Effects of changing solution chemistry on Fe^{2+}/Fe^{3+} isotope fractionation in Fe-Cl solutions

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Iron isotope ($^{56}Fe/^{54}Fe$) fractionation in nature is usually attributed to redox effects, and is used as an indicator of past oxygen fugacity. However, both theoretical models and experiments show that non-redox speciation changes (in bond partner or coordination number) are also significant [1, 2], so that iron isotope signatures in nature reflect both redox state and solution chemistry.

To explore the effects of changing solution chemistry on the Fe(II)/Fe(III) fractionation, we designed experiments that take advantage of the insolubility of all Fe(II) and Fe(III) aquo and chloride complexes except $Fe(III)Cl_4^-$ in immiscible diethyl ether. Each experiment consists of a series of low pH solutions of combined ferrous and ferric chlorides in varying ratios ($Fe(II)/Fe_{total}$ = 0, 0.25, 0.5, and 0.75) at a given chlorinity, to which an equal amount of diethyl ether is added. In each set, the unique solubility of the $Fe(III)Cl_4^-$ complex in ether creates a spectator phase against which variations in $^{56}Fe/^{54}Fe$ partitioning in the aqueous solution can be quantified, by measuring changes in the fractionation between aqueous and ethereal iron. Extrapolation to $Fe(II)/Fe_{total}=1$ allows us to calculate the fractionation between the dominant ferric and ferrous complexes at a given chlorinity.

We ran two series of experiments, at chlorinities of 1.5M and 2.5M. At 1.5M chlorinity, the dominant ferric species is $FeCl_2(H_2O)_4^+$ while the dominant ferrous species is $FeCl(H_2O)_5^+$. As chlorinity increases to 2.5M, $FeCl_2(H_2O)_4^+$, although still dominant, decreases in abundance as $FeCl_3(H_2O)_3^0$ increases, and $FeCl_2(H_2O)_4^0$ becomes the leading ferrous species. The experimental fractionation between the ferric and ferrous species at $[Cl^-]$=1.5M is 3.3‰ and 2.7‰ at $[Cl^-]$=2.5M, showing a decrease in fractionation with increasing chlorinity. Our first-principles models predict a smaller sensitivity (~0.2‰ / M $[Cl^-]$) for overall ferrous/ferric fractionation vs. chlorinity.

To our knowledge, these are the first experiments demonstrating that aqueous speciation affects the Fe redox fractionation signature.

[1] Hill *et al.* (2006) *GCA Supp.* **70**, 251. [2] Hill & Schauble (2008) *GCA*, doi, 10.1016/j.gca.2007.12.023

The effect of QSA on S, C, O and Si isotopic ratio measurements

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The Cameca NanoSIMS 50 is being increasingly used to measure high-precision isotope ratios at the micron to sub-micron scale. The relatively weak ion signals obtained from smaller analysis areas necessitate the use of electron multipliers (EM) for the simultaneous detection of multiple ion species. EMs are however susceptible to the phenomenon of quasi-simultaneous arrivals (QSA) [1], which occurs when a single incoming primary ion produces multiple secondary ions that are then recorded at the EM as a single event. The number of counts recorded by the EM for the major isotope is lower than the actual number of secondary ions emitted and thus the calculated ratio appears artificially high. This is particularly problematic for elements with high ionisation efficiency, such as S, C, O, Si and N.

From the ratio of secondary to primary ions, K, the first-order relationship (based on the Poisson statistics) between a measured and true isotopic ratio is $R_{meas} = R_{true}*(1+\beta*K)$. Slodzian *et al.* (2004) [2] showed, however, that at least for sulphur, β deviates significantly from the theoretical correction factor of 0.5.

We have measured the effect of QSA for a number of elements by recording isotope ratios at different values of K, obtained by decreasing the secondary ion current with the entrance, aperture and energy slits. The data for $\delta^{34}S$ and $\delta^{33}S$ in Archean pyrite, CDT, Balmate pyrite and the chalcopyrite standard CP-1 and $\delta^{17}O$ and $\delta^{18}O$ in magnetite consistently gave $\beta \approx 0.75$. The data for $\delta^{13}C$ measured in graphite, Archean pyrobitumen, carbon foils and resin-embedded organic material gave $\beta \approx 1.0$. The data for $\delta^{29}Si$ and $\delta^{30}Si$ measured on Si wafer gave $\beta \approx 0.6$.

[1] Slodzian *et al.* (2001) EPJ *App. Phys.* **14(3),** 199-231. [2] Slodzian *et al.* (2004) *App. Surf. Sci.* **231-232**, 874-877.