Available online at www.sciencedirect.com
SCIENCE DIRECT®
Earth and Planetary Science Letters 217 (2004) 223–236
EPSL Frontiers
www.elsevier.com/locate/epsl

Frontiers

Iron stable isotopes: beyond biosignatures

A.D. Anbar [a,b,*]

[a] Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, USA
[b] Department of Chemistry, University of Rochester, Rochester, NY 14627, USA

Received 2 June 2003; received in revised form 10 October 2003; accepted 12 October 2003

Abstract

The stable isotope geochemistry of Fe has attracted intense interest in the past five years. This interest was originally motivated by the possible use of Fe isotopes in biosignature applications, particularly in sediments from the ancient Earth or Mars. This application is still being developed, with particular attention to fractionation mechanisms. Understanding such mechanisms should also provide new insights into the environmental biogeochemistry of Fe. At the same time, the Fe isotope system holds promise for other exciting frontiers, including applications in oceanography, solid Earth geochemistry and biomedicine. Such applications will be increasingly attractive as Fe isotope analysis becomes routine.

Keywords: iron; iron isotopes; fractionation; stable isotope geochemistry; transition metals; biosignatures; MC-ICP-MS

1. Introduction

Recent analytical advances have accelerated the development of new research areas in the isotope geosciences. Few have drawn as much interest, from as many subdisciplines, as the stable isotope geochemistry of transition elements and other 'heavy' elements.

Mass-dependent variations in isotopic composition are being seriously investigated for a dozen elements from the middle part of the periodic table (Fig. 1). The isotope geochemistry of Fe has drawn the most attention. This is not surprising in an era of increasing interest in the interface between geosciences and life sciences – both fields in which Fe is an element of central importance.

In the geosciences, the chemistry and physics of Fe are ubiquitous: Fe is the final product of nuclear fusion in stars because of its high binding energy per nucleon, and hence is the most abundant transition element in the cosmos; the structure and composition of the silicate Earth is grossly influenced by the 'siderophile' tendencies of the elements because the high density of metallic Fe makes it the dominant constituent of the Earth's core; the magnetic properties of Fe-bearing minerals dominate rock magnetism in the crust, where Fe is the 4th-most abundant element; and the mobility of Fe at the Earth's surface is strongly affected by the redox potentials of aqueous systems, causing the environmental abundance of Fe to vary markedly with location and through time.

* Tel.: +1-585-275-5923.
E-mail address: anbar@earth.rochester.edu (A.D. Anbar).

0012-821X/03/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S0012-821X(03)00572-7

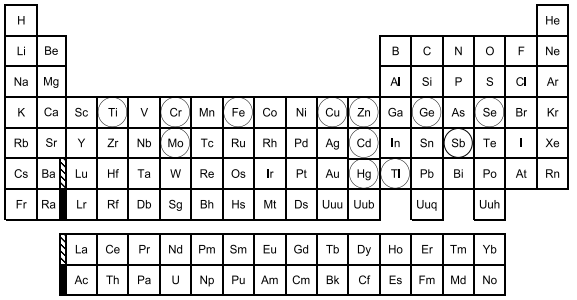

Fig. 1. 'Heavy' stable isotope systems under active investigation (highlighted): Ti [71]; Cr [72]; Fe (see text); Cu, Zn [18]; Ge [73,74]; Se [75,84]; Mo [76–78]; Cd [79,80]; Sb [85]; Tl [85]; Hg [82,83].

Biologically, Fe mediates electron transfer in a host of enzymes, such as the nitrogenase enzyme which catalyzes N_2 fixation, and hence is an essential element for almost all organisms. Combined with the low solubility of Fe^{3+}–oxides in oxygenated seawater, this biological role makes Fe a limiting nutrient in large parts of the ocean [1,2]. Fe can also act as an electron donor or receptor in microbial metabolism. And, in magnetite (Fe_3O_4), Fe is a constituent of a sometimes biogenic mineral that may serve as a biosignature in rocks from ancient Earth or Mars (recently reviewed in [3]).

The possibility that Fe isotope variations could be used to differentiate biological from non-biological processing of Fe, particularly in the formation of magnetite or other minerals, motivated much of the initial research in Fe isotope geochemistry (e.g., [4–6]). This potential continues to tantalize, but the reality has proven challenging. At the same time, the range of Fe isotope fractionation processes that have been revealed hold much promise for future research.

Below we consider some of this potential, highlighting critical issues and giving some historical perspective. The intent is not to provide a comprehensive review of Fe isotope research, but a broad overview showing how much has been achieved in a few short years, and directing attention to some particularly promising frontiers.

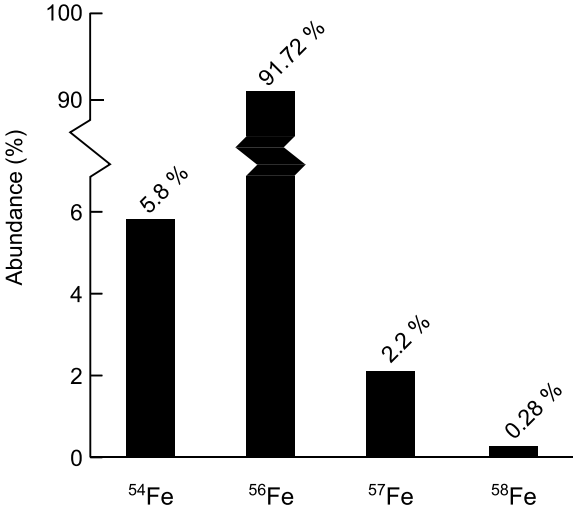

Fig. 2. The isotopes of Fe. Relative abundances are recommended average values from IUPAC [12].

2. Precise pursuits

Iron has four naturally occurring stable isotopes (^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe; Fig. 2). Natural mass-dependent variations in the isotopic composition of Fe are small: $\delta^{56/54}Fe$ (Box 1) covers a

Box 1: Iron Stable Isotope Concepts, Notation and Relations

Equilibrium isotope fractionation: A difference in isotope composition between compounds A and B at chemical equilibrium. Commonly expressed in terms of an equilibrium isotope exchange reaction, e.g., $^{54}Fe(H_2O)_6^{3+} + {}^{56}Fe(H_2O)_6^{2+} = {}^{56}Fe(H_2O)_6^{3+} + {}^{54}Fe(H_2O)_6^{2+}$. The equilibrium constant for this reaction, $K_{eq} = {}^{56}K/{}^{54}K$, where ${}^{m}K$ are equilibrium constants for oxidation of $^{m}Fe(H_2O)_6^{2+}$ to $^{m}Fe(H_2O)_6^{3+}$.

Kinetic isotope fractionation: A difference in isotope composition between reactant, A, and product, B, of a unidirectional process or an unequilibrated chemical reaction. For a chemical reaction, a kinetic isotope effect follows from mass-dependent rate constants (i.e., for the reaction A -> B, ${}^{54}k \neq {}^{56}k$).

Fractionation factor (α): $\alpha_{A\text{-}B} = R_A/R_B$, where R_A and R_B are isotope ratios in compounds A and B (here, $\alpha_{A\text{-}B} = (^{56}Fe/^{54}Fe)_A/(^{56}Fe/^{54}Fe)_B$). α may reflect an equilibrium (α_{eq}) or kinetic isotope effect.

$\delta^{56/54}Fe = [(^{56}Fe/^{54}Fe)_{sample}/(^{56}Fe/^{54}Fe)_{standard} - 1] \times 1000$, expressed as ‰ (per mil). Data are reported relative to the IRMM-014 standard.

$\Delta^{56/54}Fe_{A\text{-}B} = \delta^{56/54}Fe_A - \delta^{56/54}Fe_B$
$\alpha_{A\text{-}B} \sim \exp(\Delta^{56/56}Fe_{A\text{-}B}/1000)$; $\Delta^{56/54}Fe_{A\text{-}B} \sim 1000\ln(\alpha_{A\text{-}B})$
(hence, if $\alpha_{A\text{-}B} = 1.001$, A and B are fractionated by 1‰)

$\alpha_{eq} = K_{eq}^{1/n}$, where n is the number of atoms exchanged (for the Fe exchange reaction above, n = 1)

$K_{eq} = {}^{56}K/{}^{54}K = ({}^{56}k_f/{}^{56}k_r)/({}^{54}k_f/{}^{54}k_r)$ where ${}^{m}k_f$ and ${}^{m}k_r$ are rate constants for forward and reverse reactions, respectively.

Box 1.

range of only ~3.5‰. Therefore, advances in mass spectrometric methods have been essential to the emergence of Fe stable isotope geochemistry, and will continue to drive progress.

Fe isotope analytical efforts extend back more than half a century [7]. Thermal ionization mass spectrometry (TIMS) was applied to this problem in the 1980s and 1990s by a number of research groups [8–14]. While TIMS data are exquisitely precise in isotopic studies of radiogenic isotope systems, stable isotope analyses are more challenging because of the need to correct for mass discrimination by the mass spectrometer ('mass bias') without masking pre-existing natural fractionation. In principle this effect can be accurately characterized by analyzing standards, to generate a correction function that can be applied to samples measured under identical instrument operating conditions. However, in practice $\delta^{56/54}$Fe determined by such methods yielded data with a reproducibility of only 1–3‰/amu (atomic mass unit) [11], insufficient to reliably detect natural mass fractionation. TIMS analyses of Fe are also hampered by low ionization efficiency.

The application of the isotopic double spike technique [13–15], yielding precision of ~ ±0.6‰ (2σ), solved this problem. This precision was sufficient to provide the first convincing evidence of Fe isotope fractionation in nature [13]. These and subsequent findings are discussed more fully below.

Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) offers a number of advantages applicable to stable isotope studies [16]. Despite the large mass bias in ICP systems (1–2%/amu), methods have been developed that avoid the use of a double spike for Fe and other systems [4,17–20]. These methods simplify analytical procedures, and hence have dominated the initial wave of Fe isotope research.

Fe isotope analysis by MC-ICP-MS is not without challenges, however. Most significant is the problem of isobaric interferences at masses 54, 56 and 57 from ArN^+, ArO^+ and $ArOH^+$. There are now several solutions to this problem including sample desolvation [4,17], collision cells [20,21] and most recently high-resolution multicollection (Fig. 3) [22,23].

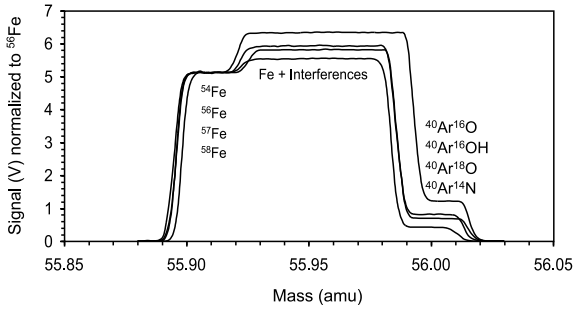

Fig. 3. Peakshape scans in the vicinity of masses 54, 56, 57 and 58 on the ThermoFinnigan Neptune, a high-resolution MC-ICP-MS [22]. The figure shows 'plateaus' corresponding to pure analyte isotopes (left plateau), analyte+interference (central plateau) and interferences (right plateau). Such novel analytical techniques promise to make Fe isotope analysis routine. Figure modified after [22].

The accuracy of Fe isotope data is not easily tested. In particular, at high precision the effects of sample matrix on mass bias in MC-ICP-MS remain unclear. Even in nominally purified samples, emerging reports indicate that residual matrix can cause isotopic shifts between samples and standards of 0.1–0.5‰ in the case of Fe [23] and perhaps other elements (e.g., [24]). Such effects can be monitored and corrected (at least in part) using an 'element spike' [18,23]. High-purity chemical separation can also minimize this problem [20]. A combination of isotopic double spike and MC–ICP–MS may be the best solution.

Using such approaches with second-generation MC-ICP-MS instruments, $\delta^{56/54}$Fe is now routinely measured to a reported external precision of ±0.1‰ (2σ) in samples <1 μg [20,23,25]. Such data are more than adequate to examine Fe isotope fractionation in nature, and so Fe isotope analyses are increasingly routine.

3. Biosignature beginnings

Iron's prominence at the crossroads between geology and biology, combined with analytical advances, motivated rapid progress in Fe isotope research in the last five years (summarized in Figs. 4 and 5).

In their seminal study, Beard et al. reported that dissolved Fe^{2+} produced by the dissimilatory

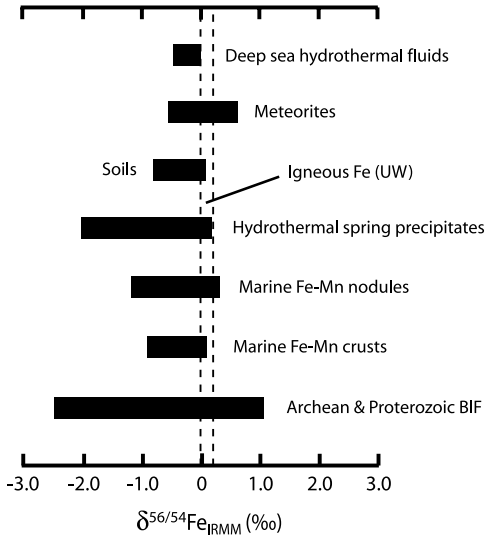

Fig. 4. Fe isotope variations in different natural materials. Bars represent range of isotopic compositions in indicated categories. All values renormalized to the IRMM-014 standard. See text for references.

Fe-reducing bacterium *S. alga* was fractionated ~−1.3‰ from ferrihydrite substrate [5], consistent with contemporaneous work by Bullen and McMahon [14]. Variations of similar magnitude were reported in a handful of analyses of sedimentary Fe: $\delta^{56/54}$Fe of marine ferromanganese nodules and Precambrian BIF ranged from −1.6 to 0.9‰, respectively, relative to the mean of ~30 terrestrial and lunar basalts. In contrast, a uniform isotope composition was observed among these basalts to the limits of analytical precision at that time (±0.6‰ at 95% confidence) [13,15].

Based on the hypothesis that Fe isotope fractionation by enzyme-catalyzed kinetic processes would produce much larger effects than would inorganic fractionation, particularly at equilibrium, it was proposed that $\delta^{56/54}$Fe variations in ferromanganese nodules and BIF were of biogenic origin [5,13]. It was further suggested that, as a result, Fe isotopes might be used to study microbial activity in the geologic record [5].

The initial observations have held up remarkably well. In particular, subsequent studies tightened the uniformity of the igneous rock database to within ±0.1‰ [20]. Meteorites exhibit more variability, but are confined to ±0.6‰ [26,27]. In contrast, in sediments, Zhu et al. reported a range of variation of ~1‰ in a high-resolution study of an Atlantic ferromanganese crust [26].

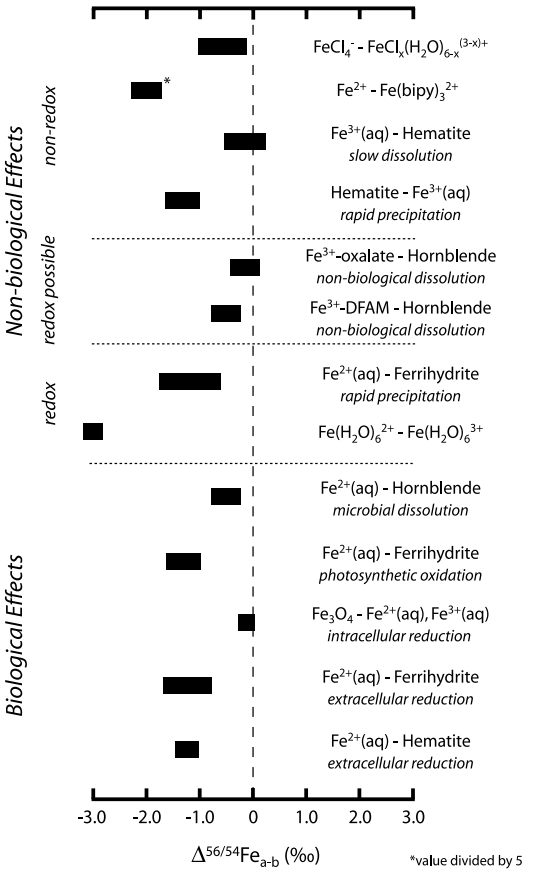

Fig. 5. Fe isotope fractionation effects. $\Delta^{56/54}Fe_{a-b} = \delta^{56/54}Fe_a - \delta^{56/54}Fe_b$. Fractionation factors are reported where possible. Uncertainties, represented by width of bars, ±2σ. All values in ‰. From top to bottom, non-biological experiments: $FeCl_4^-$–$FeCl_x(H_2O)_{6-x}^{(3-x)+}$, −0.1 to −1 [4,33]; Fe^{2+}–$Fe(bipy)_3^{2+}$, −10 [43]; Fe^{3+}(aq)–hematite (dissolution), −0.10±0.40 [42]; hematite–Fe^{3+}(aq) (precipitation), −1.32±0.24 [42]; Fe^{3+}–oxalate–hornblende (dissolution), −0.2±0.3 [32]; Fe^{3+}–DFAM–hornblende (DFAM = desferrioxamine B mesylate; dissolution), ≤−0.6±0.3 [32]; Fe^{2+}(aq)–ferrihydrite (oxidative precipitation), −0.9±0.3 [34]; $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$, 3.00±0.14 (22°C) [35]. Biological experiments: Fe^{2+}(aq)–hornblende (dissolution), −0.6±0.3 [32]; Fe^{2+}(aq)–ferrihydrite (anoxygenic photosynthesis, precipitation), −1.1 to −1.7 [30,31]; Fe_3O_4–Fe^{2+}(aq) (intracellular, magnetotactic Fe_3O_4), Fe^{3+}(aq), <−0.3 [6]; Fe^{2+}(aq)–ferrihydrite (extracellular, reductive dissolution), −1.3±0.6 [5,20]; Fe^{2+}(aq)–hematite (extracellular, reductive dissolution), −1.27±0.28 [20].

Although these particular data have recently been questioned [28], variations of up to ~0.7‰ are seen in a separate study of three Pacific crusts [29]. A detailed examination of a Late Archean–Early Proterozoic BIF from the Transvaal Supergroup (S. Africa) reveals the greatest variations: −2.5 to 1.0‰ across a range of mineral phases [30].

Biological results have been extended to different growth conditions, substrates and other Fe-metabolizing bacteria (including anoxygenic photosynthesizing Fe oxidizers) [20,30,31]. Fractionations of ~1.3–1.5‰ between substrates and products are typical, in all cases favoring heavy isotopes in Fe^{3+} phases. Fractionations of ‰ magnitude have also been reported between dissolved Fe^{2+} and Fe_3O_4, $FeCO_3$ and $(Fe,Ca)CO_3$ produced by Fe-reducing bacteria grown on ferrihydrite [30]. Dissolved Fe is fractionated by −0.5 to −0.6‰ after mobilization from hornblende in the presence of *Bacillus* sp. and *Streptomyces* sp. (interestingly, neither of these soil bacteria uses Fe as an electron donor or receptor in respiration) [32]. In contrast, the only study to date of Fe isotope effects in magnetite produced by magnetotactic bacteria revealed no fractionation [6] – an ironic finding in view of the prominence of magnetite in biosignature debates.

Hence, after several years of research, it continues to be the case that the variations of $\delta^{56/54}Fe$ in sediments dwarf those among igneous rocks, and that variations comparable to those in sediments are observed in most microbial experiments (Figs. 4, 5).

However, the biosignature hypothesis has proven less robust because non-biological chemical fractionation of Fe isotopes has been found ubiquitous and of comparable magnitude to biological fractionation (Fig. 5). The first such evidence came in the form of ~7‰ variations observed during anion exchange chromatography of Fe in HCl media [4]. These variations were attributed to chromatographic amplification of 0.1–1‰ equilibrium fractionation (Box 1) between coexisting Fe^{3+} chloro–aquo complexes. Although this interpretation has been challenged [20], it still seems most likely [33]. Extrapolating from these data, Anbar et al. hypothesized that isotope effects were likely to occur generically during equilibration of dissolved Fe species with significant differences in bonding energetics such as arise from differences in coordination geometry, ligand identity or Fe redox state.

Bullen et al. subsequently reported fractionation of ~0.9–1.8‰ favoring heavy Fe in the oxidized precipitate during non-biological oxidation and precipitation of ferrihydrite from dissolved Fe^{2+} at near-neutral pH, as well as variations of ~2‰ in probable abiotic ferric precipitates from an Fe-rich groundwater spring [34]. The precise mechanism of this fractionation is disputed. Equilibrium fractionation between $Fe(H_2O)_6^{2+}$ and rapidly oxidizing $FeOH(H_2O)_5^{+}$ was proposed [34]. However, an equilibrium fractionation of ~3‰ was subsequently determined between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, favoring heavy isotopes in the oxidized species [35,36]. Equilibrium fractionation experiments and their interpretations are not trivial, as witnessed by recent debate [37,38], but isotope effects between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ are likely to be important in natural systems. This matter is discussed more fully in the next section.

A theoretical examination of equilibrium isotope fractionation between inorganic Fe complexes, calibrated against spectroscopic data, indicates that variations of ~1–5‰ are expected [39], generally consistent with experiments. Even larger effects were predicted between coexisting Fe-bearing minerals in a novel study based on Mossbauer data [40,41]. The uncertainties on these theoretical estimates, of order 1‰, are relatively large. Reconciling theoretical predictions with observations remains a challenge (e.g., [30]).

Kinetic isotope effects (Box 1) are also significant. A fractionation of ~1‰ is seen during rapid precipitation of hematite from dissolved Fe^{3+} [42], favoring *light* isotopes in the precipitate. This is presumed due to a kinetic isotope effect during precipitation. A kinetic effect as large as ~10‰ has been inferred to occur when the Fe–N bond is broken when Fe^{2+}–bipyridine complexes are converted to Fe^{3+}–chloro complexes [43]. A kinetic isotope effect is also given as the explanation for fractionation of ~0.6‰ during abiotic leaching of Fe from horn-

blende in the presence of strong chelating ligands [32].

Collectively these studies indicate that, despite important ambiguities, non-biological chemistry in nature can produce $\delta^{56/54}$Fe variations comparable to those seen in sediments. Redox reactions should be particularly important; the equilibrium fractionation between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ encompasses the entire range of observed natural variation.

It must be emphasized that these findings do not invalidate the potential utility of Fe isotopes in biosignature applications, even as they obviously present complications for the interpretation of sedimentary $\delta^{56/54}$Fe. In many ways, the early evolution of the Fe isotope system parallels that of the C isotope system, for which there were similar debates about the importance of biogenic vs. non-biological effects in the fractionation between organic and inorganic compounds [44]. Even today, organic carbon with $\delta^{13}C = -20$ to -30‰ is not by itself indisputable evidence of biogenicity [45,46]. Yet the C isotope system is unquestionably useful in such research! The same can be said for the S isotope system, although interpretation of δ^{34}S in nature is substantially more complicated than δ^{13}C.

As with S isotopes, the most productive research path for Fe isotopes as biosignatures lies in controlled laboratory studies to determine the processes that fractionate Fe isotopes and their sensitivities to variables such as T, pH, reaction mechanism and reaction rate. Such studies can be coupled to contextual information in natural materials, such as mineralogy or other geochemical tracers, to provide insights into ancient processes. An early example of this strategy is the recent study of $\delta^{56/54}$Fe in Transvaal BIF, which matches mineralogical context with analogous laboratory experiments to infer a role for photosynthetic microbial Fe oxidation in Late Archean and Early Proterozoic oceans [30]. While not conclusive, $\delta^{56/54}$Fe data provide new constraints that must be met by models of Fe chemistry in these systems. In future efforts, coupling of $\delta^{56/54}$Fe data to other geochemical (and especially isotopic) tracers is likely to be especially powerful.

The following sections provide an initial framework for mechanistic understanding of Fe isotope systematics with an eye toward biosignature applications, along with a consideration of research frontiers beyond biosignatures.

4. Mechanisms and metabolism

Fe isotope studies are likely to be especially useful in unraveling mechanistic details of Fe environmental chemistry and biochemistry. This potential emerges from efforts to explain the relative magnitudes of Fe isotope fractionation in different experimental systems.

4.1. Kinetic or equilibrium isotope effects?

Among the more striking observations from Fig. 5 is that Fe isotope fractionation during biologically mediated Fe redox transformations is substantially *smaller* than the equilibrium fractionation between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$. Microbially mediated reduction of ferrihydrite or goethite discriminates between ^{54}Fe and ^{56}Fe by 1.3‰, corresponding to a fractionation factor, $\alpha_{Fe(III)-Fe(II)}$, of $\sim$1.0013 (Box 1) [20]. A similar effect has recently been reported to occur during microbially mediated oxidation of dissolved Fe^{2+} [31]. By comparison, $\alpha_{Fe(III)-Fe(II)} \sim 1.0030$ for non-biological redox equilibrium [35,36]. These relative magnitudes are contrary to the expectations of earlier studies which anticipated that biogenic effects would dominate over abiotic [13], but may nevertheless constitute a 'vital effect' useful in biosignature applications [20,30].

Expectations of large biogenic effects were not entirely unreasonable. Microbial reduction of Fe is presumably enzymatically catalyzed, which could result in expression of kinetic isotope effects. Iron biochemistry involves dissociation of Fe–O or Fe–N bonds that coordinate Fe in solution in order to bind Fe to enzyme active sites, and similar dissociation when Fe is released back to solution (O coordination is typical of inorganic Fe coordination in aqueous solution; biogenic chelating ligands may bind through O or N coordination). The magnitude of isotope fractionation associated with bond dissociation can be esti-

mated using transition state theory (TST) [47]. When the structures of the reactant and activated complex are similar, TST predicts $\alpha = {}^{54}k/{}^{56}k \sim ({}^{56}\mu/{}^{54}\mu)^{1/2}$, where k is a dissociation rate constant and μ is the reduced mass of the diatomic bond being dissociated. For dissociation of Fe–O or Fe–N bonds, $\alpha \sim 1.0040$ (Fig. 6). Larger effects are possible if the structure of the activated complex is similar to the dissociation product [43].

Why, then, are biological Fe isotope effects comparatively small? Possibly, Fe isotope fractionation in biological systems is not the result of a simple kinetic isotope effect, at least not related to bond dissociation. This supposition is strengthened by the observation that biogenic reaction products are lighter than reactants in the case of Fe^{3+} reduction [20], but heavier in the case of Fe^{2+} oxidation [31,48]; kinetic isotope effects generally favor reaction of lighter isotopes.

It is tempting to conclude that biogenic effects are controlled by ferrous–ferric equilibrium, based on the similar fractionation seen in biogenic Fe reduction and oxidation experiments [20,31]. However, if so, biogenic Fe isotope effects are too small to be consistent with simple control by the redox equilibrium between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$.

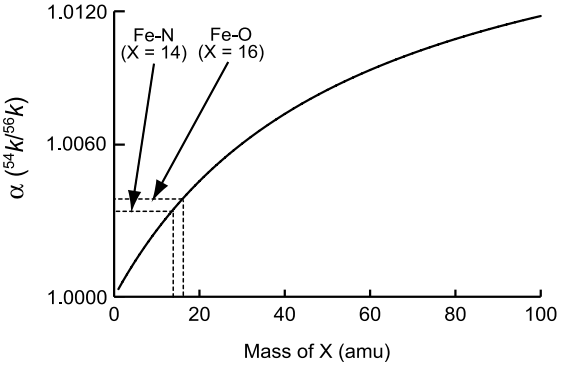

Fig. 6. Fractionation factor (α) resulting from kinetic isotope effect ($^{54}k/^{56}k$) associated with dissociation of the bond Fe–X, where X is any element having mass $m_X = 0$–100 amu. The effects from Fe–N ($m_X = 14$) and Fe–O ($m_X = 16$) dissociation are indicated. Following TST, $\alpha = {}^{54}k/{}^{56}k \sim ({}^{56}\mu/{}^{54}\mu)^{1/2}$, where ${}^{m}\mu = (m \times m_X)/(m+m_X)$ (see text).

4.2. Kinetics, equilibrium and speciation: toward an integrated approach

It is probable that Fe isotope fractionation during microbially mediated Fe redox reactions is the result of a series of equilibrium and/or kinetic effects which combine to produce less overall fractionation than would be expected from a simple, single-step process. This concept is broadly analogous to multi-step models of biological fractionation of C and N isotopes [49–51].

Fe complexation in solution is also likely to be critical, as suggested by several workers [4,20,32,34]. Aqueous speciation of Fe is dominated by $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ at strongly acidic pH in the absence of other ligands, but this is not typical of natural systems where pH is commonly higher and Fe speciation more complicated. Although chloro complexation has little effect on the ferric–ferrous isotope equilibrium in laboratory studies [35], there is evidence of at least some fractionation between coexisting mixed chloro–aquo Fe^{3+} species [4,33], and many other Fe-coordinating ligands are present in biological systems, and in nature, including organic ligands with high affinity for Fe.

A rigorous model of these factors is still difficult to develop for biological Fe redox systems because of their complexities [20,21,31]. However, the same concepts should apply to non-biological systems which are more amenable to analysis, such as oxidation and precipitation of ferrihydrite under steady-state conditions [34]. As with biogenic Fe isotope effects, fractionation in this reaction is smaller than the equilibrium between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ (Fig. 5). Additionally, fractionation varies by $\sim 2\times$ as a function of the relative importance of $FeHCO_3^+$ over the pH range 5.4–6.2 [34]. Can these observations be explained?

Consider a two-stage model:

$$Fe^{2+} - L_n \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} Fe^3 - L_n \quad (1)$$

$$Fe^{3+} - L_n \xrightarrow{k_2} Fe^{3+} - \text{oxide} \quad (2)$$

where L is the ligand binding Fe in solution (or ligands, if $n > 1$), and k_1, k_{-1} and k_2 are rate constants (concentrations of other reactants are

assumed constant, so rate constants are pseudo-first-order). This model includes a number of simplifications. The rate constant for dissolution of Fe^{3+}–oxide is neglected because it is likely to be trivially small compared to k_2, and an unlikely source of isotope discrimination [42]. More significantly, Fe speciation is assumed to be dominated by only one type of ligand complex for each redox state. Speciation in natural systems is more complicated. Nevertheless, this model illustrates some important points.

In the kinetic analysis of such a system, the rate of product formation, and hence the overall reaction rate (v), is equal to $k_2[Fe^{3+}–L_n]$. It is commonly assumed that intermediates like $[Fe^{3+}–L_n]$ rapidly attain 'microscopic steady state' or 'pseudoequilibrium' even as concentrations of reactant and final product are evolving, and this seems reasonable for the steady-state reactor system of [34]. Therefore:

$$d[Fe^{3+} - L_n]/dt =$$

$$k_1[Fe^{2+} - L_n] - (k_{-1} + k_2)\cdot v/k_2 = 0 \quad (3)$$

Isotopically, variants of Eq. 3 can be written for ^{56}Fe and ^{54}Fe. These equations can be related and simplified to obtain the ratio of rates for the overall reaction, $^{56}v/^{54}v$ [52]:

$$\frac{^{56}v}{^{54}v} = \frac{^{56}k_2[^{56}Fe^{3+} - L_n]}{^{54}k_2[^{54}Fe^{3+} - L_n]} =$$

$$\frac{\frac{^{56}k_1\ ^{56}k_2}{(^{56}k_{-1} + ^{56}k_2)}[^{56}Fe^{2+} - L_n]}{\frac{^{54}k_1\ ^{54}k_2}{(^{54}k_{-1} + ^{54}k_2)}[^{54}Fe^{2+} - L_n]} =$$

$$\frac{^{56}k_{eff}[^{56}Fe^{2+} - L_n]}{^{54}k_{eff}[^{54}Fe^{2+} - L_n]} = \alpha_{eff}\frac{[^{56}Fe^{2+} - L_n]}{[^{54}Fe^{2+} - L_n]} \quad (4)$$

where α_{eff} is the effective fractionation factor for the overall reaction [52].

It follows from these relations that a simple kinetic isotope effect is expressed if $k_2 \gg k_{-1}$, in which case $\alpha_{eff} \sim {}^{56}k_1/{}^{54}k_1$. At the other extreme, when $k_2 \ll k_{-1}$, $\alpha_{eff} \sim {}^{56}k_2/{}^{54}k_2 \times {}^{56}k_1/{}^{56}k_{-1} \times {}^{54}k_{-1}/{}^{54}k_1 = {}^{56}k_2/{}^{54}k_2 \times \alpha_{eq}$ where α_{eq} is the equilibrium fractionation factor between Fe^{2+}–L_n and Fe^{3+}–L_n (Box 1). In this case, the magnitude of overall fractionation depends on the relative magnitudes and directions of $^{56}k_2/^{54}k_2$ and α_{eq}. Apparently, α_{eq} cannot be cleanly observed, unless $^{56}k_2 = {}^{54}k_2$. Inferring from the fractionation seen during precipitation of hematite from dissolved Fe^{3+}, $^{56}k_2/^{54}k_2 \sim 1/1.0013 = 0.9987$ [42]. Hence, as previously suggested, based on this model it should come as no surprise that α_{eff} observed in the experiments of Bullen et al. [34] does not match α_{eq} observed by Johnson et al. [36].

Quantitatively, the relative magnitudes of k_2 and k_{-1} are in some dispute. It has been argued that electron transfer between Fe complexes is rapid relative to the rate of precipitation so that $k_2 \ll k_{-1}$ [35–37]. Others suggest this condition only applies at low pH, and reverses at near-neutral pH because of rapid hydrolysis of Fe^{3+} [34,38]. Intriguingly, if it is assumed that $k_2 \ll k_{-1}$ and that Fe is present only in hexaquo complexes for which $\alpha_{eq} = 1.0030$, the model predicts $\alpha_{eff} \sim 1.0030 \times 0.9987 = 1.0017$ [35]. This result is similar to observations of 1.0009–1.0018 at pH 5.4–6.2 [34], suggesting that this limiting case reasonably approximates an environmentally relevant range of conditions and explains why $\alpha_{eff} < \alpha_{eq}$.

This model also helps illustrate how Fe speciation may 'modulate' α_{eff}. Several possibilities arise. First, the identity of L may affect α_{eq} [4,20,34]. Second, because different species react at different rates, and via different reaction pathways, the relative sizes of k_2 and k_{-1} and the value of $^{56}k_2/^{54}k_2$ may be speciation-dependent. Third, in the presence of more than one type of ligand, it is possible to have multiple ferrous reactants with different equilibrium isotopic compositions. In this case, speciation may have an important effect on α_{eff} even if $k_2 \ll k_{-1}$. Such considerations may explain why α_{eff} during oxidative precipitation varies systematically with Fe speciation [34].

4.3. *Implications for applications and future research*

The preceding analysis has several implications. First, despite the complexities of Fe aqueous geochemistry, such models seem capable of reconcil-

ing some early experimental datasets and of explaining some experimental phenomenology, offering a template for future research.

Second, it reinforces caution in the interpretation of 'vital effects'. Fractionation of ~1.0–1.5‰ may be typical of systems in which Fe undergoes oxidative precipitation because equilibrium and kinetic isotope effects are intertwined. If so, the deviation from $\alpha_{Fe(III)-Fe(II)} \sim 1.0030$ is not strictly a biological phenomenon.

Third, as noted previously [30,31], it is striking that the fractionation discussed above is similar to that in biologically mediated Fe oxidation *and* reduction experiments (Fig. 5). This suggests – but does not prove – similar mechanisms. It is possible that a combination of reactions like Eqs. 1 and 2 occur in biological systems as well. Enzymatic activity may serve not so much to generate kinetic isotope effects as to catalyze ferric–ferrous equilibration. Uniquely biological effects, if they exist, may lie in the modulation of α_{eff} by Fe speciation [20]. Quantitative analysis requires consideration of a number of other processes as well, such as uptake of Fe^{3+}–L_n by microorganisms and adsorption of Fe^{2+} to ferrihydrite surfaces [31,53,54].

Clearly, unraveling such complications will require careful, reductionist laboratory experiments focused on Fe speciation and reaction kinetics. Such experiments should be a high priority.

At the same time, it must be recognized that rigorous Fe isotope laboratory experiments approximating natural conditions can be very challenging (e.g., [21]). Therefore, the development of accurate and precise theoretical models to predict isotope effects is also important. Initial theoretical efforts utilizing vibrational spectra and the classical computational approach of Urey [55] and Bigeleisen [56] predicted $\alpha_{Fe(III)-Fe(II)} \sim 5.4$‰ [39], nearly twice experimental observations [21,35]. This has been a source of some concern [30,35,36]. However, recent theoretical work using density functional theory (DFT) predicts fractionation consistent with experiments (Fig. 7) [57]. DFT is a well-established computational approach in modern theoretical chemistry that requires no a priori vibrational spectra and more realistically simulates molecular vibrations than do classical methods. Theory therefore seems to be converging with experiments, and is poised to begin making useful predictions of equilibrium Fe isotope effects between aqueous Fe species, predictions that can guide experiments, inform their interpretations, and perhaps substitute for experiments too challenging to conduct in a cost-effective manner.

As experimental and theoretical results accumulate, Fe isotopes should prove especially useful in examining Fe coordination in complex biological and environmental systems, particularly by ligands with high affinity for Fe [25]. The presence or absence and identities of Fe-coordinating ligands are central questions in Fe biochemistry and environmental biogeochemistry, with potentially global implications (e.g., [58]). The magnitude of Fe isotope effects should be sensitive to ligand identities.

In geological settings, a ligand effect is reported during Fe leaching from hornblende [32,59]. The underlying fractionation mechanism in this system remains unclear, but may help explain $\delta^{56/54}$Fe in soil systems [32,60,63]. Such data further suggest that $\delta^{56/54}$Fe of weathering products could carry information about the presence or absence of biogenic Fe chelating ligands in ancient environments. In this way, detailed mechanistic understanding may ultimately provide a solid footing for biosignature applications.

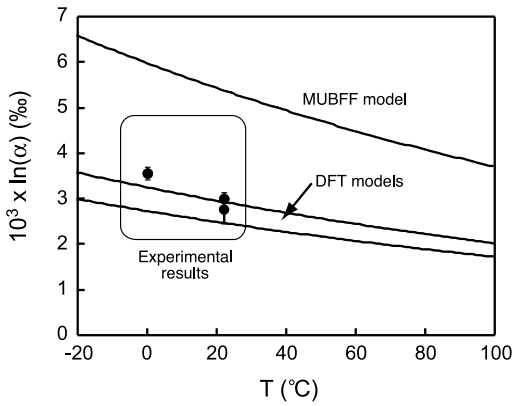

Fig. 7. Comparison of equilibrium fractionation factors for $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$ obtained experimentally [35,36] with those predicted by MUBFF [39] and DFT [57] models. Figure modified after [57].

5. Beyond biology

Interest in Fe isotopes in biogeoscience applications should not blind us to the utility of this isotope system in more traditional areas of geoscience.

For example, equilibrium fractionation between dissolved Fe^{2+} and Fe^{3+} complexes encompasses the range of most natural variations observed to date [36] (Figs. 4, 5). Thus fractionations of 2–3‰ in nature at least suggest aqueous, Fe redox chemistry. This may be useful in understanding Fe chemical history in specific systems, particularly paleoenvironmental systems. $\delta^{56/54}$Fe in ancient metamorphic rocks of uncertain origin could be used to differentiate between sedimentary and igneous histories; an offset of 1–3‰ from average crustal Fe would be consistent with a sedimentary origin. Similarly, a 1–3‰ offset between Fe in Martian dust and basalts could provide evidence of pervasive aqueous alteration.

Independent of mechanistic understanding of Fe isotope fractionation, $\delta^{56/54}$Fe contrasts could prove useful in tracing Fe sources to different regions of the ocean, a topic of considerable paleooceanographic interest because of the importance of Fe for marine biota. For example, Fe in deep sea hydrothermal fluids is fractionated $\sim$0.5‰ relative to Fe in igneous rocks [61,62]. After injection into the oxygenated water column, preferential loss of heavy isotopes during Fe oxidation and precipitation should result in an even lighter source of dissolved Fe to the deep sea [62]. In contrast, Fe reaching the oceans in the form of detrital particles may be relatively unfractionated [61], while dissolved Fe entering via rivers may exhibit isotopic variability related to weathering [63,64]. $\delta^{56/54}$Fe in ocean sediments could therefore provide information about the relative importance and/or source(s) of detrital, riverine and hydrothermal inputs. Such information is likely to be local and variable with time because of the short ocean residence time of Fe ($<$300 years), an expectation consistent with geographic and temporal variability reported in recent high-resolution sediment data [29]. Such variability may be advantageous given interest in correlating changes in Fe supply with temporal and geographic changes in primary production.

Perhaps most intriguing are recent reports of small (typically $<$0.5‰) variations in $\delta^{56/54}$Fe between igneous minerals [25,65–67]. These include $\delta^{56/54}$Fe variations of $\sim$0.2‰ between Fe metal and olivine in pallasite meteorites, $\sim$0.4‰ between amphibole and olivine in terrestrial mantle xenoliths, and $\sim$0.2‰ between igneous rocks from the Moon and Mars. These observations are challenging because they approach current analytical limits, particularly with respect to matrix effects. However, such variations may open the door to the use of Fe isotopes to study processes in solid Earth geochemistry and planetary formation, such as the effects of giant impacts (e.g., [67]) or mantle redox state, as well as to using Fe isotopes to differentiate among Fe sources. Careful, systematic studies of such variations are needed. The potential rewards are well worth the effort.

6. Future frontiers

While the Fe stable isotope community obviously does not suffer from a lack of research topics, it is not too early to peer beyond current horizons to more distant frontiers. A glance at the trajectory of light stable isotope research is thought-provoking. There, 'compound-specific' analyses are proving extremely useful, particularly in the case of C isotopes. Analogous measurements of Fe-bearing biomolecules are possible, and could prove useful both for elucidating metal metabolism and as a means of looking for evidence of particular metabolisms in nature.

On another frontier, the light stable isotope community is just beginning to come to grips with the fact that mass fractionation in multi-isotope systems follows different rules when kinetics, rather than chemical equilibrium, governs mass fractionation; the slope on a plot of δ^{18}O vs. δ^{17}O is not invariant as often assumed, but depends on reaction mechanism [68]. The same is surely true of Fe isotopes. Such measurements would be a powerful tool in Fe biogeochemical studies, but require a substantial improvement in

analytical precision – a worthy goal for the emerging generation of instruments.

Finally, although the primary motivation for Fe stable isotope research has come from the geosciences, important applications may await in other areas. Variations of $\delta^{56/54}$Fe have been reported up the food chain, and between male and female blood plasma [25,69], suggesting applications in ecology and biomedical research. Fe speciation and redox chemistry are as important in human biology as in the environment. Indeed, pathogenic bacteria and the human immune system routinely struggle for control of Fe in vivo [70]; manipulation of Fe speciation to reduce free Fe availability is one of the body's basic defenses against infection. Hence, it would be surprising if research into Fe isotope fractionation did not ultimately prove useful in biomedicine.

Acknowledgements

I am grateful to the students of EES 263/463 for helping me to see old papers in a new light, to Alex Halliday for early encouragement and recent patience, and to Francis Albarède for first demonstrating MC-ICP-MS stable isotope possibilities. The 'heavy' stable isotope research community is thanked for five memorable years of innovation. Comments by Bridget Bergquist, Ed Boyle, Tom Bullen, Clark Johnson, Tom Johnson, Mark Rehkämper and an anonymous reviewer substantially improved the manuscript. This work was supported by NSF (EAR 0003565) and the NASA Astrobiology Institute.*[AH]*

References

[1] K.H. Coale, K.S. Johnson, S.E. Fitzwater, R.M. Gordon, S. Tanner, F.P. Chavez, L. Ferioli, C. Sakamoto, P. Rogers, F. Millero, P. Steinberg, P. Nightingale, D. Cooper, W.P. Cochlan, M.R. Landry, J. Constantinou, G. Rollwagen, A. Trasvina, R. Kudela, A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, Nature 383 (1996) 495–501.

[2] P.G. Falkowski, R.T. Barber, V. Smetacek, Biogeochemical controls and feedbacks on ocean primary production, Science 281 (1998) 200–206.

[3] K.H. Nealson, B.L. Cox, Microbial metal-ion reduction and Mars: extraterrestrial expectations?, Curr. Opin. Microbiol. 5 (2002) 296–300.

[4] A.D. Anbar, J.E. Roe, J. Barling, K.H. Nealson, Nonbiological fractionation of iron isotopes, Science 288 (2000) 126–128.

[5] B.L. Beard, C.M. Johnson, L. Cox, H. Sun, K.H. Nealson, C. Aguilar, Iron isotope biosignatures, Science 285 (1999) 1889–1892.

[6] K.W. Mandernack, D.A. Bazylinski, W.C. Shanks, T.D. Bullen, Oxygen and iron isotope studies of magnetite produced by magnetotactic bacteria, Science 285 (1999) 1892–1896.

[7] G.E. Valley, H.H. Anderson, A comparison of the abundance ratios of the isotopes of terrestrial and of meteoritic iron, J. Am. Chem. Soc. 69 (1947) 1871–1875.

[8] J. Volkening, D.A. Papanastassiou, Iron isotope anomalies, Astrophys. J. 347 (1989) L43–L46.

[9] T. Walczyk, Iron isotope ratio measurements by negative thermal ionisation mass spectrometry using FeF4-molecular ions, Int. J. Mass Spectrom. Ion Proc. 161 (1997) 217–227.

[10] A. Gotz, K.G. Heumann, Iron isotope ratio measurements with the thermal ionization technique using a compact quadrupole mass-spectrometer, Int. J. Mass Spectrom. Ion Proc. 83 (1988) 319–330.

[11] P.R. Dixon, R.E. Perrin, D.J. Rokop, R. Maeck, D.R. Janecky, J.P. Banar, Measurement of iron isotopes (Fe-54, Fe-56, Fe-57, and Fe-58) in submicrogram quantities of iron, Anal. Chem. 65 (1993) 2125–2130.

[12] P.D.P. Taylor, R. Maeck, P. Debievre, Determination of the absolute isotopic composition and atomic-weight of a reference sample of natural iron, Int. J. Mass Spectrom. Ion Proc. 121 (1992) 111–125.

[13] B.L. Beard, C.M. Johnson, High precision iron isotope measurements of terrestrial and lunar materials, Geochim. Cosmochim. Acta 63 (1999) 1653–1660.

[14] T.D. Bullen, P.M. McMahon, Using stable Fe isotopes to assess microbially-mediated Fe^{3+} reduction in a jet-fuel contaminated aquifer, Mineral. Mag. 62A (1998) 255–256.

[15] C.M. Johnson, B.L. Beard, Correction of instrumentally produced mass fractionation during isotopic analysis of Fe by thermal ionization mass spectrometry, Int. J. Mass Spectrom. Ion Proc. 193 (1999) 87–99.

[16] A.N. Halliday, D.-C. Lee, J.N. Christensen, A.J. Walder, P.A. Freedman, C.E. Jones, C.M. Hall, W. Yi, D. Teagle, Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry, Int. J. Mass Spectrom. Ion Proc. 146 (1995) 21–33.

[17] N.S. Belshaw, X.K. Zhu, Y. Guo, R.K. O'Nions, High precision measurement of iron isotopes by plasma source mass spectrometry, Int. J. Mass Spectrom. Ion Proc. 197 (2000) 191–195.

[18] C.N. Marechal, P. Telouk, F. Albarede, Precise analysis

of copper and zinc isotopic composition by plasma-source mass spectrometry, Chem. Geol. 156 (1999) 251–273.
[19] A.D. Anbar, K.A. Knab, J. Barling, Precise determination of mass-dependent variations in the isotopic composition of molybdenum using MC-ICPMS, Anal. Chem. 73 (2001) 1425–1431.
[20] B.L. Beard, C.M. Johnson, J.L. Skulan, K.H. Nealson, L. Cox, H. Sun, Application of Fe isotopes to tracing the geochemical and biological cycling of Fe, Chem. Geol. 195 (2003) 87–117.
[21] C. Johnson, B. Beard, S. Welch, L. Croal, D. Newman, K. Nealson, Experimental constraints on Fe isotope fractionations during biogeochemical cycling of Fe, Geochim. Cosmochim. Acta 66 (2002) A371.
[22] S. Weyer, J. Schwieters, High precision Fe isotope measurements with high mass resolution MC-ICP-MS, Int. J. Mass Spectrom. Ion Proc. 226 (2003) 355–368.
[23] G.L. Arnold, S. Weyer, A.D. Anbar, Fe isotope variations in natural materials measured using high mass resolution MC-ICP-MS, Anal. Chem., in press, 2003.
[24] R.W. Carlson, E.H. Hauri, C.M.O.D. Alexander, Matrix-dependent isotope mass fractionation in the ICP-MS, in: J.G. Holland, S. Tanner (Eds.), Plasma Source Mass Spectrometry: The New Millenium, The Royal Society of Chemistry, Cambridge, 2001, pp. 288–297.
[25] X.K. Zhu, Y. Guo, R.J.P. Williams, R.K. O'Nions, A. Matthews, N.S. Belshaw, G.W. Canters, E.C. de Waal, U. Weser, B.K. Burgess, B. Salvato, Mass fractionation processes of transition metal isotopes, Earth Planet. Sci. Lett. 200 (2002) 47–62.
[26] X.-K. Zhu, K. O'Nions, Y. Guo, B.C. Reynolds, Secular variation of iron isotopes in North Atlantic Deep Water, Science 287 (2000) 2000–2002.
[27] X.K. Zhu, Y. Guo, R.K. O'Nions, E.D. Young, R.D. Ash, Isotopic homogeneity of iron in the early solar nebula, Nature 412 (2001) 311–313.
[28] S. Levasseur, M. Frank, J.R. Hein, A.N. Halliday, Iron isotope variations in marine ferromanganese deposits, Geophys. Res. Abstr. 5 (2003) 11009.
[29] N.-C. Chu, C.M. Johnson, B.L. Beard, C.R. German, R.W. Nesbitt, A. Usui, Secular Fe isotope variations in the NW and Central Pacific Ocean, Geochim. Cosmochim. Acta 67 (2003) A66.
[30] C.M. Johnson, B.L. Beard, N.J. Beukes, C. Klein, J.M. O'Leary, Ancient geochemical cycling in the Earth as inferred from Fe isotope studies of banded iron formations from the Transvaal Craton, Contrib. Mineral. Petrol. 144 (2003) 523–547.
[31] L.R. Croal, C. Johnson, B. Beard, D.K. Newman, Iron isotope fractionation by Fe(II)-oxidizing photoautotropic bacteria, Geochim. Cosmochim. Acta, in press, 2003.
[32] S.L. Brantley, L. Liermann, T.D. Bullen, Fractionation of Fe isotopes by soil microbes and organic acids, Geology 29 (2001) 535–538.
[33] J.E. Roe, A.D. Anbar, J. Barling, Nonbiological fractionation of Fe isotopes: evidence of an equilibrium isotope effect, Chem. Geol. 195 (2003) 69–85.
[34] T.D. Bullen, A.F. White, C.W. Childs, D.V. Vivit, M.S. Schulz, Demonstration of significant abiotic iron isotope fractionation in nature, Geology 29 (2001) 699–702.
[35] S.A. Welch, B.L. Beard, C.M. Johnson, P.S. Braterman, Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(II) and Fe(III), Geochim. Cosmochim. Acta, in press.
[36] C.M. Johnson, J.L. Skulan, B.L. Beard, H. Sun, K.H. Nealson, P.S. Braterman, Isotopic fractionation between Fe(III) and Fe(II) in aqueous solutions, Earth Planet. Sci. Lett. 195 (2002) 141–153.
[37] C.M. Johnson, B.L. Beard, P.S. Braterman, S.A. Welch, Reply to Comment on 'Isotopic fractionation between Fe(III) and Fe(II) in aqueous solutions' by Thomas D. Bullen, Arthur F. White and Cyril W. Childs, Earth Planet. Sci. Lett. 206 (2003) 233–236.
[38] T.D. Bullen, A.F. White, C.W. Childs, Comment on 'Isotopic fractionation between Fe(III) and Fe(II) in aqueous solutions' by Clark Johnson et al. [Earth Planet. Sci. Lett. 195 (2002) 141–153], Earth Planet. Sci. Lett. 206 (2003) 229–232.
[39] E.A. Schauble, G.R. Rossman, H.P. Taylor, Theoretical estimates of equilibrium Fe-isotope fractionations from vibrational spectroscopy, Geochim. Cosmochim. Acta 65 (2001) 2487–2597.
[40] V.B. Polyakov, Equilibrium fractionation of the iron isotopes: Estimation from Mossbauer spectroscopy data, Geochim. Cosmochim. Acta 61 (1997) 4213–4217.
[41] V.B. Polyakov, S.D. Mineev, The use of Mossbauer spectroscopy in stable isotope geochemistry, Geochim. Cosmochim. Acta 64 (2000) 849.
[42] J.L. Skulan, B.L. Beard, C.M. Johnson, Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(III) and hematite, Geochim. Cosmochim. Acta 66 (2002) 2995–3015.
[43] A. Matthews, X.-K. Zhu, K. O'Nions, Kinetic iron stable isotope fractionation between iron (-II) and (-III) complexes in solution, Earth Planet. Sci. Lett. 192 (2001) 81–92.
[44] H. Craig, Geochemical implications of the isotopic composition of carbon in ancient rocks, Geochim. Cosmochim. Acta 6 (1954) 186–196.
[45] S.J. Mojzsis, G. Arrhenius, K.D. McKeegan, T.M. Harrison, A.P. Nutman, C.R.L. Friend, Evidence for life on Earth before 3,800 million years ago, Nature 384 (1996) 55–59.
[46] M.A. van Zuilen, A. Lepland, G. Arrhenius, Reassessing the evidence for the earliest traces of life, Nature 418 (2002) 627–630.
[47] J. Bigeleisen, The relative velocities of isotopic molecules, J. Chem. Phys. 17 (1949) 675–678.
[48] S. Levasseur, R.J. Warthmann, A.N. Halliday, Fractionation of Fe isotopes by anaerobic phototrophic bacteria, Geochim. Cosmochim. Acta 66 (2002) A450.
[49] M.H. Fogel, M.L. Cifuentes, Isotope fractionation during primary production, in: M.H. Engel, S.A. Macko (Eds.),

Organic Geochemistry: Principles and Applications, Plenum, New York, 1993, pp. 73–98.
[50] J.M. O'Leary, Carbon isotope fractionation in plants, Phytochemistry 20 (1981) 553–567.
[51] R. Park, S. Epstein, Carbon isotope fractionation during photosynthesis, Geochim. Cosmochim. Acta 21 (1960) 110–126.
[52] L.C.S. Melander, W.H. Saunders, Reaction rates of isotopic molecules, R.E. Krieger Publishing Co., Malabar, 1987.
[53] G.A. Icopini, S.L. Brantley, S. Ruebush, M. Tien, T.D. Bullen, Iron fractionation during microbial reduction of iron, EOS Trans. AGU 83 (2002) B11A-0706.
[54] N. Teutsch, U. von Gunten, D. Porcelli, A.N. Halliday, Iron isotope fractionation in groundwater, Geochim. Cosmochim. Acta 66 (2002) A769.
[55] H.C. Urey, The thermodynamic properties of isotopic substances, J. Chem. Soc. (1947) 562–581.
[56] J. Bigeleisen, M.G. Mayer, Calculation of equilibrium constants for isotopic exchange reactions, J. Chem. Phys. 15 (1947) 261–267.
[57] A.D. Anbar, A. Jarzecki, T. Spiro, Theoretical investigation of equilibrium iron isotope fractionation between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, Geochim. Cosmochim. Acta, submitted, 2003.
[58] N.M. Price, F.M.M. Morel, Biological cycling of iron in the ocean, in: Metal Ions in Biological Systems, Vol. 35, 1998, pp. 1–36.
[59] S.L. Brantley, L.J. Liermann, A.D. Anbar, G.A. Icopini, R.L. Guynn, J. Barling, Fe isotopic fractionation during mineral dissolution with and without bacteria, Geochim. Cosmochim. Acta, submitted.
[60] J.G. Wiederhold, F. von Blanckenburg, Iron isotope variations in a complete natural soil catena with lateral iron mobilization and reprecipitation, Geochim. Cosmochim. Acta 66 (2002) A834.
[61] B.L. Beard, C.M. Johnson, K.L. Von Damm, R. Poulson, Iron isotope constraints on Fe cycling and mass balanced in oxygenated Earth, Geology 31 (2003) 629–632.
[62] M. Sharma, M. Polizzotto, A.D. Anbar, Iron isotopes in hot springs along the Juan de Fuca Ridge, Earth Planet. Sci. Lett. 194 (2001) 39–51.
[63] M.S. Fantle, D.J. DePaolo, The isotopic composition of continental iron and implications for the global iron cycle, EOS Trans. AGU 83 (2002), Fall Meeting Suppl., Abstract V22B-1234.
[64] B.A. Bergquist, E.A. Boyle, Iron isotopic composition of the Amazon River, EOS Trans. AGU 83 (2002), Fall Meeting Suppl., Abstract OS12C-0290.
[65] B.L. Beard, C.M. Johnson, High temperature inter-mineral Fe isotope fractionation, Geochim. Cosmochim. Acta 67 (2003) A35.
[66] H. Williams, D.C. Lee, S. Levasseur, N. Teutsch, F. Poitrasson, M. Rehkamper, A.N. Halliday, Iron isotope composition of mid-ocean ridge basalts and mantle peridotites, Geochim. Cosmochim. Acta 66 (2002) A838–A838.
[67] F. Poitrasson, A.N. Halliday, D.C. Lee, S. Levasseur, N. Teutsch, Iron isotope evidence for the origin of the Moon through partial vaporization, Geophys. Res. Abs. 5 (2003) 05120.
[68] E.D. Young, A. Galy, H. Nagahara, Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, Geochim. Cosmochim. Acta 66 (2001) 1095–1104.
[69] T. Walczyk, F. von Blanckenburg, Natural iron isotope variations in human blood, Science 295 (2002) 2065–2066.
[70] C. Ratledge, L.G. Dover, Iron metabolism in pathogenic bacteria, Annu. Rev. Plant Biol. 54 (2000) 881–941.
[71] X.K. Zhu, A. Makishima, Y. Guo, N.S. Belshaw, R.K. O'Nions, High precision measurement of titanium isotope ratios by plasma source mass spectrometry, Int. J. Mass Spectrom. 220 (2002) 21–29.
[72] A.S. Ellis, T.M. Johnson, T.D. Bullen, Chromium isotopes and the fate of hexavalent chromium in the environment, Science 295 (2002) 2060–2062.
[73] A. Galy, O.S. Pokrovsky, J. Schott, Ge-isotopic fractionation during its sorption on goethite: an experimental study, Geochim. Cosmochim. Acta 66 (2002) A259.
[74] A. Galy, C. Pomies, J.A. Day, O.S. Pokrovsky, J. Schott, High precision measurement of germanium isotope ratio variations by multiple collector-inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 18 (2003) 115–119.
[75] T.M. Johnson, T.D. Bullen, P.T. Zawislanski, Selenium stable isotope ratios as indicators of sources and cycling of selenium: Results from the northern reach of San Francisco Bay, Environ. Sci. Technol. 34 (2000) 2075–2079.
[76] J. McManus, T. Nägler, C. Siebert, C.G. Wheat, D. Hammond, Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge flank alteration, Geochem. Geophys. Geosyst. 3 (2002) 1078.
[77] C. Siebert, T.F. Nägler, F. von Blanckenburg, J.D. Kramers, Molybdenum isotope records as a potential new proxy for paleoceanography, Earth Planet. Sci. Lett. 211 (2003) 159–171.
[78] J. Barling, G.L. Arnold, A.D. Anbar, Natural mass-dependent variations in the isotopic composition of molybdenum, Earth Planet. Sci. Lett. 193 (2001) 447–457.
[79] F. Wombacher, M. Rehkamper, K. Mezger, C. Munker, A. Bischoff, Stable isotope compositions of cadmium in stony meteorites, Geochim. Cosmochim. Acta 66 (2002) A844.
[80] D.G. Sands, K.J.R. Rosman, J.R. de Laeter, A preliminary study of cadmium mass fractionation in lunar soils, Earth Planet. Sci. Lett. 186 (2001) 103–111.
[81] M. Rehkamper, M. Frank, J.R. Hein, D. Porcelli, A. Halliday, J. Ingri, V. Liebetrau, Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits, Earth Planet. Sci. Lett. 197 (2002) 65–81.
[82] H. Hintelmann, S.Y. Lu, High precision isotope ratio

measurements of mercury isotopes in cinnabar ores using multi-collector inductively coupled plasma mass spectrometry, Analyst 128 (2003) 635–639.
[83] D.S. Lauretta, B. Klaue, J.D. Blum, P.R. Buseck, Mercury abundances and isotopic compositions in the Murchison (CM) and Allende (CV) carbonaceous chondrites, Geochim. Cosmochim. Acta 65 (2001) 2807–2818.
[84] O. Rouxel, J. Ludden, J. Carignan, L. Marin, Y. Fouquet, Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry, Geochim. Cosmochim. Acta 66 (2002) 3191–3199.
[85] O. Rouxel, L. Ludden, Y. Fouquet, Antimony isotope variations in natural systems and implications for their use as geochemical tracers, Chem. Geol. 200 (2003) 25–40.

Ariel D. Anbar obtained an A.B. at Harvard in 1989 and escaped from the Lunatic Asylum at the California Institute of Technology with a Ph.D. in 1996. He subsequently joined the faculty at the University of Rochester, where he was among the first to investigate the geochemistry of 'non-traditional' stable isotope systems using MC–ICP–MS. Now an Associate Professor, Anbar and his research group focus on transition metal biogeochemistry and the application of Fe and Mo stable isotopes to study ancient life and environments. Anbar was the recipient of the Donath Medal (Young Scientist Award) of the Geological Society of America in 2002.