Experimental constraints on Fe isotope fractionations during biogeochemical cycling of Fe

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Experimental calibration of Fe isotope fractionation factors in the system Fe(II)-Fe(III)-Fe_2O_3/FeOOH in both inorganic and biologic systems allows us, for the first time, to quantify the "vital" effects that are associated with biological processing of Fe during both Fe reduction and oxidation. Equilibrium isotope fractionation between hexaquo Fe(III) and Fe(II) varies from +2.7 to +3.5 per mil for $^{56}Fe/^{54}Fe$ from 22 to 2 °C, and is independent of Cl^- substitution into the inner hydration sphere up to a stoichiometry of $[Fe(III)(H_2O)_5Cl]^{2+}$ for ferric Fe. In contrast, equilibrium isotope fractionation between hexaquo Fe(III) and Fe_2O_3 at low temperatures is nearly zero, which is distinct from the significant (~ 1 per mil) kinetic fractionations that may be produced by rapid precipitation of ferric oxides. Combining these results indicates that equilibrium isotope fractionations between Fe(II) and ferric oxides is ~ -3 per mil for $^{56}Fe/^{54}Fe$.

Fe isotope fractionation produced during dissimilatory Fe reduction, as well as anoxygenic photosynthetic Fe oxidation, produces remarkably similar fractionations in $^{56}Fe/^{54}Fe$ between ferrous and ferric components of ~ -1.5 per mil, which is half that measured for "equivalent" inorganic systems. We may define this contrast as a "vital" effect, and we interpret this to reflect the unique organic ligands that are involved in complexing ferric and ferrous Fe during biological processing of Fe.

Combined, the experimental data explain several aspects of Fe isotope variations observed in nature, as well as those expected during biogeochemical cycling of Fe:

1) The moderately positive $\delta^{56}Fe$ values of primary hematite in some Late Archean Banded Iron Formations are best explained by Fe oxidation by photosynthetic bacteria,

2) The low $\delta^{56}Fe$ values for ferrous-rich fluids and minerals are consistent with both inorganic or biological processing of Fe,

3) The $\delta^{56}Fe$ values of oxide minerals are likely to directly reflect the Fe isotope compositions of Fe(III) in ancient fluids,

4) Redox cycling of Fe by bacteria will produce Fe deposits that are strongly zoned in Fe isotope compositions.

Grain formation, processing and survival in, and transport through, the ISM

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The major dust-forming environments are the circumstellar environments of `old' stars, principally asymptotic giant branch (AGB) stars and supernovae (SNe). While AGB stars seems to dominate the galactic dust budget, in terms of the variety (crystalline and amorphous silicates, amorphous aliphatic/aromatic hydrocarbons and SiC) and the quantity of the dust that they produce, the SNe dust input contribution is not entirely clear. The total dust input rate to the Galaxy is of the order of $8\text{-}30 \times 10^{-6}$ M_Sun kpc^{-2} yr^{-1} (Jones 2001). If we assume that dust makes up some 1% of the galactic gas mass then it would take of the order of 3 billion years to replenish the entire galactic dust mass.

Interestingly, not all of the dust materials formed in AGB and SNe circumstellar environments are, however, detected in circumstellar regions or in the interstellar medium (ISM). Some of them, e.g., SiC, graphite, Al2O3 and Si3N4, have been extracted from primitive meteorites and have been extensively analysed but are never seen in the ISM.

The derived lifetimes for grains in the ISM appear to be short (400-600 million years, e.g., Jones et al. 1996) compared to the time-scales for their re-formation. This discrepancy in timescales is about order of magnitude. Thus, a lifetime and propagation problem is posed for dust in the ISM. Apparently, it is necessary to re-form and grow grains in the ISM, through accretion and coagulation processes, in order to explain interstellar dust observations. Clearly we see presolar dust in meteorites and this dust must therefore have traversed the ISM before incorporation into primitive Solar System bodies. This paper will discuss: dust formation in circumstellar and interstellar environments, dust sources and their contributions to the galactic dust budget, and dust survival in, and propagation through, the ISM.

References

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