Frontiers of stable isotope geoscience


A Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, United States
B Department of Earth Sciences, University of Toronto, Toronto, Ontario M5S 3B1, Canada
C Earth Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720, United States
D Laboratoire de Géochimie des Isotopes Stables Institut de Physique du Globe de Paris, PRES Sorbonne Paris Cité, Univ Paris-Diderot, 1 rue jussieu, 75005 Paris, France
E Department of Geology, University of Maryland College Park, College Park, MD 20742, United States
F School of Oceanography, University of Washington, Seattle, WA 98195, United States
G Woods Hole Oceanographic Institution, Woods Hole, MA 02543, United States
H Weizmann Institute of Science, Rehovot 76100, Israel
I Department of Chemistry, Franklin & Marshall College, Lancaster, PA 17604, United States
J Jackson School of Geosciences, University of Texas at Austin, Austin, TX 78712, United States
K Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, United States
L Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095, United States

A R T I C L E  I N F O

Article history:
Received 21 June 2013
Received in revised form 31 January 2014
Accepted 7 February 2014
Available online 28 February 2014

Editor: David R. Hilton

Keywords:
Stable isotope geochemistry
Mass independent
Clumped isotope
Position-specific isotope effects

A B S T R A C T

Isotope geochemistry is in the midst of a remarkable period of innovation and discovery; the last decade (or so) has seen the emergence of 'nontraditional' stable isotopes of metals (i.e., variations in isotopic compositions of Mg, Fe, Cu, etc.), a great expansion of mass-independent isotope geochemistry, the invention of clumped isotope geochemistry, and new capabilities for measurements of position-specific isotope effects in organic compounds. These advances stem from the emergence of multi-collector plasma mass spectrometry, innovations in gas source mass spectrometry, infrared absorption spectroscopy, and nuclear magnetic resonance techniques. These new observations demand new connections between isotope geochemistry and the chemical physics that underlie isotopic variations, including experimental study and modeling of vibrational isotope effects, photochemical isotope effects, and various nuclear volume and magnetic effects. Importantly, such collaborations also have something to offer chemists and physicists because the novel observations of emerging branches of stable isotope geochemistry hold the potential to reveal new insights into the nature of chemical bonds and reactions. This review looks broadly across the frontiers of new methods and discoveries of stable isotope geochemistry and the fundamental chemical-physysics problems they pose, focusing in particular on the most pressing problems in: kinetic isotope effects in complex systems; mass independent isotope geochemistry (both the strong effects in photochemical reactions and the subtle variations of more conventional reactions); clumped isotope geochemistry; and the position-specific isotopic anatomy of organic molecules.

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⁎ Corresponding author.
E-mail address: eiler@gps.caltech.edu (J.M. Eiler).

http://dx.doi.org/10.1016/j.chemgeo.2014.02.006
0009-2541/© 2014 Published by Elsevier B.V.
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1. Introduction

The nuclear, physical and biological chemistry of isotopes has profoundly influenced the geosciences; these fields underpin the calibration of geological time scales (e.g., Patterson et al., 1955; Bowring and Schmidiz, 2003), reconstructions of past climates (e.g., Epstein et al., 1951; Zachos et al., 2001), ‘tracer’ studies in the hydrosphere and atmosphere (e.g., Dansgaard, 1964; Jouzel et al., 1997), and numerous other geological and geochemical tools. This discipline is in the midst of a sustained burst of innovation and discovery as dramatic as any period since its foundation in the 1940’s and 50’s. New analytical techniques for isotope geochemistry have increased the scope of the discipline, adding to both the list of elements that can be analyzed and the properties of isotope distribution that can be interrogated, including mass laws of fractionations, position-specific isotope effects and isotopic ordering or ‘clumping’. These methodological innovations have led to a variety of discoveries that are playing central roles in the study of earth history and processes. But, many of these discoveries involve phenomena beyond our basic understanding of the chemistry of isotopes.

Recent decades have also seen noteworthy advances in ab initio and molecular dynamic models of the structures and energetics of chemical compounds (e.g., Becke, 1993). These advances have enabled the first-principles modeling of molecular structures and isotope effects on molecular properties and dynamics for complex materials with unprecedented levels of accuracy (Car and Parrinello, 1985; Panagiotopoulos, 1987; Laio and Parrinello, 2002), including solute–solvent interactions and phase interfaces, (e.g., Kolmodin et al., 2002; Sharif et al., 2006) — the sorts of materials most relevant to many earth science problems (Varma and Rempe, 2006; Bourg and Sposito, 2011; Stack et al., 2012). These methods are capable of illuminating the chemical physics of isotope fractionations (Dreisinger et al., 2000; Hill et al., 2010; Rustad et al., 2010) and have been widely applied to classic problems in traditional stable isotope geochemistry (e.g., the carbon isotope fractionation associated with photosynthetic carbon fixation; Tcherkez et al., 2006). But this work has not yet been brought to bear on most of the new observations coming from novel branches of stable isotope geochemistry.

Thus, isotope geochemistry and the chemical physics of isotopes are both in an unusual period of their development — each has separately made substantial progress on their own, but would benefit by turning their attention on common sets of new goals. Some of the greatest past discoveries and advances in understanding of the isotope geosciences have come from such collaborations — for example, the invention of quantitative paleoclimate reconstructions was based on isotope effects on vibrational energies of chemical bonds (Urey, 1947); the discoveries of metabolic and other biological isotopic fractionations (e.g., Dole and Jenks, 1944) led to new insights into biochemical kinetics and new biogeochemical tools (e.g., Farquhar et al., 1989); discoveries of mass-anomalous isotope effects in nature (i.e., departures from canonical mass laws followed by common fractionation mechanisms; Clayton et al., 1973; Mauersberger, 1987), led to fundamental research in isotope effects in photochemistry and other gas phase reactions dominated by electronic transitions (e.g., Thiemens and Heidenreich, 1983; Mauersberger et al., 1999; Thiemens et al., 2012) and fundamental chemical–kinetic theory (e.g., Gao and Marcus, 2001), which in turn has led to further discoveries regarding the history of the Earth’s atmosphere (Farquhar et al., 2000a). From a geoscientist’s point of view, the
purpose of this dialog between geochemistry and chemistry is to develop a deep understanding of isotopic tools for deciphering natural environments. From the physicist's or chemist's point of view, such research permits a wide-ranging exploration of natural laboratories in search of new isotope effects that can be used to refine our understanding of chemical structures and reaction mechanisms.

The purpose of this paper is to review the last decade (or so) of developments in isotope geochemistry, principally in an effort to tempt the present generation of chemists and geoscientists into productive and insightful collaborations. The remainder of this introduction briefly reviews some of the most relevant recent developments in isotope chemistry and geochemistry; the remainder of this paper is then organized around a series of case studies that we feel best exemplify future opportunities. This paper is an outgrowth of a 2011 workshop on these subjects, organized by the Department of Energy and attended by 25 geochemists, chemists and geologists, including the authors and others listed in the Acknowledgments.

1.1. Recent analytical innovations

Twenty years ago, a young stable isotope geochemist needed to be aware of only one sort of analytical instrument — the Nier-type gas source isotope ratio mass spectrometer — and the field rarely considered subjects beyond the bulk isotopic compositions of the light, volatile elements (H, C, N, O, S). The emergence of multi-collector plasma mass spectrometers has extended this field to metals that could not be analyzed routinely and precisely by traditional gas source and thermal ionization instruments (e.g., Cu, Fe, Zn, Ni; e.g., Halliday et al., 1995). Improvements in ion microprobes have enabled in situ, micron-scale measurements of solids with precision approaching that achieved by chemical extraction and gas source mass spectrometry (Kita et al., 2009). Improved analytical methods and approaches to standardization have resulted in measurements of elements with more than two stable isotopes (i.e., O and S isotopes; e.g., Luz et al., 1999) with unprecedented precision, revealing subtle variations in mass laws governing stable isotope fractionations. Most recently, a high-resolution gas source multi-collector mass spectrometer has been created (Eiler et al., 2012) that is capable of analyzing isotopologues of molecules and their fragments with resolution of isobaric interferences (e.g., 13CH4 from 12CD4), extending the field of clumped isotope geochemistry — i.e., analysis of multiply substituted isotopologues (Eiler, 2007) from simple compounds like CO2 and O2 to a wide range of isotopic systems and compounds, including volatile and semi-volatile organics. All of these technical developments figure prominently in the subjects discussed in this paper. Outside the realm of sector mass spectrometry, absorption spectroscopy has emerged as a precise and highly efficient and field-portable method for isotope ratio measurements of simple molecular gases (see recent review by Griffis (2013)). And, nuclear magnetic resonance spectroscopy has demonstrated the capacity to make precise measurements of C and H isotope ratio at natural abundances for individual structural sites in complex organic molecules; this effect was demonstrated over 30 years ago (Martin and Martin, 1981), but only recently expanded to a wide range of applied problems (e.g., the n-alkanes; Gilbert et al., 2013). These more specialized but potentially powerful emerging technologies also figure prominently in some sections of this review.

1.2. Discoveries

This recent surge in analytical capabilities has led to observational discoveries that have transformed our approaches to and understanding of some of the major problems in Earth science: The stable isotope geochemistry of metals has emerged as a large, multi-faceted discipline that is perhaps the fastest growing tool in environmental geochemistry, paleoclimate research and cosmochemistry (Johnson et al., 2004). The mass-independent isotope geochemistry of S has revolutionized the study of the rise of atmospheric oxygen early in Earth history (Farquhar et al., 2000a). More subtle variations in mass laws for S and O isotope fractionations provide a new basis for studying modern biogeochemical and atmospheric cycles of these elements (e.g., Farquhar et al., 2007). Similarly, the 17O/16O–18O/16O systematics of water have provided hydrology with a powerful new tool (e.g., Landais et al., 2008). Measurements of multiply substituted (13C and 18O) isotopologues of CO2 and carbonate have led to a new approach to paleothermometry that is changing the way we study ancient earth climate, alitmetry, and related problems (e.g., Finnegan et al., 2011). Isotope ratio measurement by absorption spectroscopy has enabled field-deployable devices that are revolutionizing environmental stable isotope geochemistry (e.g., Griffis et al., 2004). Site-Specific Natural Isotope Fractionation-Nuclear Magnetic Resonance (SNIF-NMR) is a relatively specialized technique at present, but has demonstrated applications to the forensics of agricultural compounds and explosives (Remaud et al., 1997), and could grow to form the basis of a wide range of new sub-disciplines in environmental geochemistry, geobiology, and meteoritics and cosmochemistry. High-resolution gas source mass spectrometry recently produced the first precise ‘clumped isotope’ thermometer for an organic molecule (methane; Stolper et al., 2014, submitted for publication), and ongoing work suggests that this tool will significantly impact our understanding of petroleum deposits and the biogeochemistry of methane (Stolper et al., submitted for publication), and may soon be extended to a variety of more complex organic compounds (Eiler et al., 2013b).

1.3. Puzzles

Many of these new measurements and applications are concerned with properties of isotopic substances that are relatively unfamiliar and little understood. The stable isotope geochemistry of metals can be interpreted generally through conventional models of equilibrium and kinetic fractionations, but detailed understanding currently lags far behind that accumulated through decades of research in ‘traditional’ branches of light-element stable isotope geochemistry. Furthermore, many metal systems seem to experience kinetically controlled fractionations that are at the murky outer edges of our understanding of conventional isotope effects. The interpretation of ‘mass independent’ isotope fractionations (or, more generally, the isotope systematics of elements like O, S or Hg that have 2 or more stable isotope ratios) has encountered two problems: The largest mass independent isotopic anomalies examined by this field arise from photochemical, magnetic and/or nuclear volume effects that have been studied in detail for only a few chemical compounds and reactions (e.g., ozone and SO2 photochemistry). There is much about such fractionations that we do not understand (although there is a recent progress with experimental and theoretical study of these and other species, such as CO2; Chackraborty et al., 2012). And, second, mass dependent fractionations of elements having multiple isotope ratios can exhibit subtle but measurable variations in mass law (i.e., mass dependent slope in a plot of one isotope ratio vs. another). These variations arise from understood principles of chemical physics and are potentially useful in that they could give rise to new geochemical tools. But, there is very little substantive information showing how these mass laws vary in geochemically interesting systems. Similarly, the intramolecular fractionations that are the subject of clumped-isotope and SNIF-NMR measurements can be understood as consequences of the same fractionation mechanisms commonly used to interpret conventional (bulk) stable isotope data, but have been investigated in detail for only a handful of examples (e.g., ordering, or ‘clumping’, of 13C with 18O in CO2 and carbonates; Eiler, 2011).

1.4. The dialog with chemistry

The geochemical tools we think of as core to traditional stable isotope geochemistry — e.g., carbonate-water thermometry, the vapor
pressure isotope effect for water, or the photosynthetic fractionation of carbon isotopes — arose from a dialog between the, at that time, cutting-edge discoveries in physical chemistry (quantum mechanics), technical advances in analytical chemistry (e.g., the Nier mass spectrometer), and experimental and field-based discoveries in geochemistry and biochemistry. Similarly, a deep, physically based understanding of the emerging stable isotope disciplines must involve first-principle models rooted in the experimental and computational tools of physical and biological chemistry. These tools have evolved in a variety of ways that should facilitate this kind of interdisciplinary dialog. Software that allows ab initio and molecular dynamics simulations of isotopic fractionations has become widely available and relatively easy to learn and use, and computers capable of making such calculations, even for relatively large and complex chemical structures, are increasingly available to earth science research groups. And, there is a growing appreciation that widely known methods for evaluating isotope effects on molecular vibrational energies must be replaced with more sophisticated and accurate approaches when examining the subtle, second-order isotope effects involved in some of the emerging disciplines of stable isotope geochemistry (e.g., Webb and Miller, 2014).

This paper aims to illuminate both the need and opportunity for multidisciplinary studies that combine innovations in analysis, experiment and fundamental chemical theory to push forward the emerging disciplines of stable isotope geochemistry. Most of the following sections present case studies where analytical advances, discoveries and physical–chemistry theory come together in focused problems in stable isotope geochemistry. But we start first with a subject that underlies many of the others — a persistent problem that confronts nearly every tool in every branch of stable isotope geochemistry.

2. On beyond equilibrium

Many of the problems on the frontiers of stable isotope geochemistry involve the struggle to understand isotopic fractionations inconsistent with models of the equilibrium thermodynamics of isotope exchange reactions first described by Urey in the 1930’s and fleshed out by a community of founding figures in the chemical physics of isotopes in the 1940’s and 50’s. Some of the best known of these cases involve peculiar photochemical or nuclear effects; we address these in their own sections below. But there also exists a family of non-equilibrium, or ‘kinetic’, isotope effects that can occur in nearly every geochemical transformation: evaporation and condensation (Richter, 2004; Luz et al., 2009), diffusive transport (Bourg and Sposito, 2008; Beekman et al., 2011), mineral growth and dissolution (Kiczka et al., 2010; Nielsen et al., 2012), redox reactions (Anbar and Rouxel, 2007; Zink et al., 2010), and metabolic reactions (Ripperger et al., 2007; Cobert et al., 2011). Fig. 1 illustrates some of the fundamental processes in such systems that are the focus of this section, several of which are significant for subsequent sections.

Kinetic isotope effects often limit our ability to interpret the stable isotope compositions of natural materials; for example, kinetic controls are implicated in some ‘vital effects’ that complicate paleoclimate records, and are major complication in the isotope geochemistry of natural waters and water vapors. However, if the kinetic fractionation factors associated with these non-equilibrium processes can be determined experimentally and/or theoretically (cf., Bourg and Sposito, 2008; Maggi and Riley, 2009; Zink et al., 2010; Nielsen et al., 2012), then these effects can provide powerful applied tools, such as novel biomarkers or measures of previously poorly known paleoenvironmental variables (e.g., humidity).

2.1. Some founding principles

A useful first step in the discussion of chemical kinetics is to define a nomenclature for discussing the case of a one-step transformation of element A from state $A_{\text{initial}}$ to state $A_{\text{final}}$, with forward and backward reaction rates $R_f$ and $R_b$ (such that the overall rate $R_o = R_f - R_b$):

$$\frac{R_f}{R_b} = \frac{A_{\text{initial}}}{A_{\text{final}}}$$

For a trace isotope i, the overall transformation rate $\dot{R}_o$ can be expressed as a function of the isotopic compositions of the initial and final states (expressed here as mole fractions $x_{\text{initial},i}$ and $x_{\text{final},i}$, which are both assumed to be much less than 1 to simplify the algebra) and

Fig. 1. Illustration of the chemical and physical processes at play in phase transformations and other chemical reactions, any or all of which may contribute to isotopic fractionations.
the kinetic isotope fractionations (‘KIF’) associated with the forward and backward transformations ($\alpha_f$, $\alpha_b$):

$$i R_0 = \frac{R_f - R_b - X_{\text{initial}}}{R_f - X_{\text{final}}} \alpha_f R_i - X_{\text{final}} \alpha_b R_0$$

(2)

The KIF factors $\alpha_f$ and $\alpha_b$ are related to the equilibrium isotopic fractionation through $\alpha_{eq} = \alpha_f \alpha_b$; i.e., the equilibrium state corresponds to an exact balance between the forward and backward reactions. If we assume steady-state conditions ($dX/dt = 0 = R_f - X_{\text{final}} R_0$) and define the overall fractionation of trace isotope $i$ as $\alpha_{eq} = R_f / (X_{\text{final}} R_0)$, we obtain the following equation for the overall isotopic fractionation associated with Eq. (1) (DePaolo, 2011):

$$\alpha_f = \frac{R_0}{1 + \frac{R_0}{R_b}} \left( \frac{\alpha_{eq} - 1}{\alpha_{eq}} \right)$$

(3)

Inspection of Eq. (3) shows that the overall isotopic fractionation factor associated with one-step, steady-state geochemical transformations depends significantly on kinetic isotope effects unless $R_0 \ll R_b$. The same significant role of kinetic isotope effects is predicted (with a more complex form of Eq. (3)) if we relax the condition that $X_{\text{initial}}$ and $X_{\text{final}}$ are both much less than 1.

Kinetic isotope fractionation almost always arises from Newtonian dynamics, i.e., the motions of atoms and molecules (Vineyard, 1957). A notable exception is chemical reactions involving light elements such as H, O, N, or C where quantum mechanical effects (quantum tunneling, zero-point energies) may contribute significantly to the kinetic isotope effect (Bigeleisen, 1949; Eyring and Cagle, 1952; Bigeleisen and Wolfberg, 1958; Schepple, 1972; Kliman, 2010; Gómez-Gallego and Sierra, 2011); even in this case, the Newtonian contribution to the KIF is present (Bigeleisen, 1949; Eyring and Cagle, 1952; Bigeleisen and Wolfberg, 1958; Matthews et al., 2001) and often dominates the KIF of elements as light as C (Nowlan et al., 2003; Kelly et al., 2009).

The manner in which KIF arises from atomic or molecular motions is best understood for three types of elementary transformations: evaporation and condensation, diffusion in gases and liquids, and metal ligand-exchange reactions.

2.2. Evaporation and condensation

In conditions where diffusive boundary layers are believed to be negligible, such as evaporation of silicate melts (Richter et al., 2007) or liquid mercury (Estrade et al., 2009), mass fluxes across liquid–gas interfaces are determined by the rates of evaporation and condensation. These rates follow relations derived from the kinetic theory of gases (Knudsen, 1911; Langmuir, 1913; Hirth and Pound, 1960; Richter et al., 2007):

$$i R_i = \frac{n_i \sigma_i P_{\text{sat}}}{\sqrt{2m_i kT}}$$

and

$$R_b = \frac{n_{i} \sigma_{i} P_{i}}{\sqrt{2m_{i} kT}}$$

(4)

where $R_i$ and $R_b$ are evaporation and condensation fluxes per surface area, $n_i$ is the number of atoms of $i$ in the gas phase material containing $i$, $\sigma_{i}$ is the condensation coefficient (the probability that an incident molecule will condense into the liquid phase), $P_{\text{sat}}$ is the saturation vapor pressure of isotope $i$, and $P_i$ is the actual vapor pressure of isotope $i$. For two isotopes $i$ and $j$, $n_i$ being independent of isotopic mass and $\alpha_{eq}$ being equal to $P_{\text{sat}} X_{\text{liquid}} / P_{\text{sat}} X_{\text{liquid}}$, we have:

$$\alpha_f = \frac{\sigma_{i} m_j}{\sigma_{j} m_i} = \frac{1}{\sqrt{\alpha_{eq}}}$$

(5)

If $\alpha_{eq}$ and $\sigma_{i} / \sigma_{j}$ are close to 1, Eq. (5) simplifies to $\alpha_i = (m_j / m_i)^{0.5}$, a relationship that is consistent with studies of Fe evaporation from molten FeO (Wang et al., 1994) and K evaporation from a melt of chondrule-like composition (Yu et al., 2003). Fractions closer to 1 have been observed for the evaporation of pure Hg [($\alpha_{202/198}$Hg) = 0.9933 ± 0.0011 at 22 °C, whereas ($m_j / m_i)^{0.5} = 0.9900$ (Estrade et al., 2009)] and for the evaporation of Mg from molten mixtures of SiO$_2$, Al$_2$O$_3$, MgO and CaCO$_3$ [($\alpha_{25/24}$Mg) = 0.98704 ± 0.00025 on average at 1600 to 1900 °C, decreasing with temperature, whereas ($m_j / m_i)^{0.5} = 0.97980$ (Richter et al., 2007)]. These results suggest that, in certain cases, the condensation coefficient $\alpha_{eq}$ may increase with isotopic mass (Richter, 2004; Richter et al., 2007). Molecular dynamic (MD) simulations, which are widely used for obtaining molecular-scale insight into the condensation coefficient $\alpha_{eq}$ (Tsuruta and Nagayama, 2004; Kolb et al., 2010; Cheng et al., 2011), may provide a means to probe the isotopic mass-dependence of $\alpha_{eq}$.

2.3. Molecular diffusion in gases and liquids

Molecular diffusion in gases and liquids can cause significant KIF, for example, in the gas-phase diffusive boundary layer during water evaporation (Luz et al., 2009; Kim and Lee, 2011), in the aqueous–phase diffusive boundary layer during air–water exchange of volatile gases (Bourg and Sposito, 2008), in pore water of low-permeability sedimentary formations (Lavastre et al., 2005; Bourg et al., 2008; Beekman et al., 2011), and in crystals formed during magmatic differentiation (Teng et al., 2011). For a solute of mass $m_i$ diffusing in a solvent of mass $m_0$, in the idealized case where solute and solvent interact only through instantaneous, uncorrelated binary collisions, the kinetic theory of gases predicts that the diffusion coefficient $D_{ij}$ has an inverse square root dependence on the reduced solute–solvent mass $\mu_{ij} = m_{ij} / (m_i + m_j)$ (Chapman and Cowling, 1960; Hansen and McDonald, 1986; Ali et al., 2002). Under these circumstances, the KIF of isotopes $i$ and $j$ ($\alpha_f = D_i / D_j$) should equal:

$$\alpha_f = \sqrt{\frac{p_j}{p_i}} = \sqrt{\frac{m_j (m_i + m_j)}{m_i (m_i + m_j)}}$$

(6)

Attempts to confirm Eq. (6) using gas-phase measurements are arduous because of the difficulty of ensuring pure diffusive transport. Experimental measurements of D/H and $^{18}$O/$^{16}$O isotope fractionation during water vapor diffusion are inconsistent with Eq. (6) \[\alpha_j(D/H)/\alpha_{eq}(^{18}\text{O}/^{16}\text{O}) = 0.84–0.88 for diffusion in air at 20 °C (Merlivat, 1978; Luz et al., 2009), whereas Eq. (6) predicts a value of 0.52 for diffusion in air\]. Whether this discrepancy arises from experimental difficulties (Kim and Lee, 2011) or from a failure of the kinetic theory of gases to explain H$_2$O diffusion in air is currently unknown.

Data are more widely available on the isotopic mass dependence of solute diffusion coefficients in liquids, particularly in water (Mills, 1973; O’Leary, 1984; Jähne et al., 1987; Richter et al., 2006; Bourg and Sposito, 2007, 2008; Eggenkamp and Coleman, 2009; Bourg et al., 2010; Aupiais, 2011) and in silicate melts (Richter et al., 2003, 2008, 2009; Watkins et al., 2009, 2011). These data generally indicate smaller $\alpha$-values than Eq. (6). Experiments and MD simulations yield identical $\alpha$-values, confirming that this KIF is a classical mechanical effect (Bourg and Sposito, 2007; Bourg et al., 2010). Where data are available for more than two isotopes of the same solute, they are consistent with an inverse-power-law dependence of $D$ on isotopic mass (Bourg and Sposito, 2007, 2008; Bourg et al., 2010):

$$D_i \propto m_i^{-\beta}$$

(7)

with $\beta$-values that range from 0 to 0.22 (Bourg et al., 2010; Watkins et al., 2011). Mode coupling theory calculations suggest that the failure of kinetic theory in gases in these instances is caused by solute–solvent interactions having long-time correlations rather than occurring through instantaneous uncorrelated collision (i.e., the colliding...
molecules interact chemically rather than simply through hard-sphere collisions; Bhattacharyya and Bagchi, 2000; Ali et al., 2002). This view is supported by the fact that the β-values of solutes are inversely correlated with: 1) the residence times of water molecules in their first solvation shell (Bourg et al., 2010); and 2) with the ratio of solvent to solute diffusion coefficients (Watkins et al., 2011), two properties that express the long-time coupling of solute and solvent motions.

2.4. Metal ligand-exchange reactions

A recurring theme in studies of the biogeochemistry of metals in aquatic environments is the importance of ligand-exchange reactions — particularly, binding to organic ligands (Zhu et al., 2002; Corry and Chung, 2006; Gussone et al., 2006; Lacan et al., 2006) or to mineral surfaces (Stumm and Morgan, 1996; Sposito, 2004; Ohlin et al., 2009; Black et al., 2010; Stack et al., 2012) — as the rate-controlling steps in metal cycling. The important kinetic role of these reactions suggests that they may contribute significantly to metal kinetic isotope effects in natural settings.

At first glance, the very wide range of rates and molecular-scale details of metal ligand-exchange reactions (Richens, 2005) would appear to preclude any generalization on the KIFs associated with these reactions. A path towards a general model of these KIFs is suggested, however, by the observation that the forward rate constants of metal-ligand exchange reactions often scale with the water-exchange rate constant of the metal of interest, a relationship expressed by the well-known Eigen–Wilkins–Werner relation (Eigen, 1963; Stumm and Morgan, 1996; Sposito, 2004; Richens, 2005; Ohlin et al., 2009):

\[ k_{\text{binding}} \propto k_{\text{wex}} \] (8)

Eq. (8) suggests that knowledge of the mass dependence of \( k_{\text{wex}} \) may be sufficient to predict the KIF associated with the forward rate of many ligand-exchange reactions, particularly in the case of the more labile metal ions for which \( k_{\text{wex}} \) is relatively insensitive to the nature of the incoming ligand (Richens, 2005).

2.5. Questions and needs

The preceding review makes it evident that there already exists a detailed theoretical and experimental infrastructure from understanding isotopic fractionations controlled by physical and chemical kinetics in relatively simple systems. Nevertheless, the most obvious need of the fundamental study of kinetic isotope effects is simply more data on more systems and processes of geological relevance. We’ve achieved a useful critical mass of experimental constraints and connections to natural materials for only a few model materials that are important in the environment and geological record — evaporation and condensation of water; growth of carbonate from aqueous solution. Much must be done before these concepts can be molded into predictive, quantitative models of the isotopic compositions for diverse geologically important authigenic solids (silica, clays, sulfates, etc.) and products of biologically controlled or mediated mineral growth.

3. Why can’t authigenic minerals just behave?

Our first case study builds immediately on the general principles of kinetic isotope effects laid out in Section 2, by considering the kinetic isotope effects that underlie the common failure of minerals to grow in equilibrium with the geological fluids in their environments. Studies of metal isotopic fractionations during mineral growth from aqueous solutions (e.g., Johnson et al., 2004; Baskaran, 2011) generally find large spreads in isotopic fractionations that cannot be accounted for by theoretically predicted equilibrium fractionation factors (Yamaji et al., 2001; Griffith et al., 2008; Hill and Schauble, 2008; Jahn and Wunder, 2009; Hill et al., 2010; Rustad et al., 2010; Kowalski and Jahn, 2011; Schauble, 2011). These findings constitute a first-order barrier to the application of the emerging field of metal stable isotopes to paleoclimate, paleooceanography and other geochemical problems.

As a general rule, kinetic isotopic fractionations during precipitation of solids from liquids or gases enrich the solid in light isotopes (e.g., Böttcher et al., 2011; Nielsen et al., 2011; Wunder et al., 2011) — generally opposite the direction of equilibrium fractionations in these systems (Bigeleisen and Mayer, 1947; Bigeleisen, 1965). This presumably reflects the generally faster rate of transport of light isotopic species through a liquid or vapor to a growing solid, or faster ‘motion’ through the reaction coordinate during irreversible precipitation (Bigeleisen, 1949). An open question is whether we can understand these effects in enough mechanistic detail to develop a general description of the isotopic compositions of natural materials.

3.1. Diffusion alone?

A recent series of studies combining molecular dynamic (MD) simulations and laboratory experiments has shown that isotopes of Li\(^+\), K\(^+\), Ca\(^{2+}\), Cl\(^-\), and the noble gases are fractionated via diffusion in liquid water (Richter et al., 2006; Bourg and Sposito, 2007; Bourg and Sposito, 2008; Bourg et al., 2010). For example, in the absence of other kinetic processes, diffusion of dissolved Ca\(^{2+}\) species through water to a growing solid (e.g., calcite) can enrich the precipitating solid (relative to the fluid) by ca. 0.4‰ in \(^{40}\text{Ca}\) relative to \(^{44}\text{Ca}\) at 348 K (Bourg et al., 2010). Laboratory precipitation experiments and natural samples of calcite and aragonite indicate a range in \(\delta^{44/40}\text{Ca}\) from ca. +0.5 to −4.0‰ (DePaolo, 2004 and references therein; Nielsen et al., 2011 and references therein), where the equilibrium Ca isotope fractionation between Ca\(^{2+}\)(aq) and calcite is predicted to be of order 0.0 ± 0.1‰ (Fantele and DePaolo, 2007). These experiments clearly imply a kinetic control of the fractionation, but diffusion of dissolved Ca\(^{2+}\) to the growing mineral surface is clearly too small (and expected to be too constant) to explain such widely varying experimental results.

3.2. Desolvation

Experiments and molecular-dynamic (MD) simulations indicate that the kinetics of crystal growth from aqueous solutions can be controlled or influenced by the chemical kinetics of desolvation of ions and/or attachment to a growing crystal surface (deBoer, 1977; Mucci and Morse, 1983; Casey, 1991; Casey and Westrich, 1992; Dove and Czank, 1995; Kersit and Parker, 2004; Piana and Gale, 2006; Kowacz et al., 2007). It is conceivable that these processes are responsible for the common observation of large, apparently kinetically controlled fractionations of metal stable isotopes during crystal growth (Gussone et al., 2003). Recent MD simulations by Hofmann et al. (2012) show that the desorption rates (i.e., water exchange rates; \(k_{\text{wex}}\)) of isotopes of Li\(^+\), K\(^+\), Rb\(^+\), Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\) all follow an inverse power-law dependence on cation mass (\(k_{\text{wex}} \propto m^{-n}\)). This mass dependence predicts enrichment of the light isotope in precipitating solids relative to the surrounding fluid by amounts broadly in the range of experimental results, suggesting cation desolvation is a plausible mechanism for causing non-equilibrium metal isotope fractionation in aqueous systems.

3.3. Questions and needs

While these recent MD models provide suggestive evidence regarding the role of desolvation in kinetic isotope effects during mineral growth (perhaps modified by the more subtle effects of diffusion), there are significant limitations in the models themselves: they consider systems that are likely too small and time scales too brief to capture all of the relevant chemical physics, largely because of limits to computational power (e.g., Geissler et al., 1999; Stack et al., 2012).
The next significant advance in this area may come from MD simulations, which allow for quantum calculations of atomic velocities and bonding energetics at the scale of molecules and can provide more realistic and comprehensive thermodynamic and kinetic data, or rare-event modeling techniques like metadynamics (e.g., Stack et al., 2012) and transition-path sampling (e.g., Kerisit and Rosso, 2009), which enable an evaluation of reaction mechanisms and calculation of rate constants via the sampling of the relevant energy landscape(s) for processes that occur on long timescales otherwise inaccessible by direct MD. At present, however, even these approaches will likely still be limited to small molecular systems. As suggested by Rustad (2001), constructing near-molecular-scale (i.e., on the order of 100 s to 1000 s of nanometers) systems accessible by both simulation and experimental observations is the necessary next step forward. One possible solution could come from studies of the reactivity and exchange rates of metal and oxygen sites in small (i.e., fewer than 50 atoms) inorganic molecules that are symmetrically analogous to phases of geochronological interest (e.g., Rustad and Casey, 2012). Such systems can be probed via a combination of straightforward analytical methods (e.g., spectroscopies) and calculations based on ab initio or molecular dynamics theory (e.g., Casey et al., 2009).

Finally, in addition to diffusion— and desolvation— limited induced kinetic isotope fractionation, non-equilibrium isotope fractionation is also observed in cases where it seems inevitable that crystal—chemical controls dominate; for example, chemical and isotopic sector zoning in minerals, where crystallographically non-equivalent regions grow from the same solutions at broadly similar rates but have markedly different compositions (Boyd et al., 1988; Dickson, 1991). This process may reflect local equilibrium of the chemical or isotopic species between the fluid and a ‘proto-site’ at the surface of the growing crystal—a structural site that differs in coordination, size, or shape from the final site in the crystal interior (Watson, 2004). If crystals grow rapidly enough, then the proto-sites may transform into their final bulk—solid configurations more quickly than the time needed for isotopic re-equilibration of those sites with the adjacent fluid (Watson, 2004). While the basic outline of the proto-site hypothesis has been applied to several problems and seems like a leading contender to explain some non-equilibrium phenomena (e.g., sector zonation), much will have to be learned about the structures and chemical kinetics of growing crystal surfaces and the crystal—liquid boundary layer before we can understand the isotopic fractionations that occur at this interface.

4. The outer limits of ‘mass dependent’ isotopic fractionation

Several fields of meteoritics, cosmochemistry, atmospheric chemistry and Precambrian geology are concerned with comparisons of the fractionation behaviors of two or more isotope ratios of the same element; for example, comparison of 34S/32S with 33S/32S, or 18O/16O with 17O/16O. In these cases, measured isotopic compositions are generally compared with a reference frame of expected mass dependent fractionation behavior; i.e., where the magnitudes of fractionations for two isotope ratios are a simple function of their relative differences in mass. For example, mass dependent S isotope fractionations are generally assumed to follow the power law dependence, $\alpha_{33} = \alpha_{34}^{33/34}$ where $\alpha$ is the fractionation of the $^{33}S/^{32}S$ ratio and $\lambda_{33,34}$ is a constant that depends upon the mass difference between the $^{34}S$ and $^{32}S$—bearing compound of interest (~2 amu) vs. that between $^{33}S$ and $^{32}S$—bearing compounds (~1 amu). Note $\lambda_{ij}$ may be referred to as the mass law exponent or mass exponent. See Fig. 2.

Equilibrium isotope fractionation in the high temperature limit is associated with (in the case of sulfur): $\lambda_{33,34} = (1/32)^{33}/(1/32)^{34} - 0.515$ (see below; note all masses are reported in atomic mass units). This is often taken to be a suitable reference frame for defining mass dependent sulfur isotope fractionations (Hulston and Thode, 1965; Farquhar and Wing, 2003; Otake et al., 2008). Other mass dependent fractionations include chemical kinetic isotope effects, diffusion and gravitational fractionations; these generally have broadly similar behavior (though often subtly lower) mass exponents.

There are several cases where natural materials violate these mass dependent fractionation behaviors, e.g., anomalously high or low 34S/32S ratios at a given 34S/32S ratio in sulfides and sulfates from Archean sedimentary rocks (Farquhar et al., 2000a), anomalously low 17O/16O ratios at a given 16O/16O ratio in components of primitive meteorites (Clayton, 1993), and anomalously high 16O/16O ratios at a given 18O/16O ratio in ozone from the earth’s stratosphere (Heidenreich and Thiemens, 1983). These exceptions to reference mass dependent fractionation laws are generally described as ‘mass independent fractionations’ and are generally measured as a departure from the trend of a mass dependent line in a triple isotope reference frame; e.g., a plot of 34S/32S vs. 33S/32S (Fig. 2). These departures have been illustrated through $\Delta$ values, such as: $\Delta^{33S} = \delta^{33S} - 0.515 \times \delta^{34S}$, where $\delta^{32S} = 1000 \times \ln(\delta^{32S}/1000 + 1)$, $\delta^{33S} = ((^{33}S/^{32}S)_{sample}/(^{33}S/^{32}S)_{standard} - 1) \times 1000$, and the constant, 0.515, is the mass law exponent ($\lambda_{33,34}$). This definition is closely similar to Farquhar and Wing’s, 2003 definition, $\Delta^{33S} = (\delta^{33S} - (\delta^{34S}/1000 + 1)0.515 - 1) \times 1000$.

The discoveries of large mass—dependent isotope anomalies, particularly the sulfur isotope anomalies in minerals in Archean rocks are explored in a later section, below. These effects are mostly interpreted to result from atmospheric reactions in which large mass dependent effects are associated with photo-dissociation and other photochemical reactions and, in the case of ozone, reflect the effect of molecular symmetry on rates of dissociation of unstable species. However, interest in these effects have also inspired a broader study of the mass laws that describe nominally mass—dependent processes (i.e., chemical equilibria, chemical kinetics, diffusion). Some of this work specifically asks whether such fractionations might be directly responsible for the multiple—per—mil sulfur isotope anomalies in Archean...
4.1. Unusual mass laws associated with equilibrium processes

A premise of the study of mass independent isotope geochemistry is that equilibrium and conventional (non-photochemical) chemical kinetic fractionsations exhibit only subtle variations in $\lambda$, similar to canonical values (e.g., for sulfur isotopes, $\lambda_{33,34} = (1/32^i/33)/(1/32^i/34) - 0.515$ and $\lambda_{36,34} = (1/32^i/36)/(1/32^i/34) - 1.889$). For equilibrium fractionsations, these mass exponents are functions of the partition function ratios for individual molecules, which vary with temperature, bond stiffness and reduced mass, over a range of ~0.5%, relative (Fig. 3; with exceptions discussed below).

It is recognized that anomalous mass laws (i.e., mass laws that differ significantly from the canonical values) can occur in conventional (i.e., non-photochemical) chemistry as a result of nuclear volume effects (discussed below). However, Schauble (2007) estimates that such effects should be negligible for sulfur isotopes. Slight deviation from canonical mass laws can arise in reaction networks through the effects of mass-conservation on systems undergoing distillation or other dynamic reactions. These effects are typically expected in reaction networks that combine mixing, open-system fractionation and sets of multiple stepwise and/or branched reactions (Matsuhisa et al., 1978; McEwing et al., 1983; Farquhar et al., 2007). These effects are usually well accounted for and involve no novel chemical physics, so we do not discuss them further.

Significant deviations from canonical mass laws can also occur when equilibrium (i.e., thermodynamically controlled) fractionations display ‘crossovers’ – changes in the sign of values of ln($\alpha$) (Fig. 4). The temperatures at which crossovers occur differ subtly among different isotope ratios (i.e., the crossover temperature for $\alpha_{33}$ generally will not exactly equal that for $\alpha_{34}$). The gaps between crossover temperatures are typically expected to be just a few °C (though few such cases are actually demonstrated by experiment or observations of natural systems). Within this temperature range, the mass law exponent ($\lambda_{ij}$) can take on any value and can vary wildly with small changes in temperature (Skaron and Wolfsberg, 1980; Oi et al., 1985; Kotaka et al., 1992; Deines, 2003). Perhaps more importantly, the mass law can differ more subtly, but still significantly, over a broader range of temperatures near these crossovers. And, more subtly still, the same chemical–physics phenomena that lead to crossovers (and related peculiarities in temperature dependence of isotopic fractionsations) lead to variations in mass law. Such variations are best known in molecules that have little geological relevance (e.g., between SPCI and H$_2$S, and between SOBr or SOCl and SO$_2$). Nevertheless, there are very few direct observations of mass laws for sulfur isotope fractionations accompanying well understood and thermodynamically controlled reactions, and theoretical explorations of such systems are generally restricted to the small, vibrationally simple molecules (see Otake et al., 2008).

Lasaga et al. (2008) suggested that small differences in the vibrational energy between the bound states of sulfate during adsorption onto organic matter could result in a threshold behavior, whereby one or more S isotopes are stably bound to a surface while the others are not, causing isotopic fractionsations that appear mass independent (or at least violate common expectations regarding mass dependent fractionsations). Subsequent re-evaluation of this problem suggested that the threshold effect in question arose from a truncation error in the approximations of Lasaga et al.’s theoretical treatment, and that a more accurate description of such systems yields only strictly canonical mass-dependent isotope effects (Balan et al., 2009). However, this conclusion applies only to simple harmonic oscillators, not to vibrationally complex materials having a variety of modes of vibration and rotation that may combine or compete with each other to produce a net fractionation.

Eiler et al. (2013a) recently observed a non-canonical mass exponent, $\lambda_{33,34} = 0.551$ accompanying the vapor pressure isotope effect for SF$_6$ ice and sorbate. This is significantly greater than the canonical value of 0.515 or any calculated equilibrium mass law (Fig. 3), and appears to have occurred in systems that reached a reversible, time-invariant equilibrium (i.e., this appears to be a thermodynamically controlled fractionation). This effect might be the result of competition between isotope effects on intra and intermolecular vibrations that differ markedly in reduced mass. Analogous effects are previously
recognized for the mass law governing D/H and T/H fractionations among phases of methane (Kotaka et al., 1992), and it seems possible that this could be more widespread than is generally recognized. Initial attempts to test this hypothesis with first-principle models failed, likely due to poor description of the phonon spectrum of SF₆ ice; this is an attractive target for further, more refined models.

4.2. Mass laws of non-equilibrium processes

The kinetic theory of gases predicts that diffusive or gravitational fractionations are associated with mass laws that differ subtly but measurably from those describing isotope exchange equilibria (Bigeleisen and Wollfberg, 1958; Young et al., 2002). For example the mass law describing the oxygen isotope fractionation accompanying Knudsen diffusion of CO₂ is \( \lambda_{17,18} = \ln(44/46)/\ln(44/46) = 0.507 \), which is significantly lower than the range of values for thermodynamic equilibria involving oxygen isotopes (roughly described in the high temperature limit by the approximation, \( \lambda_{17,18} = (1/16^{-1/17})(1/16^{-1/18}) = 0.529 \)).

Anomalous mass laws could also arise during networks of irreversible reactions (including those that contain an equilibrium step), even if no one step in that network has an anomalous mass law. One example is a two-step reaction in which a kinetically controlled step cleaves a bond in a transition state molecule that is maintaining an isotope exchange equilibrium with another substrate. Examples of such complex systems can be found in experiments showing inverse kinetic isotope effects (i.e., where products are enriched in heavy isotopes compared to reactants; e.g. Casciotti, 2009). As illustrated in Fig. 5, anomalous mass laws can be produced if the kinetic and equilibrium fractionations are opposite in direction but similar in magnitude. It is possible that these behaviors of complex reaction networks account for previous experimental observations of mass anomalous behavior in sulfur isotope fractionations. For example, thermochemical sulfate reduction in the presence of water and amino acids at temperatures between 170 and 200 °C generated \( \Delta^{33}S \) values as high as \(-2\%\) (Watanabe et al., 2009). Similar experiments have yielded \( \Delta^{35}S \) as high as \(-13\%\) (Oduro et al., 2011). Oduro et al. ascribed these anomalous \( \Delta^{35}S \) fractionations to magnetic isotope effects (Buchachenko, 2001 and references therein) based on the relatively subtle accompanying \( \Delta^{33}S \) anomalies (they suggested that nonzero \( \Delta^{35}S \) in the experiments of Watanabe et al. (2009) were the result of mixing).

Additional experimental observations of anomalous mass laws during non-photochemical reactions include a report by Miller (2002) of thermal decomposition of carbonates and evidence presented by one of us (Cartigny) at the Basic Energy Science workshop, describing mass laws varying from \( \lambda_{13,34} \) of \(-0.505 \) to \(-0.621 \) during the partial fluorination of sulfides. These effects may be due to heterogeneous solid/gas reactions on surfaces, though the exact mechanism remains unknown. Finally, mass–anomalous effects have been observed during mass transport of vapor through a temperature gradient (Sun and Bao, 2011).

It is possible that effects like those discussed above contribute to non-zero \( \Delta^{32}S \) and/or \( \Delta^{34}S \) values of geological samples, though generally the effects observed experimentally to-date are too subtle to explain mass–independent fractionations in Archean sedimentary rocks, or are not consistent with the observed trends of co-varying \( \Delta^{34}S, \Delta^{32}S \) and \( \delta^{34}S \) in natural samples (see below). These experiments demonstrate, however, that processes yielding anomalous isotopic fractionations likely remain to be discovered.

4.3. Questions and needs

The principal limitation to our current understanding of the mass laws of processes we conventionally think of as ‘mass dependent’ (chemical equilibria; chemical kinetic isotope effects; diffusion) is simple: we have experimentally observed only a small fraction of those relevant to geologically important processes. This field has largely depended on empirical observations of ‘average’ mass laws implied by compositional variations of natural materials having only the loosest relationships to one another (e.g., terrestrial rocks; meteoric waters), and theoretical predictions regarding simple, idealized systems. It is essential that this subject engages in more basic experimental exploration. Such work may simply confirm prejudices and reinforce interpretations. Or it might be eye opening. It is noteworthy that most of the recent efforts in this direction (Miller, 2002; Watanabe et al., 2009; Sun and Bao, 2011; Eiler et al., 2013a; P. Schiano’s unpublished experiments described above) have produce results that vary from unexpected to unbelievable. A key element needed in any future experiments is controlled isolation of well-known mechanisms, as opposed to the complex, largely uncontrolled reactions examined by most of these initial studies, and interpretation of experimental results using detailed models of the relevant chemical physics.

5. O-isotope mass laws as a tool for study of the water cycle

The abundance of \(^{17}O\) in natural materials is generally described as a departure from a reference line in a plot of \( ^{18}O/^{16}O \) vs. \( ^{17}O/^{16}O \) (or equivalent functions), most often defined as: \( \Delta^{17}O = \delta^{17}O - \lambda \times \delta^{18}O \), where \( \delta^{18}O = 1000 \times \ln(\delta^{18}O/1000 + 1) \), \( \delta^{16}O = (\delta^{16}O/\delta^{18}O)_{\text{standard} -1} \times 1000 \), and \( \lambda \) is a constant that describes the observed or assumed mass law of nominally mass dependent fractionations (commonly 0.52 or 0.529; e.g., Miller, 2002; Fig. 6). Large positive values of \( \Delta^{17}O \) in atmospheric compounds (Fig. 6a) have been attributed to mass independent isotopic fractionations that can arise in the chemistry of ozone and are then passed to other species (CO₂, N₂O, sulfate, etc.) through O-exchange reactions (Thiemens et al., 1995, 2012). And, the sum of these enrichments is balanced by a small but measurable negative \( \Delta^{17}O \) value in atmospheric O₂ (Luz et al., 1999). Indirect evidence for similar mass independent atmospheric effects is found in ancient mineral deposits on Earth and Mars (Farquhar et al., 1998; Bao et al., 2000, 2009), and subtle variations in the \( \Delta^{17}O \) of atmospheric O₂ trapped in ice cores have been used as a measure of secular variation in biological productivity and respiration (Blunier et al., 2002, 2012).

However, in addition to these large mass independent atmospheric fractionations, it is recognized that small variations in \( \Delta^{17}O \) in waters and minerals can arise from mass-dependent isotopic fractionations,
due to subtle variations in their mass laws (Matsuhisa et al., 1978; Luz et al., 1999; Young et al., 2002; Hendricks et al., 2005). These effects are generally overlooked in the analysis of terrestrial materials, either because they are presumed not to exist or because they are below the level of detection at which most oxygen isotopic measurements are made.

The past 8 years have seen several analytical developments that dramatically improved the precision of measurements of $\Delta^{17}$O in water and, most recently, CO$_2$ (Barkan and Luz, 2005, 2012; Pack et al., 2013 and references therein); these technical advances have catalyzed new sub-disciplines of stable isotope geochemistry of Earth’s hydrosphere and paleoclimatology.

5.1. $\Delta^{17}$O in the Hydrosphere

High-precision measurements of $\Delta^{17}$O in water have enabled a variety of recent studies of the hydrologic cycle, climate dynamics and paleoclimate research (Landais et al., 2008; Landais et al., 2010; Luz and Barkan, 2010; Risi et al., 2010; Uemura et al., 2010; Risi et al., 2012; Winkler et al., 2012). The triple oxygen isotopic composition of meteoric waters defines an average trend on a plot of $\delta^{17}$O vs. $\delta^{18}$O with a slope of 0.528 (Barkan and Luz, 2010). Note that this slope differs from the mean terrestrial value of 0.52 or 0.524 assumed in many previous studies (e.g., Rumble et al., 2007) – one of several instances in which the community of scientists working on $^{17}$O abundances in natural materials have made different assumptions about the reference frame of expected mass dependent fractionations. This empirical slope differs very subtly from that for equilibrium fractionation between liquid and vapor water ($\ln^{17}O_{eq}/\ln^{18}O_{eq} = 0.529$; Risi et al., 2010). In contrast, gas-phase diffusion of water is defined by a slope (or, equivalently, a mass law exponent, $\lambda$) of 0.518 (Barkan and Luz, 2007; Fig. 6b). The mass law that describes the fractionation between water vapor and its liquid source can vary between these extremes, as a function of the relative humidity at the site of evaporation; i.e., high humidity evaporation will lie closer to the canonical 0.528 slope line and low humidity evaporation will have a lower slope, producing vapors that lie above the reference line in Fig. 6b (and, if evaporation is extensive, residual liquids beneath the line with a slope of 0.528). Therefore, $\Delta^{17}$O values of precipitation can be used to evaluate the humidity of the site where the vapor source of that precipitation first entered the atmosphere (Luz and Barkan, 2010; Risi et al., 2010). In addition to source water conditions, the conditions of ice condensation, re-evaporation, convective intensity and mixing of waters can affect $\Delta^{17}$O in precipitation, vapor and surface water (Landais et al., 2010; Risi et al., 2010; Risi et al., 2012).

The combination of these factors can make it complicated to tease apart the source of $\Delta^{17}$O variation in meteoric waters, but this task becomes tractable when $\Delta^{17}$O is used in concert with other measurements such as $d$-excess (where $d$-excess = $1000\times\delta^{17}$O; Landais et al., 2008; Risi et al., 2012). In conditions where evaporation is the main process driving oxygen and hydrogen isotope fractionation in precipitation, $\Delta^{17}$O and $d$-excess covary linearly because they are both determined by relative humidity and the isotopic composition of the surrounding vapor (Landais et al., 2010). The relationship between $\Delta^{17}$O and $d$-excess has been used in paleoclimate studies of ice cores, using $\delta^{17}$O as a means to measure and correct for the role of humidity on $d$-excess, such that the corrected $d$-excess value can be used as a proxy for temperature (another of its controlling variables; Landais et al., 2008). This...
approach may be compromised by the finding that $\Delta^{17}O$ and $d$-excess are often poorly correlated, and $\Delta^{17}O$ and relative humidity are poorly correlated in tropical storm systems (Fig. 7). These findings suggest that there are other processes (e.g., moisture source, continental recycling, and convective activity) in addition to relative humidity that influence $\Delta^{17}O$ variation in rainfall.

5.2. $\Delta^{17}O$ in CO$_2$

In the 1990’s Thiemens and colleagues discovered a large, positive $\Delta^{17}O$ value in stratospheric CO$_2$ (Fig. 6a), which is recognized as a consequence of mass independent fractionations in ozone chemistry coupled with exchange of O among ozone, CO$_2$ and other atmospheric constituents (Thiemens et al., 1991, 1995). Continued experimental study of relevant reactions, in molecular beam lines and using other methods, has led to a significant understanding of the chemical physics responsible for these effects (see review of Thiemens et al., 2012).

Because tropospheric CO$_2$ is a mixture of stratospheric CO$_2$ having a high $\Delta^{17}O$ value and terrestrial sources (respiration, ocean outgassing) with near-zero $\Delta^{17}O$ values, the $\Delta^{17}O$ value of tropospheric CO$_2$ has been proposed as a measure of the relative sizes of terrestrial vs. stratospheric fluxes to the tropospheric CO$_2$ pool. The catch is that stratospheric sources are a small part of the tropospheric CO$_2$ budget, so this application is possible only if the $\Delta^{17}O$ value of CO$_2$ can be measured precisely (Boering et al., 2004; Hoag et al., 2005).

Recent advances in the precision of triple-oxygen-isotope measurements of CO$_2$ have opened up new possibilities for using $\Delta^{17}O$ in atmospheric CO$_2$ to monitor the global carbon budget. In particular, initial evidence suggests that such measurements can distinguish between wood combustion, gas combustion and respiration, so that there is potential for it to be used as a tracer for anthropogenic CO$_2$ emissions, particularly in urban environments. These emerging methods also provide opportunities to precisely measure $\Delta^{17}O$ values in carbonate minerals, i.e., by converting them to CO$_2$ for isotopic measurements. This ability will open up new ways to examine water cycles in the geologic record and as a paleo-CO$_2$ barometer (e.g., Gehler et al., 2012; Pack et al., 2013). The coupling of $\Delta^{17}O$ and $\Delta^{18}O$ measurements in carbonates (i.e., carbonate clumped isotope analyses; see below) will be particularly powerful because the temperature constraints on $\delta^{18}O_{\text{water-mineral}}$ provided by $\Delta^{18}O$ will make it possible to construct $\delta^{17}O$ values of the formation water such that $\Delta^{17}O$ values of carbonates can be used to estimate the $\Delta^{17}O$ of that water, free of assumptions about the magnitude of the carbonate–water fractionation, and thereby get at hydrological conditions (degree of evaporation, precipitation/climate regime, moisture sources) at the time of mineral formation.

5.3. Questions and needs

The principal challenge of studies of $\Delta^{17}O$ values of meteoric waters and the authigenic minerals that grow from those waters is that the $\Delta^{17}O$ variation in rainfall reflects not only the humidity of its moisture sources but also continental recycling, convective activity and other factors. Most studies of $\Delta^{17}O$ in terrestrial waters to-date have focused on documenting natural variability and understanding the fundamental processes involved in triple oxygen isotope fractionation (Landais et al., 2006; Barkan and Luz, 2007; Luz and Barkan, 2010). The existing database includes a sparse but broad global survey of meteoric waters (Luz and Barkan, 2010), tropical rainfall (Landais et al., 2010), and plant and soil waters (Landais et al., 2006). These studies have been interpreted in light of models simulating Rayleigh distillation of air masses, either as idealized 1-dimensional columns or using general circulation models (Landais et al., 2008; Risi et al., 2010, 2012). And, there have been some exploratory efforts to reconstruct paleoclimate from ice cores (e.g., Landais et al., 2008; Winkler et al., 2012). However, the complexity of the meteoric water cycle and the diversity of environmental and geological problems that it touches mean that there is a great need to expand these studies. Particularly pressing needs include documenting variations in low- and mid-latitude settings and where evaporation is not the main driver of oxygen isotope fractionation. This work should include coupled $\Delta^{17}O$ and $d$-excess studies of precipitation and associated ground waters, on both the scale of individual storms and across large regions to understand the full dynamics of the relationship between these parameters. Studies of surface and ground waters, in particular, will be the key towards developing $\Delta^{17}O$ as a tool for studying paleoclimate and paleohydrology.

6. Illuminating mass independent sulfur isotope fractionations

The search for mass independent sulfur fractionations (S-MIF) started in the 1960’s with the work of Hulston and Thode (1965). Mass-independent signatures, ascribed to solar nebula photochemical processes or cosmic ray spallation, were first documented in Allende by Rees and Thode (1977) and later in iron and achondrite meteorites (e.g., Gao and Thiemens, 1991; Thiemens et al., 1994) and in organic sulfonic acids from the Murchison carbonaceous chondrite (Cooper et al., 1997). Subsequently, anomalous sulfur isotope ratios were found in meteorites from Mars (i.e., the SNC’s), and it was demonstrated experimentally that ultraviolet photolysis of SO$_2$ (but not of H$_2$S) yielded S-MIF compositions; on this basis S-MIF isotopic anomalies in the SNC meteorites were ascribed to Martian atmospheric chemistry (Farquhar et al., 2000b, 2001).

This field expanded greatly in scope and significance with the discovery that pyrite (FeS$_2$) and barite (BaSO$_4$) in sedimentary rocks of Archean and early Paleoproterozoic age, but not in younger rocks, commonly exhibit large (several per mil) mass-independent sulfur isotope fractionations (Farquhar et al., 2000a; Fig. 8). Since this discovery, the geological record has been more extensively and finely sampled and the range of observed Archean S-MIF fractionations has reached approximately $\Delta^{34}S = -4$ to $+14$‰ (Farquhar et al., 2000a; Johnston, 2011; Guy et al., 2012; Phillipot et al., 2012). On the basis of SO$_2$ photolysis experiments (Farquhar et al., 2000b, 2001) and atmospheric chemistry models (Pavlov and Kasting, 2002), these isotope anomalies were ascribed to sulfur photochemistry in an atmosphere with less than $10^{-5}$ times the modern atmospheric O$_2$ partial pressure. S-MIF anomalies in modern atmospheric aerosols and in volcanic dust-rich horizons in Antarctic ice cores (Romero and Thiemens, 2003; Baroni et al., 2007, 2008) demonstrate that the chemistry required for S-MIF generation occurs in parts of the modern O$_2$-rich atmosphere, though the signal is only preserved in atmospheric aerosol. I.e., the key role of O$_2$ is not to completely suppress generation of S-MIF anomalies, but rather to prevent them from being preserved in the geological record by promoting conversion of atmospheric S compounds to sulfate that eventually mixes into the large marine reservoir.

While it is widely accepted that the large S-MIF anomalies of Precambrian sedimentary rocks reflect the reduced character of the Archean atmosphere, there are still major hurdles to our understanding of their physical and chemical meaning, the processes that transmitted this signature from its presumed atmospheric source into the rock record, and the quantitative constraints that might be derived from the details of the S-MIF record — its magnitude and spatial and temporal variations. We focus here on these questions and refer the reader to recent reviews for a more complete survey of S-MIF (Farquhar and Wing, 2003; Johnston, 2011).

6.1. Generation of Archean–Proterozoic S-MIF

Distinctly nonzero $\Delta^{33}S$ values in Archean–Proterozoic rocks (Fig. 8) are generally correlated with non-zero $\Delta^{34}S$; this appears to rule out magnetic isotope effects, which should influence only $^{35}S$ (the only S isotope with a nuclear magnetic moment) as the source of S-MIF (e.g., Ohmoto et al., 2006; Oduro et al., 2011). Additional constraints on the source of S-MIF are suggested by trends in $\delta^{34}S$–$\Delta^{33}S$–$\Delta^{34}S$
space defined by Archean sedimentary rocks. These materials form arrays in $\Delta^{33}S - \delta^{34}S$ space with slopes typically between 0.5 and 1 (or, slopes between 1 and 2 in Fig. 8; Ono et al., 2003; Kaufman et al., 2007), arguing against processes with modestly anomalous mass laws (which generally have near-zero slopes in this space, or near 0.5 slopes in Fig. 8). Typical Archean slopes of $-0.9$ in $\Delta^{36}S - \Delta^{33}S$ space (e.g., Kaufman et al., 2007) differ distinctly from values between $-7$ and $-9$ that are characteristic of mass-dependent processes (Ono et al., 2006; Johnston et al., 2007). These inconsistencies have been taken to reinforce the leading hypothesis that $SO_2$ photolysis is the cause of S-MIF in Archean rocks.

Despite the general consensus that the Archean S-MIF record was generated by UV–photochemistry in a $SO_2$-bearing, anoxic atmosphere, several essential details are unclear. Laboratory experiments examining $SO_2$ photolysis yield products ($H_2SO_4$, $S_8$ aerosols, organo-sulfur compounds) and residual $SO_2$ with $\delta^{33}S - \delta^{34}S$ fingerprints that depend on the wavelength of light driving the reactions, the bath gas composition and, and on the optical thickness of the photolysis column (Farquhar et al., 2001; Masterson et al., 2011; Whitehill and Ono., 2012; Ono et al., 2013a, 2013b). While some broadband photolysis experiments successfully match observations of S-MIF in present-day stratospheric sulfate aerosols (Ono et al., 2013a, 2013b), none have been able to reproduce the Archean array. Moreover, there is no mechanistic understanding of the variability in $\delta^{33}S - \Delta^{33}S - \Delta^{36}S$ relationships for these experimental products.

Difficulties in matching Archean S-MIF through direct experiments have motivated fundamental studies of the absorption spectrum of $SO_2$, in hopes of finding a part of the spectrum having fractionations that can explain the rock record. Subtle differences among the absorption cross sections of all $SO_2$ isotopologues (Lyons et al., 2010). Studies, suggesting that the spectral resolution of existing cross sections is too low to resolve all of the relevant differences among the isotopologues (Lyons et al., 2010).

In an optically thin atmospheric $SO_2$ column (i.e., one in which self-shielding does not occur) S-MIF fractionations arise because, at any given wavelength, the absorption cross sections differ between the $SO_2$ isotopologues but not following a simple (or at least easily predicted) dependence on mass. Measured cross sections for isotopologues of sulfur dioxide have improved considerably over the past 5 years, and differences among these cross sections appear to account for a significant amount of the observed S-MIF fractionation in experiments and perhaps in nature (Danielache et al., 2008; Ueno et al., 2009; Halevy et al., 2010). However, S-MIF from preliminary calculations with newly-measured, high-resolution absorption cross sections differs from these previous studies, suggesting that the spectral resolution of existing cross sections is too low to resolve all of the relevant differences among the isotopologues (Lyons et al., 2010).

Mass-independent effects may also arise because isotopologues differ in their oscillator strengths and in their probabilities that photo-excited molecules relax to the ground state and avoid dissociation. The latter effect has been suggested to explain mass-independent effects in the photo-polymerization of $CS_2$ (Zmolek et al., 1999). A combination of such effects, which lead to adiabatic crossings and differences in dissociation dynamics, has been suggested to explain mass-independent effects in the photodissociation of $CO_2$ (Bhattacharya et al., 2000) and $CO$ (Chackraborty et al., 2012). The dependence of experimentally produced S-MIF on the pressure of an inert bath gas and on the water vapor content (Farquhar et al., 2001; Masterson et al., 2011) hints at similar effects during $SO_2$ photodissociation, though quantitative model predictions cannot yet be made because of the absence of a sufficiently accurate potential energy surface for the dissociation of photo-excited $SO_2$.

6.2. Carriers of Archean–Proterozoic S-MIF from atmosphere to surface

The identities of the molecules that carried the Archean S-MIF isotopic anomaly to the surface and the sign and magnitude of S-MIF in the different carriers are unclear. Photolysis experiments done to-date were invariably performed with $SO_2$ density orders of magnitude higher than realistic atmospheric abundances. Oligomerization of elemental sulfur to ultimately yield $S_8$ aerosols is favored under more realistic conditions, leading to the prevailing view that S-MIF was delivered to
Earth’s surface in H$_2$SO$_4$ and S$_8$ aerosols as well as in the residual SO$_2$ (e.g., Farquhar et al., 2000a, 2001; Pavlov and Kasting, 2002; Ono et al., 2003; Zahnle et al., 2006).

Experiments with more realistic SO$_2$ abundances (as low as 2 ppm), and in the presence of realistic abundances of small, gaseous hydrocarbons (CH$_4$, C$_2$H$_4$, and C$_2$H$_2$) have yielded methanesulfonic acid (CH$_3$SO$_2$H), dimethylsulfone [(CH$_3$)$_2$SO$_2$] and similar molecules (DeWitt et al., 2010; Oduro et al., 2012). Sulfur isotope ratios in these organo-sulfur products are mass-independent (Oduro et al., 2012), leading to suggestions that organo-sulfur compounds generated by reaction of photo-excited SO$_2$ with atmospheric hydrocarbons carried S-MIF to Earth’s surface (Halevy, 2013).

6.3. Preservation of S-MIF in the geological record

The process (or processes) responsible for S-MIF generation has been translated and modified by the biogeochemical sulfur cycle before being written in the observable geologic record. On the one hand, this presents a problem to the interpretation of the geological record as a simple constraint on past atmospheric chemistry. On the other hand, if the patterns of S-MIF in the geologic record (i.e., spatial and temporal variations in amplitudes of signals) were observed in sufficient detail and decoded through models of appropriate complexity, it might be possible to constrain not only the origin of S-MIF but also the species and processes that carried that signature into minerals. A complete and successful model of the observable S-MIF record mayvaluably constrain the characteristics of Earth’s early surface environment.

Models of increasing sophistication account for biogeochemistry and transport in the oceanic sulfur cycle (Halevy et al., 2010; Halevy, 2013), and for communication of the marine sulfur pool with the reservoir of sulfur minerals on land (Reinhard et al., 2013). One important conclusion derived from these models is that future observations should focus on non-marine and shallow marine environments, where the S-MIF preserved should most closely resemble the original signal delivered by the atmospheric carriers (Halevy, 2013). And, a recent model of the Archean sulfur cycle links increases in the magnitude of S-MIF as well as its asymmetry (i.e., difference between sulfide and sulfate anomalies) to increasing subaerial volcanism (Halevy et al., 2010). Some parts of the Archean S-MIF record may be too poorly sampled to reach confident conclusions of this kind (particularly where the marine sulfate record is relatively sparse). Nevertheless, recent discovery of Archean volcanic sediments with the highest S-MIF magnitude and asymmetry observed to date has reinforced the importance of subaerial volcanism to the Archean sulfur cycle (Philippot et al., 2012). Whatever their challenges, models of this kind have the potential to convert geological records of S-MIF into specific statements about the sulfur cycle, and to identify important targets for future observations and experiments.

6.4. Questions and needs

Major theoretical and experimental efforts will be required to understand the isotopic effects of the various mechanisms suggested to generate S-MIF. A potential energy surface for excited SO$_2$ must be calculated to facilitate modeling of kinetic isotope effects during SO$_2$ photodissociation. High-resolution absorption spectra of all four $^{34}$SO$_2$ isotopologues must be measured to allow calculations of differences in photo-excitation probabilities. An inherent challenge with such measurements is that SO$_2$ photo-dissociates at the spectral intervals of interest, making it difficult to achieve high spectral resolution and signal-to-noise ratios while maintaining a stable column optical thickness of SO$_2$. Experimental photolysis at low integrated column opacities and sub-ppm concentrations of SO$_2$ are required to determine S-MIF generated under realistic atmospheric conditions. To study the chemical mechanisms of SO$_2$ photolysis, the products must be identified and separated more carefully than in past experiments, and their multiple-isotope compositions measured. Improvements in the analysis of small samples (e.g., Paris et al., 2013) will facilitate this.

A broader challenge is to understand the specific chemical pathways by which S-MIF signals are deposited on the Archean surface and recorded in rocks; much work will be required to develop a detailed and realistic picture of these processes. It will be particularly important to investigate the anoxic gas-phase and aqueous chemistry of organo-sulfur compounds — something that is presently very poorly constrained.

7. Mass independent fractionations of heavy metals

Interest in mass independent fractionation of the isotopes of heavy elements began with laboratory experiments on uranium isotope fractionation in oxidation/reduction equilibria [U(VI) vs. U(IV) and U(IV) vs. U(III)] (e.g., Fujii et al., 1989). In these experiments, heavy uranium isotopes were concentrated in chemically reduced species. Equilibrium mass dependent fractionation usually favors heavy isotopes in oxidized species (e.g., Bigeleisen and Mayer, 1947), because these species’ vibrational zero point energies are more sensitive to isotope substitution. Furthermore, the magnitude of observed fractionation was not proportional to differences in isotopic mass — $^{234}$U/$^{238}$U changed only 14% more than $^{235}$U/$^{238}$U despite a 33% greater mass difference (Fujii et al., 1989; Nomura et al., 1996). And, more generally, common mass dependent chemical isotope effects generally scale inversely with isotopic mass and should be negligibly small for U.

7.1. Nuclear volume effects

Jacob Bigeleisen (1996a) and Nomura et al. (1996) showed that these fractionations correlated with spectroscopic observations of nuclear field shifts in uranium — changes in the energies of electronic transitions caused by variation in the volume (and to some extent the shape) occupied by the positive charge in the atomic nuclei. Specifically, they found qualitative correspondence between measured nuclear field shift energies in atomic vapor (−1 cm$^{-1}$ = 12 μmol) and the amount of energy needed to drive the observed fractionations. Nuclear spin effects were found to be much smaller.
In spectroscopy, the nuclear field shift effect (schematically illustrated in Fig. 9) occurs because electron densities (especially for s-orbitals) in atoms overlap with the nucleus. For the simple case of a spherical nuclear charge distribution, when an electron is inside the nucleus, the nuclear charge exterior to its location does not exert any net electrostatic attraction. Such electrons are not bound as strongly to a finite-volume nucleus as they would be to a point-charge nucleus. When comparing isotopes of the same element, nuclei that take up more space will contain more electron density, and the electrons will be bound more weakly. Smaller nuclei of that element hold onto electrons more tightly. Geochemical isotope fractionation will occur when species with different electronic structures exchange isotopes with different nuclear charge distributions. As a rule, species with more s-electrons preferentially incorporate small (usually neutron-poor) isotopes, while s-orbital-depleted species prefer larger isotopes. P-, d- and f-electrons screen s-electrons, reducing their electron density inside nuclei, so they tend to have the opposite effect on isotope fractionation. The nuclear field shift effect is particularly interesting for geochemistry because atomic spectroscopy shows that nuclear field shifts increase rapidly towards the bottom of the periodic table, suggesting that fractional nuclear charge. The nuclear field shift effect is due to the nuclear field's ability to alter the electron density inside nuclei, so they tend to have the opposite effect on isotope fractionation. The nuclear field shift effect can be produced in triplet (T) or singlet states (S). Triplet states are spin forbidden from recombining to form the starting product and must undergo T → S intersystem crossing in order to recombine. Because of the interaction of the magnetic moment of the odd nuclei with the unpaired electron, odd isotopes undergo intersystem crossing much faster than the even isotopes resulting in the enrichment or depletion of odd Hg isotopes in the reaction products depending on whether the radical pair started in a triplet or singlet state (Buchachenko et al., 2007). In order for intersystem crossing to compete with dissociation into free radicals, it is necessary for the radical pair to be in a solvent cage to extend the lifetime of the radical pair. For aqueous photochemical reduction, the water acts as a solvent cage.

Despite this relatively detailed understanding of MIF in Hg, there are reasons to think that it is not the whole story. First, nuclear volume effects may also significantly impact the odd isotopes of Hg, and the balance of nuclear volume and magnetic isotope effects is not clear in every instance. And, recent studies of atmospheric samples also show that the even isotopes of Hg also display small non-mass dependent fractionation (Gratz et al., 2010; Chen et al., 2012; Demers et al., 2013; Rolison et al., 2013). Because the nuclear volume and magnetic isotope effect should only result in non-mass dependent isotope fractionations for the odd isotopes in Hg, the mechanism for the even isotope mass independent fractionation is unknown, but may be related to gas phase reactions and mechanisms similar to those for oxygen and sulfur.

Much current research is aimed at distinguishing magnetic from mass-dependent and nuclear-field shift fractions as the cause(s) of the odd-isotope mass-independent fractionation of Hg. Because Hg has seven isotopes, two of which are odd, it has been suggested that the ratio of the mass independent fractionations (ΔHg/ΔHg) might be unique to the different mechanisms. Theoretically, the ratio of ΔHg/ΔHg for the nuclear volume effect is predictable from measured nuclear charge radii and should be the same for different transformations. Theoretical predictions of this ratio range from 1.6 to 2.7 depending on the nuclear charge radii estimates used (Schauble, 2007; Ghosh et al., 2008; Estrade et al., 2009; Wiederhold et al., 2010; Zheng and Hintelmann, 2010; Ghosh et al., 2013). However, earlier experiments were not able to confirm what estimate was most accurate because nuclear volume associated mass independent fractionations are very small and the error in the ratio was too high. More recently, Zheng and Hintelmann, 2010, reported a ratio of 1.61 ± 0.06 (2SE) for a dark kinetic reaction and suggested that it was the result of the nuclear volume effect. However, both the nuclear volume effect and magnetic isotope effect can occur during kinetic reactions and it was unclear whether the signature could have been produced by the magnetic isotope effect in the dark. In order to avoid the magnetic isotope effect, Ghosh et al., 2013, performed Hg liquid–vapor equilibrium experiments (similar to Estrade et al., 2009) and confirmed a ratio for the nuclear volume effect of 1.59 ± 0.06 (2SE). Thus the theoretical prediction for the ratio of 1.6 by Wiederhold et al., 2010, using nuclear charge radii compiled in Fricke and Helling (2004), appears to be the most accurate estimate.

The ratio of ΔHg/ΔHg for the nuclear volume effect of ~ 1.6 does appear to be significantly different from the ratios observed for the magnetic isotope effect, which range from ~ 1 to 1.4 for experimental photochemical transformations involving different Hg species and ligands (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009; Chandan et al., submitted for publication). Because the theory behind the magnetic isotope effect is relatively qualitative, it is difficult to explain the ratios observed in different photochemical reactions, nor even why they differ from one another. However, the magnetic isotope effect is sensitive to numerous factors including hyperfine coupling, lifetime of the radical pair, coupling strength of the radical pair, spin-orbital coupling, diffusion factors, and the nature of the solvent cage (space) in which the reaction occurs (Buchachenko, 2001). Therefore, changing the ligand that the Hg is associated with may affect many of the factors that affect the magnetic isotope effect and change the relative rates at which 199Hg and 201Hg undergo T → S state intersystem conversion. Despite a range of ratios observed in experiments, natural
samples are much more consistent. Biological samples that are dominated by monomethylmercury have ratios close to 1.3, which is consistent with monomethylmercury photo-degradation (Bergquist and Blum, 2009; Sonke, 2011). Whereas, samples dominated by inorganic $\text{Hg}^{2+}$ have ratios close to 1.0, which is consistent with the photochemical reduction of $\text{Hg}^{2+}$ in the presence of dissolved organic matter (Bergquist and Blum, 2009; Sonke, 2011).

7.3. Questions and needs

First, experimental and theoretical studies of mass-independent fractionations of heavy elements have focused on gas-phase and aqueous species, in part because condensed phases are not readily modeled using current relativistic electronic structure software codes. Substances with metallic bonding, in particular, may be difficult to model successfully using molecular methods. Second, nuclear shape effects stemming from non-spherical nuclear charge distributions in odd isotopes have mostly been neglected. One study (Knyazev et al., 1999) suggests that volume effects are the dominant component of nuclear field shift fractionation, but it is possible such shape effects are more important for some elements and materials. Third, a quantitative or even semi-quantitative theory of magnetic-isotope fractionation is needed. At present there is no tractable framework for predicting these fractionations, even though they apparently dominate $\text{Hg}$-isotope MIF. Fourth, we are aware of no attempts to incorporate nuclear field shift effects into transition state theory. This means that our understanding of kinetic processes of mass-independent fractionation in heavy elements is largely empirical and phenomenological, despite the critical importance of chemical–kinetic isotope effects in geochemistry (above). Finally, disagreements between calculated $\text{Hg}$-isotope fractionations and experiments have highlighted uncertainties in tabulated nuclear charge radii (e.g., Schauble, 2007; Ghosh et al., 2008; Estrade et al., 2009; Wiederhold et al., 2010; Ghosh et al., 2013), indicating for instance that the Fricke and Heilig (2004) tabulation is more accurate than Angeli (2004). This suggests that careful measurement of nuclear field shift fractionation is a potential tool for determining nuclear structure parameters of high-Z isotopes.

8. Clumped isotope geochemistry of carbonate species

Recent advances in isotope ratio mass spectrometry make it feasible to precisely determine the abundances of doubly-substituted isotopologues at their low natural abundances, leading to a new field of isotope studies—clumped isotope geochemistry (Eiler and Schauble, 2004; Eiler, 2007, 2013). The most notable tool to emerge from this young field is ‘carbonate clumped isotope thermometry’ (Eiler, 2011), which is based on the fact that abundances of doubly substituted isotopologues of carbonate ions containing both a $^{13}\text{C}$ and one $^{18}\text{O}$ (i.e., $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$) in equilibrated systems are controlled by a homogeneous equilibrium:

$$^{13}\text{C}^{16}\text{O}_3^{-2} + ^{12}\text{C}^{18}\text{O}^{16}\text{O}_2^{-2} = ^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{-2} + ^{12}\text{C}^{16}\text{O}_3^{-2}$$

The equilibrium constants for reactions of this form are a function of temperature, and thus provide the basis of a paleothermometer (Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2011); perhaps the most important feature of this method of paleothermometry is that it can be used to constrain temperatures without knowing the $\delta^{18}\text{O}$ of waters from which carbonate minerals grew.

One significant challenge faced by carbonate clumped isotope thermometry is the possibility that kinetic fractionations, including both ‘vital effects’ and abiological processes, might disturb the homogeneous equilibrium on which the method is based. Both speleothems and corals show significant deviations from equilibrium with co-existing waters, for both carbon and oxygen isotope compositions (Fig. 10a and b). In the case of speleothems and surface corals, these are accompanied by clumped isotope compositions that also differ markedly from equilibrium (Fig. 10a and b). In the case of speleothems and surface corals, these are accompanied by clumped isotope compositions that also differ markedly from equilibrium (Fig. 10c). Here we discuss recent attempts to understand kinetic isotope effects in these carbonate materials, focusing on two questions: (1) Under what circumstances is isotopic ‘clumping’ in carbonate controlled by kinetics rather than equilibrium? And, (2) what do these examples teach us about the chemistry of dissolved inorganic carbon and carbonate minerals? More generally, the studies discussed below present the first well-

![Fig. 10. Isotopic compositions of representative speleothems (a and c, red symbols), deep-sea corals (blue, b and c) and surface corals (yellow, b and c). Values of $\delta^{13}\text{O}$ and $\delta^{18}\text{O}$ of both (a, b) deviate from expected equilibrium with coexisting waters for all three materials, but (c) whereas speleothems and surface corals deviate strongly in clumped isotope compositions from expected equilibrium values, deep-sea corals conform to equilibrium. Data from Adkins et al., 2003; Mickler et al., 2004; Affek et al., 2008; Daeron et al., 2011; Thiagarajan et al., 2011; Saenger et al., 2012; Kluge and Affek, 2012; and Affek, 2012.](image-url)
developed example in which complex, kinetically controlled clumped isotope fractionation has been examined from several perspectives — experimental, theoretical and as expressed in natural materials.

8.1. Speleothems and degassing of DIC solutions

Carbonate clumped isotope analyses of modern speleothems typically yield apparent temperatures significantly higher than known growth temperatures (i.e. assuming a calibration of the thermometer based on nominally equilibrated calcite) — here we use the term ‘apparent’ temperature to mean the clumped-isotope derived temperature that may or may not relate to the actual formation temperature. These differences can be up to ~22 °C, and are typically on the order of ~10 °C (Fig. 10c). Speleothem precipitation is driven by the fact that drip waters (calcium bicarbonate solutions) are exposed to high partial pressures of CO2 as they percolate through soil and rock, but once they enter a ventilated cave they encounter the relatively low pCO2 of air. Dissolved CO2 in the drip water outgasses in response to this drop in pCO2. As CO2 leaves the solution, bicarbonate decomposes by dehydroxylation (and, similarly, the small amount of carbonic acid dehydrates). This decrease in dissolved inorganic carbon at constant total alkalinity increases the carbonate saturation state, driving growth of calcite or aragonite from the drip water (a simpler way to describe this process is that the reaction, Ca2+ + 2xHCO3-> CaCO3 + CO2 + H2O, is driven to the right when pCO2 decreases). The δ13C and δ18O values of speleothem carbonates commonly deviate from expected compositions, given their temperatures of growth and compositions of their parent waters, indicating that this process involves kinetic isotope effects, and proceeds more rapidly than re-equilibration with water. For this reason, it has been hypothesized (and demonstrated in some detail) that the failure of carbonate clumped isotope compositions to record equilibrium at the known growth temperature reflects the influences of kinetic isotope effects associated with dehydroxylation of bicarbonate.

Solution to this problem required a combination of theoretical, experimental, and field-based approaches. Guo et al. (2007) and Guo (2009) use first principle transition state calculations to simulate the kinetic fractionations of all isotoxopologues of HCO3− during dehydroxylation, and predicted these fractionations would lead to a lower proportion of 13C-18O substituted isotoxopologues in the residual HCO3− as compared to that expected at equilibrium, and thus to overestimations of carbonate growth temperatures based on carbonate clumped isotope thermometer. These calculations also predict HCO3− dehydroxylation will lead to increases in the δ18O of residual DIC species, which is also passed on to speleothems; thus, there should be a correlation between anomalously low abundances of clumped isotope species and anomalously high δ18O values, with a slope of ~−0.025 at 25 °C. These theoretical predictions are broadly consistent with the experimental observations in modern speleothems, and have been used to correct measured compositions of natural speleothems for these kinetic effects (Guo et al., 2007; Guo, 2009; Wainer et al., 2011). However, the model-predicted correlation between clumped isotope depletion and oxygen isotope enrichment is significantly smaller, by a factor of ~2, than what is observed in modern speleothems. This indicates that either the kinetic model of HCO3− dehydroxylation is incorrect, or that kinetic processes other than degassing reactions, such as kinetic isotope effects associated with precipitation of dissolved carbonate (Nielsen et al., 2012), also affect the clumped isotope composition of speleothems.

8.2. Corals

The clumped isotope composition of deep-sea corals exhibit no apparent deviations from expected equilibrium values, despite having well documented and large vital effects in their carbon and oxygen isotope compositions (Fig. 10b and c; Thiagarajan et al., 2011). In contrast, surface corals appear to exhibit pronounced enrichments in 13C-18O ‘clumps’ relative to expected proportions for their known growth temperatures (and thus apparent temperatures lower than known growth temperatures; Saenger et al., 2012; Fig. 10c).

The lack of a kinetic signature in clumped isotope temperatures of deep-sea corals appears to be most consistent with the pH model of stable isotope vital effects in biogenic carbonates, which hypothesizes that they arise due to differences between the equilibrium stable isotope compositions of CO3− and HCO3− ions and the differences in pH between environmental and body waters from which biominerals precipitate (Zeebe, 1999; Adkins et al., 2003; Guo et al., 2009; Thiagarajan et al., 2011). Dissolved HCO3− and CO3− in an equilibrated solution differ in δ18O by ~6.8‰ at 25 °C (Beck et al., 2005), such that basic solutions (pH >9), which are dominated by carbonate ion, tend to precipitate low δ18O carbonate, whereas higher pH solutions (pH from ~6 to 9), which are dominated by bicarbonate ion, grow higher δ18O carbonate. Thus, an organism that increases the pH of its body waters to induce carbonate precipitation will tend to exhibit a negative ‘vital effect’ in δ18O (Fig. 10b).

Guo et al. (2008) and Guo et al. (2012) predict a subtle difference of ~0.04‰ between the equilibrium clumped isotope compositions of bicarbonate and carbonate ions (also at 25 °C), using first principle quantum mechanical calculations of isotope effects on the vibrational energies of HCO3−·(H2O)n and CO3−·(H2O)n clusters. Based on these predictions, Guo et al. concluded that modest variations in pH could lead to observable changes in δ18O (per mil level) when the corresponding changes in clumped isotope composition remain similar to analytical errors (~0.01–0.02‰). These expectations are generally consistent with initial experiments constraining the difference in Δct between HCO3− and CO3− (Guo et al., 2012) and with later theoretical calculations by Hill et al. (2014). However, a larger experimental data set presented by Tripati et al. (in press) suggests a somewhat larger effect (0.06 ± 0.02‰). These effects are just strong enough that they may well lead to observable vital effects in clumped isotopes and/or equivalent differences in temperature dependence of Δct for inorganic carbonates grown from high and low pH solutions. It is possible that this effect plays some role in explaining discrepancies between some calibrations of the carbonate clumped isotope thermometer (e.g., Ghosh et al., 2006 vs. Dennis et al., 2010).

The non-equilibrium enrichment in isotopic ‘clumps’ in surface corals is less well understood at present, and might reflect diffusion of CO2 across cell membranes, chemical kinetics of the hydration and hydroxylation of aqueous CO2 (Saenger et al., 2012; see also McConnaughey, 1989; Cohen and McConnaughey, 2003) or, perhaps,

![Fig. 11. Schematic illustration of important reactions affecting the isotopic composition of dissolved inorganic carbon.](image-url)
the equilibrium fractionation factors between solutions and the distinct surface layers of growing grains (Watson, 2004; see Fig. 11). There are currently no experimental constraints on the clumped isotope effects associated with hydration and hydroxylation of CO₂, Guo et al. (2007) and Guo (2009) made first-order theoretical estimates of these processes, assuming no isotope effects on the forward reactions (i.e., O from water is added to CO₂ unfraccionated), and predicted that this process should yield bicarbonate species with clumped isotope compositions significantly higher than the expected equilibrium values, at least in the direction of the kinetic isotope effects observed in surface corals (Saenger et al., 2012). If this process is responsible for the surface coral vital effect, it could be thought of as a mirror image of the kinetic effect in speleothems; i.e., whereas speleothems are depleted in 13C-18O clumps due to rapid dehydroxylation of bicarbonate and degassing of CO₂, enrichments in those clumps in surface corals are due to rapid hydration of excess CO₂.

An essential process that must influence whether or not kinetic isotope effects can be manifested in the clumped isotope compositions of DIC species is the rate of their isotope exchange with water. i.e., if chemical or physical fractions drive the DIC pool out of equilibrium with respect to the homogeneous equilibria that control clumping, exchange with co-existing water may allow a return to the equilibrium state. This may be an important factor that mitigates the effect of CO₂ degassing on the isotopic compositions of speleothems (and thus perhaps explains the range in offsets between apparent and independently known temperatures; Fig. 10c). Although the kinetics of oxygen isotope exchange of DIC species have been well constrained by experimental studies (Beck et al., 2005), only recently has there been any such data for clumped isotope equilibria (Affek, 2013).

8.3. Questions and needs

The greatest gaps in our understanding of the clumped isotope geochemistry of carbonate minerals and related dissolved species is the relative paucity of experimental constraints on the exchange equilibria and kinetics of all the relevant species (Fig. 11). Particularly important goals include: (1) establishing whether pH effects arising from differences between carbonate and bicarbonate ions influence the temperature dependence of Δ47 values for biogenic carbonates and previous attempts to calibrate the method by inorganic experiments; (2) constraining the kinetic fractionations associated with CO₂ hydration and hydroxylation reactions; (3) studies of clumped isotope effects associated with variations in solid growth rates, which may inform kinetic isotope effects associated with the solution/solid interface (Fig. 1, above); and (4) kinetics of clumped isotope exchange between DIC species and water. And, it will be important that this work considers the effects of carbonic anhydrase or other catalysts (Uchikawa and Zeebe, 2011).

A final more general point to keep in mind is that all clumped isotope studies examine second-order isotope effects more subtle than those responsible for most stable isotope signals. It has recently been shown that the theories commonly used to predict and interpret chemical isotope effects (i.e., models of vibrational isotope effects based on Urey theory) lead to small but analytically significant errors due to approximations in the handling of anisotropy and ro-vibrational coupling (Webb and Miller, 2014). It may be important for the future growth of this field that higher-level theory (e.g., Feynman path integral approaches) be brought to bear on these problems.

9. Position-specific and clumped isotope effects in organics

Isotopic measurements of organic compounds are generally approached using methods that constrain only the bulk isotopic composition of an element of interest, averaged across all molecular sites in the analyte. This is because these methods generally convert complex molecules to simpler gases such as CO₂, CO, H₂, O₂, SO₂, and SF₆. However, each distinctive ‘site’ in the molecule need not have the same isotopic composition. For example, acetate (CH₃COO⁻) has two distinct carbon containing groups, a methyl group (CH₃) and carboxyl group (COO⁻) which differ in the 13C/12C ratio by up to 20% in natural samples (Blair et al., 1985). Additionally, clumping in organic molecules has been both predicted (Ma et al., 2008) and demonstrated in synthetic and natural compounds (Stolper et al., 2012; Clog et al., 2013; Stolper et al., 2014, submitted for publication). Much of the potential richness in the isotope geochemistry of organic compounds arises from this fact that isotopic tracers and fractionations can be tied to specific atomic sites in complex molecular structures.

There have been several attempts to measure natural-abundance isotopic compositions at the site-specific level in organic compounds, motivated by the constraints such measurements could provide on chemical, biological and environmental processes, and their potential as forensic tracers of foods, illicit drugs, explosives and other materials. This sub-discipline of isotope chemistry has been contemplated in some form since the 1930’s, but only recent advances in analytical instruments and methods have made it tractable. Eiler (2013) reviews the history of approaches to this subject. Here, we focus on three emerging methods: NMR, high-resolution sector mass spectrometry, and IR absorption spectroscopy.

9.1. Natural abundance NMR (‘SNIF-NMR’)

Nuclear Magnetic Resonance (NMR) has several characteristics that make it a promising technique for site-specific isotope analysis. First, the NMR effect (i.e., coupling of nuclear spin with an applied oscillating magnetic field) provides a measurement of the electronic structure, and thus chemical environment, of atoms in a molecule. NMR spectra distinguish, for example, between saturated and unsaturated carbons, and members of rings vs. side branches, based on the magnitude of the energy shift that is measured by an NMR analysis. Thus NMR is inherently ‘site specific’. Second, NMR experiments are sensitive to isotopic composition because the NMR effect is proportional to magnetic moment, which varies among some isotopes. This feature of NMR effectively removes problems of interferences present in mass spectrometry and reduces the importance of abundance sensitivity (i.e., difficulty observing a rare species against the background created by some other, more abundant species). On the other hand, no NMR shift is observed when both the number of protons and neutrons in a nuclide are even; i.e., H, D, 12C and 16O are ‘seen’; 13C, 18O and 18O are not. Thus, an NMR measurement may be used to directly compare relative concentrations of 13C in two sites of a molecule, but 12C/13C ratios in each site generally require some sort of additional constraint, such as a known bulk isotope ratio for the molecule.

NMR has long been used to analyze the site-specific isotopic compositions of artificially enriched materials, or of the products of reactions that have been driven to high extents of completion, such that the unreacted residues manifest exceptionally large heavy-isotope enrichments (Singleton and Thomas, 1995). This is a relatively routine analysis that could be made by a large number of laboratories. However, making such measurements on materials with natural isotope abundances and at the precisions necessary for geochemical studies requires exceptional stability and extraordinary signal integration times (‘site-specific natural isotope fractionation (SNIF)-NMR’ techniques). The basic technologies used by SNIF-NMR are available in many NMR facilities, but only a very few have established the methodologies to do it in practice. SNIF-NMR has been developed for both site-specific δD and δ13C, and has been used sporadically for nearly 30 years to study the forensics of agricultural products and illicit drugs and mechanisms of metabolic pathways (Caer et al., 1991; Hays et al., 2000; Schmidt et al., 2003). This work has increased in pace and taken significant steps toward broader geochemical use with the demonstration that site-specific δD of cellulose may be a paleoclimate archive (Betson et al., 2006) and
with the characterization of site-specific C isotope ananomies of sugars and alkanes of different origins (Gilbert et al., 2012, 2013).

As an example of the potential of site-specific carbon isotope measurements for forensic studies we present results from an experiment one of us (T. Larson) recently performed to study the isotopic structure of dimethyl methylphosphonate (DMMP), a common precursor for chemical weapons (Fig. 12). We examined the carbon isotope composition of phosphorous-bound carbon in dichlor synthesized by the Arbuzov reaction (i.e. the reaction of a trialkyl phosphate with an alkyl halide to produce an alkyl phosphate). The $^{13}$C of the whole DMMP molecule, as determined by conventional combustion followed by IRMS of CO$_2$, is identical to the starting reagent CH$_3$OH ($^{13}$C$_{DPD} = -45.9$). However, when the two methoxyl groups of DMMP are chemically removed, leaving only the single carbon on phosphorus, the $^{13}$C value of the remaining methyl phosphonic acid (MPA) becomes $-84.0\%e$; i.e., the isotope effect associated with forming the P–C bond is observed. This effect was demonstrated by relatively laborious chemical decompositions of DMMP. However, it should be measurable by SNIF-NMR because that method differentiates the C–P from C–O bonds; i.e., it provides a site-specific measurement that should reveal the exceptionally low $^{13}$C/$^{12}$C ratio diagnostic of the P–C bond when it is formed by the Arbuzov reaction. If, as we suspect, other methods of DMMP synthesis do not exhibit this distinctive site-specific isotopic fractionation, it is easy to imagine using a SNIF-NMR measurement to recognize the specific methods used to synthesize this chemical weapons agent.

9.2. High-resolution gas source mass spectrometry

It is imaginable that mass spectrometry could produce a general (or at least very broad) approach to studies of position specific and multiply substituted isotopologues in organics. Electron bombardment of organic molecules yields a wide range of fragmentation products, separate analysis of which could be used to constrain site-specific isotopic compositions (much as analysis of N$_2$O and NO$^+$ can yield site-specific $^{15}$N composition of N$_2$O; Yoshida et al., 2000). And, mass spectrometry is the only well demonstrated method for analysis of multiply substituted isotopologues at their low natural abundances (but see the discussion of spectroscopy below).

However, any such approach must contend with the existence of a complex family of isotopic interferences at nearly every cardinal mass in the mass spectra of many organic molecules. As the number of atoms in a molecule increases, so do the number of species (both isotopologues and species that differ in stoichiometry) with the same cardinal mass. Unambiguous analyses of these species can only be made if these isobaric interferences are resolved or somehow corrected for (e.g., the H$_2^+$ correction that is commonly made to determine HD/H$_2$ ratios by gas source mass spectrometry). Fragmentation and other ion source reactions complicate this problem. For example, resolving the $^{12}$CD$_3$H$_3$ isotope of methane from $^{13}$CH$_4$ requires a mass resolving power of more than 5800 (M/ΔM), an order of magnitude higher than typical commercial gas source isotope ratio mass spectrometers; also separating these species from the adduct $^{13}$CH$_3$H$_2^+$ requires a formal mass resolution of nearly 11,000 (and, to cleanly separate all these species, something closer to 20,000 is preferred).

These problems were recently overcome using a prototype high mass resolution gas-source mass spectrometer (Eiler et al., 2012). This instrument, the Thermo 253 Ultra, combines the inlet system and ion source of a conventional gas source isotope ratio mass spectrometer (it most resembles the Thermo 253) with a double focusing analyzer and multi-collector array (resembling the Thermo Neptune ICPMS and Triton TIMS). Most importantly, it achieves mass resolutions up to $-27,000$ (M/ΔM), can be easily re-configured for a wide range analytes from 1 to 300 amu (because it possesses moveable collectors with both a Faraday cup or SEM detector at every position), and has relatively good abundance sensitivity (as good as a few times 10$^{-12}$). This prototype instrument was installed at Caltech at the end of 2011 and remains the only machine of its kind; however, several more of broadly similar constructions are in development by Thermo and Nu Instruments and we expect that several laboratories will be making measurements with such machines in the coming years.

High resolution gas source mass spectrometry will be used to study a broad range of site-specific and multiply-substituted isotopologues of organics and other molecules. A simple representative application is the doubly substituted isotopologues of methane, which is already the basis of a calibrated ‘clumped isotope’ thermometer (Stolper et al., 2012, 2014, submitted for publication; Fig. 13). Methane is important commercially and as a greenhouse gas (Lelieveld et al., 1998) and is a key metabolite in some microbial ecosystems. The sources and geochemical and biochemical budgets of methane are often poorly constrained (Mroz, 1993; Walter et al., 2006), in part because bulk isotopic measurements ($^{13}$C and $^{18}$O values and $^{14}$C abundances) often have non-unique interpretations. Measurements of one or more of the multiply substituted isotopologues of methane (the most abundant of which is $^{13}$CH$_3$D) could contribute to this problem by providing a thermometer that distinguishes high temperature, thermogenic sources from low temperature sources from biological sources or serpentinization (much as carbonate “clumped isotope” measurements have contributed to paleoclimate research; see Eiler, 2011 and above). The basis for this approach is the temperature dependence of equilibrium constants for reactions such as:

$$^{13}$CH$_4$ $^+$ $^{12}$CH$_3$D $^-$ $^{13}$CH$_3$D $^+$ $^{12}$CH$_4$$^-$

The temperature sensitivity of this reaction is such that useful geothermometry calls for measurements of the equilibrium constant with errors of a few tenths of per mil or better. Also note that, just as for the clumped isotope geochemistry of CO$_2$ and carbonate, there is every reason to suspect that kinetic isotope effects, physical fractionations and mixing effects will compromise the interpretation of such measurements, and the ‘blocking temperature’ of the system may interfere with the attainment and/or preservation of environmentally meaningful temperatures. Current applied research with this tool is just beginning to come to grips with these complexities.

The methane clumped isotope thermometer was recently calibrated by experimental equilibration over Ni catalyst at elevated temperatures (200–500 °C), and the first exploratory applications to natural gas samples and cultured methanogens are underway. Fig. 13 presents a summary of some of these first results (from Stolper et al., 2014, submitted for publication).
At present it appears that straightforward first-principle models of the temperature dependent excesses of $^{13}$CH$_3$D are accurate (or at least indistinguishable from experimental data at the present ~0.2‰ errors), that suspected natural thermogenic gases yield apparent temperatures in the range ~150–250 °C (within what is conventionally regarded as the ‘gas window’ for petroleum deposits), and that natural biogenic methane yields apparent temperatures consistent with its known growth conditions. Taken together, these results suggest that natural methane commonly forms in equilibrium with respect to methane clumping reactions and preserves the composition corresponding to that formation temperature over geological time-scales and through sampling and sample processing. Nevertheless, previous experiments on photochemical lifetimes of isotopologues of methane strongly suggest that atmospheric samples will deviate from this equilibrium condition, perhaps in ways that will offer new constraints on the oxidation reactions that destroy methane in air (Kaye and Jackman, 1990). And, the most recent data for cultured methanogens suggest they are capable of manifesting kinetic isotope effects under some conditions, artificially raising apparent temperature (D. Stolper, pers. com.), and suggesting some of the subtle isotope geochemistry of some natural environments could be more complex than suggested by work to date.

The Ultra is also being used to develop novel measurements of other previously unexplored isotopologues of higher-order alkanes, including $^{13}$C$_2$H$_6$ and preferential distribution of $^{13}$C between the central and terminal positions of propane (i.e., $^{12}$CH$_3$–$^{13}$CH$_2$–$^{12}$CH$_3$ vs. $^{13}$CH$_3$–$^{12}$CH$_2$–$^{13}$CH$_3$; a simple form of position-specific isotope effect; Clog et al., 2013; Piasecki et al., 2012; similar work demonstrates the capabilities of this instrument for multiple isotopologues of N$_2$O; Magyar et al., 2012). While there are thermodynamic effects that lead to distinct predicted fractionations of these and related species, it is unlikely that the carbon isotope analogies of metastable organic compounds such as these consistently display equilibrium isotopic distributions. Rather, we suspect that multiple $^{13}$C substitutions and position specific $^{13}$C distributions in hydrocarbons are inherited from the biosynthetic reactions that create their source organic matter, modified by ‘cracking’ reactions that generate components of gas and oil, and perhaps also modified by chemical and physical processes after these components are generated (e.g., biological consumption, secondary cracking or diffusion through pores).

### 9.3. Absorption spectroscopy

Infrared absorption spectroscopy is emerging as a powerful tool for high-precision isotope ratio measurements of gases. These methods are best known for their field portability, applicability to natural, unprocessed samples of air and water, and their relatively low cost and simple operation (at least, as compared with conventional mass spectrometric devices). To-date, most of the measurements enabled by these technologies are conventional in the sense that they probe well-known isotopic properties of molecules (e.g., the $\delta^{13}$C of CO$_2$ or $\delta$D of water; Griffis, 2013). However, continued innovations (particularly extending the frequency range of light sources into the regions of the infrared with strong molecular absorptions in compounds of interest) are giving rise to a new generation of devices for measuring position-specific and clumped isotope compositions. To-date, the only instrument of this kind that is demonstrated to achieve useful precision at natural isotope abundances is one for measuring position-specific $^{13}$N in N$_2$O (i.e., distinguishing $^{15}$N$^{14}$O$^{15}$O from $^{14}$N$^{15}$O$^{15}$O; Waechter et al., 2008). However, several recent papers and abstracts have explored the possibility that these methods could lead to a useful measurement of $^{13}$CH$_3$D (Ma et al., 2008; Tsuji et al., 2012; Ono et al., 2013a, 2013b).

### 9.4. Questions and needs

The low signal-to-noise ratio of NMR resonances, a result of low nuclear spin polarization, is a major factor limiting the precision and sensitivity of quantitative NMR (Saito et al., 2004). This low sensitivity is the principal reason why SNIF-NMR methods are limited to just a few research groups, and in all cases require very large samples and long integration times. This factor also currently prevents the use of NMR to study multiply substituted isotopologues at their low natural abundances. In the long run this may be the greatest limitation of SNIF-NMR techniques because it removes from consideration most of the isotopic diversity of organic molecules. This field could be dramatically expanded by new techniques that improve the signal to noise ratio of NMR.

It seems likely that infrared absorption spectroscopy could emerge as an important tool in clumped- and position-specific isotope geochemistry: its great potential for sensitivity and freedom from isobaric interferences make it ideally suited to the study of low abundance isotopologues of molecular gases. However it isn’t clear yet whether these methods can be extended beyond the small family of vibrationally simple room-temperature gases. And, such devices are generally capable of analyzing only a few isotopic absorption features, so these methods may not be well suited to the study of molecules with diverse isotopologues (e.g., propane and higher order hydrocarbons). Finally, many clumped isotope measurements call for exceptional precision and accuracy across a wide range of bulk compositions, because anomalies are frequently sub-per-mil departures from a random distribution for isotopologues that vary in abundance by hundreds of per mil. It remains to be seen whether spectroscopic devices can be calibrated to this level of accuracy.

We suspect that continued development of these and related technologies, and experience with their application to natural organics, will lead to a wide variety of novel geochemical tools. For example, recent experiments combining data from the Ultra with other novel mass spectrometric methods demonstrate that we may be close to having measurements that precisely constrain proportions of literally dozens of isotopologues of semi-volatile organic compounds (alkanes, derivatives of amino acids, etc.; Eiler et al., 2013b). The constituents of organic matter contain diverse enzymatically formed and modified carbon–carbon bonds, whose $^{13}$C–$^{12}$C and $^{13}$C–D clumping and position-specific fractionations may provide signatures of metabolic pathways, environmental conditions (e.g., temperature) or state of biological stress during biosynthesis (see the recent review by Eiler, 2013). If so, such measurements may let us recognize the evolutionary history of metabolic strategies through time, or could provide novel biosignatures that will aid the search for life in extreme environments or (dare to dream!) extraterrestrial samples. And, the very large number of independent compositional variables that characterize the full
isotopic structures of organic molecules may permit applications to forensics with an unprecedented level of specificity. Perhaps the greatest challenge of this field may be understanding this compositional complexity; as John Hayes so succinctly put it: "It often seems that isotopic fractionations provide too much information about too many processes, combining it all in a package that is unmanageably intricate" (2001).

10. Future prospects

This review has wandered widely through the subjects of stable isotope geochemistry — from chemistry to geology to forensics; from metals to gases to organic matter; from theory to experiment to hardware. But we have tried to wander with a few unifying goals: to illuminate the areas where this field is breaking new ground, and point to problems that presently prevent fundamental understanding of new discoveries, and to catalyze a new generation of interdisciplinary collaboration among chemists and earth and environmental scientists to solve these problems. Four of the most prominent threads that link the subjects of this paper are:

10.1 A diversifying landscape of analytical technologies

Twenty years ago, an aspiring stable isotope geochemist was faced with only one core analytical technology: low-resolution, multi-collector, gas-source sector mass spectrometry. A zoo of preparatory devices were invented to feed simple molecular gases to these machines — vacuum lines, carrier gases, preparatory GC, laser ablation — but the isotopic measurements themselves were not greatly different from those made in the 1940’s and 50’s. Today a person in this field could consider, in addition to this, multi-collector plasma source mass spectrometers, absorption spectroscopy, the emerging high-resolution multi-collector gas source mass specs, and natural abundance NMR techniques. And, we could have easily added to these a section of this paper on high-precision ion microprobe techniques for stable isotope analysis (Kita et al., 2009). Understanding, and the ability to innovate with, advanced analytical instruments is perhaps more important now than at any time since the birth of stable isotope geochemistry.

10.2 Exploration of novel isotopic properties

The recent emergence of the study of mass laws of isotopic fractionation, position-specific isotopic effects, and clumped isotope geochemistry have tremendously expanded the potential to describe the isotopic compositions of natural things. One of the simplest but most important manifestations of that physics is to explore compositional diversity, searching for the signatures that will be the foundations of new tools. The ‘space’ we are at least potentially able to explore has expanded greatly in recent years, but most of the discoveries that must follow are still waiting to be made. Some particularly obvious open playing fields include the $^{17}$O anomalies of past waters (through high precision $\Delta^{17}$O measurements of carbonates and other minerals), the expansion of clumped and position specific isotope geochemistry into methane and other organic compounds, and the mass independent geochemistry of heavy metals.

10.3 Limits of conventional theories of fractionation

The frontier of stable isotope geochemistry, taken as a whole, has surprisingly little understanding of what it is doing at the moment. For more than half a century, the kinetic theory of gases and the chemical physics of the 1930’s and 40’s served as adequate guides to most known stable isotope fractionations. Those few exceptions — mass independent oxygen isotope fractionations of meteorites and ozone — were rare beasts, confined to a few exotic settings. But the subjects of the last decade of work at the frontiers of this subject — mass independent isotope variations in S and various heavy metals; subtle variations in mass laws of S and O isotopes; clumped isotope compositions of solids, solutions and gases; position-specific isotopic fractionations — involve either poorly understood chemical physics (photochemical, magnetic and nuclear volume effects) or poorly understood aspects of the conventional chemical isotope effects we thought we knew (secondary isotope effects; sorption; etc.). There is a great need in these rapidly growing sub-disciplines of stable isotope geochemistry for predictive, quantitative and fundamental models of the physical causes of these novel forms of isotopic fractionations.

10.4 First-principle computational tools

One motivation for this paper (and the workshop from which it grew) is the recognition that the computational tools for first-principle chemical models of isotope effects (e.g., DFT and MD simulations) have become so advanced and so widespread that it is realistic to imagine integrating them with experimental and applied stable isotope geochemistry studies. The community that develops and routinely works with these tools generally is not involved in applied isotope geochemistry and so is unaware of many of this field’s emerging focus areas. And, the models themselves are sufficiently complex and imperfect that uneducated users from the geochemistry community are likely to create nothing but confusion unless they get help or invest effort in learning the relevant tools. Nevertheless, application of first principle theoretical models could advance our understanding of many novel stable isotope measurements, particularly subtle variations in mass laws for S and O, isotopic ‘clumping’, and position specific effects in chemical reactions and equilibria. These are instances where the chemical physics, stripped to its most fundamental level, is known, yet the manifestations of that physics are challenging because they involve second-order isotope effects, dynamics of surfaces or solvated compounds, or other structural complexities. Finally, it will be essential that such theoretical studies carefully consider the approximations and errors inherent in their methods, and broaden their scope to encompass alternate visions of how such problems could be (perhaps should be) approached (e.g., Webb and Miller, 2014).

Acknowledgments

This paper is an outgrowth of a workshop, “The Chemistry of Novel Isotope Effects in the Geosciences”, organized and supported by the Department of Energy office for Basic Energy Sciences, and in particular by the Geosciences section of DOE’s Chemistry division. We thank everyone involved in that program, and its administrative staff in particular, for helping us organize and run this productive workshop. This paper is significantly influenced by the talks and discussions at that workshop given by the participants in addition to the authors, including: Michael Bender, Joel Blum, Bill Casey, Don DePaolo, David Johnston, Abby Kavner, Boaz Luz, Shuhei Ono, Alison Plasecki, Jim Rustad, Alex Sessions, Gary Sposito and Mark Thiemens. Finally, this paper is dedicated to the memory of Jake Bigeleisen, whose seven-decade career of creativity and vision is an inspiration to the field of isotope geochemistry.

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