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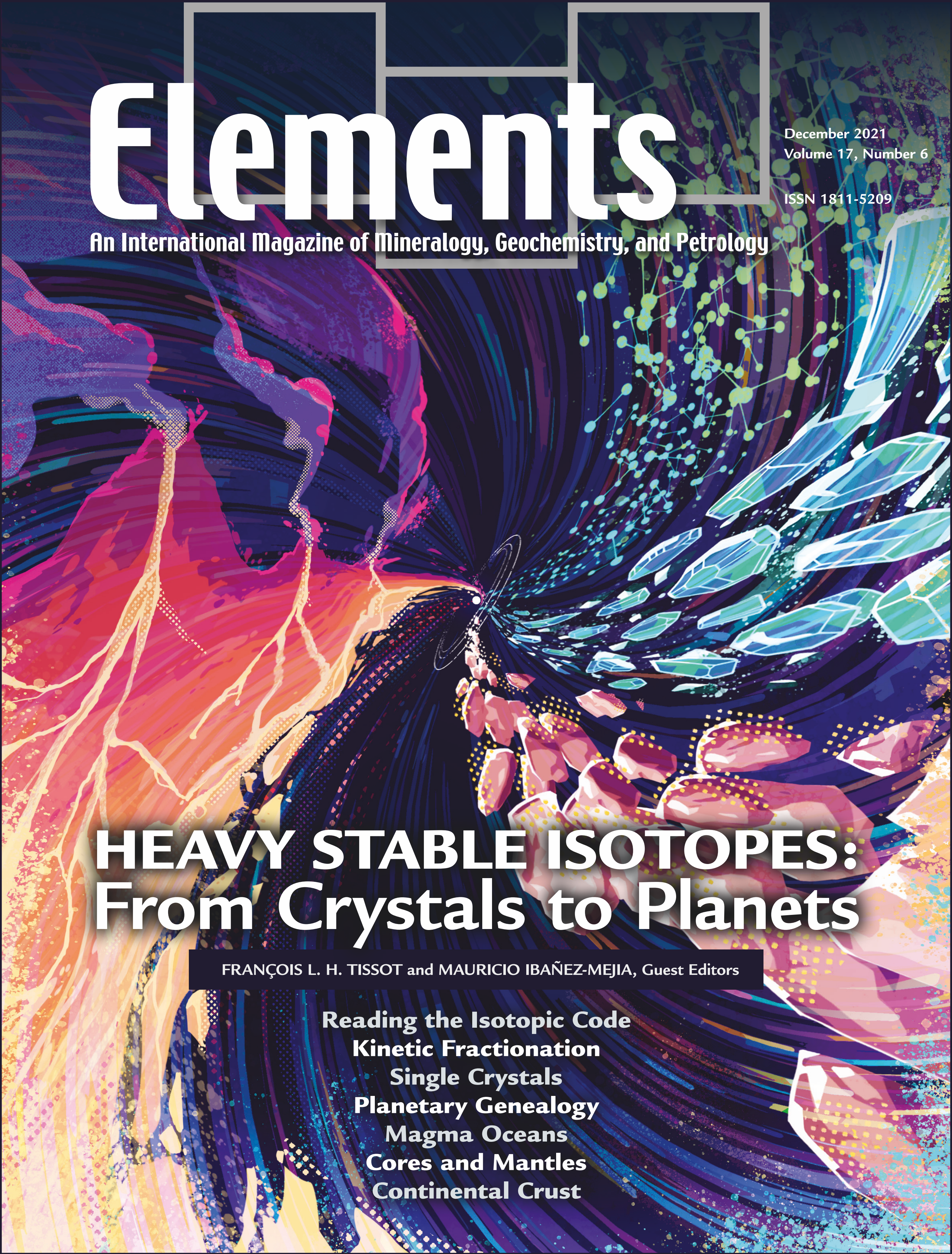

HEAVY STABLE ISOTOPES:
From Crystals to Planets

FRANÇOIS L. H. TISSOT and MAURICIO IBAÑEZ-MEJIA, Guest Editors

Reading the Isotopic Code
Kinetic Fractionation
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Reading the Isotopic Code of Heavy Elements

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The isotopic variability of the elements in our planet and Solar System is the end result of a complex mixture of processes, including variable production of isotopes in stars, ingrowth of daughter nuclides due to decay of radioactive parents, and selective incorporation of isotopes into solids, liquids, or gases as a function of their mass and/or nuclear volume. Interpreting the isotopic imprints that planetary formation and evolution have left in the rock and mineral record requires not only precise and accurate measurements but also an understanding of the drivers behind isotopic variability. Here, we introduce fundamental concepts needed to "read" the isotopic code, with particular emphasis on heavy stable isotope systems.

Keywords: geochemistry; cosmochemistry; non-traditional stable isotopes

INTRODUCTION

Just as the history of humankind is archived in scrolls and books, the history of our Solar System and its planets is recorded in the isotopic variability of the chemical elements. From the moment that elements are created in stars, through their incorporation into gas clouds, planetesimals, and throughout the complex evolution of planets, a myriad of isotopic signatures develop that provide invaluable insights into all the steps of this process. Accurately resolving isotopic differences across a variety of sample types and scales (both physical and temporal), and unraveling the processes responsible for these variations, continues to transform human understanding of our planet and Solar System. Owing to the varied geochemical behaviors that they display, the stable isotopes of heavier (so-called "non-traditional") elements have enabled investigation of processes that are beyond the reach of the more established (so-called "traditional") stable isotope systems (i.e., H, C, N, O, and S).

In this introductory article, we summarize the historical landmarks in the study of stable isotopes; the key mechanisms that induce isotopic fractionation, with an emphasis on equilibrium mass-dependent processes; define important terminology that will be used throughout this issue (see Box 1); and provide interested readers with additional resources to learn more about heavy stable isotopes.

A HISTORICAL PERSPECTIVE

In the early part of the 20th century, much research was devoted to understanding radioactive transformations (Rutherford and Soddy 1903), and, shortly after, their application to age dating (Holmes 1911). It was not until 1913, however, that Fredrick Soddy introduced the term "isotope" (Soddy 1913) and that the first experimental demonstration of their existence by J.J. Thompson was achieved (Thompson 1913). At the time, it was generally thought that the isotopic makeup of elements not involved in radioactive decay chains was fixed. Within the following decade, theoretical studies began to recognize that the relative abundances of isotopes for any given element are, to a first order, the consequence of nuclear stability during element synthesis (Harkins 1921; Urey and Bradley 1931).

Separation of isotopes was first achieved for the element mercury (Hg) by Brönsted and Hevesy (1920), and five years later, while trying to redetermine the atomic weight of boron (B), Briscoe and Robinson (1925) reported what may arguably be the first documented case of natural stable isotope variability unrelated to radioactive decay. Using gravimetric techniques, these researchers found that B-rich minerals from several worldwide localities yielded variable mean atomic weights for this element, which, after careful evaluation to rule out elemental impurities, were interpreted as variations in the relative abundances of ^{10}B and ^{11}B in their purified boron fractions. The field of quantitative stable isotope geochemistry as we know it today was heralded in the 1940s by two seminal papers: Urey (1947) and Bigeleisen and Mayer (1947). These studies outlined the quantum-mechanical nature of equilibrium stable isotopic fractionations and provided the first quantitative framework for describing the thermodynamics of isotopic exchange reactions. The first decades of stable isotope geochemistry focused primarily on light (traditional) elements (Fig. 1) (see Valley and Cole 2001), while the rest of the periodic table remained mostly unexplored.

As analytical capabilities evolved, exploring the isotopic archive of heavier elements became feasible, paving the way for "non-traditional" stable isotope geochemistry, a field that encompasses all multi-isotopic metals not included in the "traditional" systems (see Fig 1). Generally inaccessible before the mid- to late-1990s due to analytical barriers, the routine isotopic study of "heavy" elements (i.e., those heavier than Mg for stable isotope purposes) has flourished during the past couple decades since the advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the Earth and planetary sciences (Halliday et al. 1998; Marechal et al. 1999).

The dramatic expansion in the number of elements now amenable to stable isotopic investigations instigated a revolution due to their varied geochemical behavior, making certain elements (or groups of elements) sensitive

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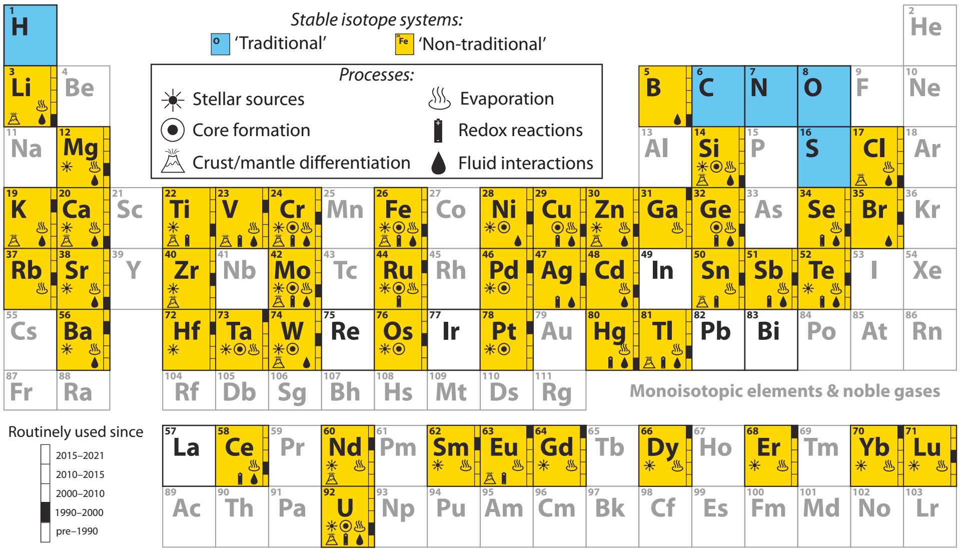

FIGURE 1 Periodic table of the elements summarizing the state-of-the-art in stable isotope geochemistry and cosmochemistry. Blue denotes the traditional stable isotope systems, and yellow the non-traditional (also called "heavy") systems for which isotope variability has been documented in the literature. Monoisotopic elements and noble gases (not considered in this issue) are in gray. Redox = reduction–oxidation. FOR MORE DETAILS AND SOURCES VISIT WWW.HEAVYSTABLEISOTOPES.ORG.

to specific geological and/or cosmological processes. For example, isotopic fractionations observed in moderately-to-strongly siderophile (or "Fe-loving") elements tell us about the conditions of metal–silicate differentiation and core formation on Earth and other planets (e.g., Weyer et al. 2005; Shahar and Young 2020). Similarly, isotopic variations observed in elements whose valence states depend on oxygen availability (i.e., fugacity) on the surface and interior of our planet provide unique insights into the evolution of redox (reductive and/or oxidative) conditions of our atmosphere, oceans, and even the deep Earth (e.g., Anbar and Rouxel 2007; Andersen et al. 2015).

Testament to this rapid development was the publication of the first Reviews in Mineralogy and Geochemistry (RiMG) volume on non-traditional stable isotopes in 2004 (Johnson et al. 2004), the significant expansion in the field as registered by a second RiMG volume on the topic in 2017 (Teng et al. 2017), and the continued growth as captured at the time of publication of this *Elements* issue (FIG. 1).

WHAT CAUSES ISOTOPIC VARIATIONS?

Isotopic variations come in many flavors: they can be either mass-independent or mass-dependent in nature, and be either driven by chemical reactions (i.e., involving bond rupture) or be independent from them. Mass-independent isotope effects are those that affect an element's relative isotopic abundances in a way that does not scale with the difference in mass of the isotopes involved; mass-dependent effects are those in which the degree of isotopic fractionation *does* scale proportionally with isotopic mass differences (FIG. 2).

Radioactive decay and nuclear transmutations by particle irradiation are examples of mass-independent effects that are not driven by chemical reactions but by nuclear ones. Consider the widely used Rb–Sr decay system as an example (FIG. 2A). Radioactive decay of an ^{87}Rb atom produces a stable nuclide of ^{87}Sr, and, thus, the abundance of ^{87}Sr in a sample relative to a non-radiogenic isotope of this element (e.g., ^{86}Sr) is a function of a sample's Rb/Sr ratio, time, and the ^{87}Rb decay constant (λ): this is the foundation of radiochronometric dating. Similarly, particle irradiation leads to isotopic variations that do not scale with atomic mass (FIG. 2B) but rather with an isotope's propensity to interact with specific irradiating particles (a property known as "nuclear cross-section"). For example, variations in neutron capture cross-section constants (known as σ_n) (FIG. 2B) lead to the synthesis of different nuclides in different stellar environments (Burbidge et al. 1957). The relatively small, but steady, neutron fluxes occurring near the burning core of massive stars lead to preferential production of the so-called *s*-process nuclides ("*s*" = slow neutron–capture), while the colossal neutron fluxes caused by supernovae explosions or neutron star mergers are responsible for the so-called *r*-process nuclides ("*r*" = rapid neutron–capture). The relative abundances of *s*-process and *r*-process nuclides in extraterrestrial samples allow us to reconstruct the architecture of the early Solar System. Other examples of mass-independent isotope effects include cosmogenic, nucleogenic, and fissiogenic nuclear transmutations.

Mass-independent isotope effects can also result from reactions involving the rupture and the formation of chemical bonds, a process known as mass-independent fractionation (MIF). While photochemically induced MIF effects have been studied extensively (e.g., MIF of Hg isotopes are used to trace sources and fluxes of this toxic element through biogeochemical cycles) (Blum et al. 2014) these effects are of limited importance in high-temperature environments. In contrast, the nuclear field shift (NFS) effect is a main driver of equilibrium MIF for heavy elements even at high temperatures and is, therefore, of greater interest to this issue. The NFS effects arise from the physical overlap that exists between an atom's electronic orbitals and the finite volume occupied by its nucleus (FIG. 2C) (Bigeleisen 1996; Schauble 2007). This overlap depends on the shape and size of the nucleus itself, and a general rule is that NFS concentrates heavy isotopes in the chemical species with the smallest electron density at the nucleus (i.e., species with fewer s-electrons or more p-, d- and f-electrons). Because nuclear volume is not a monotonic function of isotopic mass (Angeli and Marinova 2013) but instead displays an even–odd–staggering pattern, NFS isotopic effects are also even–odd–staggered. Although NFS effects can impart isotopic fractionation for multiple elements (Fujii et al. 2006), in nature this is a dominant driver of isotope fractionation only for the very heavy elements (e.g., Hg, Tl, U), for which equilibrium mass-dependent effects are exceedingly small.

Mass-dependent fractionation (MDF) of stable isotopes as driven by chemical reactions are the central theme of this *Elements* issue. These fractionations can result from the equilibrium distribution of isotopic species amongst coexisting phases and/or respond to the kinetics of chemical reactions. The following section introduces the mechanisms behind equilibrium MDF, aiming to build an intuition for the first-order processes that govern the distribution of light and heavy isotopes amongst phases.

EQUILIBRIUM MASS-DEPENDENT ISOTOPE FRACTIONATION 101

The mass-dependent equilibrium distribution of isotopes amongst coexisting phases is a quantum-mechanical effect, resulting from the influence that atomic mass has on vibrational bond energy (Bigeleisen and Mayer 1947; Urey 1947). When atoms assemble to form molecules, the

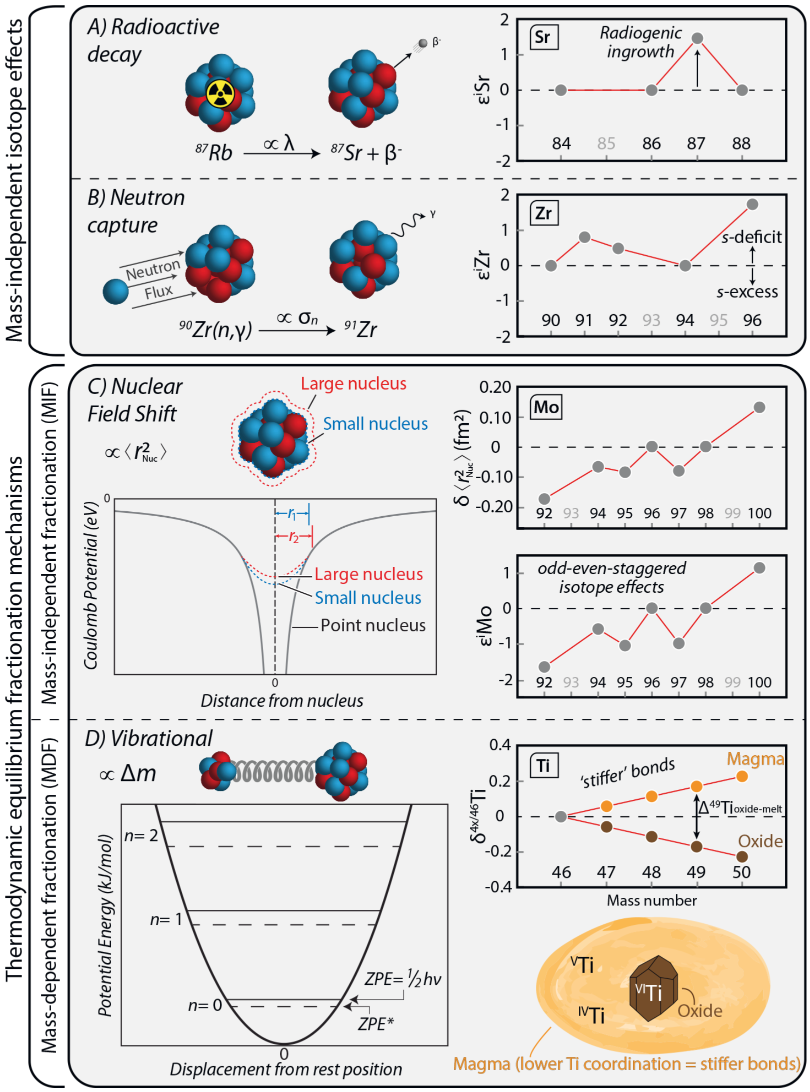

Figure 2 Main mechanisms of heavy stable isotope variability discussed in this issue. (**top; A and B**) Isotope effects caused by nuclear reactions. (**bottom; C and D**) Isotope effects caused by equilibrium chemical reactions, occurring either by mass-independent fractionation (MIF) or mass-dependent fractionation (MDF). Plots of relative isotope abundances illustrate the manifestation of each process when a measured sample is normalized with respect to a typical terrestrial standard. Symbols: λ = radioactive decay constant (in time^{-1}); β = beta negative radioactive particle; ε = epsilon offset (see Box 1); Zr(n,γ) = nuclear reaction involving capture of a neutron (n) and the emission of a gamma ray (γ); σ_n = neutron capture cross-section (in barn); δ⟨r²⟩ = change in mean-squared nuclear charge radius; the '*s*' in "*s*-deficit" and "*s*-excess" refers to slow neutron–capture processes; ZPE = zero-point energy; ZPE* = zero-point energy of an isotopically heavy molecule. For symbols in Figure 2D see text and Box 1. Nuclear field shift potential plot modified from Schauble (2007).

"links" that hold them together—i.e., chemical bonds—are far from static, but instead behave more like springs. The energy of these "spring-like" molecular vibrations is not a continuous function but rather a *quantized* one, meaning that bonds and molecules can only stretch at certain vibrational frequencies.

In its simplest form, a vibrating diatomic molecule can be conceptualized as a diatomic harmonic oscillator (Fig. 2D), where vibrational energy (E) is related to vibrational frequency (ν) by the following equation:

$$E = (n + \tfrac{1}{2})\, h\nu \qquad (1)$$

where n corresponds to the vibrational energy levels and h is Planck's constant (h = 6.626 x 10^{-34} J s). Even at absolute zero, when all molecules are in their ground state (i.e., $n = 0$), the vibrational energy of a molecule is equal to ½hν. This quantity is known as the zero-point energy (ZPE), and reflects the difference in energy between the bottom of the potential energy well of a vibrating molecule and its ground vibrational state. The vibrational frequency of the diatomic molecule can, in turn, be approximated using Hooke's law (i.e., as a frictionless spring):

$$\nu = (1/2\pi)\sqrt{k/\mu} \qquad (2)$$

where k is the spring's force constant (in N/m), μ is the molecule's reduced mass [$\mu = (m_1m_2)/(m_1 + m_2)$], and m_1 and m_2 are the masses of the atoms in our diatomic molecule. From these two simple relationships it can be seen that varying the isotopic mass (m) of the atoms forming a molecule exerts an influence on the bond vibrational frequency (ν) and, by extension, on the vibrational energy (E).

Although isotopic substitutions do not affect a bond's force constant (because bond force constants depend on *electronic* interactions), when a light isotope is replaced by a heavy isotope in a molecule its reduced mass μ increases, vibrational frequency decreases, and the net effect is a decrease in vibrational energy. Thus, because the ZPE of an isotopically heavy molecule (labeled *ZPE** in Fig. 2D) is smaller than that of its light counterpart, when all else remains equal, the molecule containing the heavy isotope is energetically more stable (i.e., minimizes potential energy) and, thus, forms preferentially, leading to selective isotope partitioning.

In addition to their inverse dependence on nuclear mass, vibrational frequencies are a function of bond force constant (k), or "stiffness" (Eq. 2). Bond stiffness is related to bond length, with shorter bonds being stiffer than longer bonds (Young et al. 2015; Blanchard et al. 2017), meaning that interionic distances play a key role in MDF. Effective ionic radii in molecules vary with valence and coordination number (Shannon 1976) where, in general, increasing an ion's coordination number leads to an increase in effective ionic radius (and, thus, interionic distance), which decreases bond stiffness. On the other hand, increasing valence while maintaining the coordination number constant decreases an atom's effective ionic radius, which increases bond stiffness. The general expectation is that, at equilibrium, heavy isotopes preferentially concentrate in phases where coordination is low and/or valence is high (i.e., phases having the stiffest bonds).

At equilibrium, isotopic differences between two substances are described using the equilibrium fractionation coefficient, α (see Box 1). There are five main ways in which these coefficients are determined: (1) modeling, using first-principles (also known as ab initio) molecular calculations (e.g., Blanchard et al. 2017); (2) isotopic equilibration experiments in the laboratory (e.g., Shahar et al. 2017); (3) investigating natural samples for which intensive variables such as temperature are reasonably well constrained and intermineral equilibration has arguably been achieved; (4) using Raman spectroscopy to determine fractionations from vibrational frequencies (e.g., Schauble et al. 2001); and (5) for elements with a Mössbauer-sensitive isotope using nuclear resonance inelastic X-ray scattering (NRIXS) (Dauphas et al. 2012) at a synchrotron facility to experimentally determine a bond's force constant. In practice, each of these approaches has limitations, and the most robust isotopic fractionation calibrations are those constrained using multiple methods.

The simple principles described above for a diatomic molecule also apply to more complex systems. Any chemical reaction involving the breakup/creation of new bonds and/or changes in ionic coordination and oxidation state (e.g., crystallization of minerals from a magma, partial melting, evaporation, ion exchange, and net transfer reactions—anything that involves a transfer of mass) are processes that can fractionate stable isotopes. The magnitude of equilibrium MDF is a strong function of temperature, and scales as $1/T^2$ in high-T environments (Urey 1947; Bigeleisen and Mayer 1947). In many geologic systems, however, MDFs of a magnitude larger than those expected at equilibrium can be driven by the kinetics of chemical reactions and/or mass-transport processes, such as diffusion (see Watkins and Antonelli 2021 this issue). Consequently, careful evaluation of whether equilibrium principles can be applied to a particular problem, element, or geologic system is needed before equilibrium fractionation coefficients can be used for data interpretation.

FROM CRYSTALS TO PLANETS

This issue of *Elements* highlights some of the exciting new ways in which stable isotopes of the heavier elements are enabling a deeper understanding of high-temperature processes, ranging from a molecular scale to a Solar System scale. Although a first survey of stable isotope variability for essentially all multi-isotopic elements in the periodic table is now close to complete (FIG. 1), many of these systems are yet to be understood in detail, and their potential has yet to be fully realized. As such, many exciting discoveries using non-traditional stable isotopes in geochemistry and cosmochemistry remain on the horizon.

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Box 1 IMPORTANT DEFINITIONS USED THROUGHOUT THIS *ELEMENTS* ISSUE

$\delta^{i/j}E = \left(\left(R^{i/j}_{\text{Sample}}/R^{i/j}_{\text{RM}}\right)-1\right)\cdot 10^3$	(*delta* notation)
$\varepsilon^{i/j}E = \left(\left(R^{i/j}_{\text{Sample}}/R^{i/j}_{\text{RM}}\right)-1\right)\cdot 10^4$	(*epsilon* notation)
$\mu^{i/j}E = \left(R^{i/j}_{\text{Sample}}/R^{i/j}_{\text{RM}}-1\right)\cdot 10^6$	(*mu* notation)
$\alpha_{A-B} = R^{i/j}_A / R^{i/j}_B$	(equilibrium isotopic fractionation coefficient)
$\Delta^{i/j}E_{A-B} \equiv \delta^{i/j}E_A - \delta^{i/j}E_B \approx 10^3\cdot\ln\alpha_{A-B}$	(‘*cap*’ or ‘*big*’ *delta*)

E: element of interest

i and j: i-th and j-th isotopes of element E

$R^{i/j}$: abundance ratio of isotopes i and j

R_{sample}: isotopic ratio of a sample

R_{RM}: isotopic ratio of reference material

A and B: two distinct substances of interest

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