Non-Traditional Stable Isotopes:
Retrospective and Prospective

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INTRODUCTION

Traditional stable isotope geochemistry involves isotopes of light elements such as H, C, N, O, and S, which are measured predominantly by gas-source mass spectrometry (Valley et al. 1986; Valley and Cole 2001). Even though Li isotope geochemistry was developed in 1980s based on thermal ionization mass spectrometry (TIMS) (Chan 1987), the real flourish of so-called non-traditional stable isotope geochemistry was made possible by the development of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Halliday et al. 1995; Marechal et al. 1999). Since then, isotopes of both light (e.g., Li, Mg) and heavy (e.g., Tl, U) elements have been routinely measured at a precision that is high enough to resolve natural variations (Fig. 1). The publication of RIMG volume 55 (*Geochemistry of Non-Traditional Stable Isotopes*) in 2004 was the first extensive review of Non-Traditional Stable Isotopes summarizing the advances in the field up to 2003 (Johnson et al. 2004). When compared to traditional stable isotopes, the non-traditional stable isotopes have several distinctive geochemical features: 1) as many of these elements are trace elements, their concentrations vary widely in different geological reservoirs; 2) these elements range from highly volatile (e.g., Zn and K) to refractory (e.g., Ca and Ti); 3) many of these elements are redox-sensitive; 4) many of them are biologically active; 5) the bonding environments, especially for the metal elements, are different from those of H, C, N, O and S; and finally, 6) many of these elements have high atomic numbers and more than two stable isotopes. These features make the different elements susceptible to different fractionation mechanisms, and by extension, make them unique tracers of different cosmochemical, geological and biological processes, as highlighted throughout this volume.
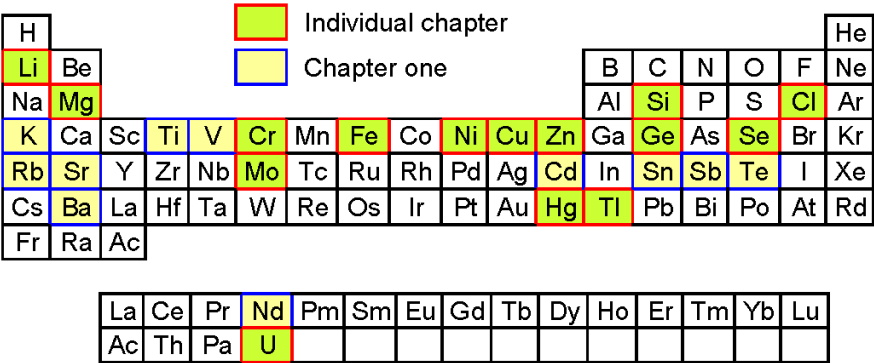
Non-Traditional Stable Isotopes

Figure 1. Non-traditional stable isotope systems covered in this volume.

Large variations have been documented in both natural samples and laboratory experiments for non-traditional stable isotopes (Fig. 2). These studies suggest that the following factors control the degree of isotope fractionation in non-traditional stable isotopes during various processes: the relative mass difference between isotopes, change of the oxidation state, biological sensitivity, and volatility. Among these elements, Li displays the largest isotopic variation in terrestrial samples, and since Li is not volatile during geological processes and is not sensitive to redox reactions and biological processes, the large isotope fractionation is controlled mainly by the large relative mass difference (Penniston-Dorland et al. 2017). For many of the other elements, other factors may be equally, if not more, important. For example, Cl exhibits the
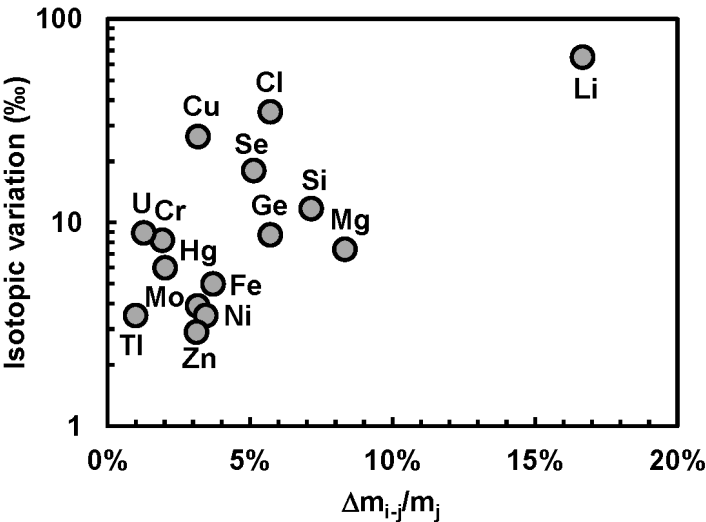

Figure 2. The terrestrial isotopic variation vs. the relative mass difference for non-traditional stable isotopes covered in this volume (Anderson et al. 2017; Barnes and Sharp 2017; Blum and Johnson 2017; Dauphas et al. 2017; Elliott and Steele 2017; Kendall et al. 2017; Moynier et al. 2017; Nielsen et al. 2017; Penniston-Dorland et al. 2017; Poitrasson 2017; Qin and Wang 2017; Rouxel and Luais 2017; Stueken 2017; Teng 2017). The $\Delta m_{i-j} = m_i - m_j$, where i and j represent the two isotopes that are used to report the isotopic variation, with $i > j$.

second largest isotopic variation, which is due to kinetic isotope fractionation during volcanic degassing (Barnes and Sharp 2017). Selenium isotopes also show large isotopic variations, but this reflects redox-controlled Se isotope fractionation (Stueken 2017), while the large Hg isotopic variations are mainly associated with biological processes (Blum and Johnson 2017).

In this chapter, we discuss guidelines and recommendations for reporting non-traditional stable isotopic data and choosing reference materials. We then provide brief introductions to some of the emerging isotope systems that are not covered as individual chapters in this volume. As Ca isotope geochemistry has been recently reviewed in the book series on Advances in Isotope Geochemistry (Gussone et al. 2016), and a similar book is also in preparation for B isotope geochemistry, both Ca and B isotopes are not discussed in this volume. For the basics of stable isotope geochemistry, we recommend prior RIMG volumes (Valley et al. 1986; Valley and Cole 2001; Johnson et al. 2004; MacPherson 2008) and stable isotope geochemistry textbooks (Criss 1999; Faure and Mensing 2005; Sharp 2007; Hoefs 2009).

THE δ NOTATION

The isotopic composition of a sample is commonly reported relative to an international standard as defined by the δ notation. For example, for Mg isotopes:

$$\delta^{26}\mathrm{Mg} = \left\{ \frac{(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}}{(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}}} - 1 \right\} \times 1000 \tag{1}$$

where DSM3 is the international standard for reporting Mg isotopic data (Galy et al. 2003). This definition of δ value has been used extensively for both non-traditional stable isotopes (e.g., this volume, Johnson et al. 2004) and traditional stable isotopes (e.g., Valley et al. 1986).

Recently, a new δ notation without the factor of 1000 has been recommended by the IUPAC for expression of stable isotope ratios (Coplen 2011). For example, the new guideline would suggest a definition of δ for Mg isotopes as:

$$\delta^{26}\mathrm{Mg} = \left\{ \frac{(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}}{(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}}} - 1 \right\} \tag{2}$$

The rationale is that when isotopic data are reported, the ‰ symbol is commonly placed following the value. Then, in the case that $(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}} = 1.00025$, the $\delta^{26}\mathrm{Mg}$ should be equal to $+0.25$ in the traditional δ notation i.e., $\delta^{26}\mathrm{Mg} = +0.25$. If the ‰ symbol is added after the value i.e., $\delta^{26}\mathrm{Mg} = +0.25$‰, then mathematically, this means $\delta^{26}\mathrm{Mg} = +0.25$‰ $= +0.00025$. In other words, $(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}} = 1.00000025$. If the IUPAC δ notation is adopted, then when the $(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}} = 1.00025$, the $\delta^{26}\mathrm{Mg} = +0.00025 = +0.25$‰.

While mathematically rigorous, the IUPAC recommendation goes against practices in the field. Retaining the factor of 1000 in the δ notation is, in the view of many in the community, critical to distinguish the δ, ε, and μ notations, which can be used concurrently in a paper.

In the literature on traditional and non-traditional stable isotopes, the δ notation (1) with the factor of 1000 still prevails. For the purpose of being mathematically correct, an alternative to the IUPAC recommendation is to keep the traditional δ notation with the factor of 1000 and omit the ‰ symbol after the δ value, e.g., $\delta^{26}\mathrm{Mg} = +0.25$, which means $(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{26}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM3}} = 1.00025$. This expression is also consistent with the usage of the ε notation where the part per 10000 is not added after any ε value.

Another alternative is to adopt the original δ notation as defined by Craig (1957). For Mg isotopes:

$$\delta^{26}Mg(\text{‰}) = \left\{ \frac{(^{26}Mg/^{24}Mg)_{sample}}{(^{26}Mg/^{24}Mg)_{DSM3}} - 1 \right\} \times 1000 \qquad (3)$$

which would read "$\delta^{26}Mg$ expressed in ‰ is equal to $[(^{26}Mg/^{24}Mg)_{sample}/(^{26}Mg/^{24}Mg)_{DSM3} - 1] \times 1000$". Under this definition, it is also mathematically correct to place the ‰ symbol after the value, e.g., $\delta^{26}Mg = +0.25$‰, which means $(^{26}Mg/^{24}Mg)_{sample}/(^{26}Mg/^{24}Mg)_{DSM3} = 1.00025$.

Although both notations (2) and (3) are mathematically correct, we recommend the notation (3) as it ensures that new publications are consistent with past practices. More important, it is the original definition of δ notation since the beginning of stable isotope geochemistry (Craig 1957). We did not enforce this notation in the present volume but recommend it be used in future publications.

Regardless of which notation is used, it is still correct, as often done by the community, to write sentences like "the $^{26}Mg/^{24}Mg$ varies 1‰ in water samples from Chicago and Seattle" or "The water sample from Chicago is enriched in heavy Mg isotopes by 1‰ relative to that in Seattle", or "The water sample from Chicago is 1‰ heavier than that from Seattle".

GUIDELINES FOR SELECTING REFERENCE MATERIALS

The field of non-traditional stable isotope geochemistry is confronted with the same issues as traditional stable isotope geochemistry regarding the selection of isotope reference materials (IRMs; Carignan et al. 2004; Vogl and Pritzkow 2010). The recurring problem is that standards used in laboratories either run out or are not readily available. This is the case for reference materials distributed by official organizations as well as in-house standards. For instance, *IRMM-014*, which is used in iron isotope geochemistry and distributed by *the Institute for Reference Materials and Measurements (IRMM),* is no longer available. Similarly, *JMC Lyon Zn* and *DSM3*, which are used in Zn and Mg isotope geochemistry, are not readily available. These issues need to be addressed because systematic errors arise when measurements are carried out against secondary standard solutions. Below, we propose some guidelines for selecting isotopic reference materials used in isotope geochemistry. These are informed by discussions with members of the community as well as our analysis of best practices in traditional and non-traditional stable isotope geochemistry.

> **Guideline #1:** *The isotopic composition of the reference material should be demonstrably homogeneous given current analytical precision and its preparation should be such that future isotopic analyses will be unlikely to reveal isotopic heterogeneities when the precision improves.*

We, as a community, should be forward-thinking in designing preparation protocols that minimize the possibility that reference materials will prove to be heterogeneous as analytical capabilities improve. The purified Mg metal isotopic standard NIST SRM 980, which was made and distributed by *National Institute of Standards and Technology (NIST),* was deemed to be isotopically homogeneous when it was created in 1966 (Catanzaro et al. 1966). However, subsequent higher precision measurements showed that it was isotopically heterogeneous, and it was replaced by a Mg solution made from dissolution of pure Mg metal from Dead Sea Magnesium Ltd, i.e., *DSM3* (Galy et al. 2003). Some steps can be taken to ensure that the maximum level of homogeneity is achieved (i.e., stable solutions, quenched glasses, stable metal sheets or bars are likely to be isotopically homogeneous to a high degree). The processes that can

potentially cause heterogeneities in isotopic composition and should be avoided are evaporation, chemical diffusion, the Soret effect, and precipitation/crystallization (e.g., Richter et al. 2009).

Guideline #2: *The reference material should be pure elements or chemical compounds that are either in diluted acids or can be easily dissolved into diluted acids.*

Any unnecessary processing performed in the lab has the potential to induce systematic errors. For example, incomplete digestion and precipitation can induce isotope fractionation, as can chemical purification of analytes in the lab. Although some of these issues can be mitigated using a double-spike approach, it is advantageous to have the reference material in a pure form or a form in which the other elements can be quantitatively removed (e.g., by drying after digestion).

Guideline #3: *The reference material should have an isotopic composition that falls within the range of natural variability, and ideally is representative or similar to a major geological reservoir.*

For non-traditional stable isotope systems, Guideline #2 imposes the reference material be purified by a third party, often at an industrial scale. A benefit is that it ensures that the reference material is available in large quantities and is unlikely to be exhausted. The process of purification can, however, induce significant isotope fractionation, such that the synthetic material can have extreme isotopic composition and may not be representative of any geochemically relevant reservoir. This can lead to all natural isotopic compositions being systematically shifted either to the negative or positive side. Therefore, the reference material should have an isotopic composition that falls within the range of natural variability and ideally is representative of a major geological reservoir for the element investigated. This can be achieved by first surveying aliquots of industrially purified material to find a batch whose isotopic composition approaches that of a geologically relevant reservoir. For example, IRMM-014 coincidentally has an iron isotopic composition that is indistinguishable from chondrites (Craddock and Dauphas 2011).

Guideline #4: *The isotopic composition of the reference material should be characterized at high-precision for all its isotopes to ensure that no measurable anomalies are present that would complicate studies of mass-independent effects and mass-fractionation laws.*

To first order, isotopic variations follow the rules of mass-dependent fractionation, meaning that the variations in isotopic ratios scale as the differences in mass of the isotopes involved. However, it is now possible to discern clear departures from mass-dependent fractionation produced by nuclear field-shift or magnetic effects, and it is also possible to precisely define the laws of mass dependent-fractionation (Dauphas and Schauble 2016). Large-scale purification processes that would fractionate isotopes would impart a certain mass-fractionation law that would complicate comparison between naturally occurring mass fractionation laws. Furthermore, it has been shown previously that some purification processes, notably the Mond-process used in purifying Ni, can create spurious isotopic anomalies (Steele et al. 2011). Characterization of mass-independent effects and mass-fractionation laws is a growing field in geochemistry (Dauphas and Schauble 2016) and it is essential that attention be paid to this issue by documenting whether the material displays spurious isotopic anomalies.

Guideline #5: *The choice of a reference material against which to report isotopic analyses should be a community-led effort and should be consistent.*

Once a standard has reached a certain level of acceptance (e.g., when more than 20 publications report isotopic compositions relative to that standard; if two reference materials have achieved this status, whichever has been more extensively used), that standard should be used in subsequent publications. If it is exhausted, a secondary reference material may be defined and an offset be applied to the isotopic analyses such that the original reference material can still be used to report isotopic compositions. For example, JMC Zn-Lyon is not readily available but future Zn isotopic analyses should still be reported relative to this

standard even if new reference materials are used such as IRMM-3702 (Cloquet et al. 2006a; Ponzevera et al. 2006; Moeller et al. 2012) or NIST SRM-683 (Tanimizu et al. 2002; Chen et al. 2016). The secondary reference material used during the measurement should be specified when the δ-notation is defined. For example, one would write: "The Zn isotopic composition is expressed as, $\delta^{66}Zn = [(^{66}Zn/^{64}Zn)_{std}/(^{66}Zn/^{64}Zn)_{JMC\,Lyon} - 1] \times 1000$, where the isotopic analyses were measured relative to IRMM-3702 to which a systematic offset of -0.29 was applied (Moeller et al. 2012) for conversion to the JMC Lyon $\delta^{66}Zn$ scale".

The exception to this guideline is that if the standard is proven to be isotopically heterogeneous as analytical capabilities improve, then a new reference material should be used to report isotopic compositions (see guideline # 1). Ideally, this new standard should have an isotopic composition that is similar to the original reference material used to define the δ scale.

Guideline #6: *The reference materials should be widely available. This implies that lab-defined and owned reference materials should be transferred to organizations that do not have a conflict of interest.*

The role of certification institutes such as IRMM or NIST is to characterize the reference materials that they distribute and ensure that they are available. In many instances, there has been a disconnect between the needs of the geochemical community and what these certification institutes can provide. This is probably due, in part, to the fact that non-traditional stable isotope geochemistry has grown at a rapid pace while preparation of certified materials can take a long time (Vogl and Pritzkow 2010). Part of the certification involves characterization of absolute isotopic abundances using gravimetrically prepared isotope mixtures. In non-traditional stable isotope geochemistry, knowing the absolute ratios is not particularly useful. To cope with the shortage or unavailability of isotopic reference materials, in-house isotopic standards have become the reference materials against which isotopic analyses are reported (DSM3 for Mg, Zn-Lyon for Zn, OL-Ti for Ti). An issue with this practice is the availability of those materials, and conflicts of interest may arise that are detrimental to the advancement of science. Investigator-controlled distribution systems do not work. Moving forward, some organizations/companies could take over that role and distribute (perhaps against a modest fee) the reference materials created by the community. Taking titanium as an example, the bar of pure Ti used to define the OL-Ti standard (Millet and Dauphas 2014; Millet et al. 2016) will be transferred to SARM (Nancy, France), where it will be available to end-users upon request.

Another aspect regarding availability is the preparation of a large enough stock so that the reference material can be used for decades and the material remains stable in time. Aqueous solutions are appealing as they ensure homogeneity (Vogl and Pritzkow 2010) but the concentration is limited by solubility constraints and long-term stability may be an issue. Solids alleviate this issue and are more cost effective for the end user.

Several isotopic systems are, or will be, in crisis if no action is taken to remediate the shortage of isotopic reference materials that can be used by newcomers to the field. There is no committee or working group overseeing the important issues related to standards and we take the opportunity of writing this chapter to propose the establishment of such a working group.

EMERGING ISOTOPE SYSTEMS

The recent advances in instrumentation have made high-precision isotopic analysis possible for almost all elements on the periodic table. Besides those systems reviewed in individual chapters of this volume, there are numerous emerging systems that show great potential as briefly summarized for some of them below.

Stable potassium isotope geochemistry

Table 1. K (atomic number = 19) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{39}K	93.2581
^{40}K	0.0117
^{41}K	6.7302

Isotopic abundance data are from Berglund and Wieser (2011).

Potassium (K) is a volatile, lithophile, incompatible and fluid-mobile element (McDonough and Sun 1995). It is a major cation in both seawater and river water (Pilson 2013), and is well mixed in the ocean because of its long residence time of ~7 Myr (Li 1982). Potassium has three isotopes, ^{39}K, ^{40}K and ^{41}K (Table 1). Among them, ^{40}K is radioactive and exhibits a branched decay scheme to ^{40}Ca and ^{40}Ar, with a half-life of 1.25×10^9 years (Faure and Mensing 2005). The stable ^{39}K and ^{41}K isotopes have > 5% mass difference, which can potentially lead to large K isotope fractionations. Indeed, fractionation of K isotopes during chemical processes has been well known and was documented as early as 1938. Taylor and Urey (1938) found a 10% variation in ^{41}K/^{39}K when K was incompletely eluted by an aqueous solution from a zeolite ion exchange column, with ^{39}K preferentially eluted from the exchange medium. This indicates that natural processes such as water-rock interactions could potentially fractionate K isotopes, and generate isotopically distinct reservoirs. Humayun and Clayton (1995a,b) found that both extraterrestrial samples (chondrites, eucrites, SNC meteorites, ureilites, and some lunar highland and mare igneous samples) and terrestrial samples (peridotites, basalts, granites, carbonatites, biotite schists and seawater) have similar K isotopic compositions within ± 0.5‰, despite variable levels of volatile element depletion among those bodies. This has been explained by vaporization under a high vapor pressure, as opposed to free evaporation. Indeed, under such conditions, evaporation would take place in an equilibrium rather than a kinetic regime (Richter et al. 2009 and references therein). Chondrules also revealed limited K isotope fractionation, again suggesting that evaporation took place under equilibrium conditions, presumably because chondrule melting and vaporization took place when the density of chondrules was high enough for a high partial pressure of K to build up around them (Alexander et al. 2000; Alexander and Grossman 2005).

The advent of high-resolution mass spectrometry has made it possible to measure K isotopes with higher precision (from ± 0.1‰ to < ±0.05‰, 2SE by MC-ICPMS) (Morgan et al. 2014; Li et al. 2016; Wang and Jacobsen 2016a,b) and TIMS (Wielandt and Bizzaro 2011; Naumenko et al. 2013).

Stable K isotopic compositions are reported in the δ notation:

$$\delta^{41}\mathrm{K}(\text{‰}) = \left\{ \frac{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{sample}}}{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{std}}} - 1 \right\} \times 1000$$

where the standard (std) is either NIST SRM 3141a (Li et al. 2016) or commercial ultrapure potassium nitrate (Wang and Jacobsen 2016a,b). There is a slight difference between these two standards based on the same geostandard and seawater data published from these two groups. Further studies are needed to better quantify the difference and to select one standard for reporting high-precision K isotopic data.

To date, >1.4‰ variation in ^{41}K/^{39}K has been reported for terrestrial and extraterrestrial samples (Fig. 3). Morgan et al. (2014) found 0.4‰ K isotopic variation in a diverse range of whole rocks and mineral separates that formed at high temperatures, which is 10 times greater than the analytical uncertainty of <±0.05‰ (2SE). Wang and Jacobsen (2016a,b) found that
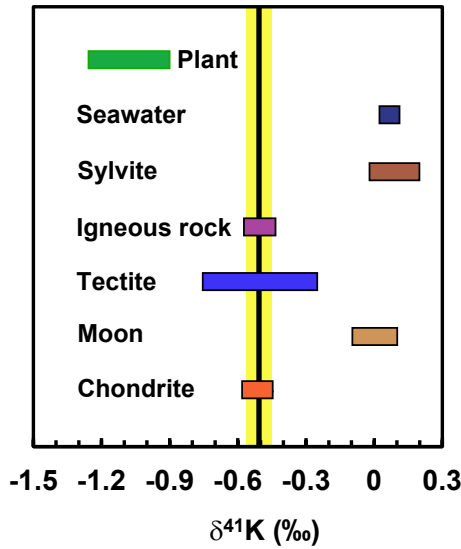
Figure 3. Natural variations in the stable K isotopic composition relative to NIST SRM 3141a. The vertical line and shaded area represent the bulk Earth as represented by igneous rock standards, with $\delta^{41}K = 0.50 \pm 0.04\permil$ (2SD). Data from Wang and Jacobsen (2016a,b) are normalized to NIST SRM 3141a by subtracting 0.58. Data are from the literature (Li et al. 2016; Wang and Jacobsen 2016a,b).

seawater samples are ~0.6‰ heavier than terrestrial basalts whereas sylvite samples from two evaporate deposits have heterogeneous K isotopic compositions and overall are also heavier than basalts. Wang and Jacobsen (2016b) reported for the first time that lunar samples are enriched in heavy K isotopes relative to the Earth and chondrites. The isotopically heavy Moon was interpreted as a result of evaporation-driven kinetic K isotope fractionation during the Moon-forming giant impact. Li et al. (2016) documented the largest K isotopic variation in natural samples, with $\delta^{41}K$ (relative to NIST SRM 3141a) ranging from -1.3 in plants to ~ 0‰ in seawater. Though the underlying processes for large K isotopic variations require further investigation, the large fractionations make K isotope geochemistry a promising avenue for tracing geological and biological processes.

Stable K isotope geochemistry might also play a significant role in refining the ^{40}K–^{40}Ar and ^{40}K–^{40}Ca dating as these methods are based on the assumption that K isotopic composition does not vary in nature to an important degree. As discussed in Naumenk et al. (2013), the $^{40}K/K$ isotopic abundance is the largest contributor to the total K–Ar age uncertainty.

Titanium isotope geochemistry

Table 2. Ti (atomic number = 22) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{46}Ti	8.25
^{47}Ti	7.44
^{48}Ti	73.72
^{49}Ti	5.41
^{50}Ti	5.18

Isotopic abundance data are from Berglund and Wieser (2011).

Titanium (Ti) shares many geochemical similarities with other high field strength elements Hf, Zr, Nb, and Ta. In particular, it has very low solubility in aqueous medium, such that it is largely insusceptible to low temperature aqueous alteration. Titanium is also a highly refractory element that condensed from solar nebula gas early in the condensation sequence (Lodders 2003). For example, refractory inclusions in meteorites (also known as Calcium-Aluminum-rich Inclusions—CAIs) contain significant amounts of Ti. In natural settings, Ti is usually present as Ti^{4+} but significant amounts of Ti^{3+} can be present under low oxygen fugacity conditions, such as those that prevailed during condensation of CAIs.

Titanium has 5 stable isotopes, ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti and ^{50}Ti (Table 2). In meteorites and their components, significant departures from mass-dependent fractionation (i.e., isotopic anomalies) have been documented (Dauphas and Schauble 2016). Hibonite inclusions from CM chondrites and CAIs display large enrichments in ^{50}Ti that correlate with anomalies in another neutron-rich isotope, ^{48}Ca (see Fig. 9 and its caption in Dauphas and Schauble 2016 for details). The anomalies measured in hibonite grains can reach ~2500 for $\varepsilon^{50}Ti$ (25%). Bulk meteorites also display isotopic anomalies affecting primarily ^{50}Ti but the effects are subtler, ranging from ~−2 to +4 ε-units (Trinquier et al. 2009; Zhang et al. 2012). Zhang et al. (2012) measured the $\varepsilon^{50}Ti$ value of lunar rocks and found that they were affected by cosmogenic effects, more specifically neutron capture effects arising from interactions between galactic cosmic rays and lunar rocks. They were able to correct for these effects by using collateral neutron capture effects on Sm and Gd. After correction, they found that lunar and terrestrial rocks have identical $\varepsilon^{50}Ti$ values within ± 0.04, despite the 6 ε-unit span of the meteorites. This suggests that either most of the Moon came from the protoEarth or the Moon-forming impactor had very similar isotopic composition to the Earth.

The mass-dependent Ti isotopic variations, similar to other non-traditional stable isotopes, are also reported in the traditional δ notation. Nonetheless, no officially certified Ti isotopic standard is available and the measurements published thus far are reported relative to a bar of high-purity metal Ti: OL-Ti (Millet and Dauphas 2014). Millet and Dauphas (2014) showed that different part of the OL-Ti reference material had indistinguishable Ti isotopic compositions. Furthermore, the Ti isotopic compositions of basalts measured by a double spike technique yield a $\delta^{49}Ti$ value of +0.004 ± 0.062‰, relative the OL-Ti reference material. Millet et al. (2016) used this technique to measure a more extensive array of mantle-derived magmas and found that they have approximately uniform isotopic compositions (variations can be found but they span less than 0.05‰). Lunar rocks also have Ti isotopic compositions very similar to the Earth. The
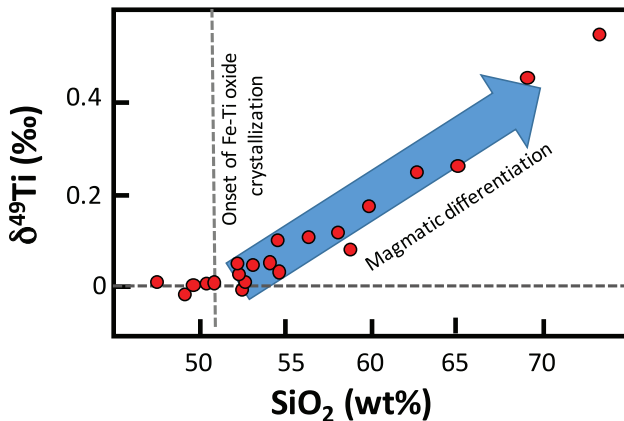

Figure 4. Trend of magmatic Ti isotope fractionation in igneous rocks (modified from Millet et al. 2016).

isotopic composition of OL-Ti is thus representative of an important geochemical reservoir. This reference material fulfills the guidelines highlighted above and we recommend that this standard continue to be used in future studies to facilitate inter-laboratory comparisons.

The available high-precision Ti isotopic data are still limited but suggest a great potential for understanding magmatic differentiation (Miller et al. 2016). Millet et al. (2016) discovered that magmatic differentiation of silicic rocks can fractionate Ti isotopes, producing rocks that have δ^{49}Ti values as high as ~+0.3‰ (Fig. 4). Such enrichment could reflect Ti isotope fractionation during magmatic differentiation, possibly associated with equilibrium fractionation between oxides (e.g., ilmenite) and melt.

Vanadium isotope geochemistry

Table 3. V (atomic number = 23) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{50}V	0.250
^{51}V	99.750

Isotopic abundance data are from Berglund and Wieser (2011).

Vanadium (V) is a biologically active trace element with multiple redox states. The ratio of V to another non-redox element of similar geochemical behavior (e.g., Sc) can provide direct information on the oxygen fugacity during magmatic processes. This approach has been used to examine the redox state of the mantle in the Archean (Canil 1997; Li and Lee 2004) and various other settings (the source of mid-ocean ridge basalts; the sub-arc mantle; Lee et al. 2005). The conclusion is that the redox conditions of melting did not change drastically with time (Canil 1997; Li and Lee 2004). Similarly, there does not appear to be much spatial heterogeneity in the present mantle (Lee et al. 2005). Those results have been questioned recently (Kelley and Cottrell 2009; Aulbach and Stagno 2016) and it is important to develop new proxies of the redox condition of Earth's mantle. Vanadium isotope fractionation could provide clues on that. Indeed, it has been shown that in magmas and minerals relevant to mantle petrology, significant isotope fractionation was present between the two redox states of iron (Dauphas et al. 2014; Roskosz et al. 2015). Similar equilibrium isotope fractionation may be present for V between for example V^{4+} and V^{5+}.

Not much work has been done on V isotope geochemistry because it possesses only two stable isotopes, ^{50}V and ^{51}V (Table 3), so a double spike technique cannot be applied and quantitative recovery is required during purification. This element is also not straightforward to purify from other elements. An additional complication arises from the fact that there is a large contrast between the abundances of ^{51}V and ^{50}V (^{51}V/^{50}V = ~400), so that it is difficult to measure its isotopic composition by mass spectrometry. Nielsen et al. (2011) addressed those difficulties and designed a protocol to measure the V isotopic composition of natural rocks. Prytulak et al. (2011) applied this technique to the analysis of igneous geostandards PCC-1, BHVO-2, BCR-2, BIR-1a, GSP-2, and AGV-2 as well as the Allende chondrite and found ~1.2‰ isotopic variation. A later comprehensive study of 64 mafic and ultramafic rocks revealed 1.6‰ V isotopic variation, and yielded a silicate Earth δ^{51}V value of -0.7 ± 0.2‰, where the reference material is a pure V solution distributed by Alfa Aesar (Prytulak et al. 2013). In this δ reference frame, all samples measured so far have markedly negative values. Nielsen et al. (2014) measured the V isotopic composition of meteorites (various chondrites, some HED meteorites, and one martian meteorite). They found that those meteorites have a δ^{51}V value of around -1.7‰, meaning that they are lower than the terrestrial composition by 1‰. The cause for this shift is uncertain but could be related to irradiation from the young Sun, which can produce enrichments in ^{50}V relative to ^{51}V (i.e., it can shift δ^{51}V towards lower values).

More recently, Wu et al. (2015) calculated V isotope fractionation factors using first-principle techniques for V species in solution or adsorbed on goethite surface. They suggested that V isotopes could record past redox conditions in seawater. Wu et al. (2016) reported on a new measurement protocol for V isotopes that yields a precision of better than ± 0.1 ‰. Schuth et al. (2016) presented measurements by femtosecond laser ablation MC-ICPMS of V-rich minerals and found a range in $^{51}V/^{50}V$ of ~1.5‰. Overall, V isotopes show a lot of promise as a tracer of metabolic pathways as well as redox conditions in the mantle and possibly in the ocean.

Stable rubidium isotope geochemistry

Table 4. Rb (atomic number = 37) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{85}Rb	72.17
^{87}Rb	27.83

Isotopic abundance data are from Berglund and Wieser (2011).

Rubidium (Rb), similar to K, belongs to the alkali metal group and is a volatile, lithophile, incompatible, and fluid-mobile element. Rb has two isotopes, ^{87}Rb and ^{85}Rb (Table 4). Between them, ^{85}Rb is stable and ^{87}Rb is radioactive and decays to ^{87}Sr, with a half-life of 48.8 billion years (Faure and Mensing 2005). In ^{87}Rb–^{87}Sr dating, the isotopic composition of Rb is often measured to determine the concentration of Rb in the rocks or minerals by isotope dilution but the demand on the precision of those isotopic analyses is not very stringent because other sources of error contribute to the overall error (Waight et al. 2002). To date, high precision Rb isotopic measurements in the literature are still limited. This is presumably due to two difficulties. One is that Rb behaves very similarly to K during most chromatography procedures, so that separating the two can be difficult. The second difficulty is that Rb possesses only two stable isotopes, so that high yield is needed to avoid isotope fractionationation during purification. Achieving both requirements (effective separation from K and high yield) is difficult. Nebel et al. (2005) developed a protocol to purify Rb and analyzed its isotopic composition. The publication does not give details on the degree of separation between Rb and K, other than after processing the K/Rb ratio is < 5. The isotopic analyses are corrected for instrumental mass bias using Zr doping and the precision of the analyses is on the order of ± 0.5‰. Nebel et al. (2011) applied this technique to the Rb isotopic analysis of chondrites and found that if any, the isotopic variations were limited to ± 1‰ around the terrestrial value. Rb is significantly more volatile than K but improvements in precision are needed to tell whether its isotopic composition was affected by vaporization in the solar system.

Stable strontium isotope geochemistry

Table 5. Sr (atomic number = 38) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{84}Sr	0.56
^{86}Sr	9.86
^{87}Sr	7.00
^{88}Sr	82.58

Isotopic abundance data are from Berglund and Wieser (2011).

Strontium (Sr) is an alkaline earth element, with four isotopes (Table 5). Of them, ^{87}Sr is the decay product of ^{87}Rb, with a half-life of 48.8 billion years (Faure and Mensing 2005). The ^{87}Rb–^{87}Sr decay scheme has been extensively used as a chronometer and fingerprint of mantle source regions (Faure and Powell 1972; Faure and Mensing 2005). Because of the

small relative mass difference, the stable Sr isotope ratios are often treated as invariable, with $^{88}Sr/^{86}Sr = 8.375209$. This value has been used to calibrate instrumental fractionations for high-precision Sr isotopic analyses.

With the developments in high precision mass spectrometry using MC-ICPMS and TIMS, significant stable isotope fractionation has been found for Sr in natural samples. The large fractionation has important implications for the measurement and application of radiogenic Sr isotopes, as well as great potential to trace various geological processes.

Stable Sr isotopic compositions are often reported in the δ notation:

$$\delta^{88}Sr(\‰) = \left\{ \frac{(^{88}Sr/^{86}Sr)_{sample}}{(^{88}Sr/^{86}Sr)_{std}} - 1 \right\} \times 1000$$

where the standard (std) is the NIST SRM 987.

Sable Sr isotopic compositions have been measured on both TIMS and MC-ICPMS. Double spike methods are usually used for TIMS (DS-TIMS) (Krabbenhoft et al. 2009; Shalev et al. 2013) and some MC-ICPMS (Shalev et al. 2013), though more MC-ICPMS protocols have adopted the standard-sample bracketing method (SSB-MC-ICPMS) (Fietzke and Eisenhauer 2006; Moynier et al. 2010; Charlier et al. 2012; Ma et al. 2013a). In general, the DS-TIMS yield the highest precision and accuracy (± 0.02 for $\delta^{88}Sr$, 1SD), followed by DS-MC-ICPMS and SSB-MC-ICPMS. To date, significant stable Sr isotope fractionation has been observed for both high-T and low-T geological processes, with the overall variation in $\delta^{88}Sr$ greater than 1.1‰ in terrestrial materials (Fig. 5).
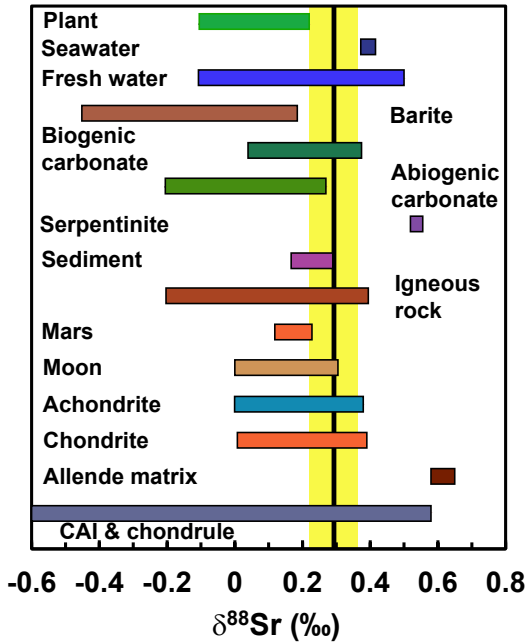

Figure 5. Natural variations in the stable Sr isotopic composition relative to the standard SRM987. The $\delta^{88}Sr$ range of CAI and chondrule extends down to −1.73‰. The vertical line and shaded area represent the mantle, with $\delta^{88}Sr = 0.29 \pm 0.07$‰ (2SD) (Charlier et al. 2012). Data are from literature (Fietzke and Eisenhauer 2006; Halicz et al. 2008; Ohno et al. 2008; Ruggeberg et al. 2008; de Souza et al. 2010; Krabbenhoft et al. 2010; Moynier et al. 2010; Bohm et al. 2012; Charlier et al. 2012; Ma et al. 2013a; Raddatz et al. 2013; Wei et al. 2013; Stevenson et al. 2014, 2016; Vollstaedt et al. 2014; Widanagamage et al. 2014, 2015).

Studies of extraterrestrial and terrestrial materials reveal significant Sr isotope fractionation. Chondrites have heterogeneous Sr isotopic compositions, with δ^{88}Sr ranging from +0.12 to +0.35‰, reflecting the mixing of different proportions of isotopically light CAIs and chondrules with the isotopically heavy matrix materials during nebular processes (Moynier et al. 2010; Charlier et al. 2012). The terrestrial mantle has an average δ^{88}Sr value of +0.29 ± 0.07‰ (2SD), similar to carbonaceous chondrites, angrites, eucrites and martian meteorites (Moynier et al. 2010; Charlier et al. 2012). By contrast, differentiated igneous rocks from the Earth and Moon have light Sr isotopic compositions, likely resulting from the crystallization of isotopically heavy plagioclase during magmatic differentiation (Charlier et al. 2012).

Large stable Sr isotopic variation has also been observed in biogenic and inorganic carbonates (Fietzke and Eisenhauer 2006; Ruggeberg et al. 2008; Krabbenhoft et al. 2010; Bohm et al. 2012; Raddatz et al. 2013; Stevenson et al. 2014; Vollstaedt et al. 2014), barite precipitation (Widanagamage et al. 2014; 2015) and weathered residues (Halicz et al. 2008; de Souza et al. 2010; Krabbenhoft et al. 2010; Wei et al. 2013; Stevenson et al. 2016), indicating the potential of using Sr isotopes as a tracer of continental weathering, marine Sr cycle, and paleoceanographic studies. In general, carbonates tend to have light Sr isotopic compositions relative to seawater, which has a homogenous δ^{88}Sr of 0.387 ± 0.002‰ (2SE mean) (Shalev et al. 2013). The large Sr isotope fractionation correlates with factors such as growth rate and temperature (e.g., Ruggeberg et al. 2008; Bohm et al. 2012; Stevenson et al. 2014). River waters draining carbonates and silicates tend to have distinct Sr isotopic compositions, reflecting the control of source lithologies (isotopically light carbonates vs. heavy silicates) (e.g., Wei et al. 2013). Stable Sr isotopes have also been used in archaeology for paleodietary studies, as there are systematic mass-dependent variations with increasing trophic level (Knudson et al. 2010).

Cadmium isotope geochemistry

Table 6. Cd (atomic number = 48) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{106}Cd	1.25
^{108}Cd	0.89
^{110}Cd	12.49
^{111}Cd	12.80
^{112}Cd	24.13
^{113}Cd	12.22
^{114}Cd	28.73
^{116}Cd	7.49

Isotopic abundance data are from Berglund and Wieser (2011).

Cadmium (Cd) is a highly volatile, chalcophile, moderately incompatible and biologically active trace element with a single oxidation state (Cd2+) in the Earth (McDonough and Sun 1995). Cadmium, together with Hg and Zn, belongs to the group-IIB element, and is toxic and widely distributed in the hydrosphere, biosphere, crust, mantle and extraterrestrial rocks. Cd has eight stable isotopes (Table 6), with a large (>9%) relative mass difference, which could lead to large mass-dependent isotope fractionation.

Stable Cd isotopic compositions are reported in either δ notation:

$$\delta^{114/x}\text{Cd}(‰) = \left\{ \frac{(^{114}\text{Cd}/^{x}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{x}\text{Cd})_{\text{std}}} - 1 \right\} \times 1000$$

or ε notation:

$$\varepsilon^{114/x}Cd = \left\{ \frac{(^{114}Cd/^xCd)_{sample}}{(^{114}Cd/^xCd)_{std}} - 1 \right\} \times 10000$$

or εCd/amu notation:

$$\varepsilon^{y/x}Cd/amu = \left\{ \frac{(^yCd/^xCd)_{sample}}{(^yCd/^xCd)_{std}} - 1 \right\} \times \frac{10000}{(m_y - m_x)}$$

where x = mass 110, 111, 112 or 113, and y = mass 114, 113, 112 or 111. The Cd isotopes are typically measured by MC-ICPMS, and the ratio of $^{114}Cd/^{110}Cd$ is the one used for reporting purposes. The standard (std), however, is quite different for different labs. Before 2013, different labs used their own in-house Cd isotopic standards (Carignan et al. 2004; Wombacher and Rehkaemper 2004; Cloquet et al. 2005; Schmitt et al. 2009a), which makes it difficult to compare Cd isotopic data reported from different labs, as those in-house standards have very different Cd isotopic compositions. Recently, Abouchami et al. (2013) examined the purity, homogeneity and Cd isotopic composition of NIST SRM 3108 and found that it is pure, homogenous and has a Cd isotopic composition close to the best estimates for the bulk silicate Earth. Thus, NIST SRM 3108 is recommended as the common reference material for reporting high-precision Cd isotopic data for future studies.

To date, >4‰ Cd isotopic variation in $^{114}Cd/^{110}Cd$ has been reported for terrestrial samples (Ripperger et al. 2007) and >24‰ Cd isotopic variation in extraterrestrial samples (Wombacher et al. 2008). As reviewed in Rehkaemper et al. (2011), these large Cd isotopic variations mainly result from evaporation and condensation during both natural and anthropogenic processes as well as biological processes.

Some ordinary chondrites, type 3 carbonaceous and most enstatite chondrites have highly fractionated Cd isotopic compositions, which reflect kinetic Cd isotope fractionation by volatilization and redistribution of Cd during open system thermal metamorphism on the parental bodies (Wombacher et al. 2003, 2008). The Cd produced during ore refineries has very different isotopic compositions relative to the natural Cd because of the evaporation-driven kinetic isotope fractionation during smelting of sulfide ores, which makes Cd isotopes a great tracer for anthropogenic sources of Cd into soils (Cloquet et al. 2006b; Shiel et al. 2010; Wen et al. 2015) and oceans (Shiel et al. 2012, 2013). Nonetheless, recent studies found significant Cd isotope fractionation during soil weathering, which may compromise the Cd isotopic signatures from pollution sources (Chrastny et al. 2015).

Seawater displays the largest Cd isotopic variation in terrestrial samples because of the large Cd isotope fractionation during biological uptake and utilization of Cd in the seawater column. During Cd uptake into marine carbonates at the ocean surface (Boyle et al. 1976; Boyle 1988), light Cd isotopes are preferentially enriched in carbonates, which leads to a concomitant enrichment of heavy Cd isotopes (> +2‰) in the surface water. The Cd isotopic composition of deep seawater (>1000 m) seems homogenous, with $\delta^{114}Cd$ = ~+0.3‰ (relative to NIST SRM 3108; Conway and John 2015, and the references therein). In addition to the vertical heterogeneity, surface seawaters from different oceans also display a large isotopic variation, which reflects both isotope fractionations and mixing among the oceans. Therefore, Cd isotope geochemistry can be used to trace not only global Cd cycle but also changes in marine biological activity in the past (Lacan et al. 2006; Ripperger et al. 2007; Schmitt et al. 2009b; Abouchami et al. 2011; Xue et al. 2013; Abouchami et al. 2014; Conway and John 2015; Georgiev et al. 2015).

Tin isotope geochemistry

Table 7. Sn (atomic number = 50) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{112}Sn	0.97
^{114}Sn	0.66
^{115}Sn	0.34
^{116}Sn	14.54
^{117}Sn	7.68
^{118}Sn	24.22
^{119}Sn	8.59
^{120}Sn	32.58
^{122}Sn	4.63
^{124}Sn	5.79

Isotopic abundance data are from Berglund and Wieser (2011).

Tin (Sn) is a chalcophile and highly volatile trace element with two oxidation states (Sn^{2+} and Sn^{4+}). Natural Sn is mainly associated with sulfide minerals though Sn oxide (cassiterite, SnO_2) is also widespread. Tin has 10 stable isotopes with a large relative mass difference (>10%) (Table 7). Sn isotope fractionation was considered negligible until 2002 when Clayton et al. (2002) developed a method for high-precision isotopic analysis of Sn based on MC-ICPMS. Since then, tin isotopes have been widely applied in archaeology to trace Sn provenance of artifacts. This is because Sn was a vital commodity in the past and Sn from different ore deposits from different locations has different isotopic compositions (Haustein et al. 2010; Balliana et al. 2013; Yamazaki et al. 2013, 2014; Mason et al. 2016). Nonetheless, the application of Sn isotopes in geochemistry is still limited. A remarkable feature of Sn is that like Fe, it possesses a Mössbauer isotope ^{119}Sn, so it is possible to predict its equilibrium fractionation factor using the synchrotron technique of Nuclear Resonant Inelastic X-ray Scattering (NRIXS) or conventional Mössbauer spectroscopy. Polyakov et al. (2005) used these techniques to predict Sn isotope fractionation for different phases and found a large control of its different oxidation states. Malinovskiy et al. (2009) showed that UV irradiation of methyltin can cause large mass-dependent and mass-independent Sn isotope fractionations. Moynier et al. (2009) observed mass-independent Sn isotope fractionation in chemical exchange reactions by using dicyclohexano-18-crown-6, which they argued are due to nuclear field shift effects.

Antimony isotope geochemistry

Table 8. Sb (atomic number = 51) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{121}Sb	57.21
^{123}Sb	42.79

Isotopic abundance data are from Berglund and Wieser (2011).

Antimony (Sb) is a siderophile, moderately incompatible trace element in the Earth (McDonough and Sun 1995), with multiple oxidation states (dominated by Sb^{3+}, Sb^{5+} and Sb^{3-}). It is toxic, with Sb^{3+} more toxic than Sb^{5+}. Antimony has two stable isotopes (Table 8). At present, the literature on high-precision Sb isotopic data is still limited. Rouxel et al. (2003) characterized the Sb isotopic compositions of seawater, silicate rocks, various environmental samples, deep-sea sediments and hydrothermal sulfides. The continental and oceanic crustal rocks have relatively restricted and lighter Sb isotopic composition than seawater, which has a homogenous Sb isotopic composition. The hydrothermal sulfides display the largest (up

to 1.8‰) Sb isotopic variation. The large Sb isotopic variation reflects both heterogeneous Sb sources and isotope fractionation during redox changes in aqueous solutions at low temperatures (Rouxel et al. 2003). Recently, Resongles et al. (2015) have found that two rivers in France, which drained different mining sites, have distinct Sb isotopic compositions, reflecting Sb isotope fractionation during complexed Sb transfer from rocks, mine wastes and sediments to the river water. Overall, Sb isotope systematics may be a useful tool for tracing redox processes, pollution sources and biogeochemical processes in riverine and oceanic systems (Rouxel et al. 2003; Resongles et al. 2015).

Stable tellurium isotope geochemistry

Table 9. Te (atomic number = 52) isotopes and typical natural abundance,

Isotope	Abundance (%)
^{120}Te	0.09
^{122}Te	2.55
^{123}Te	0.89
^{124}Te	4.74
^{125}Te	7.07
^{126}Te	18.84
^{128}Te	31.74
^{130}Te	34.08

Isotopic abundance data are from Berglund and Wieser (2011).

Tellurium (Te) belongs to the same group as S and Se, and is a volatile, chalcophile trace element with multiple oxidation states (Te^{6+}, Te^{4+}, Te^{2+}, and Te^{2-}). Tellurium has eight isotopes with > 8% relative mass difference (Table 9). Among them, ^{126}Te is the decay product of ^{126}Sn, with a half-life of 0.2345 million years (Oberli et al. 1999). In addition, the eight Te isotopes were produced by *r*-, *s*-, and *p*- processes during stellar nucleosynthesis. Hence, Te isotopes have been mainly used in cosmochemistry for searching the short-lived ^{126}Sn in order to use the ^{126}Sn–^{126}Te chronometer to understand early solar system processes, or for searching the nucleosynthetic anomaly in order to understand the solar nebular processes (Fehr et al. 2004, 2005, 2006, 2009; Moynier et al. 2009; Fukami and Yokoyama 2014). To our knowledge, there is only one study that focuses on stable Te isotope geochemistry. Fornadel et al. (2014) developed a method for high-precision (~±0.10‰, 2SD for ^{130}Te/^{125}Te) analysis of Te isotopes in tellurides and native tellurium from various ore deposits and documented an over 1.6‰ Te isotopic variation. Though the processes responsible for the large fractionation is unknown, Te isotope geochemistry, could become an excellent complement to S and Se isotope geochemistry.

Barium isotope geochemistry

Barium (Ba) is an alkaline earth element with seven stable isotopes (Table 10). Most of the work in Ba stable isotope geochemistry has focused on Ba isotope anomalies in extraterrestrial materials (Eugster et al. 1969; McCulloch and Wasserburg 1978; Hidaka et al. 2003; Savina et al. 2003; Ranen and Jacobsen 2006; Andreasen and Sharma 2007; Carlson et al. 2007; Hidaka and Yoneda 2011). The past several years have seen a rapidly growing literature on Ba isotopes in terrestrial materials.

The Ba isotopic compositions are most often reported using isotopes ^{137}Ba and ^{134}Ba:

$$\delta^{137}\text{Ba}(‰) = \left\{ \frac{(^{137}\text{Ba}/^{134}\text{Ba})_{\text{sample}}}{(^{137}\text{Ba}/^{134}\text{Ba})_{\text{std}}} - 1 \right\} \times 1000$$

where δ^{137}Ba has been reported relative to one of three different standards in the recent literature: (1) a Ba(NO$_3$)$_2$ solution from Fluka Aldrich (Von Allmen et al. 2010; Miyasaki et al. 2014; Pretet et al. 2016), (2) a BaCO$_3$ solution (IAEA-CO-9), and (3) a Ba(NO$_3$)$_2$ solution from the National Institute of Standards and Technology (SRM3104a; Nan et al. 2015, Horner et al. 2015).

Table 10. Ba (atomic number $= 56$) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{130}Ba	0.106
^{132}Ba	0.101
^{134}Ba	2.417
^{135}Ba	6.592
^{136}Ba	7.854
^{137}Ba	11.232
^{138}Ba	71.698

Isotopic abundance data are from Berglund and Wieser (2011).

The total natural variation in ^{137}Ba/^{134}Ba of natural terrestrial materials is $\sim 1.5\%$ (Fig. 5). Although this range is quite restricted (owing to the small relative mass difference between Ba isotopes), modern MC-ICPMS methods are able to yield a reproducibility of about $\pm0.03\%$ to $\pm0.05\%$ (Miyazaki et al. 2014; Nan et al. 2015), which is more than an order of magnitude smaller than the natural variations.

The most recent applied studies have focused primarily on the Ba cycle in seawater because the concentration of Ba closely tracks the concentration of dissolved Si(OH)$_4$ and other nutrients (von Allmen et al. 2010; Horner et al. 2015; Pretet et al. 2015; Cao et al. 2016). The thinking behind these studies is that Ba isotopes coupled with Ba concentration measurements may be useful to probe nutrient cycling, biologic productivity, and water mass mixing (Horner et al. 2015; Cao et al. 2016). Ba enters the oceans from rivers with a δ^{137}Ba of about 0 to $+0.3\%$ (Fig. 6). From there, precipitation of BaSO$_4$ in organic microenvironments or adsorption of Ba onto organic particulates leads to light isotope enrichment in the solid phase, and consequently, seawater becomes isotopically heavy with respect to Ba (Fig. 6; Horner et al. 2015; Cao et al. 2016). This general process leads to a strong correlation between Ba^{2+} concentrations and δ^{137}Ba, and imparts a distinct chemical and isotopic signature on different water masses. Hence, coupled Ba–δ^{137}Ba systematics can be used to trace the mixing of different water masses (Horner et al. 2015; Cao et al. 2016). An open question is whether other factors such as hydrothermal activity, submarine groundwater discharge, or atmospheric inputs, are important within the oceanic Ba cycle or simply have effects that cancel out (Cao et al. 2016).

Like particulate matter, corals are isotopically lighter than seawater (Fig. 6; Pretet et al. 2015). Most of the corals measured so far were analyzed without information regarding the isotopic composition of the host seawater, but the expectation from laboratory cultures is that coral is lighter than seawater by 0.01 to $0.26\pm0.14\%$ (Pretet et al. 2015).

To aid the interpretation of δ^{137}Ba in nature, several studies have investigated isotope fractionation by diffusion (Van Zuilen et al. 2016) and between experimentally grown *inorganic* minerals and their host solution. Von Allmen et al. (2010) grew BaCO$_3$ and BaSO$_4$ from aqueous solutions at 21 and 80 °C. Like many previous experiments using other isotopic systems, they observed that the solid phase was isotopically light relative to the aqueous solution. For BaCO$_3$, the fractionation ranges from 0.1 (fast growth) to 0.3‰ (slow growth). An interesting result for both BaCO$_3$ and BaSO$_4$ is that the fractionations are insensitive to temperature between 21 and 80 °C. Mavromatis et al. (2016) precipitated BaCO$_3$ at 25 °C and documented light isotope enrichment in the solid phase by $0.07\pm0.04\%$, a value that is in
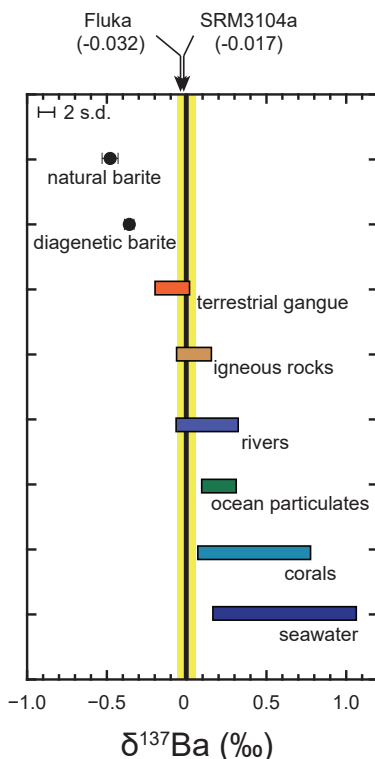
Figure 6. Natural variations in the Ba isotopic composition of terrestrial materials relative to the standard IAEA-CO-9. The vertical line and shaded area represent the standard value with $\delta^{137}Ba = 0.00 \pm 0.02$ (2SD). A different choice of standard, shown by the two arrows, would not shift δ values significantly (Miyazaki et al. 2014; Nan et al. 2015). Data are from the literature (Von Allmen et al. 2010; Miyazaki et al. 2014; Horner et al. 2015; Nan et al. 2015; Cao et al. 2016; Pretet et al. 2016).

good agreement with the "fast growth" experiments of Von Allmen et al. (2010). Mavromatis et al. (2016) went a step further and monitored the Ba isotope composition of the aqueous solution over time after chemical (but not isotopic) equilibrium between $BaCO_3$ and fluid was established. After about 6–8 days, the solution had evolved isotopically to a composition that was indistinguishable from the solid phase, indicating a $BaCO_3$–fluid equilibrium fractionation factor of ~0‰. Such a small equilibrium effect is consistent with similarities in the Ba–O bond length of witherite (2.80 Å) compared to aqueous Ba (2.79 Å) (Mavromatis et al. 2016). One other experimental study by Böttcher et al. (2012) showed that $BaMn(CO_3)_2$ grown at 21 °C yields a similar light isotope enrichment in the solid phase of $0.11 \pm 0.06‰$.

Stable neodymium isotope geochemistry

Neodymium (Nd) is a rare earth element, with seven isotopes (Table 11). Of them, ^{142}Nd is the decay product of ^{146}Sm, with a half-life of 68 million years (Kinoshita et al. 2012) and ^{143}Nd is the decay product of ^{147}Sm, with a half-life of 106 billion years (Faure and Mensing 2005). The ^{147}Sm–^{143}Nd and ^{146}Sm–^{142}Nd have been extensively used as chronometers and fingerprints of mantle source regions (DePaolo 1988; Boyet and Carlson 2005; Faure and Mensing 2005). Because of the small relative mass difference, the stable Nd isotope ratios are often treated as invariable, with $^{146}Nd/^{144}Nd = 0.7219$. This value has been used to calibrate instrumental fractionations for high-precision Nd isotopic analyses.

Table 11. Nd (atomic number = 60) isotopes and typical natural abundance.

Isotope	Abundance (%)
^{142}Nd	27.152
^{143}Nd	12.174
^{144}Nd	23.798
^{145}Nd	8.293
^{146}Nd	17.189
^{148}Nd	5.756
^{150}Nd	5.638

Isotopic abundance data are from Berglund and Wieser (2011).

With the developments in high precision mass spectrometry using MC-ICPMS and TIMS, significant stable isotope fractionation has been found for Nd in natural samples. The large fractionations have important implications for the measurement and application of radiogenic Nd isotopes, as well as great potential to trace various geological processes.

The stable Nd isotopic compositions are often reported in the ε notation:

$$\varepsilon^x\text{Nd} = \left\{ \frac{(^x\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^x\text{Nd}/^{144}\text{Nd})_{\text{std}}} - 1 \right\} \times 10000$$

where the standard (std) is the JNd$_{i-1}$ and x = mass 145, 146, 148 and 150. When x = 142 and 143, the ε^{142}Nd and ε^{143}Nd represent the radiogenic Nd isotopic compositions.

The literature on stable Nd isotope geochemistry is still very limited. Nonetheless, the data so far reveal significant Nd isotope fractionation (Fig. 7). Wakaki and Tanaka (2012) reported high-
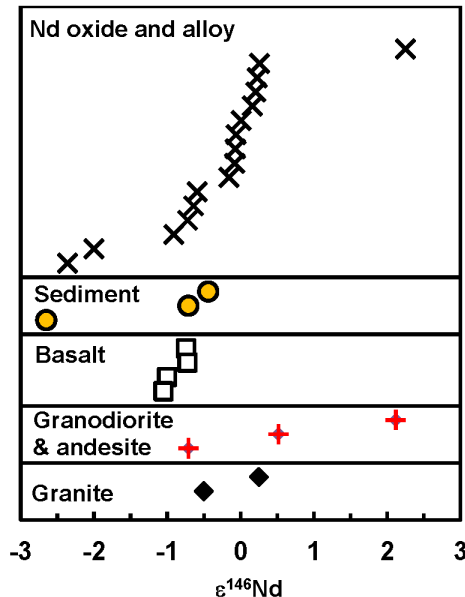

Figure 7. Natural variations in the stable Nd isotopic composition of terrestrial materials relative to the standard JNd$_{i-1}$. The La Jolla Nd has different δ^{146}Nd value than the JNd$_{i-1}$. Data are from Wakaki and Tanaka (2012), and Ma et al. (2013b).

precision (±0.3 for ε^{146}Nd, 2SD) stable Nd isotope analysis by using DS-TIMS method and found large mass-dependent Nd isotope fractionation during column chemistry, with ε^{146}Nd varying from +4.60 at the early stage of elution to −9.44 at the late stage of elution. They also found significant Nd isotopic variation in commercial high-purity Nd reagents (ε^{146}Nd = −2.36 to +0.23). In particular, the La Jolla Nd (ε^{146}Nd = −1.97 ± 0.23) has different stable Nd isotopic composition than JNd_{i-1}. Ma et al. (2013b) developed a method of using MC-ICPMS to measure stable Nd isotopes and achieved similar precision (better than ±0.4 for ε^{146}Nd, 2SD) to DS-TIMS. They found a large Nd isotopic variation in 15 rocks and polymetallic nodules (mainly geostandards), with ε^{146}Nd ranging from −2.65 in a stream sediment (JSD-1) to +2.12 in a granodiorite (JG-1a). The in-house Nd standard (Nd-GIG) has the heaviest Nd isotopic composition, with ε^{146}Nd=+2.25. Overall, relative to basalts, river and marine sediments tend to have light Nd isotopic compositions while granites and granodiorites have heavy Nd isotopic compositions.

CONCLUSIONS

Our knowledge of the behavior and utility of non-traditional stable isotopes has expanded greatly since the publication of the RIMG volume 55: *Geochemistry of Non-Traditional Stable Isotopes* in 2004. A testament to the rapid progress in this field is that many of the stable isotope systems that were in their infancy in 2004 have a dedicated chapter in this volume. We anticipate that the isotope systems summarized in this introductory chapter or not even mentioned (e.g., Ga, Br and Zr) will warrant their own dedicated chapter in the not too distant future.

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