Combining Metal Stable Isotope Fractionation Theory with Experiments

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INTRODUCTION

Precise measurements of isotope abundance variations are now available for many elements, with more being added all the time. A general aim of isotope geochemistry is to understand the geochemical mechanisms that generate isotope signatures for each of the elements, so that measurements of natural samples can be interpreted as robustly as possible. Theory and experiments can both contribute to this understanding.

The isotopes of an element are powerful geochemical tracers. They have nearly identical electronic structures, and therefore their chemical behaviors are similar, but small differences in mass produce small differences in reaction rates. This results in slight chemical partitioning, in which isotopes are partially separated or fractionated during incomplete chemical reactions, phase changes, advective transport, and diffusion. Because these differences are subtle, they are recorded in natural materials as small deviations (usually expressed in per mil, ‰) in isotope composition (see Bullen and Eisenhauer 2009 this issue). Isotope fractionation is mass dependent in most cases, which means that the change in any isotope ratio, for a given element in a given reaction, varies roughly in proportion to the difference in mass between the isotopes. Early attempts to understand the thermodynamic basis for isotope fractionation during chemical and physical reactions focused on the light elements (H, B, C, N, O, and S), which generally show the greatest fractionation (Bigeleisen and Mayer 1947; Urey 1947). These studies established the central role of vibrational energy in controlling the distribution of isotopes among different phases and species at equilibrium. They also showed that equilibrium isotope separation is highly dependent on temperature. A general observation is that substances with strong bonds tend to concentrate heavier isotopes, whereas substances with weak bonds concentrate lighter isotopes (e.g. Fe3+aq versus Fe2+aq; Fig. 1). Several reviews present detailed descriptions of the thermodynamic relationships between vibrational frequencies, vibrational zero-point energies, and isotope fractionation factors (e.g. Chacko et al. 2001; Schauble 2004).

A simplified formula for estimating mass-dependent fractionation (adapted from Bigeleisen and Mayer 1947) is suitable for molecules if one assumes rigid rotation and harmonic vibration:

\[
\beta = \frac{3n-6}{n} \prod_{i=1}^{n} \frac{U_i^*}{U_i} \exp \left( \frac{U_i - U_i^*}{2kT} \right) \frac{1 - \exp (-U_i)}{1 - \exp (-U_i^*)} \quad (1)
\]

where \( \beta \) is the fractionation factor of a molecule relative to an ideal atomic gas, \( n \) represents the number of atoms in the molecule (3n–6 is thus the number of vibrational frequencies in the molecule; for a linear molecule this would be 3n–5), \( U_i = \hbar \nu_i/k_B T \) for the \( i \)th vibrational mode, \( \hbar \) is Planck’s constant, \( \nu \) represents the vibrational frequency, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( U_i^* \) is the analogous term for a molecule where one atom is substituted with a heavier isotope \( ^{18}X \). Although we are rarely interested in isotope properties of a monoatomic gas (with the exception of Hg\(^\text{aq} \) vapor), this formulation serves as a simple point of comparison: the equilibrium fractionation factor between any two substances is simply the ratio of their \( \beta \)'s.

\[
\alpha_{A-B} = \frac{(X/X)_A}{(X/X)_B} = \frac{\beta_A}{\beta_B} \quad (2)
\]

where \( \alpha_{A-B} \) is the equilibrium isotope fractionation factor between substances \( A \) and \( B \). The critical input for a theoretical calculation thus includes the vibrational frequencies of the substances of interest and the effects of isotope substitution on those frequencies. Bigeleisen and Mayer (1947) analyzed the chemical systematics of these equations and derived a series of approximate formulae for...
Bond strength strongly affects isotope fractionation. Aqueous Fe$^{3+}$ (green, at left) forms weaker bonds with water molecules than Fe$^{2+}$ (violet, at right). This is illustrated by the shape of the 0.05 e$^–$/bohr$^3$ electron-density isosurface, which pinches out (arrow) near the midpoint of each Fe$^{2+}$–OH$_2$ bond, but persists for Fe$^{3+}$–OH$_2$ bonds. Greater electron density along the bond axes correlates with stronger, more covalent bonds, which also tend to have higher force constants. At room temperature, $^{56}$Fe/$^{54}$Fe is ~3‰ higher for aqueous Fe$^{3+}$ than coexisting Fe$^{2+}$ (Johnson et al. 2002). Electron-density surfaces are derived from hybrid density functional theory (DFT) calculations.

Fractionation factors in terms of fundamental constants, isotopic masses, temperatures, and bond properties. Following a similar approach, it is possible to derive the following expression:

$$\alpha_{A-B} \approx 1 + \frac{\Delta m}{m^2} \frac{h^2}{96\pi^2 k^2 T^2} \left(\frac{F_A - F_B}{m^2} - \frac{\Delta m}{m^2} \right)$$

where $m$ represents the atomic mass of the element being investigated; $\Delta m$, the difference in the mass for the isotopes of interest; $F_A$, the sum of the bond force constants for substance $A$ that oppose displacement of the atom of interest in each of three perpendicular directions; and $F_B$, the corresponding sum of force constants for substance $B$. This expression correctly predicts that most fractionation varies as the reciprocal of the square of the temperature. It also indicates a general tendency for mass-dependent isotope fractionation to become much smaller in heavy elements (~$m^{-2}$). The strong temperature dependence of equilibrium fractionation is the basis of much stable isotope paleothermometry, including the carbonate–water oxygen isotope thermometer. The equation also shows how chemical bonding properties control isotope fractionation (for example, through the tendency of oxidized compounds to have high force constants, i.e. stronger, shorter, and thus stiffer bonds). The theoretical basis for isotope fractionation in light elements is well established. Although some early theoretical studies investigated fractionation in heavier elements and metals (e.g. Bigeleisen and Mayer 1947), geochemists paid relatively little attention to these “nontraditional” elements until the resolution of analytical techniques improved.

**METAL ISOTOPES**

It is reasonable to expect that metal isotope fractionation would be similar to the well-studied light isotope systems—that is, show strong sensitivity to temperature and oxidation state—with generally less fractionation with increasing atomic mass. Observations are consistent with these expectations: metal isotope fractionation in natural materials is on the order of a few per mil or less, much smaller than the percent-level fractionation found for carbon, oxygen, and sulfur (lithium, the lightest metal, is an exception). The largest fractionations are generally found in low-temperature materials and are often associated with oxidation–reduction (redox) reactions (e.g. Fe$^{2+}$ versus Fe$^{3+}$), although significant isotope abundance variations are also found in nonredox metals such as calcium and magnesium. In summary, metal isotope relationships are broadly consistent with those observed in light-element systems. Thus it is not surprising that the efforts of theorists have focused on adapting mass-dependent fractionation models to metal isotope systems that have recently become interesting.

Measurements and theoretical arguments also provide strong evidence that one or more processes leading to mass-independent fractionation are important for the heaviest elements (Fuji et al. 1989, 2006; Bigeleisen 1996; Bergquist and Blum 2007; Schauble 2007; Abe et al. 2008). For uranium, the element best studied in the laboratory, reduction–oxidation experiments [U(VI) versus U(IV)] show that $^{235}_{\text{U}}$/$^{238}_{\text{U}}$ fractionates only 14% more than $^{238}_{\text{U}}$/$^{235}_{\text{U}}$, in spite of a 33% greater mass difference (Fuji et al. 1989). Furthermore, heavy uranium isotopes are concentrated in reduced U(IV) species, opposite to typical mass-dependent fractionation. Bigeleisen (1996) showed that this mass-independent fractionation correlates with spectroscopic observations of nuclear field shifts in uranium—i.e. changes in the energy of electronic transitions caused by differences in the volume and the shape of atomic nuclei. Nuclear field shift energy in uranium (0.4 cm$^{-1}$ = 5 J/mol) roughly matches the energy needed to drive the fractionation that is observed (3.5 J/mol per mil at 420 K). These shifts increase toward the lower rows of the periodic table, suggesting that this effect is most important for the heaviest elements. Evidence for geochemical nuclear field shift fractionation is known for thallium and uranium (Schauble 2007; Weyer et al. 2008), but also extends to lighter elements such as ruthenium and molybdenum (Fuji et al. 2006).

Mass-independent fractionation observed in mercury, particularly in fish and other biological samples, cannot be explained by the nuclear field effect, and is currently explained as a kinetic process, possibly magnetic coupling in spin-forbidden reactions (Bergquist and Blum 2007). Unfortunately, at present we lack a tractable quantitative theory of magnetic fractionation of metal isotopes. The fascinating fractionation behavior of mercury is discussed in another paper in this issue (Bergquist and Blum 2009 this issue).

**FIRST-PRINCIPLES CALCULATIONS**

Equilibrium, mass-dependent isotope fractionation is driven primarily by changes in molecular and crystalline vibration frequencies when one isotope is substituted for another. In practice, except in simple cases, the complete set of frequencies is not available. Some researchers have dealt with this shortcoming by reformulating Equation 3 in terms of other, more easily measured properties that depend on vibration energy, such as heat capacity, or by applying resonant and near-resonant X-ray scattering techniques (including Mössbauer and synchrotron methods; e.g. Polyakov 1997; Polyakov et al. 2007). X-ray scattering methods are excellent for directly probing the vibrational
properties of an element, even when it is embedded in a complex structure. These methods are becoming more useful as more spectroscopic data are collected.

Another approach is to model vibrational spectra, either by fitting an empirical potential field to known properties of the substances of interest and using the potential to calculate isotope vibration frequencies, or, more recently, by using first-principles electronic structure calculations. In these models, uncertainties in frequency estimates are typically the main limitation for the accuracy of calculated fractionation.

Ongoing advances in computer power and the wide distribution of both commercial and free computational chemistry software, such as Gaussian03 (Frisch et al. 2004) and Quantum Espresso (Baroni et al. www.pwscf.org), have made it possible to calculate the vibrational frequencies of many simple molecules and crystalline compounds using first-principles electronic structure theory. In these methods, an approximate solution to Schrödinger’s equation (or an analogous expression) is obtained for the material of interest. Vibrational frequencies then follow from analysis of the second derivative of the electronic energy with respect to atomic displacements (i.e. force constants). Isotope substitution is expected to have a negligible effect on electronic structure, so a matrix of force constants for the common isotope in a molecule or a crystal can be recycled to estimate vibrational frequencies of uncommon isotope-substituted species.

First-principles methods have two important advantages. First, isotope effects on vibrational frequencies can be calculated self-consistently, using a single set of force constants for each molecule. These effects are often small and may be beyond achievable precision for common spectroscopic methods, such as Raman and IR. So even in cases where spectral data are available for isotopically substituted species, it may not be practical to use them to predict isotope fractionation. First-principles vibrational models also have limited absolute accuracy, usually requiring empirical correction factors (e.g. Scott and Radom 1996); however, the errors are expected to be highly systematic and thus largely cancel when calculating isotope frequency shifts. In such a case, metal isotope models have an advantage: β-factors for most metal elements are quite small in natural materials [ranging from ~30–40‰ for 28Mg/24Mg (Schauble unpublished data) to 4–9‰ for 56Fe/54Fe (e.g. Polyakov 1997)] and ~1‰ for 202Hg/198Hg (Schauble 2007) to 4–9‰ for 56Fe/54Fe (e.g. Polyakov 1997) and ~1‰ for 202Hg/198Hg (Schauble 2007), all at 298 K, so a typical systematic error of 5–10‰ for calculated vibrational frequencies for one of the heavier elements is likely to be responsible for <1‰ of error in an estimated fractionation factor (Table 1). An equivalent error in a calculation using measured frequency shifts would require an accuracy of ca. 0.5 cm−1/mode (~1 cm−1 over all modes). Light elements (including H, C, and O) have larger β-factors (~60–16,000‰ at 298 K), so they are much more sensitive to scaling factor uncertainties. Another advantage of first-principles vibrational models is that other output from a model (e.g. bond lengths) can be directly compared with observations to test the accuracy of the model. Because a consistent procedure, with the same basic assumptions, can be applied to a range of materials, confirmation that a model does well for one molecule is good evidence that other, less well-studied sister species can also be modeled.

Recently, the first studies applying stable isotope fractionation theory to heavy elements in crystals have appeared, adapting periodic boundary condition density functional theory methods (e.g. Méheut et al. 2007). These methods have shown great success in predicting light-element stable isotope properties and in principle should be applicable to many elements. At present there are few direct points of comparison between first-principles crystal model results and experiments, but there is evidence of at least qualitative agreement for silicon isotope fractionation in clay minerals (Méheut et al. 2007).

A shortcoming of first-principles calculations is that complex systems are difficult to treat, especially aqueous solutions. The computational time (t) required for a first-principles vibration frequency calculation typically varies as a power of the number of atoms (N) in the system, i.e. $t = t_0 N^a$ (the exponent is higher for high-precision electronic structure methods). To keep computer time within practical limits, additional assumptions are required. Several exponents have been tested, including cluster models (for example, treating aqueous Fe$^{3+}$ as a gas-phase Fe(H$_2$O)$_{6}^{3+}$ molecule (Anbar et al. 2005) or as an Fe(H$_2$O)$_{6}^{3+}$ + 12 H$_2$O nanodroplet (Liu and Tang 2006; Hill and Schauble 2008)] and immersing a molecule in a cavity surrounded by a continuum approximating the dielectric properties of the solvent. Simpler analogues of complex biological molecules can also be modeled (e.g. Domagal-Goldman and Kubiicki 2008). In the best-studied case of redox fractionation between ferric and ferrous iron, even highly simplified methods give reasonable agreement (within 1‰ at 298 K) with exchange experiments (Johnson et al. 2002). Less has been done to examine solid solutions, crystal defects, and absorption phenomena. As computers become less expensive, more powerful, and more reliable, we expect improvements in the treatment of complex species.

**KINETIC PROCESSES**

Natural fractionation does not always reflect equilibrium. Diffusion, evaporation, and biological reactions all commonly produce isotope signatures, and these signatures have driven much of the excitement in metal isotope geochemistry. Although a substantial theoretical literature addresses kinetic fractionation processes for light elements, theoretical studies currently lag behind experimental and empirical observations.

Perhaps the most fundamental cause of kinetic isotope fractionation is diffusion. Molecules containing light isotopes diffuse fastest, so the products of transport-limited reactions are usually enriched in light isotopes. In the limiting case of pinhole diffusion, where the reaction consists simply of a molecule diffusing through a pore smaller than the mean free path of the gas, a simple rule applies:

$$\alpha_{\text{pinhole}} = \left(\frac{X/X}{X/X}_{\text{Initial}}\right)_{\text{Diffused}} = \left(\frac{M}{M^*}\right)$$

where $M$ represents the mass of the molecule containing the most abundant isotope, and $M^*$, the mass of a molecule containing an isotope of lesser abundance. This formulation assumes that substituted molecules are rare, that only one atom of element X is present in the molecule, and that only a small part of the initial reservoir diffuses.

Diffusion through solutions, minerals, and membranes shows qualitatively similar behavior, despite interfering interactions with neighboring atoms and molecules. For example, aqueous molybdenum isotope fractionation is largest when the diffusing molecule is small (so that $M/M^*$ is most different from 1) (Malinovsky et al. 2007). A more quantitative theoretical understanding of aqueous diffusion fractionation is beginning to emerge through computational...
Comparison of errors in estimated fractionation factors at 298 K because of systematic scaling of vibrational frequencies calculated with first-principle models. The error induced by a 0.5 cm$^{-1}$ error in a measured isotope shift in a 500 cm$^{-1}$ vibrational frequency is also shown.

<table>
<thead>
<tr>
<th>Exchanging molecules</th>
<th>Isotopes</th>
<th>Fractionation at 298 K (%)</th>
<th>Effect of 5% frequency scale factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(H$_2$O)$_6$]$^{3+}$ vs. [Fe(H$_2$O)$_6$]$^{2+}$</td>
<td>$^{56}$Fe/$^{54}$Fe</td>
<td>2.9</td>
<td>0.3</td>
</tr>
<tr>
<td>CO$_2$ vs. H$_2$O</td>
<td>$^{18}$O/$^{16}$O</td>
<td>49.4</td>
<td>5.1</td>
</tr>
</tbody>
</table>

0.5 cm$^{-1}$ shift error at 500 cm$^{-1}$ 0.4

molecular dynamics studies (e.g. Bourg and Sposito 2007). This is a promising area of joint theoretical and experimental development.

**“MESSY” REACTIONS**

A focus of interest in metal isotope biogeochemistry is identifying signatures of biological uptake of metals as nutrients and in metabolic reactions. Metals such as iron can undergo changes in oxidation state during these reactions and may acquire isotope signatures related to the activation energy of reactions during their interaction with enzymes, during transport (including diffusion), during fractionation between cellular reservoirs, and during reduction/oxidation. One of the first low-temperature fractionations observed, induced by respiration and reduction of ferric iron (Fe$^{3+}$ in ferrihydrite) to ferrous iron by anaerobic bacteria (Beard et al. 1999), belongs to this hybrid group. Experiments on the reverse process (oxidation of ferrous iron by photosynthesizing bacteria) show fractionation in the opposite direction, but neither reaction yields the full 3‰ reduction/oxidation equilibrium signature (Croal et al. 2004).

Webs of biogeochemical reactions are often too complex and incompletely characterized to be captured by current first-principles modeling. Progress is being made toward an understanding of simpler analogous systems, especially electrochemical reduction reactions (Kavner et al. 2008 and references therein).

**COMPARING THEORY AND OBSERVATIONS**

Experimental data and theoretical calculations have somewhat complementary strengths. Calculations are only feasible for simplified analogues of natural systems (for example, an *ab initio* model for a few functional groups attached to a metal atom, instead of a whole enzyme). Some aspects of theoretical models appear to be robust, in spite of the simplifications. The best example of this robustness is the temperature dependence of fractionation. The most notable drawback of the experimental approach is the slow rate of exchange of isotopes in crystals and in some biological molecules. Mineral–mineral and mineral–solution equilibration on practical laboratory timescales may require high temperatures (hundreds of °C). Several experimental strategies have been used to partially circumvent these problems in light-isotope calibration experiments, and these are being adapted to other systems. These include synthesis (inorganic or biogenic precipitation) from solutions and/or melts, use of isotopic tracers to extract equilibrium fractionation factors from experiments with incomplete exchange, and empirical calibrations based on natural sample suites formed under more or less well-controlled conditions. Empirical and synthesis studies have been the most common, but isotope tracing of exchange has been applied in some low-temperature studies (e.g. Johnson et al. 2002). Recent studies that take advantage of the complementary strengths of theory and experiment are showing particular promise.

As an example, theory and experiment have worked together to explore the question “How important are nonredox effects in Fe fractionation?” The largest iron isotope signatures in rock samples have been attributed to redox effects, suggesting use as a proxy of past O$_2$ fugacity (e.g. Rouxel et al. 2005). However, theoretical calculations (e.g. Polyakov 1997, 2007; Hill and Schauble 2008) predicted that changes in bond partner or coordination number can also drive fractionation, implying that Fe isotope signatures reflect both the redox state and the solution chemistry from which iron minerals precipitate. In a follow-up study, Hill et al. (2009) conducted experiments on nonredox $^{56}$Fe/$^{54}$Fe fractionation among ferric aquo-chloro species, using this system as an easily modeled analogue of other geochemically important, iron-bearing compounds such as sulfides and organic complexes.

At low pH, Fe$^{3+}$–Cl–H$_2$O solutions contain a mixture of species or complexes ranging from Fe(H$_2$O)$_6$$^{3+}$ (6 waters and no chloride bound to an iron cation) to FeCl$_4$$^-$ (4 chlorides, no water), with weaker Fe$^{3+}$–Cl– bonds substituting for stronger, stiffer Fe$^{4+}$–OH$_2$ bonds. Complexes with high Cl/Fe ratios (and fewer Fe–O bonds) become increasingly abundant in Cl–-rich solutions. $^{56}$Fe/$^{54}$Fe ratios are thus expected to decrease, relative to any equilibrated phase, in chloride-rich solutions. To test the models, Hill et al. (2009) placed diethyl ether (an immiscible organic liquid) in contact with Fe$^{3+}$–Cl–H$_2$O solutions. Only one of the Fe$^{3+}$–Cl species, FeCl$_4$$^-$, dissolves into ether, providing a liquid-phase, rapidly exchanging reference frame for detecting changes in the fractionation properties of the aqueous solution. Figure 2 compares these experiments with theoretical results from several *ab initio* models. Theory and experiments both show decreasing $^{56}$Fe/$^{54}$Fe in the aqueous phase relative to the ether, as chloride concentration increases. Although the results of the various models vary somewhat, the overall trend demonstrates that variations in aqueous speciation can affect iron isotope fractionation, even when oxidation state does not change. More recent experiments (Hill et al. unpublished data) have shown a difference of ~0.3‰ per mole of Cl$^-$ in $^{56}$Fe/$^{54}$Fe isotope fractionation between aqueous Fe$^{3+}$ and Fe$^{4+}$, indicating that speciation can also modify isotope signatures in redox reactions.

Even in systems that have not been subjected to detailed theoretical study, the principles of fractionation may provide insight into the origins of natural and experimental isotope signatures. One such example is calcium carbonate precipitation between biologically precipitated calcium carbonate (aragonite or calcite) and dissolved Ca$^{2+}$ in seawater. This is an example of a potentially messy reaction, strongly controlled by the shell-building organism but also showing promise as a proxy for the inorganic environment (Eisenhauer et al. 2009 this issue). When carbonate-precipitating foraminifera are grown under
Comparison of ab initio model predictions and observations for iron isotope fractionation in solution. The thick shaded lines show model fractionation between aqueous (aq) Fe\(^{3+}\)–H\(_2\)O–Cl species and FeCl\(_4^–\)–dissolved in ether (et), calculated with several electronic structure methods. The thin solid (red) line is a logarithmic best fit to experimental data. Higher chloride concentration increases the abundance of Fe–Cl bonding, decreasing the average force constant sum acting on each Fe\(^{3+}\) ion in the aqueous phase. This causes a decrease in 56Fe/54Fe in the aqueous solution compared with FeCl\(_4^–\) dissolved in ether (adapted from Hill et al. 2009).

controlled conditions, two distinct types of calcium isotope fractionation appear. Most organisms show behavior broadly similar to what is observed in *Orbulina universa*—the triangles in Figure 3 (data from Gussone et al. 2003). Precipitated calcite is enriched in light isotopes (in this case 44Ca/40Ca is roughly 1‰ lower than seawater). Another species, *Globigerinoides sacculifer*, shows fractionation of up to 4‰ (Nägler et al. 2000). Given that both organisms grow under roughly similar conditions of water chemistry and temperature, it can be concluded that at least one of them displays nonequilibrium fractionation. But is equilibrium relevant at all for this biologically complex system? This question is important, because equilibrium fractionation between two substances of fixed composition is controlled mainly by temperature (e.g. Equation 3) and thus should not be affected by (or convey information about) parameters such as growth rate or nutrient availability. A nonequilibrium fractionation does, by definition, reflect the dynamic conditions of precipitation—potentially giving a record of the biological status of the organism but likely giving a less robust record of growth temperature.

No good quantitative theoretical model of equilibrium calcium isotope fractionation between calcite and seawater exists, but it is still possible to use the expected temperature dependence of equilibrium fractionation to gain insight. Figure 3 shows calcium isotope fractionation for both organisms plotted against the reciprocal of the square of temperature. Considering Bigeleisen and Mayer’s (1947) approximation (i.e. Equation 3), we should expect equilibrium fractionation to plot along a straight line intersecting the origin (zero fractionation at infinite temperature). The gray line indicates the approximate trend through the *O. universa* data. A regression through the same data is not quite coincident with the expected equilibrium trend, but given the scatter in the data and the approximate nature of Equation 3, the discordance is not great. The *G. sacculifer* data, however, are strikingly divergent from the equilibrium expectation. *O. universa* tests (shells) may or may not preserve an equilibrium fractionation of CaCO\(_3^–\) seawater, but *G. sacculifer* almost certainly does not. Biological and inorganic calcite precipitation experiments most commonly show weakly temperature-dependent fractionation (e.g. Gussone et al. 2003). This is to be expected, given the temperature derivative of Equation 3:

\[
\frac{d\alpha}{dT} \approx -2(\alpha - 1) \frac{1}{T}
\]

(5)

So a 1‰ equilibrium seawater–CaCO\(_3^–\) fractionation at 300 K (\(\alpha = 1.001\)) is expected to decrease by only -0.007‰/°C. Analytical precision (and isolation of confounding factors) will thus be critical to the development of new metal isotope geothermometers. We still do not know if any of the measured calcium isotope fractionations reflect equilibrium. At least one empirical calibration (Fantle and De Paolo 2007) suggests that there is no significant calcium isotope fractionation between calcite and seawater at exceptionally slow reaction rates, i.e. in conditions likely to be close to thermodynamic equilibrium.

**SUMMARY**

The basic principles of stable isotope fractionation theory are well established, particularly for equilibrium processes, but quantitative models are lacking for many elements and classes of substances that geochemists would like to understand and use. In particular, the key areas where modeling techniques need to be advanced include:

1. Fractionation involving one or more dissolved species, including solid solutions and defect substitution.

2. Mass-independent fractionation. Nuclear volume fractionation has been studied for only a few elements (mercury, thallium, and uranium). Tantalizing signatures...
in other heavy and medium-weight metals have not yet been explained. Nuclear shape effects are essentially unstudied. A quantitative or even semi-quantitative theory of magnetic isotope fractionation is also needed.

3. Kinetic and biological fractionation. Fractionations associated with forced reactions are ubiquitous in natural and technological environments, but we are just beginning to refine our understanding of them.

There are clear and important benefits in planning experimental and analytical campaigns with basic theoretical concepts in mind. Even in systems lacking detailed theoretical characterization, considering qualitative principles of equilibrium and kinetic fractionation could help to isolate and define fractionation processes and feed intuition about potential applications of new isotope measurement techniques.

ACKNOWLEDGMENTS

The authors thank J. Kubicki, V. Polyakov, T. Bollen, and S. Stipp for helpful reviews and encouragement. New electronic structure calculations were supported by grants from the National Science Foundation (EAR0643286) and UCLA.REFERENCES


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