

distribution of the kinetic energy into sample fragmentation, system expansion and mass transport. These experiments have shown that variations in the process controlling parameters, i.e.: the multiphase system viscosity (due to the presence of the melt + crystals + bubbles) and the water injection modes (due to the water relative amount and velocity) can produce strongly different distributions of the mechanical energy produced by the water interaction. The flow regime of the injected water (injection rate and injection gradient) appears to be the most critical parameter controlling the energy distribution between the system expansion and the mass transport processes. Isobaric versus impulsive injected water experiments, in progress still, show that for the same sample composition temperature and pressure, isobaric injected water experiments favour the system expansion and melt fragmentation while the impulsive ones produce more mass transport. This latter is relevant for volcanic hazard evaluation and appears to be firstly controlled by the aggregation state of the interacting melt and then, given a fixed M^m/M^w (melt/water masses ratio), by the interaction time.

V21F-10 1605h

Unzen Dome Dacite Density: Influence on Fragmentation Threshold.

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Preliminary experimental investigation of the fragmentation of dome lava from Unzen volcano, Kyushu, Japan, has indicated that the fragmentation is influenced by density. Thus to apply our experimental analysis to Unzen we have conducted two field campaigns (2000 and 2001), with the aim of obtaining extensive density information for the pyroclastic flow deposits of the 1990 to 1995 eruption. This permits the characterisation of the pre-collapse dome density.

Further, such density data allow us to evaluate the effect of transport processes on the density distribution of the deposits. No evidence for simple transport-related density distribution has been found.

Experiments have been conducted to determine the fragmentation threshold for rapid decompression of hot, pressurised specimens (60 x 26mm). The energy source is pressurized gas (argon) inside the open porosity. The fragmentation bomb simulates well the conditions for volcanic fragmentation induced by rapid decompression. At 850°C dense dacite (< 25% vesicularity) requires an initial pressure difference >20MPa to overcome the threshold. Less than 20% of the dacite samples, with vesicularity > 25% exhibit a lower threshold. Using a layered model of the dome interior, derived from abundant layered blocks at the dome and in the deposits, a quantitative reconstruction of the collapse is being developed.

V21F-11 1620h

Fragmentation Speed (FS), Sound Speed (Vp) and Fracture Velocity (FV) in Dome Dacite.

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The fragmentation speed is a vital parameter for numerical modeling of explosive eruptions. This is because the speed of fragmentation, in combination with gas expansion influences the effusion rate during explosive eruptions. Thus, the propagation speed of the fragmentation front relative to the flow rate in the conduit has the potential to establish a dynamic situation where the fragmentation depth may be either stable, deepening or shallowing with time during the eruptive event.

Using statistically relevant density variations of pyroclastic blocks determined in the field (Kueppers et al. 2001) we have selected representative samples of varying density for experimental investigation. Two types of experiments have been performed. (1) Fragmentation speeds have been determined at constant differential pressure using the fragmentation bomb. (2) Elastic wave velocities have been determined using a cubic anvil press.

Existing empirical relationships indicate further that the fracture velocity (FV) correlates with sound speed (Vp ~ 3FV). Thus, through a combination of

Vp and FS measurements, together with the FV-Vp relationship we derive the fracture propagation speed for dome lavas and its correlation with fragmentation speed, as a function of vesicularity. In a case study of Unzen dacite, first results indicate a negative correlation between fragmentation and sound speeds. The fragmentation experiments further indicate that 5 vol% vesicularity appears as a limit in the decompressive fragmentation through bubble overpressure in these experiments under these conditions.

V21A MC: Hall D Tuesday 0830h

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

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

V21A-0958 0830h POSTER

High-Temperature Fractionation of Fe Isotopes

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Fe isotope fractionations of as much as 3 permil have been reported for the 57Fe/54Fe ratio in low-temperature environments. For high-metamorphic and magmatic temperatures, Polyakov and Mineev (2000, *Geochim Cosmochim Acta* 64, 849) used Mossbauer spectroscopic data to predict that a range of ca. 1 permil might be resolvable between different Fe-bearing phases. According to Polyakov, heavy Fe isotopes are enriched in minerals that tend to concentrate ferric iron relative to those that incorporate mainly ferrous iron. Further, the degree of these fractionations is predicted to be inversely correlated with temperature. We analysed, using a Nu-Instruments MC-ICP-MS, Fe isotopes in minerals from greenschist and upper amphibolite facies conditions. Differences were found in Delta57Fe between Fe3+ containing magnetite and Fe2+ based sheet silicates (Biotite, Chlorite) of as much as 1.2 permil. Contrary to the predictions of Polyakov, however, these are entirely uncorrelated with temperature. Furthermore, in a well-studied Alpine migmatite setting, Fe in magnetites is always lighter than in minerals containing ferrous iron. Differences in Delta57Fe of magnetites of as much as 0.8 permil are found between residue, leucosome, and protolith. These are correlated with the Fe2+/Fe3+ ratio of the bulk rock. Similar relationships are found in an alkaline intra-continental volcanic suite. Delta57Fe (relative to IRM14) is almost zero in bulk rocks of a highly reducing carbonatite melt, and increases to 1 permil to the most oxidising phonolitic melt. These preliminary data indicate that, contrary to predictions, Fe isotopes are a potential proxy for oxidation state rather than a geothermometer.

V21A-0959 0830h POSTER

Iron Isotopes in Meteorites

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The recent identification of naturally occurring isotopic mass fractionation of the transition metals on the Earth has prompted a search for similar variability in meteorites. Studies of Cu, Zn, and Fe, for example, have revealed per-mil level and larger mass fractionations between different bulk meteorites. Such variations can result from temperature-sensitive isotope exchange reactions and kinetic processes, and therefore may reflect conditions in the solar nebula and on meteorite parent bodies.

Recent advances in ICP-MS have permitted isotope studies of transition metals and other elements with similarly small isotopic mass dispersions. Among the transition metals, Fe is perhaps the most difficult to analyze by ICP-MS because plasma sources are copious producers of argide molecules that interfere with the measurement of iron isotopes. However, the stable isotope behavior of Fe is of special interest because it is a non-refractory major element in meteorites, present in a variety of mineral associations and redox states.

Considerable effort has gone into overcoming the inherent analytical difficulties of measuring Fe using ICP-MS. We recently reported on a technique that achieves argide reduction by operating the plasma source in so-called 'cold' mode. In this presentation, we report results from this ongoing work.

To date, analyses of nine different meteorites, and eight individual Tieschitz (H3) chondrules have been completed, along with a number of measurements of the Hawaiian basalt sample K11919. All of the bulk meteorite compositions, which include both chondrites and irons, have identical 56Fe/54Fe to within ~ 0.14 per mil (2 sigma), and are indistinguishable from the composition of the terrestrial basalt. The Tieschitz chondrules, on the other hand, tend to have isotopically light compositions. This could reflect formation from fractionated starting material. Alternatively, Fe condensation, under non-equilibrium conditions can enrich light isotopes. Future work will focus on determining the extent of Fe mass fractionation in chondrules from Tieschitz as well as other chondrites. This growing database will help us to understand the conditions in which chondrules formed, potentially placing stringent constraints on theories of their formation.

V21A-0960 0830h POSTER

High Precision Iron Isotope Compositions in Components From the Allende CV3 Meteorite by MC-ICP-MS

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Four chondrules and one matrix sample of Allende were examined for Fe-isotope fractionation, using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Iron is the most volatile major constituent of chondrules and a recent study [1] suggested that solar system Fe was initially isotopically homogeneous. Thus, any isotopic variation is likely due to mass fractionation during nebular processing.

The chondrule samples were split. One portion was subject to a standard acid dis-solution whilst the other was polished, enabling textural and compositional characterisation. Fe, Cu and Zn are separated from the remaining matrix elements [2], removing potential interfering ions from the solution. 100 % elemental recovery (within error) is achieved, ensuring that chromatographic fractionation does not occur [2]. Hydrogen is bled into the collision cell, minimising Ar polyatomic species interferences. Typical precisions of 0.1‰/‰ (2σ) for 54Fe/56Fe ratios are achieved for 75 replicates. Instrumental mass bias is assessed using (1) sample-standard bracketing and (2) doping with Cu.

A variation of 0.8‰/‰ is observed, which is approximately 18 times the analytical uncertainty at the 2σ level. Our high precision data show that: (1) Allende chondrules and matrix exhibit clear isotopic variation in iron. (2) δ54Fe val-ues appear to be correlated to the bulk FeO content, with the more iron rich samples enriched in the lighter 54Fe isotope. (3) δ54Fe values appear to be unrelated to texture, and consequently to the temperature of chondrule formation.

Bulk Fe-content may be a proxy for the amount of volatilisation experienced, and volatilisation of Fe in chondrule precursor material has resulted in a residue of the heavier Fe isotopes. Chondrules are known to have often experienced several heating events, and their texture primarily reflects the nature of the last event. Thus, the lack of correlation between the δ54Fe value and chondrule texture suggests that Fe-isotope composition was derived from chondrule precursor material.

[1] Zhu et al. (2001) *Nature* 412, p.311 [2] Mullane et al. (2001) *LPS XXXII*, No.1545.

V21A-0961 0830h POSTER

Widespread Evaporation/Condensation Related Cadmium Isotope Fractionation in Chondritic Meteorites

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The stable isotope cosmochemistry of highly volatile elements may provide new constraints on condensation/evaporation processes in the early solar system. Therefore, we used multiple collector - ICP - mass spectrometry (NuPlasma, Zurich) to investigate mass-dependent Cd isotope fractionation in chondritic meteorites. The results are reported in ϵ -units (10^{-4}) per atomic mass unit (amu) relative to the Cd isotope composition of an in-house standard. The external reproducibility of ± 1.6 ϵ Cd/amu (2σ) is conservatively estimated from 14 repeated measurements of an in-house rock standard. Results for the Semarkona, Brownfield and Orgueil meteorites agree with TIMS data obtained with a double spike method (Rosman et al. 1980, Rosman and De Laeter 1988). Terrestrial minerals, sediments and igneous rocks show only limited Cd isotope fractionation of about ± 2 ϵ Cd/amu. This suggests that major rock and mineral forming processes do not result in significant fractionation of Cd isotopes. In contrast, a Muong-Nong type tektite displays a pronounced enrichment of the heavy isotopes ($+7.8$ ϵ Cd/amu) that is probably due to the evaporative loss of light Cd. The Cd isotope compositions of six carbonaceous chondrites (CC) are indistinguishable from the Cd standard. However, ordinary chondrites (OC), enstatite chondrites (EC) and Rumuruti chondrites (RC) display strong isotope fractionation with ϵ Cd/amu ranging from -27 to +39. The large isotope effects and the observed variations in Cd abundances can be explained by evaporation and condensation processes. It is presently not known, whether Cd isotope fractionation occurred on the meteorite parent bodies or during nebular processes. In principle, fractionation of stable isotopes is expected to occur during melting of chondrule precursors in a nebular environment. In this case, the absence of Cd isotope fractionation in bulk CC samples would require significantly different conditions for formation of chondrules that are now found in CC and for chondrules found in OC, EC and RC (i.e., different ambient gas pressures). Cd isotope fractionation may as well occur on parent bodies. The Cd isotope compositions of chondrites are not correlated with the degree of shock metamorphism. Hence, heating by shock metamorphism is an unlikely mechanism for Cd isotope fractionation. The metamorphosed OC of petrological type 4 to 6 have very low Cd concentrations, whereas unequilibrated OC are commonly enriched in Cd. Possibly, Cd that was volatilised from buried chondritic material by thermal metamorphism recondensed in the cooler outer regions of the respective parent body. Further redistribution of Cd by evaporation/condensation processes in the regolith may have established the present-day Cd abundances and isotope signatures. This scenario is in accord with the lack of Cd isotope fractionation in the CC, because strong thermal metamorphism in CC is limited to few samples.

V21A-0962 0830h POSTER

Isotopic Analysis of Copper and Zinc by multiple collector-ICP-mass spectrometry

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It is now widely recognized that isotopic composition for various elements heavier than S (e.g., Fe, Cu, Zn) were fractionated. Although mechanisms of isotopic fractionation are not well understood, biological activity can be particularly important. In order to make clear the possible link between isotopic fractionation of heavier elements and biological activity, determination of isotopic exchange constant (Kex) through various chemical processes is very important. In this study, among the heavy elements, precise isotopic ratio measurements of Cu and Zn was carried out using multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS) in order to understand the mechanisms of large isotopic fractionation. External correction technique was applied to correct the mass discrimination effect observed on MC-ICPMS (Zn-doping technique for Cu-isotope analysis, Cu-doping technique for Zn-isotope analysis).

In this study, precision and reproducibility of the isotopic ratio measurement could be successfully improved when ion extraction voltage was strictly controlled. The resultant $65\text{Cu}/63\text{Cu}$ ratio for JMC 09643 (0.447781 ± 0.00017 , 2SD) was significantly lower than that for NIST 976 SRM (0.447877 ± 0.00027 , 2SD), and it is now possible to detect small variation ($<0.01\%$)

in isotopic ratio of Cu and Zn. This indicates clearly that the isotopic composition of terrestrial Cu was significantly fractionated through geochemical processes.

In order to discuss the quantitative degree of isotopic fractionation, the isotopic exchange constant (Kex) for Cu and Zn through ion exchange chromatography (as inorganic process) were measured. In this presentation, we will discuss the difference in Kex between Cu and Zn through the inorganic process. This will provide important information about the mechanisms of isotopic fractionation for Cu and Zn through inorganic as well as organic processes possibly occurred in nature.

Reference : Marechal et al.(1999); Zhu et al.(2000)

V21A-0963 0830h POSTER

Chromium Stable Isotope Fractionation An Indicator of Hexavalent Chromium Reduction.

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Chromium is a common anthropogenic contaminant in surface water and ground water, and is also of interest in oceanography. It is redox-active; the two common valences in natural waters are Cr(VI), which is highly soluble and toxic, and Cr(III), which is relatively insoluble. Redox reactions thus control Cr mobility in aqueous solutions, and reduction of Cr(VI) to Cr(III) is the most important reaction controlling attenuation of Cr in groundwater. Our results show that Cr(VI) reduction favors the lighter isotopes and leads to enrichment of heavier isotopes in the remaining Cr(VI). Cr isotope measurements thus show great promise as indicators of Cr(VI) reduction.

We report here the first measurements of the magnitude of Cr isotope fractionation during Cr(VI) reduction and variations in $\delta^{53}\text{Cr}$ Cr values obtained from three contaminated sites. Experiments were conducted to measure Cr isotope fractionation during Cr(VI) reduction by suspensions of magnetite and unamended sediments from a local pond, Urbana, IL and San Francisco Estuary near Martinez, CA. Suspensions were incubated anaerobically with constant shaking, and complete Cr(VI) reduction occurred within a few days. Cr(VI) from intermediate time points in the experiments was purified via ion exchange and $^{53}\text{Cr}/^{52}\text{Cr}$ ratios were measured via TIMS with a double isotope spike. The instantaneous per mil fractionation, ϵ , was calculated assuming a Rayleigh fractionation model. The ϵ for Cr(VI) reduction on magnetite surfaces yielded a fractionation of -3.5 ‰. The ϵ values for the pond and estuary sediments were -3.5 ‰ and -3.3 ‰, respectively. The size of this Cr isotope fractionation is encouraging, as current precision is 0.2 ‰. $\delta^{53}\text{Cr}$ Cr values in dissolved Cr(VI) from three contaminated sites range from 1.1 ‰ to 5.8 ‰, suggesting that Cr(VI) reduction has occurred and has induced isotopic fractionation in these settings. $\delta^{53}\text{Cr}$ Cr values measured from Cr(VI) in plating baths show little or no fractionation during plating operations during up to 5 years of use. These results demonstrate that Cr stable isotope analyses should be a highly practical indicator of the critical chromate reduction reaction, and an otherwise useful geologic and oceanographic tool.

V21A-0964 0830h POSTER

High Precision Iron Isotope Measurements With High Mass Resolution MC-ICPMS

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The interest in Fe isotope compositions in Geo- and Cosmochemistry has increased within the last few years, since improved analytical techniques led to the discovery of natural mass dependent isotope fractionation. Relative mass differences of the various Fe isotopes are relatively small, resulting in small isotopic fractionations (typically in the range of a few per mil), requiring precise and reliable methods to detect natural isotope fractionations. The preferred techniques for such

measurements are thermal ionization mass spectrometry (TIMS) and multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS). Compared to TIMS, MC-ICPMS has a larger mass bias, about 3% per a.m.u. for Fe. However the mass bias is stable, at least for short term measurements, and fast sample/standard switching is possible. Unfortunately, most Fe-isotope peaks suffer from molecular interferences, e.g. $^{40}\text{Ar}^{14}\text{N}$ on ^{54}Fe , $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe , $^{40}\text{Ar}^{16}\text{OH}$ on ^{57}Fe , and $^{40}\text{Ar}^{18}\text{O}$ on ^{58}Fe , respectively. These interferences can effectively be excluded by high mass resolution. The Thermo Finnigan NEPTUNE is the first commercial high mass resolution MC-ICPMS instrument that can perform high mass resolution measurements with flat top peaks on multiple collectors. The dynamic range of the NEPTUNE's current amplifiers is extended to 50V, improving the precision for large isotopic ratio measurements (e.g. $^{58}\text{Fe}/^{56}\text{Fe}$). Samples were introduced either using a dual glass spray chamber, giving a high signal stability and low memory, or using a CETAC Aridus desolvating nebulizer, that gave a 3-4 fold increase in sensitivity (ca. 10V/ppm on ^{56}Fe in high resolution mode). Only about 500ng of Fe is necessary for a high precision measurement (with internal precision of better than 20ppm IRSD for $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$). The external precision of the method was tested by measuring several samples with various isotopic compositions. Accuracy was checked by adding variable amounts of an isotopically enriched (in ^{57}Fe) tracer to the standard (IRMM014). All samples were measured using an alternating sample - standard method. In high mass resolution mode blank subtraction has only to be performed if there are large concentration differences between the standard and the sample solutions, since the small blank is mainly iron itself and isotopic variations are rather small. The reproducibility of the delta $^{56}\text{Fe}/^{54}\text{Fe}$ and delta $^{57}\text{Fe}/^{54}\text{Fe}$ was below 0.1 ‰ (1RSD). The results for the spiked samples agreed within uncertainties with the values calculated from the certified spike values. For external mass bias correction, Ni was added to some sample solutions. For purified samples this correction method did not significantly improve precision and accuracy. However, for matrix-containing samples this technique could be used to some extent to correct for matrix introduced instrumental drift.

V21A-0965 0830h POSTER

Precise and accurate determination of silicon isotope ratios by multiple collector ICP-MS.

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Silicon isotope ratios in rocks show variations in $\delta^{30}\text{Si}$ units of over 5 ‰, and it is likely that weathering processes and soil formation processes give rise to significant degrees of Si isotopic fractionation. Conventionally Si isotope ratios have been measured to a limited degree of success by fluorination of silicate rocks followed by analysis using a gas source mass spectrometry. The advent of multiple-collector ICP-MS offers a new technique with enhanced capabilities over conventional instrumentation. Measurement of silicon isotope ratios by multiple collector ICP-MS is plagued by the isobaric interferences of $^{14}\text{N}_2$ on ^{28}Si and $^{14}\text{N}^{16}\text{O}$ on ^{30}Si . However, using collision cell technology on the Axiom multiple collector ICP-MS, these isobars have been significantly reduced to enable accurate Si isotope ratios to be measured. We have investigated the use of H, He, Ne and ammonia collision gases to reduce these isobaric interferences and these results will be presented. In addition, we will show how data on the Axiom compare for the same samples with those that have been measured by gas source isotope ratio mass spectrometry.

V21A-0966 0830h POSTER

Unravelling the Complexities of MC-ICP-MS Isotope Analysis: A Study Using Cu and Zn.

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In recent years, MC-ICP-MS has become the method of choice for studying a wide range of transition and heavy metal isotope systems. This technique is still, however, relatively new, and the complexities related to using an ICP ion source for high precision isotope measurements are only now becoming apparent. We present a systematic evaluation of how matrix composition, analyte concentration and sample nebulisation influence the precision and accuracy of Cu and Zn measurements by MC-ICP-MS. This will be illustrated using data for both synthetic and natural samples collected on two MC-ICP-MS instruments: a Micromass Isoprobe and a ThermoElemental Axiom.

Isobaric and polyatomic interferences are prevalent in the Cu-Zn mass range. Separation of the sample matrix from the analyte element, using ion-exchange chromatography, eliminates the majority of interfering ions. There are, however, some important exceptions. Entrapment of atmospheric N and O by the torch results in significant ArN⁺ and ArNO⁺ interferences on ⁶⁸Zn and ⁷⁰Zn respectively, while generation of ⁶⁴ZnH⁺ under wet plasma conditions severely hinders measurements of ⁶⁵Cu. As will be shown, the influence of these interferences can be reduced using a combined acid blank subtraction and concentration matching procedure.

The precision of isotope measurements by MC-ICP-MS is primarily controlled by the ability to correct for instrumental mass bias effects. Two approaches for mass bias correction have been assessed: (1) sample-standard bracketing and (2) the empirical external normalisation technique (as proposed by Maréchal and co-workers). The precision offered by each method is strongly influenced by the magnitude of mass bias drift experienced during an analytical session; the former favouring mass bias stability, and the latter improving with increased mass bias drift. For $\delta^{65}\text{Cu}/^{63}\text{Cu}$ and $\delta^{66}\text{Zn}/^{64}\text{Zn}$ measurements both procedures are capable of long-term reproducibilities of $>0.1\text{‰}$ (2σ), enabling mass dependent isotopic anomalies to be identified in natural and anthropogenic samples.

V21A-0967 0830h POSTER

Magnesium Isotope Variation in River Basin Between Carbonate and Silicate Environments: the Example of the Moselle (France)

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With the development of new MC-ICPMS, it is now possible to measure Mg isotopic composition with a sufficient precision to interpret variations in geological samples (e.g. Galy et al. 2000). We tested the potential of Mg isotopes as hydrochemical tracer by analysing dissolved Mg in river water and Mg in source rocks and soils. We analysed samples from the Upper Moselle River watershed (northeastern France). The upstream basin drains pure silicate rocks and then flow across limestone of the eastern Paris basin. Dissolved Mg and Ca and Sr isotopic composition well reflect the drainage lithologies and allow to quantify their relative contributions along the mainstream.

We have developed a chemical separation technique of Mg in water, rocks and soils, using ion exchange resin. This allow a 100 % recovery of Mg with efficient separation from Ca, K and Na. Isotopic analysis are carried out by MC-ICPMS using standard bracketing acquisition sequence and drift correction. ²⁵Mg/²⁴Mg ratios are expressed as $\delta^{25}\text{Mg}$ (‰) relative to SRM980. Overall external reproducibility on samples and standards is between 0.05 and 0.15 ‰ (1 sigma SD). Chemical separation of a synthetic solution with matrix similar to samples does not introduce any significant isotopic fractionation.

Dissolved Mg in the Moselle River cover a range of 1.2 ‰, with high values related to water draining silicate rocks and low values in the limestone drainage. One granite and one limestone from the basin show only 0.3 ‰ difference, the granite being heavier. At a given location, the isotopic budget of dissolved Mg and Sr are consistent implying that Mg isotopic compositions can also be used as a tracer of source. Granitic source rocks has $\delta^{25}\text{Mg}$ slightly higher than those of river in granitic drainage and soils developed on the granite show significant enrichment in ²⁵Mg up to 0.5 ‰ compared to the parent rock. These few data on soil suggest that there could be an isotopic fractionation of Mg during weathering of silicate rocks.

V21A-0968 0830h POSTER

Antimony Isotope Variations in Natural Systems Determined by MC-ICP-MS

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Sb has two stable isotopes of mass 121 and 123 with average abundance of 57.362% and 42.638% respectively and to date no geochemical or cosmochemical investigations of the variations of these isotopes have been attempted. In fact, the development of Sb isotope measurements for biogeochemical studies is challenging as Sb isotopes have a low percentage mass differences (1.6%) precluding large mass fractionation and Sb is a trace element below 100 ng/g for most geological samples and below 100 ng/l for seawater. However, it is anticipated that the redox changes of Sb(V) and Sb(III) species as well as biological activity and Sb volatilization or transport in hydrothermal systems can produce significant isotope fractionation in natural systems.

The isotopic analyses of Sb have been performed using a continuous flow hydride generation system coupled to a Micromass MC-ICP-MS and the instrumental mass fractionation is corrected using a standard-sample bracketing approach. Total Sb, as well as Sb(III) and Sb(V) aqueous species are chemically purified prior to HG-MC-ICP-MS analysis. Using this analytical scheme, the minimum Sb required per analysis is 10 ng and the estimated external precision of the ¹²³Sb/¹²¹Sb isotope ratio is 0.4 ‰-units (2σ). The data are reported relative to our internal standards (MERCK elemental standard solution). The isotopic fractionation factors between the coexisting species Sb(III) and Sb(V) have been investigated both on-line and after chemical separation. For the kinetic reduction experiment of Sb(V), the reducing agent used was KI as classically used for Sb(V) reduction and we obtained an instantaneous fractionation factor of 8.6 ‰-units. For off-line experiments, we separated Sb(III) from a partially oxidized Sb solution and obtained a fractionation factor ranging from 5 to 6 ‰-units.

Preliminary results on Sb isotopic composition of selected terrestrial materials including seawater, soils, sediments and hydrothermal sulfides have been determined and show a variation of 20 ‰-units, which is 50 times higher than the analytical precision. This demonstrates the existence of natural variations of the Sb isotopic composition, which can be analyzed at the ng level by MC-ICP-MS. For seawater and Mn-nodules, we obtained negative Sb isotopic composition between -2 and 0 ‰-units which contrast with the composition of continental sediments, ranging from 1 to 4.8 ‰-units. Highly fractionated Sb isotopes (between -2.5 to 13.5 ‰-units) characterise seafloor hydrothermal sulfides and in particular the alteration products of black smokers as well as low temperature sulfides in near vent locations. This suggests that redox change from reduced environment in hydrothermal fluid to oxidized environment in seawater and subsequent Sb redox change is the major parameter controlling the Sb isotopes signatures. Possible scavenging of Sb from seawater in hydrothermal deposits may also combine to produce such variations. The natural variations of Sb isotopes obtained in this study highlight the potential use of this element as a tracer in hydrothermal and environmental systems and probably also in other fields of cosmochemistry and biogeochemistry.

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Theoretical Estimates of Equilibrium Chlorine Isotope Fractionations

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An improved understanding of equilibrium fractionations of chlorine isotopes will help to interpret observed variations in natural systems, and will allow us to determine what natural processes can be effectively studied. To this end, we have estimated equilibrium ³⁷Cl/³⁵Cl fractionations among geochemically interesting crystalline and molecular substances using both published vibrational spectra and force-field modeling. We use the theoretical approach summarized by Urey [1], in which equilibrium fractionations are calculated from the changes in vibrational frequencies caused by isotope substitution. Lattice-dynamics modeling predicts vibrational spectra for isotopically substituted halite (NaCl) and sylvite (KCl), as well as crystalline RbCl, FeCl₂, and MnCl₂. FeCl₂ and MnCl₂ were chosen as analogues for chloride in silicate minerals, because their nearest-neighbor structures around chlorine are similar to those of the OH⁻/Cl⁻ sites in

amphibole and mica. Vibrational frequencies of ³⁷Cl-substituted molecules and complexes are derived from published spectra, empirical force-fields, and *ab initio* models. *Ab initio* models reliably predict the effects of isotope substitution on molecular vibrational frequencies. Calculated fractionations agree in both direction and rough magnitude with fractionations inferred from experiments and natural samples. Halite will concentrate ³⁷Cl relative to sylvite (by ~ 0.7 per mil at 298 K). Experiments by Eggenkamp et al. [2] suggest that saturated brines will be intermediate between halite and sylvite. Based on this observation, and the predicted behavior of FeCl₂ and MnCl₂, silicates in equilibrium with either alkali halides or brine should have higher ³⁷Cl/³⁵Cl. Chlorinated organic compounds like CH₃Cl, CCl₄, C₂Cl₄, and CFC₁₃ all have similar chlorine-isotope partitioning behavior at equilibrium, and will have higher ³⁷Cl/³⁵Cl than coexisting inorganic chlorides. In general, chlorides with chlorine bonded to cations in higher oxidation states (i.e. Fe⁺² vs. Na⁺) will tend to concentrate ³⁷Cl. Compounds with oxidized chlorine (ClO, ClONO₂, Cl₂O, OClO, [ClO₄]⁻) have a progressively greater tendency to concentrate ³⁷Cl as the oxidation state of chlorine increases.

References: [1] Urey (1947) J. Chem. Soc. (London), 562-581. [2] Eggenkamp et al. (1995) GCA 59, 5169-5175.

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Fe Release and Isotopic Fractionation During Dissolution of Hornblende and Goethite in the Presence of Soil Bacteria

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Mineral dissolution experiments with a siderophore-producing soil bacterium (*Bacillus* sp.) from Gore Mountain, NY show that the microbe enhances Fe release from hornblende crystal, hornblende glass, and goethite. This enhancement is greatest with goethite, followed by hornblende crystal, and hornblende glass. Fe in solution with these bacteria, when grown with hornblende as an Fe source, is isotopically lighter than the Fe in the bulk mineral by as much as -0.73‰: the extent of Fe fractionation is similar to that observed during Fe reduction of ferrihydrite in laboratory experiments by a dissimilatory iron reducing bacteria, *Shewanella putrefaciens*, by other workers. Fe isotope fractionation of -0.2‰ to -1.2‰ is also observed when hornblende is dissolved in the presence of acetic acid, oxalic acid, citric acid, or a catecholate siderophore. The degree of fractionation is positively correlated with the equilibrium binding constant of the ligands. No fractionation is observed during dissolution of hornblende without bacteria or ligands. Fe isotope fractionation with organic ligands probably results from a kinetic isotope effect produced during ligand-promoted dissolution. This kinetic isotope effect may partially or completely account for the fractionation observed in the presence of the soil microorganism *Bacillus*, or the fractionation observed by other workers with *Shewanella putrefaciens*, a bacterium that also produces siderophores and other organic ligands. Extractions of the soil from which the *Bacillus* was isolated show that the exchangeable Fe is lighter than Fe in both oxide minerals and hornblende in the soil by -1.1‰ and -1.5‰ respectively. The results of this study suggest a mechanism for biological Fe isotope fractionation and show that Fe isotope signatures may be present in modern soil systems. These signatures could be useful in tracing biological or abiobiotic Fe transformations in the environment or paleosols.