

## Fractionation of Fe isotopes during biogenic mineral formation by dissimilatory Fe(III) reduction (DIR)

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Iron isotope fractionation between aqueous Fe(II) and biogenic magnetite and Fe carbonates produced during reduction of hydrous ferric oxide (HFO) by *Shewanella putrefaciens*, *Shewanella algae*, and *Geobacter sulfurreducens* in laboratory experiments is a function of Fe(III) reduction rates and pathways by which biogenic minerals are formed. High Fe(III) reduction rates produced  $^{56}\text{Fe}/^{54}\text{Fe}$  ratios for  $\text{Fe(II)}_{\text{aq}}$  that are 2-3 per mil lower than the HFO substrate, reflecting a kinetic isotope fractionation that was associated with rapid sorption of Fe(II) to HFO. In long-term experiments at low Fe(III) reduction rates, the  $\text{Fe(II)}_{\text{aq}}$  - magnetite fractionation is -1.3 per mil, and this is interpreted to be the equilibrium fractionation factor at 22 °C in the biological reduction systems studied here. In experiments where Fe carbonate was the major ferrous product of HFO reduction, the estimated equilibrium  $\text{Fe(II)}_{\text{aq}}$  - Fe carbonate fractionations were ca. 0.0 per mil for siderite ( $\text{FeCO}_3$ ) and ca. +0.9 per mil for Ca-substituted siderite. Formation of precursor phases such as amorphous non-magnetic, non-carbonate Fe(II) solids are important in the pathways to formation of biogenic magnetite or siderite, particularly at high Fe(III) reduction rates, and these solids may have  $^{56}\text{Fe}/^{54}\text{Fe}$  ratios that are up to 1 per mil lower than  $\text{Fe(II)}_{\text{aq}}$ . Under low Fe(III) reduction rates, where equilibrium is likely to be attained, it appears that both sorbed Fe(II) and amorphous Fe(II)(s) components have isotopic compositions that are similar to those of  $\text{Fe(II)}_{\text{aq}}$ .

The relative order of  $\delta^{56}\text{Fe}$  values for these biogenic minerals and aqueous Fe(II) is: magnetite > siderite  $\approx$   $\text{Fe(II)}_{\text{aq}}$  > Ca-bearing Fe carbonate, and this is similar to that observed for minerals from natural samples such as Banded Iron Formations (BIFs). Where magnetite from BIFs has  $\delta^{56}\text{Fe} > 0$  ‰, the calculated  $\delta^{56}\text{Fe}$  value for aqueous Fe(II) suggests a source from mid-ocean ridge (MOR) hydrothermal fluids. In contrast, magnetite from BIFs that has  $\delta^{56}\text{Fe} \leq 0$  ‰ apparently requires formation from aqueous Fe(II) that had very low  $\delta^{56}\text{Fe}$  values. Based on this experimental study, formation of low- $\delta^{56}\text{Fe}$   $\text{Fe(II)}_{\text{aq}}$  in non-sulfidic systems seems most likely to have been produced by dissimilatory reduction of ferric oxides by Fe(III)-reducing bacteria.

## Modeling stable isotope fractionation in crystals

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New techniques and instrumentation have made it possible to analyze the isotopic compositions of many elements to such high precision that we can now detect natural variations of  $\sim 0.1\%$  or less. In order to use these new measurements most effectively, it is crucial to work towards a quantitative understanding of the geochemical mechanisms that cause isotope fractionation. Theoretical models, based on the calculation of thermodynamic partition function ratios, are helping to establish a framework for predicting the chemical systematics of natural fractionations. Models can also help verify experimental results, and allow extrapolation to temperatures where isotopic exchange is too slow to achieve equilibrium on laboratory time scales. These models require detailed knowledge of the vibrational frequencies of both common and rare isotopic forms of the substances being modeled. The complexity and long-range order of crystals make it difficult to obtain these frequencies using conventional spectroscopy, presenting a hurdle to accurate modeling. However, minerals are the most durable repository of ancient geochemical signatures, and are a natural focus for modeling efforts despite their complexity.

One promising approach is to combine first-principles lattice dynamics with careful sampling of the vibrational density of states of each crystal to obtain an accurate representation of the complete vibrational spectrum. Early results show that accurate vibrational frequency estimates can be achieved using free open-source software like ABINIT ([www.abinit.org](http://www.abinit.org)), and that the method can be applied to many geochemically relevant materials. Case studies of zinc and calcium isotopic fractionation in oxides, sulfides and carbonates illustrate the potential of these *ab initio* techniques. Calculated Zn-isotope fractionations between ZnS and ZnO minerals suggest that  $^{68}\text{Zn}/^{66}\text{Zn}$  will be  $\sim 1\%$  higher in oxides in equilibrium with sulfides at 25°C. The results also suggest that oxides and dilute aqueous solutions with 6-coordinate Zn will have  $\sim 0.5\%$  lower  $^{68}\text{Zn}/^{66}\text{Zn}$  than coexisting phases where Zn is in 4-fold coordination with oxygen. Initial Ca-isotope modeling also shows a coordination number effect, with  $^{44}\text{Ca}/^{40}\text{Ca}$  in calcite (6-coordinate) predicted to be  $\sim 4\%$  higher than in aragonite (9-coordinate). This effect is in the same direction, but larger than experiments indicate.

## Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution

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Isotopic fractionation is observed between Mo in seawater, where it exists primarily in the form of the Mo(VI) anion molybdate,  $\text{MoO}_4^{2-}$ , and in oxic sediments, where the Mo is isotopically lighter than in sea water and evidence exists for a five- or six-coordinate Mo environment in Fe,Mn oxyhydroxides. In anoxic sediments, where the Mo(VI) is expected to exist as a sulfide, no fractionation is observed compared to seawater. This is presumably because of the stoichiometric conversion of the Mo from  $\text{MoO}_4^{2-}$  to  $\text{MoS}_4^{2-}$  and then to other sulfides. This results from the very high equilibrium constant for the sulfidation reaction. Thus, to understand isotopic fractionation both the equilibrium constants for isotopic fractionation reactions and the equilibrium constants for transformation of one chemical compound to another must be considered.

We here present quantum mechanical calculations of the isotopic fractionation equilibrium constants for the isotopes  $^{92}\text{Mo}$  and  $^{100}\text{Mo}$  between  $\text{MoO}_4^{2-}$ ,  $\text{MoO}_3(\text{OH})^-$ ,  $\text{MoO}_3(\text{OH}_2)_3$ ,  $\text{MoS}_4^{2-}$  and a number of other oxidic and sulfidic complexes of Mo (and scale the results to give Mo 97, 95 fractionations). These fractionation equilibrium constants are calculated directly from the computed vibrational, rotational and translational contributions to the free energy in the gas-phase using quantum methods. Calculated vibrational frequencies and ratios of frequencies for different isotopomers are first obtained using a number of different quantum methods and compared with available experimental data to establish the most reliable methodology. We have also calculated free energy changes in aqueous solution for a range of reactions of  $\text{MoO}_4^{2-}$  and  $\text{MoO}_2(\text{OH})_2$  with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ . We present evidence for the instability of the monomeric octahedral species  $\text{Mo}(\text{OH})_6$  commonly assumed to exist in acid solution and propose highly distorted six-coordinate  $\text{MoO}_3(\text{OH}_2)_3$  or three-coordinate  $\text{MoO}_3$  as better representations of the species present. We explain the isotopic lightness of oxic sediments as arising from an intermediate step in which a three coordinate  $\text{MoO}_3$  species is formed in aqueous solution, and subsequently attaches to the surface of a Fe,Mn oxyhydroxide mineral.

## Iron and tin isotope equilibrium fractionation factors from Mössbauer and synchrotron radiation data

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We have suggested a new method for determination of the reduced isotopic partition function ratio ( $\beta$ -factor) consisting in (i) computing the vibrational kinetic energy of the nucleus of interest from the phonon partial density of states PDOS obtained by inelastic nuclear resonant X-ray scattering (INRXS) in synchrotron radiation experiments and (ii) calculating the  $\beta$ -factor in terms of the kinetic energy and the difference of isotopic masses. Applications of this method to tin isotopes showed significant dependence of the tin  $\beta$ -factor on oxidation state previously established for iron isotopes (Polyakov and Mineev, 2000). This result enables the dependence on oxidation state to be extended to cover all transition metals. Iron isotope  $\beta$ -factors for hematite, magnetite, pyrite, siderite, etc. have been verified using new traditional Mössbauer spectroscopy data and PDOSs obtained by INRXS. Significant corrections to iron  $\beta$ -factors for magnetite have been made using synchrotron radiation data of Seto et al. (2003). Correlation between the iron  $\beta$ -factor and the iron electrostatic site potential have been found. The analogous correlation was previously observed for oxygen isotopes. (Smyth and Clayton, 1988). The correlation provides an explanation for the dependence of transition metal  $\beta$ -factors on oxidation state.

### References

- Polyakov V.B. and Mineev S.D. (1997), *Geochim. Cosmochim. Acta* **64**, 849-865.  
Seto M., Kitao S., Kobayashi Y. Haruki R. Yoda Y. Mitsui T. and Ishikawa T. (2003), *Phys. Rev. Lett.* **91**, 185505.  
Smyth J.R. and Clayton R.N. (1988), *EOS* **69**, 1514 .

## Probing crystal growth mechanisms with non-traditional isotopes

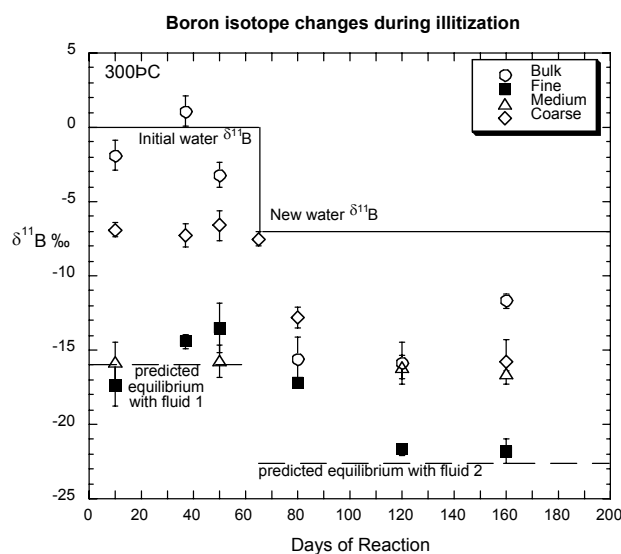
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Non-traditional stable isotopes are useful for studying the substitution of elements in specific sites in clay minerals during nucleation and growth. Boron substitutes in the tetrahedral sites of illite, while Li substitutes into octahedral sites. Their isotopic exchange with pore fluid is a sensitive indicator of when Si-O or M-O bonds are broken, and therefore provide insights to reaction mechanisms.

We conducted a hydrothermal experiment reacting smectite to illite in a B-rich solution at 300°C, 100MPa. The fluid's isotopic composition was changed after 65 days to examine the rate of illite re-equilibration during crystal growth. The bulk clay (circles) contained tetrahedral and interlayer-B. The samples were then NH<sub>4</sub>-exchanged to remove interlayer-B. The remaining clay contains only tetrahedral B and was size-separated into fine (<0.2µm; squares), medium (0.2-2.0µm; triangles) and coarse (>2.0 µm; diamonds) fractions.

Bulk clays retain variable amounts of the fluid B in the interlayer with little isotope fractionation (±3‰). The fine fraction approaches equilibrium quickly, indicating constant nucleation. The coarser fractions have not re-equilibrated. Thus, the boron isotope ratio of different size fractions of clays may record a history of fluids present during diagenesis.



## Experimental calibration of the Fe isotope fractionation between pyrrhotite and silicate melt

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While systematic differences in the Fe isotope composition of minerals in ultramafic rocks were found in several studies [1, 2, 3], others did not reveal any measurable inter-mineral high temperature Fe isotope fractionation [e.g., 4]. We tested the possibility of high temperature iron isotope fractionation by a first experimental study.

We investigated iron isotope fractionation in the pyrrhotite-silicate melt system, using a hydrous peralkaline rhyolitic glass powder and various amounts of elemental sulphur as starting materials. Pyrrhotite (Fe<sub>1-x</sub>S) was crystallised at a pressure of 500 MPa and temperatures between 840 and 1000 °C. Additionally, experiments with <sup>57</sup>Fe-enriched glass and natural pyrrhotite were performed to study the kinetics of Fe isotope exchange between pyrrhotite and silicate melt and to verify that experimental results represent equilibrium conditions. The Fe isotope composition of pyrrhotite and silicate glass were measured by MC-ICP-MS upon separation of the two phases and chemical purification of iron [5].

The  $\delta^{56}\text{Fe}$  values of pyrrhotite are significantly lower (e.g.,  $\Delta^{56}\text{Fe}_{\text{pyrr-melt}} = -0.18 \pm 0.02$  ‰ (2 $\sigma$ , n=4) at 900 °C) than those of the coexisting silicate melt. This isotope fractionation can be attributed to the difference in the iron oxidation state between pyrrhotite and silicate melt. While trivalent iron dominates in the melt, pyrrhotite contains almost exclusively Fe(II). The Fe(II)-bearing pyrrhotite then incorporates preferentially lighter iron isotopes.

Further investigation on the Fe isotope fractionation between other mineral phases and silicate melts is needed, but the presented experimental results, suggest that resolvable Fe isotope fractionation might be expected in other igneous systems, too.

### References

- [1] Williams, H. M. et al. (2004) *Science*, **304**, 1656-1659.
- [2] Weyer, S. et al. (2004) *Beih. z. Eur. J. Mineral.*, **16**, 156.
- [3] Zhu, X. K. et al. (2000) *EPSL*, **200**, 47-62.
- [4] Beard, B. L. & Johnson, C. M. (2004) *GCA*, **68**, 4727-4743.
- [5] Schoenberg, R. & von Blanckenburg, F. (2005) *IJMS*, in press

## Chromium isotope fractionation during oxidation of Cr(III) by manganese oxides

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Early investigation of environmental chromium (Cr) fractionation has focused on natural processes attenuating anthropogenic hexavalent chromium (Cr(VI)) contamination. Reduction of mobile, toxic Cr(VI) to immobile trivalent Cr (Cr(III)) preferentially reduces lighter Cr isotopes, resulting in light Cr(III) and heavy Cr(VI) near Cr(VI) contamination sites. However, environmental interactions between Cr(III) and manganese oxides can generate significant quantities of Cr(VI) without human activity. The oxidation of Cr(III) is not well understood, yet is potentially important to Cr isotopic systematics. Initial laboratory investigations of Cr(III) oxidation by birnessite ( $\delta$ -MnO<sub>2</sub>) demonstrated wide variation in the isotopic composition of the developing Cr(VI) pool ( $\delta^{53}\text{Cr} = -2.5$  to  $+0.7$  ‰, relative to NIST 979). Further, variation in isotopic composition continues after net Cr(VI) production ceases. These observations suggest that multiple oxidation mechanisms are present, even in simple systems, and individual mechanisms are discriminating against both heavy and light isotopes.

Understanding fractionation during oxidation of Cr(III) requires elucidation of the oxidation mechanisms. For example, the range of  $\delta^{53}\text{Cr}$  observed thus far in high Cr(VI) groundwaters is from 0 to  $\sim+4.4$ ‰. The data are not consistent with simple Cr reduction, suggesting that dilution or other processes are also important in cycling. In particular, Silvester *et al.* (1995) suggest that reaction rates in Mn oxide limited systems are controlled by production of the Cr(IV) intermediate species. If the associated reprecipitation of Cr(IV) (i.e.,  $3\text{Cr(IV)} \rightarrow 2\text{Cr(III)} + \text{Cr(VI)}$ ) imparts the theoretical maximum fractionation between Cr(VI)O<sub>4</sub><sup>2-</sup> and Cr(III)(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> predicted by Schauble *et al.* (2002),  $\delta^{53}\text{Cr}$  of the resulting Cr(VI) should be  $\sim+4.4$ ‰ and that of Cr(III)  $\sim-2.2$ ‰. Improved understanding of this mechanism may be key in allowing differentiation between anthropogenic and “natural” Cr(VI) and provide a powerful probe for investigation of the Cr cycle.

### References

- Schauble, E.; Rossman, G. R.; Taylor, H. P., Jr. (2004) *Chem. Geol.* **205**, 99-114.  
Silvester, E.; Charlet, L.; Manceau, A. (1995) *J. Phys. Chem.* **99**, 16662-16669.

## Copper isotope fractionation at high temperature: Investigating copper mineralization at Corocchohuayco, Perú

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Copper isotopes from mineralization in the high temperature hydrothermal skarn system at Corocchohuayco, Perú, show a range in  $\delta^{65}\text{Cu}_{\text{NIST SRM 976}}$  from -1.29 to +1.17 per mil ( $\pm 0.08$ ‰,  $2\sigma$ ). These analyses come from vein and disseminated chalcopyrite and bornite. Locally the copper isotopes are strongly zoned from isotopically light in proximal/early mineralization to heavy in distal/later mineralization. The fractionation mechanism proposed by Marechal and Albarede [1] at low temperatures between different copper complexes may be applicable at higher temperature. Isotopic fractionation between copper complexes of different thermodynamic stabilities would lead to isotopic differences between early and later mineralization produced from the same fluid. Geologic constraints indicate the hydrothermal fluids responsible for mineralization at Corocchohuayco were high salinity brines (ave 43 % wt NaCl eq) that precipitated copper sulfides between 300-350° C. Mineralization is initiated by thermodynamic instability of one of the copper complexes [2], leading to instability of the other important complexes and massive precipitation. Early mineralization would receive its isotopic signature from the first unstable copper complex and later mineralization would be characterized by the isotopic composition of the remaining complex(es). If copper is significantly fractionated between different copper complexes (“ligand-choice”) in higher temperature hydrothermal solutions then an “apparent” Rayleigh-style fractionation trend should be expected in the resulting mineralization. The large fractionation observed at Corocchohuayco is likely produced by both a true Rayleigh-type fractionation mechanism (related to differing stabilities of <sup>63</sup>Cu and <sup>65</sup>Cu in the same complex) and the “ligand-choice” mechanism. This “ligand-choice” fractionation mechanism would be most important in those hydrothermal systems where more than one important copper complex is present.

### References

- [1] Marechal, C. and Albarede, F., (2002), *Geochim. Cosmochim. Acta*, **66**, 1499-1509.  
[2] Liu W., Brugger, J., McPhail, D. C. and Spiccia, L., (2002), *Geochim. Cosmochim. Acta*, **66**, 3615-3633.

## Distinguishing between kinetic and equilibrium isotopic fractionations using 3 isotopes

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The mass-dependent fractionation laws that describe the partitioning of three or more isotopes are different for kinetic and equilibrium reactions [1]. The precision with which isotope ratios can be now measured is sufficient to take advantage of these differences. Taking into account masses of isotopes and achieved analytical precision, Mg is among the most sensitive elements [2]. The use of the relationship between  $^{25}\text{Mg}/^{24}\text{Mg}$  and  $^{26}\text{Mg}/^{24}\text{Mg}$  in terrestrial material is a clear diagnostic of kinetic fractionation and equilibrium fractionation provided the fractionation is greater than 1‰/amu and/or the number of samples is large enough for a statistical approach. Evidences for equilibrium fractionation have been found for low-Mg calcite speleothems [3], olivine-pyroxene pairs from mantle xenoliths, and marine authigenic clays. On the other hand, biologically mediated precipitates or Mg-bearing organic molecules have a clear kinetic signature.

A similar approach has been applied to Ge isotopic fractionation during adsorption and co-precipitation with Fe-oxide using the relationship between  $^{74}\text{Ge}/^{70}\text{Ge}$  and  $^{72}\text{Ge}/^{70}\text{Ge}$ . This reveals a kinetic isotopic fractionation while the chemical and  $^{74}\text{Ge}/^{70}\text{Ge}$  data could have been interpreted as closed system equilibrium and implies at least 2 different processes (precipitation and adsorption) occurring at the same time.

### References

- [1] Young E.D., Galy A. and Nagahara H. (2002) *Geochim. Cosmochim. Acta*, **66**, 1095-1104.
- [2] Young E.D. and Galy A. (2004) *Rev. Mineral. Geochem.*, **55**, 197-230.
- [3] Galy A., Bar-Mathews M., et al. (2002) *Earth Planet. Sci. Lett.*, **201**, 105-115.

## Magnesium isotopes in bacterial dolomites: A novel approach to the dolomite problem.

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Bacterially associated dolomite has been reported from two modern hypersaline lagoons in Brazil and suspected in sediments from the Peru margin [1-2]. Cultures of bacteria isolated from the lagoon produce dolomite in the laboratory [3]. We have utilised magnesium isotopes to study these natural and laboratory dolomites.

Fractionation of magnesium isotopes is observed during dolomite formation in both the natural environment and in the laboratory. The dolomite is isotopically lighter than the medium it forms from by between  $\delta^{26}\text{Mg} = -0.49\%$  and  $-3.07\%$  relative to the DSM3 standard. The careful study of the behaviour of the three isotopes of magnesium reveals a kinetic isotopic fractionation process. In mono-specific laboratory cultures the isotope fractionation is seen to vary with bacterial species by up to 1.00‰. Different species of bacteria have distinct isotopic signatures. In the lagoons short cores reveal a variation in isotopic signature down-core of 1.70‰, with the most negative values coinciding with the zone of maximum dolomite formation. The value for the Peru margin dolomite of  $-3.99\%$  is similar to that seen in the other environments and supports previous suggestions of a bacterially mediated origin. Taken together our results argue for a strong biological role in magnesium fixation into dolomite and suggest bacterial processes are important in resolving 'the dolomite problem'.

### References

- [1] Vasconcelos, C., McKenzie, J.A., Bernasconi, S., Grujic, D. and Tien, A.J., (1995), *Nature* **377**, 220-222.
- [2] Meister P., McKenzie J.A., Vasconcelos C., (2002), *Geochim. et Cosmochim. Acta* **66**, A506-A506.
- [3] Warthmann R., van Lith Y., Vasconcelos C., McKenzie J.A. and Karpoff A.M., (2000), *Geology* **28**, 1091-1094.

## Mechanisms of Mg isotopes fractionation during CaCO<sub>3</sub> biomineralisation

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The Mg/Ca ratios in foraminiferal calcite show a temperature dependence due to the partitioning of Mg during calcification. Empirical Mg/Ca-temperature calibrations exist and had been used to determine Quaternary and Cenozoic sea-temperatures [1]. These calibrations are, however, empirical and some discrepancies remain between core-top to cultured estimates. It is, therefore, of primary importance to understand precisely the mechanisms affecting the partition coefficient of Mg in biogenic calcium carbonate. In this regard, we have investigated the Mg isotopic fractionation of coral aragonite and foraminifera calcite.

The  $\delta^{26}\text{Mg}$  from 5 planktonic foraminifera species in different size fractions (core top of Indian Ocean) and 2 corals (Red Sea and Japan Sea) have been measured by MC-ICPMS after chemical purification of Mg and are expressed relative to the DSM3 standard. We find the magnesium isotope composition of coral to be constant, with a  $\delta^{26}\text{Mg} = -1.8\%$ . In contrast to coral, foraminifera present small but significant variations of Mg isotopes between and within the different species (range from  $-4.9$  to  $-5.6\%$ ). Therefore, corals and foraminifera are  $1\%$  and  $4.1$  to  $4.8\%$  lighter than seawater, respectively [2]. These results suggest a marked biological control which differs from a straightforward inorganic equilibrium process [3]. Significant dependence of Mg isotope compositions on temperature has not been observed. The combined Mg, C and O isotope ratios and Mg/Ca ratios suggest that in foraminifera biomineralisation, Mg is transported from ambient seawater into the site of calcite growth by at least 2 different mechanisms inducing kinetic isotopic fractionation and cannot be incorporated directly from seawater vacuole as previously invoked [4].

### References

- [1] Elderfield H. and Ganssen G. (2000) *Nature* **405**, 442-445.
- [2] Carder E.A. et al. (2004) *Geochim. Cosmochim. Acta* **68**, A329.
- [3] Galy A. et al. (2002) *Earth Planet. Sci. Lett.* **201**, 105-115.
- [4] Erez J. (2004) *Rev. Mineral. Geochem.* **54**, 115-149.

## Process-related covariation in Mg and Ca isotopes in the riverine dissolved load

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Ca and Mg isotopes are potential tools for examining the contribution from carbonate and silicate sources and for constraining dissolution processes in the weathering environment. This is important to estimate the impact of weathering on the atmospheric CO<sub>2</sub> budget. The global range in Ca and Mg isotopes in rivers is however relatively small with ca.  $1.8\%$  range in  $\delta^{26}\text{Mg}$  and  $0.8\%$  for  $\delta^{44/42}\text{Ca}$ . Data from >50 samples from both the Himalayan-Tibetan-Plateau region and elsewhere in the world suggest that there is a restricted control of lithology on  $\delta^{44/42}\text{Ca}$  and  $\delta^{26}\text{Mg}$  in spite of investigating both large and small rivers draining a range of lithologies from silicate, limestone and dolomite dominated catchments.

A time-series from the Marsyandi River, Annapurna Himalaya, Nepal shows that variations in Ca and Mg isotopes are small but detectable. There is a marked negative correlation between  $\delta^{44/42}\text{Ca}$ , and  $\delta^{26}\text{Mg}$ . This suggests that there is single control on the variation in both isotopic systems. Given that there is no correlation with major element chemistry or Sr isotopes (hence lithology) it is likely that both Ca and Mg isotopes are controlled by a mass dependent process. The most likely process to influence both elements is incongruent dissolution reactions in the weathering environment.

## Multiple isotope effects associated with biogeochemical networks

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In a prior study (Farquhar et al., 2003) we adapted a standard treatment of isotopic flow through biosynthetic networks (c.f., Hayes, 2001) to describe the way that the four isotopes of sulfur are affected by metabolic processes. In a study that followed (Johnston et al, in press), we reported additional data for sulfate reducers and new data for sulfur disproportionators and expanded our treatment of these effects. Although our focus has been on sulfur isotopes, we note that the same principles apply to other multiple isotope systems such as O, Fe, and Se.

Here, we will describe our approach, beginning with an explanation of the mass-balance and fractionation relationships that form the underpinnings for the calculations. We will present graphical representations of several calculations to illustrate the sensitivity of the isotopic compositions of intermediate pools to the metabolic network structure, and we will illustrate this by building progressively more complex dissimilatory network examples. We will also include a generalized discussion of the principles of nesting network components and specific predictions. These predictions provide a basis to use this approach to map out the structure and the magnitude of the fractionations for the dissimilatory metabolisms. The combination of mathematical treatment and graphical solutions is meant to provide the necessary framework for adaptation of this approach to other systems and we point out that our solutions are neither restricted to biosynthetic networks nor to the sulfur isotope system. The same principles apply to reaction networks for other elements with two or more isotopes and at scales extending from that of a single-cell to that of a global biogeochemical network.

### References:

- Farquhar, J., Johnston, D. T., Wing, B. A., Habicht, K. S., Canfield, D. E., Airieau, S. A., and Thiemens, M. H. (2003), *Geobiology*, v. 1, p. 15-27.
- Hayes, J.M. (2001), *Rev. Mineral. Geochem.*, 43, 225-277.
- Johnston, D. T., Farquhar, J., Wing, B. A., Kaufman, A.J., Canfield, D. E., and Habicht, K. S. (in press), *Am. Jour. Sci.*

## Decoupled fractionation of even- and odd-mass isotopes of Pb in TIMS

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High-precision Pb isotopic analyses of the standard SRM-981, spiked with <sup>202</sup>Pb and <sup>205</sup>Pb, were undertaken to further evaluate the anomalous fractionation of <sup>207</sup>Pb relative to even-mass isotopes in thermal ionisation mass spectrometry, reported by Thirlwall 2000 (Chem.Geo. 163, 299) and Doucelance and Manhès 2001 (Chem.Geo. 176, 361). The analyses were performed using Triton TI mass spectrometer at the GSC in static multicollector mode using three different silica gel formulations: silicic acid (Merck - Gerstenberger and Haase 1997, Chem.Geo. 136, 309); hydrolysis of silicon tetrachloride, and hydrolysis of sodium orthosilicate. Ratios involving the even-mass isotopes (<sup>202</sup>Pb, <sup>204</sup>Pb, <sup>206</sup>Pb and <sup>208</sup>Pb) obey standard mass-dependent fractionation laws over a wide range of fractionation (<sup>208</sup>Pb/<sup>206</sup>Pb between 2.160-2.172). In contrast, isotopic ratios involving odd and even isotopes (e.g. <sup>205</sup>Pb/<sup>206</sup>Pb or <sup>207</sup>Pb/<sup>206</sup>Pb), exhibit mass-independent fractionation when normalized to <sup>208</sup>Pb/<sup>206</sup>Pb, and systematically decrease as the sample approaches exhaustion. The relative change of normalized <sup>205</sup>Pb/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb are between 0.02-0.05% for the Merck and silicon tetrachloride gel, and up to 0.16% for the sodium orthosilicate gel. The relative deviations of both ratios are strongly correlated, with the slope of correlation lines close to one. Thus, the fractionation between odd isotopes is similar to the mass-dependent fractionation between even isotopes, but the behaviour of even- and odd-mass isotopes is decoupled. For example, the ratio <sup>206</sup>Pb/<sup>208</sup>Pb, normalized to <sup>205</sup>Pb/<sup>207</sup>Pb, does not vary with sample exhaustion. If the ratio <sup>207</sup>Pb/<sup>206</sup>Pb, most important for high-precision Pb-isotope dating, is normalized to <sup>205</sup>Pb/<sup>202</sup>Pb or <sup>207</sup>Pb/<sup>204</sup>Pb in a double-spike procedure, the <sup>207</sup>Pb bias is reduced by 1/3 but not removed completely.

The cause of the mass independent fractionation appears related to a higher volatility and/or ionization efficiency of Pb atoms with non-zero nuclear spin. Large differences in ionization of even vs. odd isotopes have been noted for a number of elements in laser resonance ionization mass spectrometry (e.g. Wunderlich et al. 1992 Anal. Chem 65, 1411). However it remains unclear how the process by which silica gel enhances ionization is affected by nuclear spin.

## Redox fractionation of copper isotopes in sedimentary conditions

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Experimental study (Ehrlich et al., 2004) has shown that a relatively large negative copper isotope (<sup>65</sup>Cu/<sup>63</sup>Cu) fractionation (~3‰) occurs during the precipitation of Cu(I)S (covellite) from Cu(II) solution. Biogenic processes may similarly lead to heavy-isotope depletion (1-1.7‰) in bacteria (Zhu et al., 2002). This research presents a copper isotope fractionation study of sedimentary copper minerals in the Cambrian and Lower Cretaceous sedimentary sequences of the Timna Valley area, southern Israel. These rocks are emplaced on top of Precambrian igneous basement, whose weathering provided the solution source from which the copper minerals precipitated. Several cycles of copper mobilization occur within the sediments including: (1) diagenetic deposition of copper sulphides [djurleite (Cu<sub>1.93</sub>S) and covellite (CuS)] within Cambrian dolomites and their in-situ oxidation to give copper (II) minerals [malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>); paratacamite (Cu<sub>2</sub>OH<sub>3</sub>Cl); (2) epigenetic remobilization in Cambrian sandstones and shales giving veins of malachite, paratacamite and copper silicates; (3) biogenic formation of copper sulphide concretions in Lower Cretaceous sandstones and their oxidation. Isotopic measurements were made on a Nu Instruments MC-ICP-MS with nickel internal standard and ion exchange separation.

<sup>δ65</sup>Cu (SRM 976) values of copper sulphides range from ~ -4 to -1 ‰, whereas oxidized copper minerals range from -2 to +2 ‰. Fractionation factors (Δ<sub>Cu(II)-CuS</sub>) for copper oxide minerals replacing copper sulphides vary from ~ 1 to 3 ‰, with most values being around 2 ‰. Thus, there is a clearly defined positive fractionation accompanying the supergene oxidation of copper sulphides. Since the igneous source for the copper (quartz-porphyr) probably had <sup>δ65</sup>Cu values of about 0.0 ± 0.5 ‰ (published literature and our own analyses), it is also clear that a large negative isotopic fractionation is associated with the formation of copper sulphides. Thus, redox cycling of copper leads to significant isotopic fractionation, as predicted in experiments. Whereas the oxidation processes are clearly abiogenic, it appears that fractionation processes involving the formation of low <sup>δ65</sup>Cu copper sulphides are biogenic in origin.

### References

- Ehrlich et al. (2004) *Chem. Geol.* **209** 259-269.  
Zhu et al. (2002) *Earth Planet. Sci. Lett.* **200** 47-62.

## Isotopic effects during Cu sorption onto goethite

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Of the many particles found in the environment, Fe (oxy)hydroxides are among the most common and reactive in terms of contaminant uptake. Isotopic effects during the sorption process have not been widely studied but may hold application in quantifying contaminant retardation. Preliminary sorption experiments were conducted using synthetic goethite and Cu<sup>II</sup> solutions according to Parkman et al. (1999). Each batch was checked for purity by XRD. The Cu<sup>II</sup> solution and Cu-sorbed goethite particulate were then separated by centrifuge prior to sub-sampling, digestion (goethite) and purification by ion exchange. Isotopic measurements (Micromass *IsoProbe* (GV Instruments)) were conducted using simultaneous standard-sample bracketing and Zn doping methods to enable alternative correction algorithms to be applied for mass discrimination effects. The external reproducibility on the standard was typically <150ppm.

Two out of three of our triplicates showed slight <sup>65</sup>Cu enrichment in the goethite relative to the Cu<sup>II</sup> solution, whilst the third showed no change outside the propagated analytical error (±0.1‰ 2σ). For the experiments that showed a difference the respective <sup>δ65</sup>Cu were 1.08 ± 0.10‰, 1.07 ± 0.09‰, and 0.71 ± 0.09‰, 0.73 ± 0.09‰. The <sup>δ65</sup>Cu<sub>goethite-solution</sub> values for the two experiments are 0.37 ± 0.11‰ and 0.34 ± 0.10‰ and indicate that the heavier Cu isotope is sorbed onto goethite. Previous XANES has shown that the Cu complex sorbed onto goethite is similar to that of [Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>], which suggested Cu is octahedrally coordinated to O (Parkman et al. 1999). This is analogous to that discovered for Zn sorption onto goethite (<sup>δ66</sup>Zn<sub>goethite-solution</sub> = 0.15 ± 0.08‰) in which EXAFS proved octahedral coordination for sorbed Zn and for Zn in solution (Cacaly et al. 2004). Further Cu isotopic studies in conjunction with XAS are planned in order to decipher isotopic effects that depend in part on speciation and the bonding environment.

### References

- Cacaly, S., Marechal, C., Juillot, F., Guyot, F. and Benedetti, M. (2004). *Geochim. Cosmochim. Acta*, A366.  
Parkman, R.H., Charnock, J.M., Bryan, N.D., Livens, F.R. and Vaughan, D.J. (1999). *Am. Mineral.* **84**(3), 407-419.

## Mechanisms of Fe isotope fractionation during dissimilatory Fe(III) reduction (DIR)

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Iron isotopes provide a powerful means for constraining the Fe pathways involved during DIR. Previous work has measured low  $\delta^{56}\text{Fe}$  values for  $\text{Fe(II)}_{\text{aq}}$  during DIR, but it has also been suggested that sorption of Fe(II) to ferric hydroxides may produce low- $\delta^{56}\text{Fe}$   $\text{Fe(II)}_{\text{aq}}$ ; in neither case, however, has the high- $\delta^{56}\text{Fe}$  component been analyzed directly. In the present study the mechanisms of Fe isotope fractionation during DIR were investigated through direct measurement of the isotopic composition of aqueous Fe(II), adsorbed Fe(II), and the outermost layer of Fe(III) and tightly bound Fe(II) on the oxide surface. The obligate anaerobe *Geobacter sulfurreducens* was grown with hematite and goethite as its terminal electron acceptor for 280 days, over which time less than 4% of the available ferric iron was reduced; this slow rate of growth best simulates natural conditions and minimizes kinetic isotope effects. The aqueous Fe(II) was isotopically light, in agreement with previous studies, and direct measurement of the adsorbed Fe(II) shows that its isotopic composition is similar to that of aqueous Fe(II). The outermost layer of Fe(III), as determined by step-wise leaching/partial dissolution, has high  $\delta^{56}\text{Fe}$ , and this represents the first time that an isotopically heavy component (required by mass balance) has been identified in DIR experiments.

Beard et al. (2003 Chem. Geol.) proposed a ligand exchange model to explain Fe isotope fractionation during DIR, in which the major fractionation step is between ligand-bound pools of Fe(III) and Fe(II). Our results instead suggest that the major fractionation step may occur during electron transfer from sorbed or aqueous Fe(II) to Fe(III) at the ferric oxide/hydroxide surface, following the bacterial reduction step. We find no evidence that sorption produces the large Fe isotope fractionations reported by Icopini et al. (2004 Geology). Instead, the measured  $\delta^{56}\text{Fe}$  values for  $\text{Fe(II)}_{\text{aq}}$  are produced by creation of a high- $\delta^{56}\text{Fe}$  ferric oxide/hydroxide layer, where  $\text{Fe(II)}_{\text{aq}}$  is  $\sim 3$  per mil lower in  $^{56}\text{Fe}/^{54}\text{Fe}$ . At the extent of reduction in these experiments, this is equivalent to about one Fe atom thickness; it is not yet clear if this mechanism occurs at larger extents of reduction. These results provide the first evidence that redox cycling of Fe atoms occurs at the ferric oxide/hydroxide surface during DIR.

## Isotope fractionation of Cadmium on the Moon

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The absence of a lunar atmosphere enables bombardment of the lunar surface by high energy particles and micro-meteorites to occur. Some of the sputtered material escapes from the small gravity field of the Moon, and may leave the residue preferentially enhanced in "heavy" isotopes of certain elements with respect to a terrestrial standard. A mass spectrometric study of the volatile element cadmium revealed evidence of isotope fractionation (Sands et al., 2001).

To accurately ascertain the magnitude of this fractionation and the elemental abundance of cadmium, a number of lunar samples were analysed by Thermal Ionization Mass Spectrometry, using the double spike technique. Five lunar soils gave a positive isotope fractionation ranging from + 3.1 to + 5.2 ‰ per mass unit, in which the "heavy" isotopes of cadmium are enhanced relative to the "light" isotopes. A mare basalt from the lunar surface gave zero fractionation, which is identical to BCR-1, indicating that the isotope fractionation of the Moon and Earth are identical. An orange glass from Shorty Crater in the Taurus-Littrow region, however, gave a negative fractionation of  $-2.6 \pm 0.8$  ‰ per mass unit, as a result of re-deposition of cadmium from the volatile-rich cloud associated with lunar volcanism.

### Reference

Sands D., Rosman K.J.R. and De Laeter J.R. (2001) *Earth Planet. Sci. Lett.* 186, 103-111.

## Preservation of Fe isotope compositions of iron formation during contact metamorphism

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We have analyzed a suite of minerals from iron formation samples of varying metamorphic grade (<150° C to >600°) and determined that heterogeneities in  $\delta^{56}\text{Fe}$  survive contact metamorphism. The lowest grade rocks from the 1.9 Ga Biwabik Iron Formation are comprised of quartz, magnetite, siderite, greenalite and locally minnesotaite. Layering is on the scale of millimeters to a few centimeters. The contact aureole developed adjacent to the 1.1 Ga Duluth gabbro consists of 5 zones marked by the appearance of: 1) minnesotaite 2) grunerite 3) hedenbergite 4) olivine and 5) orthopyroxene.

The Fe isotopic compositions of primary, diagenetic, and metamorphic minerals were determined at the University of Hannover; results are reported relative to the IRM standard. Primary minerals analyzed include greenalite ( $\delta^{56}\text{Fe} = -0.118\%$ ), Fe-carbonate (-0.913 to -0.430%), and hematite (0.122%). Their  $\delta^{56}\text{Fe}$  are consistent with oxidative, fractionating precipitation of oxide from MOR-source aqueous fluids and precipitation of carbonates from residual  $\text{Fe(II)}_{\text{aq}}$ , although biologic involvement cannot be excluded.

Magnetite in the Biwabik Formation is predominantly a diagenetic mineral produced by reactions between hematite and ferrous iron in silicates and carbonates, or by reactions with carbonates that generate methane.  $\delta^{56}\text{Fe}$  of diagenetic magnetite varies from 0.857 to 0.212, and is heavier than that of coexisting silicates and carbonates.

During contact metamorphism magnetite may break down but only petrologically insignificant amounts of magnetite can be produced by dehydration of Fe-silicates and dissociation of water. Metamorphic silicates are formed by various reactions involving silicates, carbonates and/or magnetite; the reaction products appear to inherit the approximate isotope composition of their reactant minerals. The  $\delta^{56}\text{Fe}$  of these metamorphic minerals, which vary from -0.19 for olivine to +0.56% for grunerite, does not depend upon metamorphic grade. Instead, this study suggests that layer-to-layer heterogeneities in bulk  $\delta^{56}\text{Fe}$  composition that developed during primary precipitation and diagenesis are preserved during contact metamorphism.

## Mass-independent isotope effect in the isotope exchange reaction of chromium(III) using a crown ether

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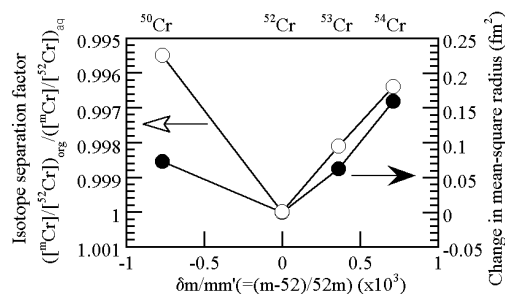
### Mass-Dependent Isotope Effect and Mass-Independent Isotope Effect

In the research field of isotope chemistry, the conventional mass-dependent theory has been extended to include a mass-independent isotope effect (nuclear size and shape effect).

#### Isotope Effect of Chromium

Chromium isotopes were fractionated by liquid-liquid extraction system using dicyclohexano-18-crown-6. We found a mass-independent isotope effect. This shows a good relationship to the change in mean-square radius,  $\delta\langle r^2 \rangle$ .

Figure 1: Isotope separation factor and change in mean-square radius of chromium.



Some continuous extraction experiments were also performed, and the mass-independent isotope effects were observed. These isotope enrichment properties give the experimental facts of the nuclear size and shape effect.

#### References

- Bigeleisen J., (1996), *J. Am. Chem. Soc.* **118**, 3676-3680.  
Fujii T., Suzuki D., Gunji K., Watanabe K., Moriyama H. and Nishizawa K., (2002), *J. Phys. Chem. A* **106**, 6911-6914.

## Isotope fractionation of Tungsten on geochemical samples using ICP-mass spectrometry

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Recent studies have revealed that natural stable isotope fractionations of many elements heavier than S (e.g., Ca, Fe, Cu, Zn or Tl) are common on the Earth. Among the heavier elements, W is especially important element, because isotopic composition of W can provide us chronological data known as Hf-W isotopic chronometer [1-5]. In the previous works, the mass discrimination effect was internally corrected by normalising a specific W isotopic pair (e.g.,  $^{186}\text{W}/^{183}\text{W} = 1.98594[1]$ ). However, this correction method is not adequate for the stable isotopic study, because not only the mass discrimination effect, but also natural isotopic fractionation of the analyses have been normalized at a same time. It is well recognized that detection of natural variation in isotopic composition of further heavy elements would be very difficult because of their small magnitude of isotopic fractionation mainly due to small relative mass differences [6]. In this study, multiple collector-ICP-mass spectrometry (MC-ICPMS) was used to measure W isotopic ratios. The extension of the capability of ICPMS is to accept external correction technique for a correction of mass discrimination effect (mass fractionation effect inside the mass spectrometer). Here we report the results of high precision W isotopic data for chemical reagents (JMC-22841 and NIST SRM 3163) and series of geochemical samples (JR-1, JR-2 and HSD-USGS), using the MC-ICPMS combined with an external correction technique using Re. The data obtained here revealed that there were no significant variations in W isotopic composition for igneous rocks, whereas W collected from the HSD-USGS was isotopically fractionated (0.15‰/amu). In this presentation, we would like to discuss the possible mechanism of the W isotopic fractionation found on this deposit sample.

### References

- [1] C. L. Harper and S. B. Jacobsen (1996) *Geochem. Cosmochem. Acta*, **60**, 1131-1153
- [2] A. N. Halliday (2004) *Nature*, **427**, 505-509
- [3] A. Scherstén et al. (2004) *Nature*, **427**, 234-
- [4] 237 Q. Yin et al. (2002) *Nature*, **418**, 949-952
- [5] G. Quitté et al. (2002) *J. Geostan. Geoana.*, **26**, 149-16
- [6] J. Völkening et al. (1991) *Int. J. mass Spectrom. Ion Processes*, **107**, 36
- [7] J. Bigeleisen and M. G. Mayer (1947) *J. Chem. Phys.*, **15**, 261

## Multiple sulfur isotope constraints on sulfur cycle in the seafloor hydrothermal systems

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Seafloor hydrothermal system fuels an unusual deep-water ecosystem that depends on the hydrothermal emission of sulfide for its energy source. Understanding chemical and isotopic systematics of such hydrothermal systems may have profound implication into the origin of life and life in the extreme environment.

We will report the first application of non-traditional isotopes of sulfur ( $^{33}\text{S}$  and  $^{36}\text{S}$ ) as a tool to decouple combination processes in the sulfur cycle in the modern seafloor hydrothermal system. Our data shows measurable variation ( $> 5\sigma$  analytical precision) in  $\Delta^{33}\text{S}^\dagger$  and  $\Delta^{36}\text{S}^\dagger$  for sulfide minerals from modern seafloor hydrothermal sulfide deposits, suggesting all four sulfur isotope system may provide new insights into sulfur cycle in the seafloor hydrothermal systems.

We will apply thermochemical and isotopic models of seafloor hydrothermal massive sulfide deposits (e.g. Ohmoto et al., 1983, Shanks, 2001), expand the model for multiple sulfur isotope systematics for a biological flow network by Farquhar et al. (2003) into the global-scale oceanic sulfate budget, and model transfer of oceanic sulfate signature into sulfide in the seafloor massive sulfide deposits. We will discuss implication of the new constraints on the sulfur cycle in the hydrothermal systems.

### References and notes

- <sup>†</sup>  $\Delta^{33}\text{S} \equiv \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$  and  $\Delta^{36}\text{S} \equiv \delta^{36}\text{S} - 1.9 \times \delta^{34}\text{S}$ , where  $\delta^{x}\text{S}$  is defined in a logarithmic formula as that used by Hulston and Thode (1965) *J. Geophys. Res.* **70**, 3475-3484.
- Ohmoto et al. (1983) *Econ Geol Mono* **5**, 570-604  
Shanks (2001) *Rev Mineral Geochem* **43**, 469-525  
Farquhar et al. (2003) *Geobiology* **1**, 27-36

## Chromium isotopic fractionation during Cr(VI) reduction in groundwaters

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Among heavy metals at trace concentration, chromium is an essential micronutrient element necessary to humans and other organism's life in its trivalent form Cr(III) at the proper concentration, but in its hexavalent oxidation state Cr(VI) becomes toxic and suspected carcinogen. The concentration of natural Cr in soils and waters is largely determined by the weathering and erosion of the parental material. Soils derived from igneous rocks can be expected to contain higher levels of Cr compared with sedimentary rocks. The two common oxidation forms of Cr in the environment are Cr(III) and Cr(VI). The two species are different in physicochemical properties and chemical and biochemical reactivity. Cr(III) has a very low solubility and a strong tendency to be adsorbed on surfaces. Cr(VI) forms anionic oxy-compounds and it is highly soluble. The most common species in natural waters is CrO<sub>4</sub><sup>2-</sup>. The Cr speciation in aqueous solutions depends on several factors, including Eh and pH but also the occurrence of competing ions, complexing agents and others.

The <sup>53</sup>δ Cr was measured in industrial Cr sources and in groundwaters interacting with ophiolitic rocks in the La Spezia Province (Italy). Cr speciation analysis reveals that in waters the dissolved Cr is essentially present in the Cr(VI) form. Due to the absence of anthropogenic Cr sources, the relatively high Cr(VI) concentration can be attributed to natural pollution.

The isotopic data suggest that Cr released from industrial sources is isotopically close to the natural value, with an average <sup>53</sup>δ Cr = 0.34 +/- 0.43 (2-σ). Most of the groundwater Cr(VI) analyses are characterized by variable enrichment in heavy Cr isotopes, with a consequent positive <sup>53</sup>δ Cr value. In particular, the higher <sup>53</sup>δ Cr values are found in samples with the lowest Cr(VI) concentration. Despite preliminary, these data indicate that lighter isotopes were preferentially removed from these waters, suggesting that along the flow path, Cr(VI) reduction was actively occurring. The data indicate that the Cr-isotopic fractionation associated with the Cr(VI) reduction follows a Rayleigh-type process.

## Lithium isotopic fractionation in pegmatites

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In order to fully utilize Li isotopes as tracers of magmatic processes it will be necessary to both characterize the Li isotopic compositions of different geological reservoirs, and quantify the magnitude of isotopic fractionations for various conditions/compositions. The continental crust appears to have lighter Li isotopic composition than the upper mantle, from which it was derived [1, 2]. Given that Li isotopes do not fractionate during high-T magmatism, juvenile crust and the mantle should have identical Li isotopic compositions. The isotopically light continental crust, therefore, is likely a result of secondary processes, e.g., weathering, metamorphism and low-T intracrustal melting. Recent studies have demonstrated large Li isotopic fractionation during surface weathering and metamorphic dehydration, but few data exist for Li isotopic fractionation during relatively low-T magmatism.

We measured Li concentrations and <sup>δ</sup>Li of coexisting quartz, muscovite, plagioclase and spodumene from the well-characterized Tin Mountain pegmatite, Black Hills, South Dakota. This pegmatite crystallized from the wall zone inwards, as temperatures decreased from >600 to <500°C [3]. Muscovite, plagioclase and spodumene in all zones display a narrow range in <sup>δ</sup>Li (+7.9 to +11.4‰), whereas quartz is more variable (+14.7 to +21.3‰). On average, quartz is the heaviest mineral (+18.1 ± 2.1‰ (1σ)) and has relatively low Li concentrations (~82 ppm), while spodumene, muscovite and plagioclase are lighter (+9.4 ± 1.2‰ (1σ)) with Li concentrations decreasing from spodumene to muscovite (~6420 ppm) to plagioclase (~570 ppm). The +6‰ difference between quartz and other minerals can be explained by the preference for heavy <sup>7</sup>Li in higher bond-energy sites. Therefore, tetrahedrally coordinated Li in quartz is expected to host more <sup>7</sup>Li than 6-fold sites in the coexisting minerals.

The isotopically heavy pegmatite body (~ +10‰) is distinct from the surrounding Black Hills metasedimentary rocks (+2 ± 1‰, n=3) and Harney Peak granites (+5 ± 1‰, n=2), consistent with <sup>7</sup>Li enrichment accompanying extensive crystal-liquid fractionation.

### References:

- [1] Teng F.Z. et al. (2004) GCA 68, 4167-4178.
- [2] Teng F.Z. et al. (2004) EOS Trans., AGU 85, V51C-0597.
- [3] Walker R.J. et al. (1984) Amer. Mineral. 71, 440-459.

## Iron isotope fractionation during goethite dissolution by oxalate

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Goethite ( $\alpha$ -FeOOH) is one of the dominant Fe oxide minerals in soils and sediments. Its dissolution behavior is closely connected to important biogeochemical processes (e.g., plant nutrition, weathering, pedogenesis, bacterial respiration). In the dark, oxalate dissolves goethite by a ligand-controlled process releasing Fe(III)-oxalate complexes to solution. In the presence of light, oxalate dissolves goethite by a photoreductive mechanism releasing Fe(II) to solution.

We studied Fe isotope fractionation during goethite dissolution by 0.5M HCl (proton-promoted) and by oxalate at pH 3 in dark and light conditions. Samples were taken at different time steps (5 min to 95 d), centrifuged, filtered (0.025  $\mu$ m) and measured by MC-ICPMS (Nu Plasma).

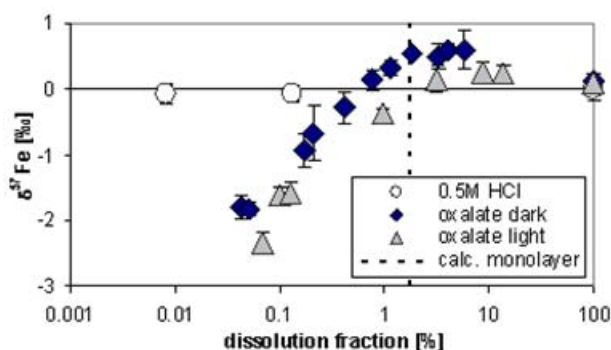


Figure 1: Fe isotopes in solution during goethite dissolution  $\delta^{57/54}\text{Fe}$  vs. bulk goethite, error bars indicate 2SD of replicate measurements (n = 3-6), 100% dissolution in 6M HCl

The 0.5M HCl experiment shows that proton-promoted dissolution does not fractionate and that our goethite is not isotopically zoned (Fig.1). In contrast, Fe isotopes are strongly fractionated during both ligand-controlled and photoreductive oxalate dissolution. The first dissolution fractions are enriched in  $^{54}\text{Fe}$ , indicating a kinetic isotope effect. However, at later dissolution fractions in the dark experiment the solution exhibits  $\delta^{57}\text{Fe}$  values  $\sim 0.5\text{‰}$  heavier than the goethite. We speculate that this is due to equilibrium isotope fractionation between Fe(III)-oxalate complexes (stronger bonding environment) and the mineral surface.