

EUG XI



Symposium PCM7

Frontiers in Stable Isotope Geochemistry: Beyond the Light Elements

Convenors

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Sunday PM Session

PCM7 : SUPm25 : G5 Fe Isotope Variations in Natural Systems: An Effective "Biosignature"?

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Fe isotopes have been proposed as a tool for distinguishing between biotic (i.e., microbially-mediated) and abiotic origins of Fe minerals in nature. The development of such a "biosignature" tracer has important implications for both the search for evidence of ancient life and our ability to remotely sense biogeochemical processes in the subsurface. A fundamental assumption of this approach has been that the amount of Fe isotope fractionation developed during biotic processes will be significantly greater than that accompanying abiotic reactions involving Fe. In an attempt to assess the validity of this assumption, we have documented Fe isotope variations along several well-defined reaction pathways in natural systems ranging from pristine and fuel-impacted aquifers to seasonally-reduced soils to Fe mineral-coated stream beds. We have found that although the relative importance of biotic and abiotic reactions involving Fe differs in each setting, the range of Fe isotope variation observed in each setting is similar and on the order of a few per mil. This observation is in agreement with recent experimental evidence that demonstrates a similar magnitude of Fe isotope fractionation during biotically- and abiotically-controlled reactions. Therefore the evidence to date suggests that although there are significant Fe isotope variations in nature, Fe isotopes considered alone will not provide a robust "biosignature" tracer. However, because biotically-controlled reactions apparently tend to favor the lighter Fe isotopes in the products while abiotic reactions apparently tend to favor the heavier Fe isotopes in the products, it may be possible to distinguish biotic and abiotic processes if a sense of reaction flowpath can be discerned for any natural system. We are currently assessing whether multi-tracer approaches, such as considering together both iron and oxygen isotope compositions of Fe-oxyhydroxide minerals, may provide a more effective discriminant of biotic and abiotic Fe mineral origins.

PCM7 : SUPm26 : G5 Iron Isotope Fractionation in Soils

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Vertical movement of Fe in soils is a common process. In Podzol soils, Fe and Al migrate downwards until they are precipitated into a dark-brown organic-rich illuvial horizon. In contrast, in soils affected by groundwater, such as gleys, Fe(II) moves upward from a reducing environment either inorganically by a change in redox conditions, or by microbial reduction of Fe. Fe is reprecipitated as Fe(III) in a more oxidising layer. Fe isotopes have the potential to characterise these inorganic and microbial processes, depending on their relative degrees of isotope fractionation.

Fe isotope measurements have been performed on a Nu-Plasma multicollector ICP-MS, using an Aridus desolvating nebuliser tuned to reduce isobaric ArX to Fe interference ratios to around 0.1 permille, where interferences are subtracted using on-peak background measurements of the acid used as solvent. ⁵⁷Fe, ⁵⁶Fe, and ⁵⁴Fe are measured simultaneously, and ⁵³Cr is monitored. In a plot of ⁵⁷Fe/⁵⁴Fe versus ⁵⁶Fe/⁵⁴Fe all samples faithfully plot on the calculated exponential fractionation line. This demonstrates absence of isobaric interferences. Sample runs are alternated with standard runs under the same conditions, and the sample's isotope ratios are calculated relative to the bracketing standards. Here, JM-Fe has been used as standard.

In a gley sequence formed in granitic alluvial sediments, bulk Fe is dominated by that contained in the minerals, and the Fe isotope ratios do not deviate significantly from the standard. However, leaching using hydroxylamine hydrochloride as reducing agent results in release of Fe from the oxidised layer that is lighter by about 2 permille in ⁵⁷Fe/⁵⁴Fe. Released Fe is isotopically stratified, with Fe being closest to bulk soil in the reduced layer, and getting lighter the higher the degree of oxidation is. It is likely that Fe reduction in the reduced soil layer favoured light Fe, thereby introducing a fractionation. Such light Fe(II), when mobilised, is reprecipitated into the oxidised layer. This light Fe is then desorbed upon leaching in the laboratory.

Fe isotopes have been also investigated in a Podzol formed in an alluvial soil sequence of the Maas catchment (the Netherlands). Soils consist to 95% of Fe-coated detrital quartz. ⁵⁷Fe/⁵⁴Fe ratios of bulk soil are again similar to the standard. However, both hydroxylamine and hydrochloride leaching release adsorbed Fe from coatings that is lighter by up to 4 permille in ⁵⁷Fe/⁵⁴Fe. Released Fe is least depleted in heavy isotopes in the organic illuvial horizon. It can be speculated that the very light Fe desorbed from coatings of the quartz grains has obtained its light composition by multiple sedimentary cycling, while the relative enrichment of heavy Fe in the illuvial horizon is a result of the podzolization process.

These results demonstrate a significant Fe isotope fractionation in the weathering environment.

PCM7 : SUPm27 : G5 Cu, Zn (and Pb) Isotopes in Aerosols and Loesses

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Introduction : Cu and Zn isotopic variations have recently been identified on various types of terrestrial samples, thanks to the use of MC-ICP-MS [1,2]. Cu and Zn isotopic compositions (expressed as ^δ⁶⁵Cu and ^δ⁶⁶Zn in permil vs. a standard in a manner similar to ^δ¹⁸O) are reported for aerosols and loesses from various localities on a global scale : W-USA, China and Europe for loesses, peri-Sahara and Southern France for aerosols. These variations may be due to redox, temperature or biological conditions - as has been shown for metal ores [1]. They may therefore bring important information on erosion processes and physico-chemical conditions, both at present and in the past, and may be useful in distinguishing between natural and anthropogenic origins for these metals.

Analytical method: A new chemical procedure, which includes that developed by Marechal for Cu [1], was developed on anion-exchange and macro-porous resins, which allows separation of Cu, Zn (and other elements: Pb, Sr, Nd) from the same solution. The whole procedure was checked for possible isotopic effects on Cu and Zn reported by previous authors: several duplicates indicate agreements within 0.05 ‰ for aliquots from a same solution processed through different chemistries. Isotopic compositions were determined on the VG Plasma 54 at ENS Lyon. Combined precision and reproducibility for Cu and Zn is ±0.04 ‰ for samples around 500 ng. Results are expressed as ^δ⁶⁵Cu vs. NBS stdt, and ^δ⁶⁶Zn vs. JMC stdt.

Results: The Loesses from various localities around the Earth display a rather constant isotopic composition in Zn (around + 0.2-0.3 ‰), a value similar to that reported for sediments by Marechal. This may provide a proxy for the mean value of "unpolluted" erodable crust. Cu is more variable.

As a group, peri-Saharan aerosols display isotopic signatures different from those collected in South-France, particularly for Zn, enriched in heavy isotope (high ^δ⁶⁶Zn). A tentative correlation shows up between Nd [3] and Zn isotopes that might indicate mixing phenomena. A source with specific (i.e. very heavy for Cu and light for Zn)

isotopic signatures has to be invoked to explain the broad negative correlation for those samples from South-Europe. Except for Cape Verde sample, which appears a very "natural" sample with radiogenic Pb ratios in the loess isotopic domain, peri-Sahara aerosols show lower Pb signatures close to those already reported for North African samples [4].

Marechal C, Telouk P, Albarède F, *Chem. Geol.*, **156**, 251-273, (1999).

Luck JM, Ben Othman D, Albarède F, Telouk P, *J Conf Abs* **5**, 619, (1999).

Grousset F et al, *Quatern. Sci. Rev.*, **17**, 395-409, (1998).

Maring H et al, *Nature*, **300**, 154-155, (1987).

PCM7 : SUPm28 : G5 Cu and Zn Isotopes in Meteorites

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Introduction : Cu and Zn isotopic variations have recently been identified on various terrestrial samples, thanks to the use of MC-ICP-MS [1,2]. Cu and Zn isotopic differences (expressed as ^δ⁶⁵Cu and ^δ⁶⁶Zn) are reported for 22 meteorites of different types : chondrites, HEDs, SNCs, iron meteorites. These variations may be due to various redox, biological or temperature conditions in terrestrial environments. For meteorites, Redox state, temperature and fractionation processes may be invoked, but volatility might also play a significant role in the case of Zn, a moderately volatile element. These elements may therefore bring important information on the physico-chemical conditions at the time of formation of the solar system, and also on other planetary processes (e.g. early history of Mars, Moon, E.P.B.).

Analytical method : Metals were separated on anion-exchange and macro-porous resins through a new chemical procedure, which includes the procedure developed by Marechal for Cu [1]. The whole procedure was checked for possible isotopic effects reported by previous authors : several duplicates and even triplicates indicate agreements within 0.05 ‰ for aliquots from a same solution processed through different chemistries. Isotopic compositions were determined on the VG Plasma 54 at ENS Lyon. Combined precision and reproducibility is ±0.04 ‰ for samples around 500 ng. Results are expressed in ^δ⁶⁵Cu vs. NBS stdt, and ^δ⁶⁶Zn vs. JMC stdt, with a notation similar to ^δ¹⁸O.

Results : The range in values for Cu isotopes is much smaller than that reported for Earth samples, while for Zn, the meteorite ranges are larger. On the whole, Irons tend to be richer in heavy isotopes for both Cu and Zn. 1-Cu isotopes : the overall variation (-1.5 ‰ to +0.5 ‰) is similar to Zn isotopes. However relative values for and within various groups are somewhat different. Orgueil has a ^δ⁶⁵Cu value close to zero, but Allende is strongly negative (triplicate analysis). Iron meteorites have negative to slightly positive values, with a pallasite having the highest ^δ⁶⁵Cu. Several iron meteorites analyzed (IIA and IIIA) show a very good isotopic homogeneity for Cu isotopes (duplicates within < 0.1‰), even when two different dissolution procedures are used, e.g. HCl and Aqua Regia.

2- Zn isotopes : the overall variation is from -1.5 ‰ (eucrite) to +1 ‰ (magnetic fraction of a chondrite). Iron meteorites of various types tend to have negative to slightly positive values (-0.72 to +0.2 ‰), although Canyon Diablo has the heaviest value measured (+2‰, duplicate). Carbonaceous chondrites (Orgueil, Allende) have very similar values, close to zero. Ordinary chondrites exhibit positive ^δ⁶⁶Zn (0.17-0.67 ‰). Non-cumulate eucrites display variable values -0 ‰. Two Shergottites are slightly negative, and their variation could be related to differentiation.

Marechal C, Telouk P, Albarède F, *Chem. Geol.*, **156**, 251-273, (1999).

Luck JM, Ben Othman D, Albarède F, Telouk P, *J. Conf. Abs.* **5**, 619, (1999).

PCM7

Frontiers in Stable Isotope Geochemistry

PCM7 : SUPM29 : G5 High-Resolution Mo Isotope Fractionation Measurements by MC-ICP-MS

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Multicollector ICP mass spectrometry has great potential for the determination of isotopic compositions of heavier stable isotopes. Molybdenum is one of the very promising elements. It is a redox-sensitive trace metal and becomes enriched in reducing, sulfidic, organic rich sediments. It is also essential for life in the oceans and therefore biological molybdenum isotopic fractionation is probable.

Further, natural, abiogenic molybdenum isotope fractionation may occur in terrestrial redox sensitive processes. The style of chemical weathering may have an influence on both the Mo concentration and Mo isotopic composition of the eroded material. Since the solubility of molybdenum is dependent on the redox state, molybdenum concentrations and isotopic composition may provide a tool in quantifying redox conditions in the early atmosphere as well as the extend of biological activity in a given paleo-environment. In addition, isotope fractionation could occur in the formation of molybdenite from hydrothermal solutions.

We present a procedure to precisely determine molybdenum isotopic compositions by MC-ICP-MS measurements. Instrumental and laboratory mass fractionation is separated from natural mass dependent fractionation by addition of a molybdenum double spike prior to chemical separation. Measurements were performed on a Nu Instruments mass spectrometer and 3-dimensional fractionation correction was carried out online. Fractionation is determined on four molybdenum mass ratios providing an internal consistency check. The external standard reproducibility is at 0.06 per mil on the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio (2σ). Using a normal micro concentric nebuliser with a cyclonic spray chamber, the minimum quantity of molybdenum has to be approximately 1 μg for reliable results. In addition, the double spike technique provides precise molybdenite concentrations. A hydrothermal molybdenite shows fractionation of -0.3 per mil on the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio relative to our standard. Preliminary results for analysed Archean and Phanerozoic sediments show natural fractionation ranging from 0.4 per mil to -1 per mil on the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio relative to our standard. Sample reproducibility on this ratio is within 0.1 per mil with the exception of the most negative sample, which reproduces within 0.3 per mil due to very low molybdenum concentrations (ca. 200 ng in analyses). Thus, the variations between different sediment samples are clearly resolveable and reproducable with our technique.

PCM7 : SUPM30 : G5 Thallium Isotope Variations in Ferromanganese Crusts

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In a recent study, Rehkamper and Halliday (1999) applied multiple collector ICP-MS to investigate the isotope geochemistry of Tl, which possesses two stable nuclides with the masses 203 and 205. Only small variations in Tl isotope compositions were identified for terrestrial igneous rocks, but fractionations of up to 1‰ were reported for two ferromanganese crusts. Based upon that result, we have commenced with a more detailed investigation of Tl isotope variations in Fe-Mn crusts. Results have been obtained for the outermost growth layer of 19 samples and a depth profile of a North Atlantic Fe-Mn crust.

Compared to the analytical uncertainty of the method ($\pm 0.5 \epsilon_{\text{Tl}}$ -units), the overall variability of Tl isotope ratios is large at about 1‰. Five crusts from the North Atlantic have intermediate ϵ_{Tl} values of between +11.5 to +12.8 (ϵ_{Tl} represents the deviation of the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of a sample relative to NIST SRM-997 Tl in parts per 10⁴). The highest ϵ_{Tl} values ($\epsilon_{\text{Tl}} = +13.1$ to +14.3) were obtained for Fe-Mn crusts from the Southern Atlantic, the Indian Ocean, and the central Pacific. Three samples from the Southern Ocean have low ϵ_{Tl} values of between +7.5 to +11.5. Such low values are also observed for four Fe-Mn crusts from coastal areas off

Northern/Central America and Indonesia. The sample with the lightest isotope composition is a diagenetic manganese nodule with $\epsilon_{\text{Tl}} = +3.3$.

The Tl isotope time series that was obtained for the North Atlantic Fe-Mn crust covers the last 2.5 Ma. Previous studies of the same sample have detected large variations of Pb, Nd and Fe isotope ratios during this time period, that are thought to reflect changes in input from different continental sources (e.g., Zhu et al., 2000). The Tl isotope composition, however, is observed to be almost constant, with ϵ_{Tl} values ranging between +11.4 to +12.3.

Because both the crust and the mantle of the Earth are probably characterized by $\epsilon_{\text{Tl}} \sim 0$ (Rehkamper and Halliday, 1999), the heavy Tl isotope compositions of the Fe-Mn crusts are likely to reflect low-temperature fractionation processes. The absence of Tl isotope variations in the North Atlantic crust for the last 2.5 Ma furthermore indicates that the overall variability of Tl isotope compositions in Fe-Mn crusts is not simply inherited from different continental sources. Rather, the Tl isotope fractionation may occur during formation and early diagenesis of the Fe-Mn crusts by co-precipitation with the Mn oxide phase, scavenging from seawater, and oxidation at the crust surface. The lighter isotopic composition of the diagenetic nodule can be explained by mixing of seawater-derived Tl with a heavy isotopic composition and sediment-derived Tl with $\epsilon_{\text{Tl}} \sim 0$.

Rehkamper M & Halliday AN, *Geochim. Cosmochim. Acta*, **63**, 935-944, (1999).
Zhu X-K, O'Nions RK, Guo Y & Reynolds BC, *Science*, **287**, 2000-2002, (2000).

PCM7 : SUPM33 : G5 Copper, Selenium and Sulphur Isotope Systematics of Seafloor Hydrothermal Systems

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The recent development of new isotopic systems such as Fe, Cu, Zn and Se considerably enlarge the potential for the study of seafloor hydrothermal systems. In this study we have used Se, Cu and S isotopes to provide further insights on the physical, chemical and biological processes in seafloor hydrothermal systems. Several hydrothermal fields were studied along the Mid Atlantic Ridge; in particular these include: (1) Lucky Strike located near the Azores Triple Junction; (2) Logatchev and Rainbow in an ultramafic hosted rock environment. Se and Cu isotopes analyses were performed using a MC-ICP-MS incorporating a Hexapole collision cell, and S isotopes by gas source mass spectrometry and by ion probe. At Lucky Strike, the setting of the hydrothermal field in a caldera system with abundant low-permeability layers of cemented breccia results in fluid cooling and mixing below the hydrothermal field. Based on vent structures, mineral abundance, and geochemistry, two types of hydrothermal deposits were identified. The $\delta^{34}\text{S}$ (between 1.5 and 4.5 ‰) and Se values (up to 2000 ppm) of Cu-rich sulphides suggest a high temperature undepleted hydrothermal fluid, whereas pyrite and marcasite generally have lower $\delta^{34}\text{S}$ values (down to -1.0‰) and low concentration of Se (<50 ppm). Se-depletion and sulphur isotope fractionation result from the sub-seafloor precipitation during the progressive oxidation of the fluid. The overall isotopic variation for $\delta^{65}\text{Cu}$ for chalcopyrite is 1.2‰ with a mean of 0.03‰ (relative to NIST 976). For $\delta^{82}\text{Se}$ the values range from meteoritic and magmatic values (near 0‰ relative to Canon Diablo Troilite) to values depleted in ^{82}Se of -3.1‰. For Se isotopes, the present results show consistent and distinct geochemical signatures for massive sulfides hosted hydrothermal deposits and Si-slab hosted active chimneys. Se isotopes are thus an important source indicator and imply the leaching and mixing of a fractionated Se source beneath hydrothermal chimneys with the hydrothermal fluid. Fluid cooling and oxidation in subsurface environment may provide suitable conditions for microbial activity which are recorded by Se isotopes. The Logatchev and Rainbow hydrothermal deposits have a restricted range of $\delta^{34}\text{S}$ of 4.6 to 6.1‰ and 2.2 to 5.5‰ respectively. The sulphur isotope variations within and between chimneys are explained the process of sulphate reduction in the near surface environment. Cu-isotope fractionation is large (up to 4.37‰) and the highest isotopic composition are found in active chimneys formed from high temperature undepleted fluid whereas negative values are recorded in

inactive vents and massive sulphides. Isotopic fractionation occurring in the upflow zone and within the deposit itself may combine to produce such an isotopic signature.

PCM7 : SUPM34 : G5 Mass-Dependent Cadmium Isotope Fractionation in Meteorites and Experiments

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Mass-dependent Cd isotope fractionation has been observed in chondritic meteorites (e.g. Rosman and De Laeter 1976), but never in terrestrial samples. In this study, multiple collector - ICP - mass spectrometry (NuPlasma in Zürich and Micromass IsoProbe in Münster) was used to determine the Cd isotope compositions of geologic, meteoritic and synthetic materials. The results are reported relative to the Cd isotope composition of an in-house Cd standard (JMC Cd ICP solution) in δ -units (‰) per amu. Positive values refer to samples that are isotopically heavy, negative values refer to isotopically light samples.

In order to assess the reproducibility of our method, a sample of Cd metal was analysed repeatedly over a period of six months. The results indicate a long-term reproducibility (2σ) of 0.05 $\delta\text{Cd}/\text{amu}$ ($n=29$). Repeated analyses of Cd extracted from a greywacke, yielded $+0.2 \pm 0.1 \delta\text{Cd}/\text{amu}$ ($n=7$). The results for the greywacke sample differ from the laboratory standard outside analytical uncertainty. In contrast, mass-dependent Cd isotope effects were not resolvable for terrestrial Cd and Zn minerals. In an experiment, molten Cd was evaporated into a vacuum. The residual Cd melt samples were found to be strongly enriched in the heavy isotopes relative to the starting material (up to $+10 \delta\text{Cd}/\text{amu}$). Assuming Rayleigh fractionation, a liquid-vapor isotope fractionation factor of $\alpha = 1.0045$ (per amu) is estimated from this experiment. For a unidirectional (purely kinetic) physical isotope effect, α is equal to the square-root of the mass ratio. For Cd this is again $\alpha = 1.0045$ (per amu). Therefore, the fractionation observed during the evaporation experiment corresponds to a unidirectional physical process that displays the maximum Cd isotope fractionation possible in a single evaporation step.

Cadmium isotopes for nine unequilibrated ordinary chondrites (UOC) and the Allende CV3 meteorite were analysed. The result for the Brownfield meteorite ($+2.84 \delta\text{Cd}/\text{amu}$) agrees with previously published data of Rosman et al. (1980). Five of the nine UOC display fractionated light or heavy Cd isotope compositions, spanning a total range of 6.5‰.

While the extent of Cd isotope fractionation on Earth appears to be fairly restricted, large Cd isotope effects were found in many UOC in this and in previous studies by Rosman and co-workers. The extent of Cd isotope fractionation in UOC is similar to that found during evaporation experiments of molten Cd into vacuum. Thus, Cd isotope fractionation in UOC is clearly due to a kinetic evaporation and/or condensation process. Since no relationship between Cd isotope fractionation and Cd concentration or the degree of shock metamorphism can be found, a complex history of evaporation/condensation and Cd redistribution must be assumed.

Rosman KJ R & De Laeter JR, *Nature*, **261**, 216-218, (1976).
Rosman KJR; Barnes IL, Moore LJ & Gramlich JW,
Geochemical Journal, **14**, 269-277, (1980).

PCM7 : SUPm35 : G5
Fractionation of Copper and Zinc Isotopes on Anion-Exchange Resin

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Recent developments in plasma-source mass spectrometry have revealed natural variations in the abundance of stable isotopes of Fe, Cu, and Zn, in ores, ferromanganese nodules, sediments, and organic samples [Maréchal et al., 2000; Beard et al., 1999; Zhu et al., 2000; Anbar et al., 2000]. As transition metals participate actively in multiple biological and low-temperature inorganic chemical reactions, their isotopic variability offers an unexplored potential as biogeochemical or geochemical tracers. Whether transition element isotopes can be fractionated at equilibrium in nature is uncertain. In a preliminary study, we reported that Cu isotopes can be fractionated by chromatographic processes [Maréchal et al., 1999] then Anbar et al. (2000) extended this observation to Fe isotopes. Demonstrating that fractionation of transition element isotopes in the laboratory takes place at equilibrium is required to support the interpretation that natural isotopic variability of Cu, Zn, and Fe results from equilibrium fractionation and not from kinetic effects.

We studied the chemical isotope fractionations of Cu and Zn in laboratory experiments at room temperature. Anion-exchange resin in HCl media was used for chromatographic and batch equilibration experiments. Solutions of Cu and Zn were eluted on an anion-exchange resin and the isotopic compositions of Cu (resp. Zn) of the eluted fractions were measured by MC-ICP-MS. It is found that, for pure Cu solutions, the elution curves are consistent with a mass fractionation coefficient of 0.46 per mil in HCl 7 M and 0.67 per mil in HCl 3 M for the isotopic pair ⁶⁵Cu/⁶³Cu. Batch fractionation experiment confirms that equilibrium fractionation of Cu between resin and HCl 7 M is ca 0.4 per mil and therefore indicates that there is no need to invoke kinetic fractionation during the elution. Zn isotope fractionation is an order of magnitude smaller with a fractionation factor of 0.02 per mil in HCl 12 M for the isotopic pair ⁶⁸Zn/⁶⁶Zn. Cu isotope fractionation results determined from a chalcocopyrite solution in 7 M HCl give a fractionation factor of 0.58 per mil, which indicates that Fe may interfere with Cu fractionation. Comparison of Cu and Zn results suggests that the extent of Cu isotopic fractionation may result from the Jahn-Teller distortion of Cu octahedral complexes. It may also signal the presence of unidentified polynuclear complexes in the solution. In contrast, we see no compelling reason to ascribe isotope fractionation to the coexistence of different oxidation states. We suggest that published evidence for iron isotopic fractionation in nature and laboratory experiments may also indicate the distortion of low-spin Fe tetrahedral complexes. The isotope geochemistry of transition elements may shed a new light on the coordination chemistry of these elements.

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Beard BL, Johnson CM, Cox L, Sun H, Neelson KH & Aguilar C, *Science*, **285**, 1889-1892, (1999).
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Zhu XK, O'Nions RK, Guo Y & Reynolds BC, *Science*, **287**, 2000-2002, (2000b).

PCM7 : SUPm36 : G5
Mechanism of Nonbiological Fractionation of Fe Isotopes

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Recent analytical advances have made possible the use of transition metal isotope systems to study environmental and, potentially, biological processes. Fe is of particular

interest because of its importance in biology and its complex environmental chemistry. Fractionation of Fe isotopes may result from kinetic isotope effects, such as might occur during diffusion or enzyme-catalyzed reactions. Equilibrium isotope effects are also possible- for example, during equilibration of dissolved Fe species having different ligands or oxidation states.

We previously reported chemical fractionation of Fe isotopes during ion exchange chromatography in HCl media on a fast-reacting macroporous resin (Biorad AG MP-1; Anbar et al., 2000). We hypothesized that fractionation occurs during equilibration between Fe-chloro complexes, driven by changes in coordination of Fe(III), and is expressed because only the anionic tetrachloro complex adsorbs to the resin. Beard et al. (2000) and Skulan et al. (2000) argued that this fractionation is due to a kinetic effect; however their experiments used a different microporous resin. To clarify the mechanisms of Fe isotope fractionation in our system, "batch" experiments were performed using a ⁵⁴Fe spike to determine the rate of equilibration of Fe isotopes between resin and solution. These experiments were agitated continuously to minimize diffusional artifacts. We also conducted chromatographic isotope fractionation experiments at different flow rates to assess the importance of kinetic factors.

The ⁵⁴Fe batch experiments demonstrate that equilibration of Fe isotopes in this system is very rapid; > 98% of the Fe in solution equilibrates with the resin-bound Fe within 1 minute. This finding is consistent with our original equilibrium interpretation, but does not completely eliminate the possibility of a kinetic effect during chromatography. In chromatographic experiments, as flow rate increased the magnitude of fractionation decreased. This observation is consistent with incomplete equilibration at higher elution rates, as should occur when the elution is too fast to permit complete equilibration between dissolved and resin-bound Fe at each "theoretical plate". Therefore, we conclude that Fe isotope fractionation during chromatography stems from an equilibrium isotope effect, but that the approach to equilibrium is easily inhibited in a laboratory chromatographic system. This implies that the magnitude of the single-step equilibrium fractionation factor inferred by Anbar et al. (2000), ~ -1.0001, may be an underestimate and that Fe isotope variations arising from changes in Fe speciation in nature may be more important than previously realized.

Anbar AD, Roe JE, Barling J & Neelson KH, *Science*, **288**, 126-128, (2000).
Beard BL, Johnson CM, Skulan JL, O'Leary J. & Sun H., *AGU Fall Meeting*, (2000).
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PCM7 : SUPm37 : G5
Effects of Organic Ligands on Iron Isotope Fractionation

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The possibility that iron isotope fractionation may provide a biomarker in some geologic systems has created great interest. However, in order for Fe isotopes to be considered useful as a reliable biosignature, more research must focus on the causes of iron isotope fractionation. We have conducted experiments using hornblende and soil samples collected from Gore Mountain, NY to study iron isotope fractionation in a natural system. Samples of the hornblende were leached in the presence of bacteria and various organic compounds (desferrioxamine mesylate (DFAM), citric acid, oxalic acid, and acetic acid). After six days of incubation, solutions without bacteria or organic ligands contained 300 ppb iron, while solutions with bacteria contained 2400 ppb iron. The concentration of iron in solutions with large multidentate ligands (DFAM and citric acid) ranged from 400 to 600 ppb; while the concentration of iron in solutions with monodentate or bidentate ligands (acetic and oxalic acid) ranged from 270 to 350 ppb. The ⁵⁶Fe/⁵⁴Fe ratio of iron dissolved without bacteria or ligands is similar to that in the hornblende. The ratio for iron

dissolved with bacteria is about -0.7 per mil relative to the hornblende. The ratio for iron dissolved with organic acids ranges from -0.2 to -0.6 per mil relative to the hornblende. The ligands known to have stronger association constants for Fe(III) show more negative iron isotope values. We believe that formation of complexes between iron and organic ligands at mineral surfaces may cause fractionation of iron isotopes in solution.

Iron present in the exchangeable and oxide fractions of the soil was extracted using magnesium chloride and citrate-dithionite respectively. Isotope analyses indicate a 1 per mil difference between the ⁵⁶Fe/⁵⁴Fe ratios for these fractions. The oxide ⁵⁶Fe/⁵⁴Fe ratio is similar to that of an Fe-containing soil mineral, hornblende, while the exchangeable ratio is closer to that for the iron in solution with bacterial cultures in hornblende dissolution experiments. These observations may be consistent with a model for a kinetic isotope effect associated with hydrolysis of Fe at the hornblende-water interface.

PCM7 : SUPm38 : G5
Analysis of Ca, Fe and Se by MC-ICP-MS: Three Solutions

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Multi-collector ICP-MS instruments are routinely used for the analysis of a broad range of elements across the mass spectrum. However, an inherent problem with all such instruments is the presence of Ar-based isobaric polyatomic species. These gas peaks limit the effective analysis elements whose major isotopes are concomitant with the polyatomic gas peaks.

There are however, ways of reducing these interferences. The VG Axiom Multi-collector ICP-MS is unique in offering three distinct methods of achieving this. The first method is to reduce the power to the plasma, typically from 1250W to 600W, and to add a metal shield to screen the plasma from the load coil. This technique is commonly known as Cool Plasma, and has the effect of greatly reducing the Ar interferences, though with a subsequent loss of sensitivity.

A second technique is to use a collision-cell device to selectively dissociate the Ar-based interferences via collisions with a gas injected into the cell. This can radically reduce a particular polyatomic species to allow interference-free measurement of the analyte, though in this case with no consequent reduction in sensitivity. However, care must be taken when choosing the collision gas, as different polyatomic species can form within the cell that may interfere with other analyte isotopes.

Though both of the above techniques allow significant reduction in the Ar-based gas peaks, they do not completely remove them. This is where high resolution becomes a valuable tool. The VG Axiom has user-definable resolution settings to beyond 10,000 RP. This allows the user to resolve out many of the gas interferences for direct measurement of the analyte. For example, Se can be resolved from Ar₂ and ⁵⁶Fe can be resolved from ArO. These three tools together allow the VG Axiom Multi Collector user unparalleled ability to analyse the traditionally problematic analytes such as Ca, Fe and Se.

Sunday PO Session

PCM7 : SUpo01 : PO Hafnium Isotope Analysis on MC-ICP-MS (IsoProbe)

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The advent of magnetic sector multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS), makes it easier to analyse high ionisation energy elements, such as Hf. The increased ionisation efficiency and resultant sensitivity means that simpler chemistry can be used with no loss of precision in the mass spectrometric method.

As a test of the chemical separation method and machine performance (Micromass IsoProbe) we have used the standard Hf solution (JMC475), rock sample (BRR) and ferromanganese nodules standard samples (NOD-A-1 and NOD-P-1). Except for JMC475, the samples are separated using a method adapted from (Lee et al., 1999). For the ferromanganese samples, we used different chemical attacks (with and without HF) in order to avoid the dissolution of the silicates that were incorporated in the nodules during growth. Our results indicate that there is a considerable Hf concentration in the silicate residues, which might affect the true Hf isotopic ratios in the nodules or crusts.

The IsoProbe at SOC has 9 Faraday collectors, 2 ion-counting channels and one Daly detector with WARP (Wide aperture retardation potential) filter. For the Hf isotopic analysis, a variety of collector configuration, static/dynamic sequences and interference corrections were tested. Precision was improved by accurately assessing inter-peak tail contribution and the Yb/Lu interferences. Consistent results were found for JMC475 concentrations greater than 20 ppb, with a mean $^{176}\text{Hf}/^{177}\text{Hf} = 0.282163 \pm 8$ (2sd; n = 21.) Total Hf ion beams were typically 270 V (2.7×10^{-9} A) per ppm.

We present Hf and Nd isotopic data for a series of ferromanganese crusts from the western Pacific and associated marginal basins.

Lee D-C, Halliday AN, Hein JR, Burton KW, Christensen JN & Gunter D, *Science*, **285**, 1052-1054, (1999).

PCM7 : SUpo02 : PO Accuracy of Isotope Ratio Measurements using ICP Multi-Collector Mass Spectrometry (ICP-MC-MS), Getting to the Truth!

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Isotope ratio analysis by ICP multicollector instruments have been shown to rival the precisions obtainable on Thermal Ionisation Mass Spectrometers (TIMS). The flexibility of the ICP source to sample both solid and liquid materials, makes these instruments increasingly attractive as alternatives for the measurement of high quality isotopic ratios. However, in order to obtain high precision measurements it is necessary to correct for the mass bias produced by the plasma and interface. The size of the mass bias is much greater than that observed in TIMS instruments, despite this, numerous authors have shown that the exponential fractionation law derived for TIMS, still provides a close approximation for the correction of the ICP mass bias. This is perhaps best illustrated by Nd isotopes. Neodymium is of special interest since the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio can be used as a chronometer of the time integrated enrichment or depletion of Sm with respect to Nd. The other isotopes of Nd are stable and do not change abundance with time. All the isotope abundances of Nd are known extremely precisely by TIMS, thus the ability of the ICP-MC-MS to reproduce these numbers is crucial in understanding the nature of the mass bias introduced by the plasma and interface. Mass fractionation corrections typically use the $^{146}\text{Nd}/^{144}\text{Nd}$ isotope ratio as the reference isotope pair. For the exponential fractionation correction to work, the

fractionation factor (beta) derived from the measurement of this ratio, must be constant for all the Nd isotopes. For TIMS this is true, but for ICP-MC-MS we observe that the larger the difference in mass between the measured isotope ratio and the $^{146}\text{Nd}/^{144}\text{Nd}$ average mass (145), the larger the inaccuracy relative to TIMS. These data show that the lower the mass of the isotopes relative to m/z 145, the exponential law undercorrects the isotope ratio, while for those isotopes heavier than m/z 145 the exponential law overcorrects. This indicates a mass dependency of beta. Modification of the exponential law is also necessary when other isotope systems are considered, in particular when one element is mass bias corrected with another. Examples of U-Tl and Fe-Cu will be presented.

PCM7 : SUpo03 : PO 213nm Laser Ablation ICP-MS – Revolution or Gimmick?

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Few, who have followed the development of laser ablation ICP-MS can have failed to notice the technique's great leap forward, following the replacement of infrared lasers for shorter wavelength ultraviolet lasers. The instrumentation, which until then, had been used primarily as a bulk sampling device, has moved on and is now accepted as a routine trace and ultra-trace element microprobe.

Whilst the performance benefits of ultraviolet as compared to infrared laser ablation were immediate and distinct, no one ultraviolet wavelength yet has been adopted universally as the industry standard. The analytical community is divided into two camps: Those using excimer lasers operating mainly at 193nm, which provide low fractionation and excellent coupling efficiency in most materials, but at the expense of ease of use, safety and cost, and those who have settled on the frequency quadrupled Nd:YAG systems operating at 266nm, which lack some of the performance quality of the excimer, but have greater ease of use, safety, stability and lower cost. That was until the recent introduction of the frequency quintupled Nd:YAG laser operating at 213nm. (Jeffries et al., 1998)

Despite its short history, laser ablation at 213nm has already been adopted by instrument manufacturers and is rapidly becoming a commercial success. Thus far the few formal studies which have been undertaken suggest that this wavelength is uniquely advantageous.

Away from the tedium of bench tests and standard reference material analysis, here a 213nm laser ablation system has been used routinely and alongside an optically similar 266nm system, in the wide range of both earth and life science applications passing through a busy ICP-MS lab. The aim, to determine if, in the varied world of real applications, we are in the midst of another great wavelength revolution, or merely witnessing the passing of a gimmick?

Jeffries, TE, Jackson, SE, and Longerich, HP, *J. Anal. At. Spectrom*, **13**, 935-940, (1998).

