust mixtures – is encountered in the marine boundary layer at the Island of Santiago.

By comparison with earlier measurements in Morocco, further analyses of the samples will yield information on the change in chemical composition, particle morphology, and mixing state of the aerosol during transport from the African continent to Cape Verde.

## New <sup>230</sup>Th dating methods applied to Chinese caves: Climate change on glacial to cultural timescales

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We present a 350,000-year record of the oxygen isotopic composition of cave calcite from Hulu, Dongge, Sanbao, and Wanxiang Caves. The record is improved in oxygen isotope resolution (3 y to several decades), range, and dating precision over published results. It is, in essence, a history of the oxygen isotopic composition of meteoric precipitation, which is related to and integrates monsoonal precipitation.

Portions of the chronology were established with new generation <sup>230</sup>Th dating methods using multi-collector, inductively-coupled plasma mass spectrometry, yielding precisions (for cave calcite) of ±1 y at 1000 y, ±10 y at 10 ky, ±100 y at 100 ky, ±10 ky at 600 ky, and a range of >700 ky. Key points include high ionization/transmission efficiency for U and Th (1 - 2%), yielding high precision on calcite with low U abundances and new half-life values for <sup>234</sup>U and <sup>230</sup>Th.

The monsoon is dominated by orbital-scale variability throughout and millennial-scale variability during glacial periods. The monsoon follows boreal summer insolation with no discernable phase shift, supporting a direct link between seasonal heating and the monsoon. At millennial scales, the last glacial record correlates strikingly with the Greenland record, with Chinese correlatives to all 25 Greenland interstadial events, and similar sequences for penultimate and antepenultimate glacial periods. The Holocene monsoon correlates significantly with proxies for solar irradiance, linking some monsoon variability to solar changes. The highest resolution portion of the record (<1800 y) establishes links between the cultural history of China and climate.

The monsoon exhibits remarkable relationships with atmospheric methane, the isotopic composition of atmospheric O<sub>2</sub>, and Heinrich Events. These links allow correlations among ice core, marine, and monsoon records, thereby establishing, for key periods, the timing and sequence of events recorded around the globe in different environments. Using this strategy, we have characterized events during the last 4 glacial terminations, placing strong constraints on the causes the rapid endings of ice age cycles.

## Changing solubility of aeolian iron in the Arctic from Greenland ice cores

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Aeolian deposition is an important source of iron (Fe) to the ocean. On a glacial-interglacial time scale, large changes in dust emissions and atmospheric transport, and hence iron, may have modulated primary production in the remote ocean. Because dust-iron is thought to be relatively insoluble (~1%) small changes in solubility resulting from changes in chemical weathering may potentially affect primary productivity. However little is known regarding the history of aeolian iron solubility.

Here we present two 200 yr Greenland ice core records of total/soluble Fe and non-sea-salt sulfur. We investigate changes in Fe solubility during well-known volcanic eruptions, the rise of anthropogenic sulfur emissions and biomass burning events.

## Iron isotope fractionation during Fe(II) oxidation and precipitation of iron in acid mine drainage (Carnoulès Mine, France)

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Acid mine drainage (AMD) is produced upon oxidation of pyrite in mining residues. In these systems Fe plays a key role in water chemistry since the redox reactions involving Fe are an important energy source for chemolithotrophic bacteria such as *A. ferrooxidans*. AMD are thus ideal sites to study Fe isotope fractionation in natural waters. Few Fe isotopes data have been published to date in AMD or in similar Fe-rich waters. Recently, Herbert et al. (2008) published iron isotope data at the redox interface of a mine tailings stock. Experiments performed in AMD like water by Balci et al. (2006) demonstrated that iron isotope fractionation during the oxidation of Fe(II)<sub>aq</sub> into Fe(III)<sub>aq</sub> by *A. ferrooxidans* was controlled by non-biological equilibrium and kinetic factors.

Our study focused on iron isotope fractionation during the Fe(II) oxidation and the subsequent precipitation of iron minerals in acid mine drainage. Iron isotopes have been measured in a small stream receiving acid mine drainage from the Carnoulès mine tailings (Gard, France), characterized by acid pH (3-5), extremely high Fe(II) ( $\approx 2\text{g/l}$ ),  $\text{SO}_4^{2-}$  ( $\approx 4\text{g/l}$ ) and As(III) (100 mg/l) concentrations and As-rich iron minerals (tooeleite, As-rich schwertmannite) that form in the streambed. Natural solid samples that precipitate in the acid stream exhibit positive  $\delta^{56}\text{Fe}$  values whereas the water presents negative  $\delta^{56}\text{Fe}$  values, leading to a fractionation of about 2-3 ‰ in agreement with the values that are expected for the oxidation of Fe(II) into Fe(III). Fractionation between water and solid tends to decrease along the stream flowpath. In laboratory experiments, different strains of *A. ferrooxidans* isolated from the field were cultivated in the AMD water. Iron isotopes were measured in the dissolved phase and in the successive minerals (tooeleite, schwertmannite, jarosite) that form through time, together with Fe speciation, cell growth, and the various physico-chemical parameters. Dissolved iron isotopic composition decreased from -0.6‰ down to -1.5‰ within the first 10 days of experiments corresponding to the precipitation of 25% of Fe during the bacterial growth period.  $\delta^{56}\text{Fe}$  equilibrated around -0.5‰ after 40 days of experiments. Results of iron isotope measurements will be discussed according to kinetics of iron oxidation, nature of minerals formed and bacterial strains involved.

## Cyclicality in Earth evolution constrained by time-series analysis of global igneous activity

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Global igneous activity provides a record of crust formation and differentiation, which are, in turn, related to larger-scale geodynamic processes such as plate tectonics and plume activity. Most compilations of igneous activity portray a spectrum of ages compiled by the Gaussian summation of available ages (Gaussian AND summation). Density function distributions constructed in this way describe the probability of an age occurring in the data compilation, which may not be equivalent to the probability distribution for original igneous activity. It has long been recognised that the age of igneous activity may be biased by issues related to selective preservation and sampling. An alternative form of calculation is the Gaussian OR approach, which provides the probability for any igneous activity occurring at a particular age. This approach provides a more robust reflection of the original age distribution.

The DateView geochronology database (available at <http://sil.usask.ca>;) currently contains approximately 60,000 records for all continents, of which ~15,000 reflect igneous crystallisation ages. A Gaussian OR pdf for these latter ages illustrates several intervals of reduced igneous activity since 3.8 Ga. The long-term variations in patterns of igneous activity appear similar for all continents. Interestingly, these 'quiescent' intervals generally coincide with suggested times of supercontinent formation.

Spectral analysis of the probability distribution demonstrates cyclic behaviour at a variety of periodicities. A noticeable feature of the long-term cyclicality is that the period for two of the wavelengths identified increases from ~650 Ma and ~440 Ma at 3.8 Ga to ~860 Ma and ~510 Ma, respectively, at the present. No abrupt changes in cyclicality are evident, suggesting that there have been no dramatic changes in geodynamic processes since 3.8 Ga. Quantification and identification of the cyclicality has important implications for geodynamic processes, including the interplay of plate tectonics and plumes and the styles of mineralisation expected at different stages of earth history.

## Carbonate 'clumped isotope' thermometry: A status report

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Carbonate 'clumped isotope' thermometry can determine the growth temperatures of carbonate minerals based on their abundances of <sup>13</sup>C-<sup>18</sup>O bonds, as reflected by the 'Δ<sub>47</sub>' value of CO<sub>2</sub> extracted by phosphoric acid digestion. This method is precise (as good as ±1 °C), thermodynamically based, and independent of the δ<sup>18</sup>O of water from which carbonate grew. However, there are many unresolved questions about the general usefulness of this new and unusual proxy. We review recent developments in its calibration and understanding.

In the last year, we conducted four empirical calibration studies of previously unstudied materials: Foraminifera, Coccolithophores, various lacustrine carbonates, and synthetic dolomites grown through microbial mediation. All of these materials exhibit temperature dependencies of abundances of <sup>13</sup>C-<sup>18</sup>O bonds that are indistinguishable from that previously published for synthetic inorganic calcite. When combined with previous data for various biogenic and inorganic precipitates, these results suggest that the carbonate clumped isotope thermometer is largely free of vital effects and/or structural or crystal-chemical controls. This could be an indication that <sup>13</sup>C-<sup>18</sup>O ordering in carbonate minerals is generally inherited from the DIC pool from which they grow. Furthermore, our results suggest that many calcifying organisms — including those with significant 'vital effects' in bulk stable isotope and trace element composition — grow in local isotopic equilibrium at the site of carbonate precipitation.

Speleothems are a notable exception: they consistently record apparent temperatures ~5-10 °C higher than actual growth temperatures. Theoretical, experimental and empirical evidence suggests that this reflects a kinetic isotope effect during rapid degassing of CO<sub>2</sub> from super-saturated solutions, which depletes the residual DIC pool in <sup>13</sup>C-<sup>18</sup>O bonds. Pedogenic carbonates remain a work in progress: a subset preserve apparent temperatures consistent with their environments of growth, while others appear to be offset to higher temperatures. We speculate that some soil environments experience disequilibrium CO<sub>2</sub> degassing analogous to that influencing speleothems.

## High-precision isotopic analysis: Lessons from 'clumped isotope' geochemistry

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Several disciplines of geochemistry demand ppm-level precision in isotope ratio measurements (e.g.,  $^{142}\text{Nd}$  excesses in ancient terrestrial rocks;  $\delta^{15}\text{N}$  in air from ice cores). 'Clumped isotope' geochemistry (the study of molecules containing more than one rare isotope) is one such field that presents several unusual analytical challenges, the solutions to which might inform high-precision isotopic measurements generally.

Clumped isotope measurements examine isotope ratios very far from 1 ( $10^5$  to  $10^6$  is typical). Therefore, one must be concerned with the effect on minor ion beams of scattered ions from the major beams (i.e., abundance sensitivity is a significant factor) as well as isobaric interferences from trace contaminants. And, one must devise strategies for collecting vast numbers of ions in order to achieve the required precision for the minor species. The solutions to these problems are technically difficult but conceptually straightforward: samples must be exceptionally pure and unusually large, and ions must be collected for unusually long times.

A more complex problem arises from the fact that measurements must have ppm-level precision and accuracy over ranges of 10's of per mil in absolute isotope ratio. For example, carbonate clumped isotope thermometry demands that  $R^{47}$  (mass 47 / mass 44) ratios in  $\text{CO}_2$  be measured with external errors of 0.005 ‰ (1s) over a range of up to ~100 ‰. This demands a firm control on or understanding of instrument linearity – i.e., how intensity ratios of registered ion beams vary with abundance ratios of isotopologues and/or absolute intensity of any given ion beam. Clumped isotope measurements address this problem by characterizing the apparent abundance ratios of all isotopologues in materials that are independently known to have a stochastic distribution of isotopes (such that measurement of one isotope ratio strictly predicts others). One can imagine using an analogous approach to precisely characterize the mass dependence of other methods of mass spectrometry, thereby improving precision.

Our presentation will also address the promise and challenges of emerging technologies for clumped isotope measurements (e.g., automated sample purification; spectroscopic analyses; high-efficiency electron bombardment ion sources).

## Seasonal changes in chemical composition and organic activity in Lake Myvatn, Iceland

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Lake Myvatn is one of the most productive lakes on the Northern Hemisphere, despite the fact that it is covered with ice about 190 days per year on the average. Samples of the dissolved and suspended material from the outlet of the lake were collected regularly during the years 1999 to 2001. Lake Myvatn was covered with ice when the research began in Nov. 1999 and ice break-up began around middle of April. The Cyanobacteria *Anabena*, which is usually common during the summertime in Lake Myvatn, was not common in the summer 2000. The concentration of dissolved elements in Lake Myvatn is largely controlled by organic activity. The pH was 7.5 - 8 during the wintertime but when photosynthesis started, pH got as high as 9.86 in July 2000. Concentrations of dissolved organic nitrogen and phosphorus were up to 96% higher during summer than winter. Equally, dissolved organic carbon reached a maximum in the summer and was 81% higher than in winter. The concentrations of the macronutrients  $\text{NO}_3$ ,  $\text{NH}_4$  and  $\text{PO}_4$  which are essential for the primary production were up to 95% lower in summer than in winter. Similarly, there was a drawdown during summer in  $\text{SiO}_2$ , the building material for diatom shells. The concentrations of the metals Mn and Cr showed similar behaviour as the macronutrients. The cations Na, K, Ca, and Mg were lower in the spring than the rest of the year and the same applied to the conductivity, probably because of snow- and ice-melt. The anions  $\text{SO}_4$ , Cl and F did not have noticeable seasonal variations but the sulphur isotopes,  $\delta^{34}\text{S}$ , did and it increased during summer, likely because of reducing bacterias and formation of light sulphides. Oxygen- and deuterium isotopes were also strongly fractionated during the annual cycle and were lighter in winter than summer. The difference was 1 and 6‰, respectively. The concentration of Mo, an essential element for nitrogen fixation, was low in the spring, possibly because of snowmelt. Its concentration fell again from July to September. The nitrogen fixing Cyanobacteria *Anabena flos-aqua* was in blooms from late July to beginning of September, thus it is possible that it affected the concentration of Mo during that time. A few trace elements, Co, Al and Ti increased consistently during the summer but B, Sr, Ba, Cd, Cu, Ni, Pb and Zn showed little or no seasonal variations.

## The application of natural divalent cation isotope (Ca, Sr, Mg) fractionation (DCIF) in earth system research

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Geochemical records of elemental and isotopic variations in magnesium (Mg), calcium (Ca) and strontium (Sr) provide key information for the chemical history of our planet, its long term climate evolution and the reconstruction of past water temperatures. In particular, the recent progress in instrumentation (e.g., multi-collector ICP-MS applications) and the improvements of isotope measurement techniques (e.g., TIMS double spike technique) showed that the divalent cation isotope ratios like  $^{44}\text{Ca}/^{40}\text{Ca}$ ,  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{26}\text{Mg}/^{24}\text{Mg}$  are spatially and temporarily not constant on Earth, but rather change as a function of the intensity of continental weathering, mineral polymorphism, pH, the precipitation rates and as a function of ambient temperature during inorganic mineral precipitation and biomineralisation. High temperature controlled, Raleigh type DCIF is observed during hydrothermal processes related to rock and mineral differentiation in magma chambers as well as during the precipitation of anhydrites, calcites and aragonites in the hydrothermal plumbing systems of the mid-ocean ridges. However, very large isotope fractionation (~4‰) values for Ca isotopes can be observed during physiologically controlled fractionation in the human body related to its trace metal homeostasis. Similar to trace element partitioning, temperature dependent DCIF is different for inorganically and biologically precipitated minerals (e.g. carbonates). In addition, there are species dependent DCIF processes which reflect the strong physiological control of uni- and multi-cellular organisms on their trace element homeostasis while sequestering trace elements in different reservoirs. In this regard the DCIF may contribute to a better understanding of the function of ion selective channels and pumps on the trace element partitioning between biominerals and the bulk solution.

## Guided nanoscale remodeling of soluble surfaces using a novel probe-based method

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A methodology for remodeling surfaces at nanometer length scales would enable the mitigation of defect or damage sites in a broad range of technologically relevant materials, such as optics used in high-fluence lasers. Here we describe a novel probe-based method to guide the remodeling of KDP (KH<sub>2</sub>PO<sub>4</sub>) surfaces that exploits two phenomena occurring at nm lengthscales: 1) the unique physical chemistry that occurs in the region surrounding a nanoscale tip-surface contact, and 2) the natural driving force for elimination of regions of high curvature. This method takes advantage of the meniscus that forms through condensation at a tip-surface contact in a humid environment. Surrounding this meniscus is a naturally occurring ultrathin aqueous film on the crystal surface. Our experimental model consists of two parts: 1) repair of a groove etched into the KDP surface by hard contact with an atomic force microscope (AFM) tip and 2) creation of pillars and beams by tip-induced overgrowth on a smooth KDP surface.

We find that the wet micro-environment formed by the meniscus, combined with tip rastering during AFM scanning over a groove site, results in local surface smoothing and filling-in of the groove such that groove depth decreases with time. We present *in situ* AFM measurements of the kinetics of this surface remodeling process. Starting with the Gibbs-Thompson relation, we present a quantitative physical analysis of damage site remodeling. With the controlling parameters in the model constrained by independent measurements, we find that the predictions are in good agreement with experimental results.

## Isobar contamination studies for Accelerator Mass Spectrometry (AMS)

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The study of rare long-lived atoms by mass spectrometry is made difficult by the presence of atomic isobars, which are often difficult to remove by chemistry alone. Using AMS the separation can often be undertaken either by exploiting anion instability, such as for  $^{14}\text{C}$ ,  $^{26}\text{Al}$ ,  $^{129}\text{I}$  and others when the anion of the isobar is unstable, or sometimes by using the rate of energy loss differences at higher (MeV) energies. The latter approach is both difficult and costly for heavy isotopes. It is therefore necessary to identify and then eliminate as much as possible the sources of isobar contaminations in the first place. In addition to the usual target contaminations during sample preparation chemistry, we have identified an intrinsic type of ion source contamination due to ion implantations accompanying  $\text{Cs}^+$  beam generation. These ions are used to generate the secondary anions for AMS. Studies of this contamination phenomenon are being carried out and will be discussed. From a particular  $\text{Cs}^+$  sputter ion source we have so far identified the cations of K, Ca, Cr, V, Mn, Fe, Rb and Mo, as well as some of their oxides, at about the  $10^{-6}$  level of  $\text{Cs}^+$  flux. Some of the isotopes of these elements will interfere with the detection of such long-lived isotopes as  $^{41}\text{Ca}$ ,  $^{53}\text{Mn}$  and  $^{92}\text{Nb}$ , for example, as they will inevitably be implanted in the target. The origin of such beams, and those yet to be determined at lower levels such as W ions, will be discussed, as well as a solution of the isobar problems in these cases currently under study at IsoTrace Lab.

## Stable isotopic tracers for variations in surface and deep water circulation in the North Atlantic since ~ 13 ka

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Stable isotopes from a well-dated Gardar Drift core, KN166-14 11JPC (eastern North Atlantic; 2707 m), show two distinct trends in Holocene circulation patterns. The Younger Dryas (YD) to early Holocene (~ 13 – 7 ka) is characterized by increasing Iceland Scotland Overflow Water (ISOW) strength and sea surface temperature (SST). The period from ~ 7 ka – present is characterized by decreasing ISOW and SST.

The benthic foraminiferal (*P. wuellerstorfi*)  $\delta^{13}\text{C}$  record for the YD to early Holocene increases gradually, interpreted as a strengthening of ISOW, consistent with reported increases in ISOW flow [1, 2]. From ~ 7 ka – present, benthic  $\delta^{13}\text{C}$  values decrease, indicating a weakening ISOW. Interestingly, decreasing ISOW strength at our site is coincident with relatively constant flow at Eirik Drift (western North Atlantic), which records combined ISOW and Denmark Straits Overflow Water (DSOW); this indicates that DSOW compensated for weakened ISOW.

Planktonic foraminiferal (*G. bulloides*)  $\delta^{18}\text{O}$  records indicate that SST warmed from ~ 13 - 7 ka, consistent with observed GISP2 warming [4]. SST cooled from ~ 7 ka – present while no long-term cooling occurs in the GISP2 record [4]. Thus, Gardar SST may be linked to variability in the Gulf Stream, which contributes warm, salty water to the modern eastern North Atlantic

Finally, millennial- to centennial-scale shifts in benthic foraminiferal  $\delta^{13}\text{C}$  values suggest that high frequency variations in ISOW flow are superimposed on the long term trends. The fluctuation timing is similar to a proximal sediment grain-size record that shows millennial-scale periodicity in ISOW strength [5]. Additional high-frequency climatic events, such as the 8.2 ka event, may also be observed in our record [3].

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## Measuring jarosite dissolution rates to determine jarosite lifetimes on Earth and Mars

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Lifetimes of metastable mineral particles in aqueous environments can be calculated based on the initial particle size and an appropriate dissolution rate for the mineral of interest using a shrinking sphere model. In this study, K- and Na- jarosite dissolution rates have been measured in the laboratory and the results applied to particle lifetimes to constrain the duration of liquid water at Meridiani Planum following the precipitation of jarosite. Na- and K-jarosite endmembers were synthesized using the methods of [1] and characterized using powder X-ray diffraction, BET surface area analysis, transmission electron microscopy, and atomic force microscopy. Batch reactor dissolution experiments were conducted at 293K. Samples were collected at predetermined intervals while pH was monitored and allowed to drift over the course of the experiment from initial pH = 6 to a final pH = 4.6-4.9 for K-Jarosite and 4.1 for Na-Jarosite. Centrifuged supernatant was measured using atomic absorption spectroscopy to determine K<sup>+</sup> or Na<sup>+</sup> concentration. Rates of K-jarosite and Na-jarosite dissolution in ultrapure water were calculated using the initial rate method [2] and were found to be  $1.5 \times 10^{-8} \text{ molm}^{-2}\text{s}^{-1}\text{g}^{-1}$  and  $4 \times 10^{-10} \text{ molm}^{-2}\text{s}^{-1}\text{g}^{-1}$ , respectively. These rates are comparable to rates extracted from dissolution data in the literature [3,4] but are slower than AFM measurements of jarosite dissolution rate [5]. Assuming initial particle size of 1 mm diameter, laboratory measurements predict K-jarosite would survive ~7 years in pure water, while Na-Jarosite would persist for ~250 years.

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## Enhanced Particulate Matter Surveillance Program: A multidisciplinary approach to understanding mineral dusts from the Middle East

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The purpose of the Enhanced Particulate Matter Surveillance Program (EPMS) in the Middle East was to provide US Central Command with scientifically founded information on the chemical and physical properties of dust collected at deployment locations within their Area of Responsibility. Results from this program are available to the US Department of Defense's Occupational and Health Physicians, as well as environmental health professionals, to assist them in assessing the potential human health risks from exposure to ambient particulate matter.

Aerosol and bulk soil samples were collected during a period of approximately one year at 15 military sites – including Djibouti, Afghanistan (Bagram, Khowst), Qatar, United Arab Emirates, Iraq (Balad, Baghdad, Tallil, Tikrit, Taji, Al Asad), and Kuwait (Northern, Central, Coastal, and Southern regions). Three collocated low volume particulate samplers, one each for the total suspended (TSP), less than 10 µm in aerodynamic diameter (PM<sub>10</sub>) and less than 2.5 µm in aerodynamic diameter (PM<sub>2.5</sub>) particulates were deployed at each of the sites and operated on a “1 in 6 day” sampling schedule.

The purpose of the trace element analysis was to measure levels of potentially harmful metals. The major element and ion chemistry provided an estimate of mineral components which themselves may be hazardous to health or could be carriers of toxic substances. X-ray diffractometry provided a measure of the mineral content of dust, which is the main component of aerosols in desert regions. Scanning Electron Microscopy with Energy Dispersive Spectroscopy was used to analyze chemical composition of small individual particles of relevance to understanding mineralogical interrelationships such as surface coatings, intergrowths and other particle features. Secondary electron images provided information on particle size and shape, which also can be linked with human health effects.

Examples of findings from the EPMS are discussed in the presentation.

## Rates of metamorphism in collisional orogeny

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### Scope and Methods

Understanding the processes that operate over a range of temporal and spatial scales, as a belt of regional metamorphism develops, is at the root of many key problems in geodynamics. Progress requires studies combining petrology and geochronology in orogens where the tectonic evolution is well known. Samples from a section across the low- and medium-grade northern part of the Central Alps were studied [1] with the aim of unravelling the dynamics of the Barrovian metamorphic evolution. Detailed petrological work, aided by thermodynamic modeling, allow us to recognize the prograde sequence of assemblages involving REE-minerals, and to obtain specific P-T conditions for each stage. By dating several of these stages (SHRIMP U-Th-Pb on monazite and allanite, Ar-Ar on micas), using exceptionally well characterized samples, a very robust P-T-t path emerges. This yields well constrained regional heating and cooling rates and, when combined with quantitative textural data obtained from the same sample sequence, growth rates of prograde metamorphic minerals, as well as fluid production rates.

### Results

Prograde allanite dated at 31.5-29 Ma grew from a (detrital) monazite precursor at 430-450°C (ctd-in); monazite appeared at 18-19 Ma in the garnet-zone (560-580°, near ctd-out). The average heating rate of 10-12 deg/My pertains to a T-interval in which major reaction progress occurs in meta-clastic rocks, for which rates of metamorphic growth can be determined. Growth-zoned porphyroblasts of chloritoid, garnet, and staurolite record the P-T conditions precisely. The spacing of isopleths ( $\partial X_C/\partial T$ ) and isomodes ( $\partial n_i/\partial T$ ) directly monitors the advance of continuous silicate reactions in response to heating at the rate ( $\partial T/\partial t$ ), hence absolute reaction progress rates ( $\partial \xi/\partial t$ ) are determined. Similarly, crystal size distributions measured for garnet populations in the same metasediments yield estimated rates of nucleation and growth ( $\partial N/\partial t$ ) for these P-T conditions. As growth of the porphyroblasts studied is related to specific dehydration reactions, the spacing of the isomodes also yields minimum rates of devolatilization. These rates appear characteristic up to ~650 °C.

[1] Janots *et al.* (2008, in press) *Jour. Metam. Geology*.

## Mercury and other trace elements in coastal South Carolina aerosols

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As part of a USGS study to investigate sources of mercury (Hg) deposition in coastal areas, aerosol samples were collected between Awendaw and Georgetown, South Carolina, USA, from April, 2006 to May, 2007, together with Hg speciation measurements, air quality parameters, and meteorological data. Intensive sampling of aerosols for Hg and other trace elements was conducted at three sites in May and July, 2006 and at one site in May, 2007.

Twelve-hour integrated total suspended particulate (TSP) Hg concentrations determined in this study are typical of background areas ( $7.8 \pm 3.6 \text{ pg m}^{-3}$ , n=85), except for the industrial city of Georgetown (Hg-TSP as high as  $43.2 \text{ pg m}^{-3}$ ). Enrichment factor calculations suggest that contributions from anthropogenic sources account for more than 90% of Se, S, Sb, Bi, Pb, and Hg in TSP samples during the sampling periods. Principal component analysis suggests that primary trace element aerosol sources in the study area include crustal input, coal-fired power plants and other anthropogenic emitters, and sea salt. Mercury was identified as its own component, suggesting its geochemical behavior is unlike other trace elements analyzed. Statistical comparison of individual trace element TSP concentrations showed that all sites exhibited similar concentrations of elements derived from crustal (Ce, Cs, La, Pr, Sn, Sr, Th, and Mg) and coal combustion sources (S, Sb, Se). The Georgetown site exhibited elevated Hg and Pb TSP concentrations relative to the other two sites, indicating greater contribution from local sources (i.e. a coal-fired power plant, a paper mill, and/or a steel production plant).

Comparison of Hg-TSP and fine particulate (PM<sub>2.5</sub>) Hg concentrations between adjacent samplers demonstrates that  $71 \pm 17\%$  of particulate-bound Hg was associated with coarse (>2.5  $\mu\text{m}$ ) particles, possibly sea salt aerosols. Modeled rates of dry deposition for coarse and fine particulate Hg are compared with reactive gaseous Hg during the sampling periods. Findings from this study suggest that atmospheric particulate matter is an important transport mode for Hg in the South Carolina coastal environment and that Hg exhibits a complex and dynamic behavior relative to other trace elements.

## Zoning in olivine xenocryst in hydrous systems

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Chemical zoning in xenocrysts may be inherited, the result of magmatic growth, or diffusive ion exchange with the host magma. To quantify magma residence times of xenocrysts based on diffusion zoning patterns thus requires knowledge of the contribution of diffusion to the zoning patterns and knowledge of appropriate diffusion coefficients. Using olivine xenocrysts (Fo 75-79) from melting experiments run for ca. 1 day, at 1000-1150 °C, 200 MPa,  $fO_2$  near NNO, and 1-5 wt% H<sub>2</sub>O, we characterize length-scales of growth versus Fe-Mg diffusion zoning, and suggest that hydrous diffusion coefficients for olivine need to be constrained to reliably model xenocryst residence times in magmatic systems. In the experiments, initially angular, unzoned olivine xenocrysts develop subhedral to euhedral crystal outlines, and continuous Fe-Mg core-rim zoning with rim thicknesses of  $\leq 40$   $\mu\text{m}$ . The euhedral crystal outlines and thick rim zones indicate that the zoning patterns partly result from growth. However, abundant healed micro-fractures, originally present in the xenocrysts, extend into the compositional rim zones, and define minimum length scales for zoning as the result of diffusion. The maximum length scale of the diffusion zoning profiles are 9.5 and 17.5  $\mu\text{m}$  in 1000 and 1150 °C experiments, and we suggest that these profiles represent diffusion close to [001]. Estimating the diffusion coefficient D as  $\sim l^2/t$  (l = diffusion length scale; t = time) gives log(D) of ca. -14.8 to -14.2  $\text{m}^2/\text{s}^{-1}$  at 1000 and 1150 °C, apparently independent of the amount of H<sub>2</sub>O present. Using the same approximation to calculate D for olivine xenocrysts in an equivalent dry system (using data from [1]), indicate that diffusion in olivine xenocrysts in low-pressure hydrous systems is over ten times faster than in equivalent anhydrous systems. To reliably quantify magma residence times of xenocrysts based on diffusion zoning patterns thus requires (i) that hydrous diffusion coefficient are rigorously constrained and applied, unless it is evident that the xenocrysts were immersed in dry magmas; and (ii) that growth contributions to xenocryst zoning patterns are constrained (e.g., using markers as above, or comparing zoning patterns for multiple elements).

[1] Costa & Dungan (2005) *Geology* **33**, 837-840.

## A novel carbon concentrating mechanism for foraminiferal calcification and its potential effects on paleoceanographic proxies

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We describe a unique carbon concentrating mechanism in foraminifera that serves mainly for calcification and to some extent for symbionts photosynthesis. Observations on the benthic species *Amphistegina lobifera* show intensive seawater vacuolization activity, with two types of vacuoles: Mega-pinocytotic vacuoles (10-20  $\mu\text{m}$  in size) and small spherical vacuoles ( $\sim 5$   $\mu\text{m}$ ). Using confocal laser microscopy and fluorescent dyes we found that the pH of the mega-vacuoles is close to 9, while the pH of the small spherical vacuoles is below 6. Under these conditions CO<sub>2(aq)</sub> diffuses from the small vacuoles through the cytosol into the large basic vacuoles. These basic vacuoles are recycled into the calcification site where they exocytose their CO<sub>3</sub><sup>2-</sup> enriched seawater to the site of biomineralization. Microelectrodes observations of pH and CO<sub>3</sub><sup>2-</sup> showed that the DIC concentration in the calcifying fluid was at least 4 mM (double than that of seawater). These observations have complex implications for paleoceanographic proxy development: The carbon isotopic fractionation of the symbiotic algae occurs from a semi-closed reservoir. The CO<sub>3</sub><sup>2-</sup> is higher than that of seawater so that the partition coefficient of other anions in seawater (B, S, P) would be low. High CO<sub>3</sub><sup>2-</sup> at the calcification site may also lower the  $\delta^{18}\text{O}$  of the shell. Planktonic foraminifera may behave differently to some extent because the symbionts are also distributed along the spines, and the system is more open for gas exchange and ions diffusion.

## Carbonatites and Large Igneous Provinces (LIPs)

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There is increasing evidence that many carbonatites are linked both spatially and temporally with large igneous provinces (LIPs), i.e. high volume, short duration, intraplate-type, magmatic events consisting mainly of flood basalts and their plumbing systems. Examples of LIP-carbonatite associations include: i). the 66 Ma Deccan flood basalt province associated with the Amba Dongar, Bhuj, Barmer, and Mundwara carbonatites and alkali rocks, ii). the 130 Ma Paraná-Etendeka (e.g. Jacupiranga, Messum); iii). the 250 Ma Siberian LIP that includes a major alkaline province, Maimecha-Kotui. iv). the ca. 370 Ma Kola Alkaline Province coeval with basaltic magmatism widespread in parts of the East European craton. In the Superior craton, Canada, a number of carbonatites are associated with the 1114-1085 Ma Keweenaw LIP and some are coeval with the Circum-Superior 1880 Ma mafic-ultramafic magmatism. In addition, the Phalaborwa carbonatite is associated with the 2055 Ma Bushveld event of the Kaapvaal craton. The frequency of this LIP-carbonatite association suggests that LIPs and carbonatites might be considered as different evolutionary 'pathways' in a single magmatic process/system. Some benefits of considering LIPs and carbonatites together are as follows: 1) mapping lithospheric thicknesses: carbonatites are from areas of thick lithosphere, voluminous basaltic magmatism from shallower depths; 2) recognizing trans-lithospheric breaks: carbonatites are emplaced along structural zones, especially large scale faults and rifts; e.g. carbonatites related to both the 1107 Ma Keweenaw and 1880 Ma Circum-Superior LIPs are emplaced along the Kapuskasing Structural Zone, a significant break across the narrow 'waist' of the Superior craton; 3) timing of magmatic activity: carbonatites often occur early relative to emplacement of flood basalts consistent with the generation of low-degree melts ahead of major melting of the plume to produce basalts/picrites; 4) recognizing plumes: isotopic signatures for carbonatites include the components FOZO, HIMU, EM1 but not DM. This, along with primitive noble gas signatures in some carbonatites, suggests a deep mantle source for carbonatites, consistent with a plume origin proposed for many LIPs.

## Holocene decadal to millennial variability of winter climate in the Pacific Northwest

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We present a well-dated, high-resolution stalagmite stable isotope record from Oregon Caves National Monument in SW Oregon (42°N, 123°W).  $\delta^{18}\text{O}$  values of rainwater collected over a three year period at the cave site shows a good correlation with temperature with an average value of  $0.6\text{‰ }^{\circ}\text{C}^{-1}$  and as a result we interpret the speleothem  $\delta^{18}\text{O}$  as reflecting mainly temperature changes. Because of precipitation seasonality in south-western Oregon (wet winters and dry summers) and the rapid transit time of meteoric water through the karst aquifer, our speleothem record reflects mostly changes in cool season climate. Speleothem  $\delta^{18}\text{O}$  values show an increasing trend for the last 9000 years which is in agreement with marine paleoproxies in the eastern Pacific Ocean showing increasing sea surface temperatures over the same period. The wavelet analysis of the speleothem data shows a persistent cycle throughout the Holocene with a period of ~2000 years, as well as more intermittent cycles with periods of ~500 years and 90-50 years. We compare our record with other proxies in western North America and discuss possible processes and mechanisms responsible for Holocene climate variability in western North America.

## Al- and <sup>14</sup>B-rich tourmaline from the Sahatany Pegmatite Field, Madagascar, and its relevance on a new barometer

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An Al-rich tourmaline from the Sahatany Pegmatite Field in Manjaka, Sahatany Valley, Madagascar, was structurally and chemically characterised. The combination of chemical (EMPA, ICP-AES, TGA) and structural data, yields an optimized formula of  $X(\text{Na}_{0.5}\text{Ca}_{0.1}\square_{0.4})^Y(\text{Al}_{1.8}\text{Li}_{1.1}\text{Mn}^{2+}_{0.1})^Z\text{Al}_6(\text{BO}_3)_3^T[\text{Si}_{5.5}\text{B}_{0.5}]\text{O}_{18}(\text{OH})_4$ , with  $a = 15.7768(2)$ ,  $c = 7.0858(1)$  Å ( $R1 = 0.017$  for 3241 reflections). The  $\langle T-O \rangle$  distance of  $\sim 1.611$  Å is one of the smallest distances observed in natural tourmalines to date. The very short  $\langle Y-O \rangle$  distance of  $\sim 1.976$  Å reflects the relatively high amount of Al at the Y site. The F content was below detection limit. This reddish tourmaline sample consists of several  $\sim$ parallel arranged idiomorphic tourmaline crystals with  $\sim 1$  mm in diameter and  $\sim 5$  cm in length, embedded in quartz.

Together with other natural and synthetic Al-rich tourmalines, a very good inverse correlation between <sup>14</sup>B and the unit cell volume with  $r^2 \approx 1.00$  was found. Marler *et al.* [1] published the crystal structure (by Rietveld refinement) of two Al-rich tourmalines which were synthesized at 600°C/2500 MPa and 650°C/2000 MPa [2].

By correlating the two well characterised synthetic tourmaline samples, which were grown under known *HP* conditions, the natural Al-rich tourmaline from Momeik, Myanmar [3], and the natural Al-rich tourmaline from this study, which crystallized at minimum *PT* conditions of  $\sim 200$  MPa/ $\sim 350^\circ\text{C}$  [4, 5], we observed a very good positive relationship ( $r^2 \approx 0.99$ ) between pressure conditions and the amount of tetrahedrally coordinated boron in Na- and Al-rich tourmaline. By correlating the pressure conditions of natural and synthetic Na-, Al- and <sup>14</sup>B-rich tourmalines with the unit cell volume we found a very good inverse correlation with  $r^2 \approx 0.99$ . Hence, we believe that the pressure conditions of Al- and B-rich tourmaline can be estimated by using either the <sup>14</sup>B content or the unit cell volume.

- [1] Marler *et al.* (2002) *Eur. J. Mineral.* **14**, 763–771.  
[2] Schreyer *et al.* (2000) *Eur. J. Mineral.* **12**, 529–541.  
[3] Ertl *et al.* (2007) *Can. Mineral.* **45**, 891–899.  
[4] Ranoroa (1986) Thesis, Université Paul Sabatier, 240 pp.  
[5] London & Burt (1982) In: Černý (ed.) *Min. Assoc. Can., Short Course Handbook* **8**, 99–133, Winnipeg.

## Arsenic mobilization associated with applied recharge of low-TDS water in Central Valley, California

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A dissolved gas tracer study, tritium/helium-3 groundwater age dating, and stable isotope and dissolved trace metal data were used in conjunction with geochemical modeling using PHREEQC to identify and characterize the recharge of low-TDS recharge water into a shallow aerobic aquifer affected by a groundwater banking project in California's San Joaquin Valley. The integrated dataset consistently points to a substantial degree of mixing of recharge water from surface ponds with ambient groundwater in nearby monitoring wells screened within 60 m of ground surface. Specific geochemical interactions associated with recharge of the low-TDS water include ion exchange (comparative enrichment of affected groundwater with Na and K at the expense of Ca and Mg) and the desorption of oxyanion-forming trace elements (As, V, and Mo) in response to the elevated pH of the recharge water. The SF<sub>6</sub> tracer arrival times for the recharge-influenced wells range from weeks to months, indicating these interactions occur over a relatively short time scale.

Recharge water is characterized by a somewhat elevated pH in comparison to site groundwater, so displacement of oxyanions by OH<sup>-</sup> on the HFO binding sites is a plausible explanation for the observed behavior of As, V, and Mo. Modeled solid-phase exchangeable arsenic concentrations compare well to reported leachable concentrations in the literature. Taken together, the results of this study indicate that mixing of recharge water with ambient groundwater creates a geochemical footprint that includes a shift in the relative abundances of major cations and the mobilization of certain trace elements. In a broader sense – beyond considerations of trace element geochemistry – this study illustrates that a set of independent and measurable indicators of the age and mixing of artificial recharge water with ambient groundwater can be self-consistent and can be modeled to constrain the local flow regime and specific geochemical processes affecting water quality. This study expands on work our laboratory has done with noble gas tracers and tritium/helium-3 in southern California (e.g. [1]).

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- [1] Clark *et al.* (2004) *Ground Water* **42**(2), 167–174.

## A preliminary investigation of chlorine XANES in silicate melts

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The nature of chlorine speciation in silicate melts affects volatile exsolution history, rheological, and thermodynamic properties of the melt, but is poorly known. XANES (X-ray Absorption Near Edge Structure) spectra, taken from 26 natural and synthetic samples, have been used to constrain Cl-speciation in silicate melts, and to test the hypothesis that Cl in silicate melts is hosted by a combination of salt-like cation-Cl complexes.

The results are consistent with the existence of a CaCl<sub>2</sub> species that has reduced short-range order compared to the CaCl<sub>2</sub> salt. Identification of a similar MgCl<sub>2</sub> species is complicated by the presence of water in the standard. It is concluded that Cl in silicate melts can be represented by a combination of salt-like cation-Cl species, with or without additional mixed cation-Cl species, polymeric cation-Cl species, lone Cl species, and Cl incorporated into network-forming polymers. Further investigations using XANES, alternative spectroscopic techniques, and forward modelling approaches are required to distinguish between these possibilities. NaCl-like features exhibited by the natural samples are attributed to NaCl present in the sample that is not hosted by the melt.

## Radiation effects in zircon and apatite

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There is increasing interest in the possible effects of radiation damage, particularly from  $\alpha$ -decay events, on the results of techniques used in thermochronometry, such as (U-Th)/He dating of apatite. During the past decade, there have been extensive studies of  $\alpha$ -decay event damage in minerals that have been considered as potential host-phases for the immobilization of actinides, particularly short-lived actinides, such as <sup>238</sup>Pu and <sup>239</sup>Pu. This presentation summarizes the results of radiation damage investigations of apatite, britholite and zircon.

An  $\alpha$ -decay event consists of a ~5 MeV  $\alpha$ -particle with a range of 10  $\mu$ m, dissipating most of its energy by ionization processes, and a 70-90 keV recoil nucleus with a range of 30 to 40 nm, losing nearly all of its energy by ballistic interactions. Damage accumulation is essentially a process of an increase in the damage fraction as the fluence increases. At the first percolation point the overlap of the displacement cascades creates interconnected pathways of amorphous material, and at the second percolation point, the crystalline domains become isolated from one another. The evolution of the nanoscale structure depends on the temperature of the irradiation and thermal history, as well as radiation-induced phenomena, such as radiation-enhanced diffusion. Damage accumulation has been studied by: *i.*) investigations of suites of natural samples whose total dose is estimated based on U/Th-content and age, *ii.*) samples doped with <sup>238</sup>Pu and <sup>239</sup>Pu, and *iii.*) systematic electron-beam and heavy ion-beam irradiations as a function of temperature. Models have been developed that quite successfully describe the damage in-growth process as a function of dose, time and temperature for zircon and apatite, and the general results of these models are consistent with observations of natural zircon.

Most recently, experiments have been completed using dual beam irradiations to simulate combined  $\alpha$ - and  $\alpha$ -recoil effects. Radiation-enhanced annealing leads to a substantial increase in the required dose for amorphization. In addition, we have completed studies that combine diamond anvil cell experiments (up to 18GPa) with very high energy irradiations (10s of GeV) to investigate the effect of pressure and temperature on damage accumulation and track formation.

## Ca isotopes and the rainfall limit of silicate weathering on Earth

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Arid (~20 mm rain  $y^{-1}$ ) to extreme hyperarid (<2 mm rain  $y^{-1}$ ) soils of the Atacama Desert reveal a threshold between limited silicate weathering and accumulation of soluble atmospheric salts. In the arid soil, silicate weathering has released 2.3 kmol Ca  $m^{-2}$ , and 1.9 kmol Ca  $m^{-2}$  is present as soluble carbonate and sulfate salts. The driest soil shows no evidence of silicate weathering, and has accumulated 3.1 kmol Ca  $m^{-2}$  (mainly as CaSO<sub>4</sub>) from atmospheric deposition.

In the driest soil, Ca isotope values (vs. bulk Earth,  $\delta^{44/40}Ca_E$ ) increase with depth and are inversely correlated with sulphate- $\delta^{34}S$  and  $\delta^{18}O$  values, indicating fractionation with incremental downward transport. In the arid soil,  $\delta^{44/40}Ca_E$  values ( $\delta^{44/40}Ca_{E, total} = -0.62\%$ ) are not decreased vs. inputs (-0.35%) to the degree expected (-1.7%) from sulfate- $\delta^{34}S$  values in the soil (14.3%) vs. atmospheric deposition (5.7%). This suggests retention of Ca from silicate weathering. At the same time, sulfate- $\delta^{18}O$  values (7-10%) comparable with atmospheric deposition (8.6%), and somewhat elevated soil  $\Delta^{17}O$  values (+0.7%), suggest a strengthened marine sulfate source in the past, with higher  $\delta^{34}S$  values.

Low carbonate- $\delta^{44/40}Ca_E$  values in the arid soil (~-1%) relative to sulfate- $\delta^{44/40}Ca_E$  (~-0.5%) suggest fractionation with downward transport of CaCO<sub>3</sub> during wetter times in the past, followed by limited dissolution during precipitation of CaSO<sub>4</sub> minerals, which favors the lighter Ca isotope. <sup>87</sup>Sr/<sup>86</sup>Sr ratios decrease in CaCO<sub>3</sub> below 1 m, indicating that the proportion of weathering derived Ca increases, and reflecting a time when wetter conditions prevailed.

## Experimental determination of Ra partition coefficients for leucite, phlogopite, and feldspars, and a re-examination of <sup>226</sup>Ra-<sup>230</sup>Th disequilibria

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<sup>226</sup>Ra-<sup>230</sup>Th disequilibrium is extensively used to date magmatic processes [1-6]. In most of the studies, the chemical behaviour of Ra was approximated by that of Ba, because Ra distribution coefficients were unavailable [1-5]. This experimental study determines  $D_{Ra}$  for the most common igneous minerals that incorporate Ra (e.g. leucite, K-feldspar, plagioclase, phlogopite), to quantify the fractionation of Ra/Ba and thus, to correctly calculate mineral ages and isochrons from Ra-Ba-Th measurements.

Different synthetic starting materials were used for each mineral to obtain crystals > 40 micron of the mineral of interest and crystal free melt pools > 200 micron of the silicate liquid. A few  $\mu$ l of <sup>226</sup>Ra solution were added such that the lower Ra-concentration was at least 1 ppm (detection limit of the LA-ICP-MS is ~ 0.01 fg). Partition coefficients for alkalis and the other earth alkalis were also determined to define Onuma type parabolas. The experiments were performed in an atmospheric furnace or in a piston cylinder apparatus at appropriate experimental conditions ( $P$ ,  $T$ ).

We found that  $D_{Ra}$  is generally different from  $D_{Ba}$ , Ra being compatible in leucite, K-feldspar and phlogopite, whereas it is incompatible in plagioclase. These results allow us to re-estimate the crystal ages of different magmatic systems [1-6] using the appropriate value of  $D_{Ra}$ . The use of the correct  $D_{Ra}$ 's value results in a 2 to 10-fold change in the ages derived from minerals (plagioclase, leucite) in which the difference between  $D_{Ra}$  and  $D_{Ba}$  is high.

[1] Volpe & Hammond (1991) *EPSL* **107**, 475-486. [2] Volpe (1992) *JVGR* **53**, 227-238. [3] Reagan *et al.* (1992) *GCA* **56**, 1401-1407. [4] Schaefer *et al.* (1993) *GCA* **57**, 1215-1219. [5] Black *et al.* (1998) *JVGR* **82**, 97-111. [6] Cooper & Reid (2003) *EPSL* **213**, 149-167.