

U-Th/He age, but in areas of slow cooling, the effect might be significant.

## V22D MC: 304 Tuesday 1330h

### Heavy Element Stable Isotope Fractionations II (joint with B, OS, P)

**Presiding:** M Rehkamper, ETH Zurich; A D Anbar, University of Rochester

## V22D-01 1330h INVITED

### Iron Isotope Variations in Natural Aqueous Systems: Further Clues to Fractionation Mechanisms

Thomas D Bullen<sup>1</sup> (650-329-4577; tdbullen@usgs.gov); Cyril W Childs<sup>2</sup> (childs@xtra.co.nz); Ron Amundsen<sup>3</sup> (earthy@nature.berkeley.edu); Kevin Mandernack<sup>4</sup> (mandern@mines.edu); Philippe Negrel<sup>5</sup> (p.negrel@brgm.fr); Joel Casanova<sup>5</sup> (j.casanova@brgm.fr)

<sup>1</sup>Water Resources Division, U.S. Geological Survey, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025, United States

<sup>2</sup>School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand

<sup>3</sup>Department of Soil Science, University of California, Berkeley, Berkeley, CA 94720, United States

<sup>4</sup>Department of Chemistry, Colorado School of Mines, Golden, CO 80401, United States

<sup>5</sup>Water Division, BRGM, Orleans, France

A number of recent pioneering studies into the potential of iron isotopes to be fractionated by natural processes have revealed a complex web of possible isotope fractionation mechanisms. For example, processes involving microbially-mediated reduction of mineral-bound Fe(III) to Fe(II) have been shown to result in fractionation of the <sup>56</sup>Fe/<sup>54</sup>Fe ratio of from 0 to 2.5‰/‰, with the lighter isotopes being concentrated in the Fe(II)-bearing aqueous or solid product. This fractionation clearly results from disequilibrium reactions, although it is as yet unclear whether the cause is strong complexation of iron at the mineral surface that limits back reaction or a true vital effect. Moreover, field and laboratory studies of abiotic iron oxidation under disequilibrium conditions reveal a fractionation of as much as 2‰/‰ with the heavier iron isotopes being concentrated in the Fe(III)-bearing product, requiring equilibrium fractionation among the coexisting aqueous Fe(II) species prior to oxidation. Furthermore, theoretical considerations predict that under equilibrium conditions large iron isotope fractionations are possible due to contrasts in ligand strength and atomic bonding environment, and that aqueous Fe(III) complexes will concentrate the heavier iron isotopes relative to Fe(II) complexes involving the same ligands. These observations provide important insights into possible isotope fractionation mechanisms, yet beg a more thorough examination of iron isotope fractionation in diverse, relatively simple natural systems. Here we present new iron isotope data that document fractionations accompanying processes such as precipitation of siderite from CO<sub>2</sub>-charged springs, of schwertmannite from acid-mine drainage and of ferrihydrite from spring waters by a presumably microbial mechanism. Considered in light of previous studies the new data underscore the importance of aqueous speciation in determining iron isotope fractionations observed in natural and experimental systems.

## V22D-02 1345h

### Iron Isotope Fractionation in Microbial and Non-Biological Precipitates, and the Human Body

Friedhelm von Blanckenburg<sup>1</sup> (fvb@mineralogie.uni-hannover.de)

Michael E. Boettcher<sup>2</sup> (mboettch@mpi-bremen.de)

Beda Hofmann<sup>3</sup> (hofmann@nmbe.unibe.ch)

Thomas Walczyk<sup>4</sup> (thomas.walczyk@ilw.agr1.ethz.ch)

<sup>1</sup>Isotope Geology, University of Berne, now at Institute for Mineralogy, University of Hannover, Callinstr. 3-9, Hannover 30167, Germany

<sup>2</sup>Max-Planck-Institut fuer Marine Mikrobiologie, Celsiusstr. 1, Bremen 28359, Germany

<sup>3</sup>Natural History Museum, Bernastr. 15, Bern 3005, Switzerland

<sup>4</sup>Laboratory of Human Nutrition, Institute of Food Sciences, ETH Zuerich, Seestrasse 72, Rueschlikon 8803, Switzerland

We have investigated biotic and abiotic stable iron isotope fractionation pathways in experiments, the low-T natural environment, and the human body. Fe samples were analysed using a Nu Plasma Multicollector ICP-MS. All measured samples plot on the theoretically predicted exponential fractionation line in the Delta57Fe versus Delta56Fe space, demonstrating absence of ArN or ArO interferences. An experimental calibration of Fe isotope fractionation during abiotic formation of iron (III) oxyhydroxide and iron(II) minerals from aqueous solution resulted in significant differences: (a) During fast precipitation of FeOOH during alkalization of a Fe(III)Cl<sub>3</sub> solution at room temperature the solid is only slightly enriched by about 0.1permil in 57Fe compared to the solution. (b) Slow precipitation of akaganeite (beta-FeOOH) from aqueous Fe(III)Cl<sub>3</sub> solution leads to a depletion of 57Fe by about -2.2permil in the solid phase without a significant influence of temperature. (c) Precipitation of FeOOH during oxidation of aqueous Fe(II) solutions by oxygen yields an enrichment of up to 4.8permil in 57Fe in the solid phase. (d) Iron(II) carbonate precipitation between 20 and 60C leads to an almost negligible depletion in 57Fe compared to aqueous ferrous ions. Interpretation: Large enrichment of the heavy isotope is observed where Fe is oxidised, whereas small to intermediate depletions of heavy Fe isotopes occur upon formation of Fe-minerals without change in redox state. Additionally, kinetic effects, the speciation of the aqueous solution, or the effect of crystal structures may have to be considered. Biotic isotope fractionation by microorganisms was investigated at two field sites. In a Fe mine (Gonzen, Switzerland), Fe-precipitating microbes (*Gallionella ferrugina* and *Leptotrichia ochracea*) have formed Fe(III)-oxyhydroxides that are ca. 0.6permil heavier in Delta57Fe than the Fe-rich parent solutions. At Cady Mts, California, filamentous fabrics of goethite, thought to represent fossil remnants of microbial mats, have been found as encrustations in chalcocopyrite. Delta57Fe is 3 permil heavier than the associated calcite (representing the Fe-rich fluids). Therefore, the fractionations found in microbial precipitates are not larger than those produced in the abiotic experiments. In contrast, major Fe isotope fractionations are produced by the human body: The major iron compartments in the human body, blood, liver, muscle tissues, and also hair, are all depleted by as much as 6 permil in the 57Fe isotope relative to 54Fe when compared to the average dietary intake. Since feces are similar to the average intake, we conclude that a significant Fe isotope fractionation occurs at the absorptive stage in the intestine. In conclusion, with respect to the hypothesis that Fe isotope effects might serve as "biosignatures" it appears that microbial and abiotic reactions cause similar isotope effects which essentially depend on redox reactions and the speciation in the aqueous solution. On the other hand, higher organisms bear distinct Fe isotope signatures.

## V22D-03 1400h

### Copper Isotope Fractionation in Porphyry Copper Deposits: A Controlled Experiment

Joaquin Ruiz<sup>1</sup> (520-621-4090; jruiz@geo.arizona.edu)

Ryan Mathur<sup>1</sup> (520-621-4090; rmathur@geo.arizona.edu)

John L Uhrig<sup>2</sup> (520-348-8105; juhrie@phelpsdodge.com)

Brent Hiskey<sup>3</sup> (520-621-4090; bhiskey@mines.arizona.edu)

<sup>1</sup>Department Of Geosciences, University of Arizona, Tucson, AZ 85721, United States

<sup>2</sup>Phelps Dodge Mining Company, Process Technology Center, Safford, AZ 85546, United States

<sup>3</sup>College of Engineering, University of Arizona, Tucson, AZ 85721, United States

Previous studies have shown that copper is fractionated in the environment. However, the mechanisms for isotope fractionation and the role of organic and inorganic processes in the fractionation are not well understood. Here we used the well controlled experiments used by Phelps Dodge Corporation aimed at leaching copper from their ore deposits to constrain the mechanism of copper isotope fractionation in natural systems.

The isotope data were collected on a Micromass Isoprobe. High temperature copper sulfides from ore deposits in Chile and Arizona yield delta 65Cu near 0 permil. The reproducibility of the data is better than 0.1 permil.

Controlled experiments consisting of large columns of rocks were fed solutions containing bacteria such as *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. Solutions from the columns were sampled for sixty days and analyzed for copper concentrations, oxidation potential, ferrous/ferric ratios and pH. The results indicate that the bacterially aided dissolution of copper

fractionated copper. Preliminary experiments of copper dissolution not using bacteria show no isotope fractionation

The original rock in the experiment has a delta 65Cu of 2.1. The first solutions that were collected from the columns had a delta 65Cu of 5.0 per mil. The liquid changed its isotopic composition from 50 to 10 during the sixty days of sampling. The greatest shift in the isotope ratios occurred the first 30 days when the copper recovered was less than 40% and the ferrous/ferric ratios were somewhat constant. At approximately 35 days after the start of the experiments, the copper recovery increases the ferrous/ferric ratio decreased and the copper isotope ratio of the fluids remained fairly constant.

The data suggest that the bacteria are required to effectively fractionate copper isotopes in natural systems and that the mechanisms of bacterial aided copper dissolution may include a direct dissolution of the sulfides by the bacteria. Experiments underway with enzymes without the bacteria may confirm this hypothesis. The data obtained in these experiments will provide some constraints in the use of copper isotopes as proxy for life in the rock record.

## V22D-04 1415h

### Heavy Stable Isotopes As Indicators of Redox-Sensitive Contaminant Dynamics: Progress With Selenium

Thomas M Johnson<sup>1</sup> (217-244-2002; tmjohnsn@uiuc.edu)

Thomas D Bullen<sup>2</sup> (650-329-4577; tdbullen@usgs.gov)

Andre S Ellis<sup>1</sup> (217-244-6048; asellis@uiuc.edu)

Mitchell J Herbel<sup>2</sup> (650-329-4473; mjherbel@xian.wr.usgs.gov)

<sup>1</sup>Dept. of Geology, Univ. of Illinois, Urbana, IL 61801, United States

<sup>2</sup>Water Resources Div., US Geological Survey 345 Middlefield Road, Menlo Park., CA 94025, United States

Selenium contamination occurs in many areas of the western USA as Se is flushed from soils into irrigation wastewater. It is also elevated where fly ash from coal-fired power plants is disposed of, and in a few other settings. Predicting the long-term impacts of anthropogenic Se inputs on various systems involves understanding the redox reactions that control Se mobility and bioavailability. Detailed Se speciation studies have provided insights into such processes, but are limited in several ways. Se isotope measurements provide complementary information about redox reactions, and thus can improve understanding of these critical processes. Other heavy stable isotope systems have similar potential. Several challenges have arisen in the development of Se isotopes, and all of these apply to other heavy stable isotope systems. Because of the geochemical complexity of Se, several studies were needed to provide an initial survey of laboratory data on Se isotope systematics. Other heavy elements have similarly complex arrays of species and reactions, and detailed laboratory studies are needed to reveal the associated fractionations. Microbially mediated and kinetically complex reactions may have variable fractionations. Our microbial reduction experiments in the laboratory showed a wide range of fractionation induced by reduction of Se(VI) to Se(IV), from <1.0 to 5.0 per mil on 8076. On the other hand, sediment slurries from three different wetland settings yielded a narrow range of fractionation (2.6 to 3.1 per mil) for this reaction. This is encouraging, but further work will be needed to extend this to a wider range of conditions. Once the isotopic systematics are understood, transport dynamics in the field come into play. The effective fractionation that occurs in surface water-sediment systems may be less than the instantaneous fractionation induced by a reaction, because the sediment can be a "partially closed" system, connected to the water column via diffusion. Detailed studies of microcosms will be needed to address this issue.

## V22D-05 1430h

### Selenium Isotopes as Biosignatures in Seafloor Hydrothermal Systems

Olivier Rouxel<sup>1</sup> (rouxel@crpg.cnrs-nancy.fr)

John Ludden<sup>1</sup> (ludden@crpg.cnrs-nancy.fr)

Yves Fouquet<sup>2</sup> (fouquet@ifremer.fr)

<sup>1</sup>CRPG-CNRS, 54501 Vandoeuvre, France

<sup>2</sup>IFREMER, 29280 Plouzané, France

Chemically similar to sulphur, Se occurs as +6, +4, 0 and -2 valences in a variety of organic compounds and geological settings. This makes the study of Se

stable isotope ratios a potential indicator of geological and biological processes. Se isotopes were first determined in the early 60's (Krouse and Thode, 1962; Rashid et al., 1978) using gas-source MS and recently by N-TIMS (Herbel et al., 2000; Johnson et al., 1999) using the double spike technique. The previous results showed that the  $^{82}\text{Se}/^{76}\text{Se}$  ratio vary by as much as  $15\text{‰}$  and indicate that abiotic and bacterial reduction of soluble oxyanions is the dominant cause of Se isotope fractionation.

Our isotopic analyses of Se were performed using a continuous flow hydride generation system coupled to a Micromass MC-ICP-MS after chemical purification. The estimated external precision of the  $^{82}\text{Se}/^{76}\text{Se}$  isotope ratio is  $0.25\text{‰}$  ( $2\sigma$ ) for a quantity of Se per analysis as low as 50 ng and the data are reported relative to our internal standards (MERCK elemental standard solution).

In this study we have used Se isotopes in conjunction with S isotopes to provide additional constraints on the fractionation processes in seafloor hydrothermal systems. Several fields were studied along the Mid Atlantic Ridge and include the Lucky Strike field where the setting is in a caldera system with abundant low-permeability layers of cemented breccia which result in fluid cooling and mixing below the hydrothermal vents. Based on vent structures, mineral abundance, and geochemistry, two types of hydrothermal deposits were identified: (1) high-T vents with  $\delta^{34}\text{S}$  between 1.5 and  $4.5\text{‰}$  and Se values up to 2000 ppm; (2) low-T vents where pyrite and marcasite generally have lower  $\delta^{34}\text{S}$  values (down to  $-1.0\text{‰}$ ) and low concentration of Se ( $<50\text{ppm}$ ). Se-depletion in low temperature hydrothermal deposits is interpreted as a result of subsurface precipitation of sulfides (scavenging Se from the fluid) during the conductive cooling of the hydrothermal fluid beneath the impermeable slabs. For  $\delta^{82}\text{Se}$  the values range from meteoritic and magmatic values (near  $-1.5\text{‰}$ ) to values depleted in  $^{82}\text{Se}$  of  $-5.5\text{‰}$ . Se isotope values of sulfides are correlated with the Se content. As Se isotopic fractionation factor between the fluid and the precipitated sulfide is likely to be very small under hydrothermal conditions (as for S isotopes), we interpreted the Se isotope signature as a result of the leaching and mixing of a fractionated Se source beneath hydrothermal chimneys with the hydrothermal fluid. For one single vent (Bairo Alto) we observed variations up to  $4\text{‰}$  for S isotopes and  $3\text{‰}$  for Se isotopes with a clear positive correlation allowing the determination of two sources for S and Se; there are (1) the "end-member" hydrothermal fluid with meteoritic Se isotopic values ( $-1.5\text{‰}$ ) and typical hydrothermal values at 3 to  $4\text{‰}$  for S isotopes (due to sulfate reduction at depth) and, (2) fractionated source hosted in slab environment with sulfur at negative  $\delta^{34}\text{S}$  values and Se likely derived from bacterial reduction of Se oxyanions. Fluid cooling and mixing with seawater in the subsurface environment may provide suitable conditions for microbial activity which is recorded by Se isotopes. Furthermore, Se isotopes have been found to be an important tool to re-interpret S isotope data suggesting that magmatic isotopic values of S isotopes does not necessarily imply a magmatic origin of S.

## V22D-06 1505h INVITED

### Stable Isotope Fractionation of Metallic Elements

Francis Albarede (albarede@ens-lyon.fr)

Ecole Normale Supérieure, 46 Allée d'Italie, Lyon 69007, France

The 70s and the 80s saw the demonstration that some anomalous isotope compositions in planetary material are inherited from heterogeneities in the Solar Nebula and that some others reflect spallation induced by strong radiation events. In addition, a variety of mass-independent fractionation processes were shown to affect the isotopic composition of atmospheric O, C, and S. In the mean time, the patterns of mass-dependent fractionation of most elements, notably metals, remained largely ignored, presumably because the state-of-the-art precision of existing analytical techniques (mostly double-spike) was inadequate. The debate largely focused on why no isotopic fractionation could actually be observed, e.g., for K and Fe in planetary objects, within the limits of the current analytical uncertainties ( $0.1$  to  $1\text{‰}$ ). The advent of multiple-collector ICP MS suddenly improved the precision on isotopic measurements to a typical 40 ppm on elements such as Cu, Zn, Fe, Mg, Mo, etc. The ongoing exploration of the stable isotope geochemistry of metallic elements is revealing that their natural isotopic variability is much more widespread and stronger than previously anticipated, typically  $1\text{‰}$  for Zn and Fe to  $10\text{‰}$  for Cu. The mechanisms of isotopic fractionation that create this variability remain to be determined. The bulk of Zn and Fe in planetary material is apparently derived from an isotopically homogeneous source. The first data on meteorites reveal, however, that the isotopic heterogeneities of Cu and Zn in planetary objects correlate with  $^{16}\text{O}$  excess. Redox reactions cannot be the deus-ex-machina of the isotope geochemistry of metals: isotope fractionation in ores and soils is far more ubiquitous and far stronger for Cu than for Fe. Cu fractionation by ion exchange in solution is

much stronger for chloride complexes than for free ions in nitric solutions. Volatilization processes also need to be better understood: the Zn isotope variability of iron meteorites is nearly an order of magnitude larger than that of the rest of planetary material altogether regardless of its apparent volatile element depletion. A careful investigation of the coordination and of molecular symmetry in vapor, aqueous solutions, solids and liquid metals is a pre-requisite to the understanding of these newly discovered isotopic effects.

## V22D-07 1520h

### Large Transition-Metal Isotope Fractionations Associated with Archaeal Microbial Communities

Corey Archer<sup>1</sup> (44-0-1784-414260; c.archer@gl.rhul.ac.uk)

Derek Vance<sup>1</sup> (44-0-1784-443615; d.vance@gl.rhul.ac.uk)

<sup>1</sup>Department of Geology, Royal Holloway University of London, Egham, Surrey TW20 0EX, United Kingdom

Transition metal stable isotopes potentially have many useful geochemical and biogeochemical applications. Because of the relatively small differences in mass between isotopes it is thought that these elements are not substantially fractionated by high temperature terrestrial processes. However low temperature, and in particular, biological processes may produce significant fractionations. Recent advances in multicollector ICP technology have overcome previous analytical difficulties and made the necessary high precision isotopic measurements possible. Here we present data that illustrate some technical aspects of transition metal isotope geochemistry by multi-collector ICP-MS. In addition, we report data for Fe and preliminary data for Zn isotopes in Archaeal sulphide samples associated with sulphate-reducing bacteria in microbial communities from the 2.7 Ga Belingwe belt, Zimbabwe.

We have employed the same chemical separation procedures reported previously<sup>1</sup>. However, we have observed fractionation artefacts associated with matrix elements (mainly Ti and Fe) in the Zn fraction which we have eradicated by the addition of a small column to further purify the separated Zn. Instrument mass bias has been corrected for Fe using standard bracketing and for Zn using Cu-doping. We have also found that careful matching of Cu/Zn ratios in standards and samples is necessary in order to avoid very systematic mass-bias artefacts associated with the instrument. For example, the  $^{66}\text{Zn}/^{64}\text{Zn}$  ratio for standards and samples, mass-bias corrected using  $^{65}\text{Cu}/^{63}\text{Cu}$ , changes by 1.1 per mil as the Cu/Zn ratio changes from 1 to 0.1. The change is only 0.3 per mil, however, as the Cu/Zn ratio changes from 1 to 10. These changes are associated with non-linear variations in the Cu signal and are tentatively attributed to space-charge effects in the ICP source/expansion area.

Multiple analyses (n=12, processed separately through the chemistry) of USGS standard basalt BCR-1, during two different analysis sessions, yield a reproducibility of 0.04 per mil for  $\delta^{56}\text{Fe}$ . Analogous to earlier findings<sup>2</sup>, this product of high-temperature processes is minimally-fractionated (+0.12 per mil for  $\delta^{56}\text{Fe}$ ) relative to our IRMM14 Fe standard. Preliminary  $\delta^{66}\text{Zn}$  values for BCR-1 are also close to the Lyons JMC standard<sup>3</sup>. In marked contrast, sulphides associated with microbial communities in the Belingwe belt have the lightest Fe yet reported for terrestrial samples. For  $\delta^{56}\text{Fe}$  the range is 1.2 to 2.8 per mil, with reference to BCR-1. The silicate portion of two black shale samples, with very negative  $\delta^{13}\text{C}$  of  $-30.4$  per mil<sup>3</sup>, have values of  $-2.5$  and  $-1.6$  per mil. Preliminary data for Zn show consistently positive fractionations with the two black shales having the highest  $\delta^{66}\text{Zn}$ , at  $+0.8$  and  $+1.0$  per mil relative to BCR-1. These fractionations are analogous to those recently obtained for sulphur from the same material<sup>3</sup> and document ancient fractionations of Fe and Zn by biological processes.

<sup>1</sup>C. Marchal, P. Telouk, F. Albarede, Chem. Geol. 156, 251-273 (2000). <sup>2</sup>B.L. Beard, C.M. Johnson, Geochim. Cosmochim. Acta 63, 1653-1660 (1999). <sup>3</sup>N.V. Grassineau et al. Proc. Roy. Soc. London B 268, 113-119 (2001).

## V22D-08 1535h

### Experimental Study of Mass-dependent Fractionation of Molybdenum Isotopes Scavenged During Precipitation of Manganese Oxyhydroxides

Jane Barling<sup>1</sup> (+1 716 275 2514; barling@earth.rochester.edu)

Ariel D Anbar<sup>1,2</sup> (+1 716 275 2514; anbar@earth.rochester.edu)

<sup>1</sup>University of Rochester, Dept. of Earth and Environmental Sciences, Rochester, NY 14627, United States

<sup>2</sup>University of Rochester, Department of Chemistry, Rochester, NY 14627, United States

We are investigating mass-dependent fractionation of Mo isotopes scavenged by Mn oxyhydroxides. Barling et al. (2001) hypothesized that this process explains the natural fractionation of Mo isotopes between Fe-Mn oxide sediments on the one hand and seawater and anoxic sediments on the other. To account for the observations, the lighter Mo isotopes must be preferentially scavenged, and the scavenging process must be inefficient. Laboratory experiments have shown that scavenging efficiency decreases with increasing pH (e.g. Chan and Riley, 1968).

In our experiments we varied the concentrations of Mo and Mn in solution (Mo = 0.1 - 8.3 ppm; Mn = 21 - 1740 ppm; Mn/Mo = 209), contact time between precipitate and solution (0 - 23 hours) and pH (2 - 9.4). At pH 2 the efficiency of removal of Mo from solution by Mn oxyhydroxides is  $>99.9\%$  and is unaffected by Mo and Mn concentrations or by contact time. We infer that Mo scavenging occurs dominantly during initial precipitation and that subsequent scavenging is of secondary importance. As expected from previous studies, scavenging efficiency varied with pH, from  $>99.9\%$  at pH 2 to 78% at pH 9.4.

The isotopic composition of residual Mo in the filtered solutions was measured for experiments at pH 4.3 (4.8% residual Mo in solution), pH 9 (12.9% Mo) and pH 9.4 (22.4% Mo). In all cases, residual Mo was heavy relative to the starting Mo solution, as hypothesized. At pH 9, the magnitude of the experimentally produced fractionation ( $\delta^{97/95}\text{Mo} = 1.4\text{‰}$ ) is close to that seen in nature between Pacific Mn nodules and Pacific seawater (pH 7.8;  $\delta^{97/95}\text{Mo} = 1.9\text{‰}$ ). Assuming a simple Rayleigh fractionation model,  $\alpha$  for these experiments varies from 1.00046 to 1.00015 with decreasing pH. This suggests that at least two different mechanisms are involved in the removal of Mo from solution by Mn oxyhydroxides and that the relative importance of these mechanisms varies with pH. Factors that might vary with pH and thus favor one mechanism over another include changes in Mo speciation and the form of Mn oxyhydroxide precipitated.

## V22D-09 1550h

### Constant Molybdenum Isotope Composition of Ocean Water and Fe-Mn crusts for the Last 70 Myr

Christopher Siebert<sup>1</sup> (+41-31-6318533; siebert@mpi.unibe.ch)

Thomas F. Nagler<sup>1</sup> (+41-31-6318752; naegler@mpi.unibe.ch)

Friedhelm von Blanckenburg<sup>2</sup> (fvb@mineralogie.uni-hannover.de)

Jan D. Kramers<sup>1</sup> (+41-31-6318789; Kramers)

<sup>1</sup>Isotope Geology, University of Berne, Erlachstr. 9A, Bern 3012, Switzerland

<sup>2</sup>Isotope Geology, University of Berne, present address: Institute for Mineralogy, University of Hannover

In the relatively new field of heavy stable isotope geochemistry, molybdenum (Mo) is one of the very promising elements. Molybdenum is a redox-sensitive trace metal. Isotope fractionation during terrestrial processes such as low-temperature redox transitions, chemical weathering, changes in the composition of the atmosphere, hydrothermal activity and sedimentary cycling is likely. Molybdenum is also an essential element for biological nitrogen fixation. Therefore, biogeochemical Mo isotope fractionation is also probable. The oceans represent an important terrestrial Mo reservoir. Dissolved concentrations in seawater are relatively high (0.01 ppm). The global ocean residence time is corresponding high with 800 kyr. The aim of this study is to characterise the principle present day oceanic Mo reservoirs and their changes with time. Molybdenum isotopic compositions were determined precisely using a Nu instruments MC-ICP-MS. Instrumental and laboratory mass fractionation is separated from natural mass dependent fractionation by addition of a molybdenum double spike prior to chemical separation (Siebert et al., 2001). The external standard reproducibility is at or below 0.1 per mil for the  $^{98}\text{Mo}/^{95}\text{Mo}$  ratio (2s.d.). We analysed ocean water samples from the Atlantic (n=3, 0m-2400m depth), the Pacific and the Indian Ocean (deep water). These yield a homogeneous Mo isotopic composition as would be expected from the long residence time of Mo in the oceans. Ocean water has the heaviest Mo isotopic composition measured to date (+2.3 per mil on the  $^{98}\text{Mo}/^{95}\text{Mo}$  ratio relative to a Johnson Matthey ICP standard solution, lot 602332B). In view of the homogeneous ocean water ratios, we propose the use of present day ocean water as an reference standard (Mean Ocean Molybdenum: MOMO). Significantly lighter compositions from  $-2.7$  to  $-3.1$  per mil on the  $^{98}\text{Mo}/^{95}\text{Mo}$  ratio relative to MOMO were determined for six Fe-Mn crust surface layers. Pelagic clay ( $-2.7$  per mil) and clastic sediments ( $-2.3$  and  $-2$

per mil) show composition inbetween. A depth profile through a 70Ma old Fe-Mn crust revealed steep gradients for Mo concentrations (300ppm to 400ppm within 2 Myr), precluding post-depositional homogenisation of Mo. In contrast, the Mo isotopic compositions are uniform throughout the entire 70 Myr profile (-3.2 +/- 0.1 per mil relative to 98Mo/95Mo MOMO). We conclude, that a constant Mo isotopic composition must be assumed for ocean water during the last 70 Myr.

## V22D-10 1605h

### Thallium Isotope Variations in Seawater and Ferromanganese Deposits

Mark Rehkamper<sup>1</sup> (markr@erdw.ethz.ch)

M Frank<sup>1</sup> (frank@erdw.ethz.ch)

J R Hein<sup>2</sup> (jhein@usgs.gov)

D Porcelli<sup>1</sup> (porcelli@erdw.ethz.ch)

A N Halliday<sup>1</sup> (halliday@erdw.ethz.ch)

<sup>1</sup>Institute of Isotope Geology and Mineral Resources, ETH Zurich, NO C61, CH-8092 Zurich, Switzerland

<sup>2</sup>US Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, United States

We have conducted an in-depth investigation of Tl isotope variations for a comprehensive suite of hydrogenetic ferromanganese crusts, diagenetic Fe-Mn nodules, hydrothermal manganese deposits and seawater samples. The natural variability of Tl isotope compositions in these samples exceeds the analytical reproducibility ( $\pm 0.05\%$ ) by more than a factor of 40.

Hydrogenetic Fe-Mn crusts have  $\epsilon^{205}\text{Tl}$  of +10 to +14, whereas seawater is characterized by values as low as -8 ( $\epsilon^{205}\text{Tl}$  represents the deviation of the  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio of a sample from the NIST SRM 997 Tl isotope standard in parts per 10<sup>4</sup>). This  $\sim 2\%$  difference is thought to result from the isotopic fractionation that accompanies the adsorption of Tl onto ferromanganese particles. An equilibrium fractionation factor of  $\alpha = 1.0021$  is calculated for this process.

Ferromanganese nodules and hydrothermal manganese deposits have variable Tl isotope compositions that range between the values obtained for seawater and hydrogenetic Fe-Mn crusts. The variability in  $\epsilon^{205}\text{Tl}$  in diagenetic nodules appears to be caused by the adsorption of Tl from pore fluids, which act as a closed-system reservoir with a Tl isotope composition that is inferred to be similar to seawater. Nodules with  $\epsilon^{205}\text{Tl}$ -values similar to seawater are found, if the scavenging of Tl is nearly quantitative. Hydrothermal manganese deposits display a positive correlation between  $\epsilon^{205}\text{Tl}$  and Mn/Fe. This trend is thought to be due to the derivation of Tl from distinct hydrothermal sources. Deposits with low Mn/Fe and low  $\epsilon^{205}\text{Tl}$  are produced by the adsorption of Tl from fluids that are sampled close to hydrothermal sources. Such fluids have low Mn/Fe ratios and high temperatures, such that only minor isotope fractionation occurs during adsorption. Hydrothermal manganese deposits with high Mn/Fe and high  $\epsilon^{205}\text{Tl}$  are generated by scavenging of Tl from colder, more distal hydrothermal fluids. At such conditions, adsorption is associated with significant isotope fractionation, and this produces deposits with higher  $\epsilon^{205}\text{Tl}$ -values coupled with high Mn/Fe.

## V22D-11 1620h

### Advances in Mg and Fe Isotope Cosmochemistry

Edward D Young (310 825 3880; eyoung@ess.ucla.edu)

Institute of Geophysics and Planetary Physics and Department of Earth and Space Sciences, UCLA, 595 Charles Young Dr. East, Geology Building, Los Angeles, CA 90095

Our recent multi-collection inductively coupled plasma-source mass spectrometry (MC-ICPMS) studies of Mg and Fe isotope ratios in meteoritic materials (Galy *et al.* 2000, *Science* 290, 1751; Zhu *et al.* 2001, *Nature* 412, 311; Young *et al.* 2001, *Geochim. Cosmochim. Acta*, in press) demonstrate the potential of these new isotope systems. Taken together, the studies show that rock-forming elements other than O were well mixed in the early solar system, and that pressures during melting to form chondrules were higher than conventional astrophysical estimates. These conclusions place severe constraints on explanations for the elemental compositions of rocky planets and asteroids.

Mass-dependent fractionation results in two distinct fractionation laws that manifest as distinct slopes in three isotope space. The slopes of equilibrium fractionation lines, or more correctly the exponent in the  $\alpha_{2,1} = \alpha_{3,1}^\beta$  fractionation law where  $\alpha_{2,1}$  is the isotope fractionation factor for isotopes 2 and 1, is  $\beta = (1/m_1 - 1/m_2)/(1/m_1 - 1/m_3)$  for isotope masses  $m_1 < m_2 < m_3$ . Kinetic fractionation lines produce shallower slopes approaching  $\beta =$

$\ln(m_1/m_2)/\ln(m_1/m_3)$  where the values for  $m_i$  can be reduced masses or even molecular masses, depending upon the process. MC-ICPMS measurements can be used to distinguish these two mass fractionation laws in natural materials.

Highly precise measurements of  $^{56}\text{Fe}/^{54}\text{Fe}$  and  $^{57}\text{Fe}/^{54}\text{Fe}$  in a diverse sampling of meteoritic materials show that Fe in all bodies of the solar system came from a single reservoir. The data span limited ranges in  $\epsilon^{56}\text{Fe}$  and  $\epsilon^{57}\text{Fe}$  (16 and 23, respectively). Despite the limited range, the precision of the data (approx.  $\pm 0.6 \epsilon$ ) is sufficient to distinguish between equilibrium exchange and kinetically controlled mass fractionation of Fe isotopes. The three-isotope slope defined by the meteorite data is  $0.678 \pm 0.004$ . The slope predicted for equilibrium exchange of these Fe isotopes is 0.6786 while the slope for kinetic fractionation is 0.6726. Good agreement between the measured slope and the predicted equilibrium slope suggests that not only was there a single Fe reservoir in the early solar system, but that variability in Fe isotope ratios reflects equilibration. In the case of chondrules, this may suggest that an approach to exchange equilibrium between vapor and liquid, requiring high vapor pressures of Fe, was responsible for precluding Fe volatilization.

Measurements of  $^{25}\text{Mg}/^{24}\text{Mg}$  and  $^{26}\text{Mg}/^{24}\text{Mg}$  in components of chondrites suggest a canonical  $\delta^{25}\text{Mg}$  (relative to SRM 980) of about  $1.6 \pm 0.1 \%$ . Whole chondrules from the Allende CV3 meteorite show a limited range in  $\delta^{25}\text{Mg}$  with values from 1.6 to 2.6  $\%$ . First results from a novel ultraviolet laser ablation MC-ICPMS method for measuring Mg isotope ratios *in situ* together with *in-situ* laser ablation oxygen isotope ratio data show that the heterogeneity in  $\delta^{25}\text{Mg}$  is in part a consequence of inheritance from refractory mineral grains with high  $^{25}\text{Mg}/^{24}\text{Mg}$  and low  $\Delta^{17}\text{O}$  and not volatilization. Therefore, the Mg isotope data, like the Fe data, suggest that Allende chondrules grew at pressures high enough to prevent loss of Mg by volatilization at temperatures above the solidus.

## V22D-12 1635h

### Cu and Zn Isotopes as New Tracers of Early Solar Nebula and Asteroidal processes

Jean-Marc LUCK<sup>1</sup> (33-4-67-14-39-39; jmluck@dstu.univ-montp2.fr)

Dalila BEN OTHMAN<sup>1</sup> (33-4-67-14-39-39; d.benothman@dstu.univ-montp2.fr)

Francis ALBAREDE<sup>2</sup> (albarede@geologie.ens-lyon.fr)

<sup>1</sup>GTS, CC 060 USTL Pl. E. Bataillon, Montpellier 34095, France

<sup>2</sup>ENS, Gologie 46 Alle d'Italie, Lyon 69364, France

Cu and Zn isotopic variations are now identified in extra-terrestrial samples, as has been the case for terrestrial samples (1). The main parameters which may cause these variations are: redox state, temperature, biological activity (Earth), and volatility (extra-terrestrial samples). We report data for meteorites from various groups and classes, including carbonaceous chondrites, ordinary and differentiated chondrites (iron meteorites, SNC and HED). All analyses have been duplicated (from powder aliquot to final measurement). Values are expressed as relative deviations from NIST and JMC standards for  $^{65}\text{Cu}/^{63}\text{Cu}$  and  $^{66}\text{Zn}/^{64}\text{Zn}$ , respectively (deltas in permil). Careful chemistry and MC-ICP-MS measurements allow an overall precision of +/-0.04 permil.

I. Carbonaceous Chondrites A very important feature is that each group seems to exhibit a specific isotopic signature: Cu gets isotopically lighter from CI to CM to CO to CV, spanning an overall range of 1.5 permil. Zn shows a reverse order, getting heavier from CI to CM to CO. Zn in CV chondrites (whole rock) seems more variable. This order is the same as that observed for trace elements. Cu and Zn isotopic compositions are generally correlated to trace element content from one group to another, particularly those of similar volatility (e.g. Mn for Cu; Ge for Zn). Cu and Zn isotopic signatures exhibit remarkable relationships with Oxygen isotopes. Each group is well identified. Cu is linearly correlated with Oxygen, whereas Zn-O data display strong curvature: the difference in shape can be related to the nearly constant Cu content in all groups, and by the decreasing Zn content from CI to CO. Since Oxygen variations (from CV to CI) are thought to reflect progressive interaction of liquid water with initial solid (asteroid), Cu isotopic variations may also reflect this progressive alteration process. It may be so for Zn too, although its more volatile character might play a role.

II-Allende Progressive leaching experiments have been conducted on various powder aliquots: HF-HCl cold (#1), HF-HCl hot (#2), HF-HNO<sub>3</sub> (#3) hot under pressure. Results show clearly that different Zn (and Cu) isotopic signatures (are preserved in early components). We stress that these are NOT anomalies for Zn: three isotopic ratios (66, 67 and 68 vs. 64) agree perfectly with a mass-dependent process. In particular Zn gets systematically lighter from the "volatile" compounds (#1) to the refractory ones (#3). The rough

correlation between O and Zn isotopes in these compounds could imply that Zinc, like Oxygen, experienced interaction between gaseous and solid states (e.g. spinels) at high temperatures.

III- Iron Meteorites Non magmatic irons do not show much variation (less than 1 permil in range for both elements). On the other hand, meteorites from the IAB-IIICD group show not only large variations (3.5 permil in Zn), but also a negative correlation between Cu and Zn isotopes: this could be interpreted as a mixing between two endmembers, one of them being strongly fractionated in Zn isotopes. Fractionation of such extent (+3.7 permil) could reflect either volatilization during impact melting, or alteration on the parent body.

Data available indicate that Cu and Zn isotopes are potentially important tracers for studying: 1- early solar nebula processes (e.g. high and low-T compounds exhibit different isotopic signatures); 2- meteorite parent body evolution (e.g. Cu and Zn isotopes correlate remarkably well with Oxygen isotopes in a well-established order: CV-CO-CM-CI).

References (1)Marchal C., Telouk P. and Albarede F. (1999) *Chem. Geol.*, 156, 251-273.

## V22E MC: 305 Tuesday 1330h

### Understanding Volcanoes Through Multiparameter Measurements and Their Interpretation: Martinelli Memorial II

*Presiding:* M Calvache, Observatorio Vulcanologico de Pasto; J Neuberg, School of Earth Sciences

## V22E-01 1330h INVITED

### Dike Emplacement Triggering the 2001 Etnas Flank Eruption

Sonia Calvari<sup>1</sup> (39-095-448084; sonia@iiv.ct.cnr.it)

INGV Scientific Staff<sup>1</sup> (39-095-448084)

<sup>1</sup>Istituto Nazionale di Geofisica e Vulcanologia - Sezione di Catania, Piazza Roma 2, Catania 95123, Italy

On 12 July a seismic swarm in the upper southern flank of Etna, between La Montagnola and the summit craters, heralded the start of a new flank eruption. The emplacement of a new feeder dyke, occurred while the summit of the volcano was still the site of persistent eruptive activity, was confirmed by a number of data, spanning from seismicity, ground deformation, petrology, volcanology, geomagnetism, gravity, tectonics and gas geochemistry. The dike emplacement was marked by the seismic swarm composed by more than 2500 events mostly concentrated in the few days preceding the opening of the eruptive fissures. Ground deformation data from permanent GPS and tilt networks showed marked variations in concomitance with the seismic swarm. The deformation pattern inferred the dike penetration. Magnetic data revealed a sharp and intense decrease in the total geomagnetic field on the upper southern flank, and an increase on the upper northern flank. The Serra La Nave continuously-running gravity station (southern slope of the volcano; 1740 m elevation) recorded a sudden gravity increase, starting on 12 July. The result on the surface was the opening of a 6-km-long field of fractures that intersected the summit of the volcano from north (Valle del Leone: 2600 m a.s.l.) to south (Rifugio Sapienza: 2100 m a.s.l.). Four eruptive fissures opened between 17 and 19 July on the south and north flanks of the volcano, from the SE Cone down to 2600 m, producing small lava flows. These formed the upper fissure system. An additional vent opened on 18 July at 2100 m elevation on the south flank producing a large lava flow that spread south towards the village of Nicolosi and traveled 6.5 km. Explosive activity, increased by the intersection of the feeder dike with a shallow aquifer, since 19 July gave rise to a new cone just north of Montagnola at 2550 m elevation. This new cone built up as a result of alternating phreatomagmatic and magmatic explosive and effusive activity. The new cone at 2550 m and the 2100 m vent formed the lower fissure system. Petrology of tephra and lava flows, and SO<sub>2</sub>/HCl ratios of magmatic gases measured by FTIR, evidenced a marked chemical distinction between the upper and lower fissure systems related to the two distinctive plumbing systems. The eruption ended on 9 August with a gradual reduction in the effusion rate and a marked decrease of the SO<sub>2</sub> flux from the four summit craters.