INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON ATOMIC WEIGHTS AND ISOTOPIC ABUNDANCES[*]
SUBCOMMITTEE ON NATURAL ISOTOPIC FRACTIONATION[**]

ISOTOPE-ABUNDANCE VARIATIONS OF SELECTED ELEMENTS[†]

(IUPAC Technical Report)

Prepared for publication by
T. B. COPLEN[1,‡], J. K. BÖHLKE[1], P. De BIÈVRE[2], T. DING[3], N. E. HOLDEN[4], J. A. HOPPLE[1], H. R. KROUSE[5], A. LAMBERTY[2], H. S. PEISER[1], K. RÉVÉSZ[1], S. E. RIEDER[1], K. J. R. ROSMAN[6], E. ROTH[7], P. D. P. TAYLOR[2], R. D. VOCKE, JR.[8], AND Y. K. XIAO[9]

[1]*U.S. Geological Survey, 431 National Center, Reston, VA 20192, USA;* [2]*Institute for Reference Materials and Measurements, Commission of the European Communities Joint Research Centre, B-2440 Geel, Belgium;* [3]*Institute of Mineral Deposits, Chinese Academy of Geological Sciences, Beijing, 100037, China;* [4]*Brookhaven National Laboratory, Upton, NY 11973, USA;* [5]*The University of Calgary, Calgary, Alberta T2N 1N4, Canada;* [6]*Curtin University of Technology, Perth, Western Australia, 6001, Australia;* [7]*103 Rue Brancas, 92310 Sèvres, France;* [8]*National Institute of Standards and Technology, Gaithersburg, MD 20899, USA;* [9]*Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai, 810008, China*

[†]For use in the classroom, Microsoft PowerPoint® files of all figures are available at <http://isotopes.usgs.gov/publications.htm>.
[‡]Corresponding author: E-mail: tbcoplen@usgs.gov

Isotope-abundance variations of selected elements

(IUPAC Technical Report)

Abstract: Documented variations in the isotopic compositions of some chemical elements are responsible for expanded uncertainties in the standard atomic weights published by the Commission on Atomic Weights and Isotopic Abundances of the International Union of Pure and Applied Chemistry. This report summarizes reported variations in the isotopic compositions of 20 elements that are due to physical and chemical fractionation processes (not due to radioactive decay) and their effects on the standard atomic-weight uncertainties. For 11 of those elements (hydrogen, lithium, boron, carbon, nitrogen, oxygen, silicon, sulfur, chlorine, copper, and selenium), standard atomic-weight uncertainties have been assigned values that are substantially larger than analytical uncertainties because of common isotope-abundance variations in materials of natural terrestrial origin. For 2 elements (chromium and thallium), recently reported isotope-abundance variations potentially are large enough to result in future expansion of their atomic-weight uncertainties. For 7 elements (magnesium, calcium, iron, zinc, molybdenum, palladium, and tellurium), documented isotope variations in materials of natural terrestrial origin are too small to have a significant effect on their standard atomic-weight uncertainties.

This compilation indicates the extent to which the atomic weight of an element in a given material may differ from the standard atomic weight of the element. For most elements given above, data are graphically illustrated by a diagram in which the materials are specified in the ordinate and the compositional ranges are plotted along the abscissa in scales of (1) atomic weight, (2) mole fraction of a selected isotope, and (3) delta value of a selected isotope ratio.

INTRODUCTION

The standard atomic weights and their uncertainties tabulated by the International Union of Pure and Applied Chemistry (IUPAC) are intended to represent most normal materials encountered in terrestrial samples and laboratory chemicals. During the meeting of the Commission on Atomic Weights and Isotopic Abundances (CAWIA) at the General Assembly of IUPAC in 1985, the Working Party on Natural Isotopic Fractionation (now named the Subcommittee on Natural Isotopic Fractionation) was formed to investigate the effects of isotope-abundance variations of elements upon their standard atomic weights and atomic-weight uncertainties. The aims of the Subcommittee on Natural Isotopic Fractionation were (1) to identify elements for which the uncertainties of the standard atomic weights are larger than measurement uncertainties in materials of natural terrestrial origin because of isotope-abundance variations caused by fractionation processes (excluding variations caused by radioactivity), (2) to provide information about the range of atomic-weight variations in specific substances and chemical compounds of each of these elements, and (3) to examine critically the definitions and consistency of use of the footnotes in the Table of Standard Atomic Weights [1] and annotations in the Table of Isotopic Compositions of the Elements [2]. The purpose of this report is to compile ranges of isotope-abundance variations and corresponding atomic weights in selected materials containing 20 chemical elements (H, Li, B, C, N, O, Mg, Si, S, Cl, Ca, Cr, Fe, Cu, Zn, Se, Mo, Pd, Te, and Tl) from published data. The information in this report complements the bi-decadal Commission reviews of the atomic

weights of the elements [3,4] and the "Isotopic Compositions of the Elements 1997" [2]. Because of its focus on extreme values, this report should not be viewed as a comprehensive compilation of stable isotope-abundance variations in the literature; rather, it is intended to illustrate ranges of variation that may be encountered in natural and anthropogenic material.

The atomic weight of an element in a specimen can be determined from knowledge of the atomic masses of the isotopes of that element and the isotope abundances of that element in the specimen. The abundance of isotope i of element E in the specimen can be expressed as a mole fraction, $x(^iE)$. For example, the mole fraction of ^{34}S is $x(^{34}S)$, which is $n(^{34}S)/[n(^{32}S) + n(^{33}S) + n(^{34}S) + n(^{36}S)]$ or more simply $n(^{34}S)/\sum n(^iS)$ or $n(^{34}S)/n(S)$, where $n(^iE)$ is the amount of each isotope i of element E in units of moles. Thus, if element E is composed of isotopes ^iE, with mole fractions $x(^iE)$, the atomic weight, $A_r(E)$, is the sum of the products of the atomic masses and mole fractions of the isotopes; that is, $A_r(E) = \sum x(^iE) \cdot A_r(^iE)$. The atomic masses from the 1993 evaluation [5] have been used by CAWIA and are listed in this report. Isotope-abundance values that are free from all known sources of bias within stated uncertainties are referred to as "absolute" isotope abundances, and they can be determined by mass spectrometry through use of synthetic mixtures of isotopes. For many elements, the abundances of the isotopes are not invariant; thus, these elements have a range in atomic weight. This report includes data for 20 such elements in natural occurrences and in laboratory reagents.

Molecules, atoms, and ions in their natural occurrences contain isotopes in varying proportions, whereby they possess slightly different physical and chemical properties. This gives rise to partitioning of isotopes (isotope fractionation) during physical or chemical processes, and these fractionations commonly are proportional to differences in the relevant isotope masses. Physical isotope-fractionation processes include those in which diffusion rates are mass-dependent, such as ultrafiltration or gaseous diffusion of ions or molecules. Chemical isotope-fractionation processes involve redistribution of isotopes of an element among phases, molecules, or chemical species. They either can be (1) equilibrium isotope fractionations, when forward and backward reaction rates for individual isotope-exchange reactions are equal, or (2) kinetic isotope fractionations caused by unidirectional reactions in which the forward reaction rates usually are mass-dependent. In equilibrium isotope reactions, in general, the heavy isotope will be enriched in the compound with the higher oxidation state, and commonly in the more condensed state. Thus, for example, ^{13}C is enriched in carbon dioxide relative to graphite, and in graphite relative to methane, and ^2H is enriched in liquid water relative to water vapor. In kinetic processes, statistical mechanics predicts that the lighter (lower atomic mass) of two isotopes of an element will form the weaker and more easily broken bond. The lighter isotope is more reactive; therefore, it is concentrated in reaction products, enriching reactants in the heavier isotope. Examples of reactions that produce kinetic isotope fractionation include many biological reactions, treatment of limestone with acid to liberate carbon dioxide, and the rapid freezing of water to ice. Sulfate reduction by bacteria in respiration is an example of a biologically mediated kinetic isotope-fractionation process. Kinetic isotope fractionations of biological processes are variable in magnitude and may be in the direction opposite to that of equilibrium isotope fractionations for the same chemical species.

Isotopic equilibrium between two phases does not mean that the two phases have identical mole fractions of each isotope (isotope abundances), only that the ratios of these mole fractions are constant. Water vapor in a closed container in contact with liquid water at a constant temperature is an example of a system with two phases in H and O isotopic equilibrium; in this case, the concentrations of the heavy isotopes (^2H and ^{18}O) are higher in the liquid than in the vapor.

The distribution of isotopes in two substances X and Y is described by the isotope-fractionation factor $\alpha_{X,Y}$, defined by

$$\alpha_{X,Y} = \frac{n_X(^iE)/n_X(^jE)}{n_Y(^iE)/n_Y(^jE)} \tag{1}$$

where $n_X({}^i E)$ and $n_X({}^j E)$ are the amounts of two isotopes, i and j, of chemical element E in substance X, in units of moles. We equally well could have used $N_X({}^i E)$ and $N_X({}^j E)$, which are the number of atoms of two isotopes, i and j, of chemical element E in substance X. In this document, the superscripts i and j denote a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. The isotope pairs used to define $n({}^i E)/n({}^j E)$ in this report are ${}^2H/{}^1H$, ${}^7Li/{}^6Li$, ${}^{11}B/{}^{10}B$, ${}^{13}C/{}^{12}C$, ${}^{15}N/{}^{14}N$, ${}^{18}O/{}^{16}O$, ${}^{26}Mg/{}^{24}Mg$, ${}^{30}Si/{}^{28}Si$, ${}^{34}S/{}^{32}S$, ${}^{37}Cl/{}^{35}Cl$, ${}^{44}Ca/{}^{40}Ca$, ${}^{53}Cr/{}^{52}Cr$, ${}^{56}Fe/{}^{54}Fe$, ${}^{65}Cu/{}^{63}Cu$, ${}^{66}Zn/{}^{64}Zn$, ${}^{82}Se/{}^{76}Se$, ${}^{98}Mo/{}^{95}Mo$, ${}^{110}Pd/{}^{104}Pd$, ${}^{130}Te/{}^{122}Te$, or ${}^{205}Tl/{}^{203}Tl$. In general, isotope-fractionation factors are near unity. For example, the value of the equilibrium $n({}^{18}O)/n({}^{16}O)$ fractionation factor α between water liquid and water vapor at 15 °C is 1.0102. Thus, ${}^{18}O$ is enriched in liquid water at 15 °C by 1.02 % relative to its concentration in water vapor.

Variations in stable isotope-abundance ratios typically are small. Stable isotope ratios commonly are expressed as relative isotope ratios in $\delta({}^i E)$ notation (pronounced delta) according to the relation

$$\delta\left({}^i E\right) = \left[\frac{n_X\left({}^i E\right)\big/ n_X\left({}^j E\right)}{n_{\text{ref}}\left({}^i E\right)\big/ n_{\text{ref}}\left({}^j E\right)} - 1 \right] \tag{2}$$

where $\delta({}^i E)$ refers to the delta value of isotope number i of element E of sample X relative to the reference ref, and $n_X({}^i E)/n_X({}^j E)$ and $n_{\text{ref}}({}^i E)/n_{\text{ref}}({}^j E)$ are the ratios of the isotope amounts in unknown X and a reference ref. A positive $\delta({}^i E)$ value indicates that the unknown is more enriched in the heavy isotope than is the reference. A negative $\delta({}^i E)$ value indicates that the unknown is depleted in the heavy isotope relative to the reference. In the literature, $\delta({}^i E)$ is commonly shortened to $\delta^i E$. In the literature, $\delta({}^i E)$ values of isotope ratios have been reported in parts per hundred (% or per cent), parts per thousand (‰ or per mill), and parts per ten thousand. In this report, $\delta({}^i E)$ values are given in per mill; thus, the expression can be written

$$\delta\left({}^i E\right) = \left[\frac{n_X\left({}^i E\right)\big/ n_X\left({}^j E\right)}{n_{\text{ref}}\left({}^i E\right)\big/ n_{\text{ref}}\left({}^j E\right)} - 1 \right] \cdot 1000 \text{ ‰} \tag{3}$$

because a per mill is 1/1000, and 1000·1/1000 = 1. Note that per mill also is spelled per mil, permil, and per mille in the literature. The International Organization for Standardization [6] spelling is used in this report.

A single isotopic reference material defines the isotope-ratio scale of most of the elements listed in this report; however, it has been recognized that a single isotopic reference material can define only the anchor point of an isotope-ratio scale and not the magnitude (expansion or contraction) of the scale. Two reference materials are required to calibrate both scale magnitude and anchor point, as is done for the scales of H and O. Most isotopic reference materials are naturally occurring materials or are manufactured from materials of natural terrestrial origin; others have been produced from reagents whose isotopes have been artificially fractionated.

For each element E in this report, the standard atomic weight, $A_r(E)$, from "Atomic Weights of the Elements 1999" [1] is listed with its estimated uncertainty (in parentheses, following the last significant figure to which it is attributed). For zinc and molybdenum, the new standard atomic weights adopted at the 41st IUPAC General Assembly in Brisbane in July 2001, based, respectively, on the work of Chang et al. [7] and Wieser and de Laeter [8], are listed instead.

For most elements, data are graphically illustrated by a diagram in which the materials are specified in the ordinate and the compositional ranges are plotted along the abscissa on three scales: atomic weight, $A_r(E)$, mole fraction of a selected isotope, $x({}^i E)$, and relative isotope ratio expressed as deviation from the isotope ratio reference, $\delta({}^i E)$. Mole fractions of the selected isotope are calculated from the relative isotope ratio by using the "absolute" isotope-abundance measurements of the reference for

the delta scale. Atomic-weight values are calculated from atomic masses and mole fractions of the isotopes, assuming mass-dependent fractionation among the isotopes. The three scales are related exactly for elements with two isotopes for which "absolute" isotopic compositions of the references are known. However, the scales may be mismatched in some cases: (1) for some elements, the "absolute" isotopic composition of the reference may not be known to within the precision of the common relative isotope-ratio measurements; (2) calculations of atomic weights for polyisotopic elements are subject to additional, usually negligible, adjustments based either on additional isotope-abundance measurements or on an assumption about the mass-dependent isotope fractionation of isotopes that commonly are not measured. The section for each element tabulates the isotopic composition of a real or hypothetical material with delta value of 0 ‰; commonly, this material has been used for the best "absolute" isotope measurement as reported by Rosman and Taylor [2]. For many elements, the atomic weight derived from the best measurement is significantly different from the standard atomic weight. This difference results because (1) the standard atomic-weight uncertainty is limited to a single digit and the two cannot match exactly, or (2) $A_r(E)$ was assigned to be in the center of a range of natural isotopic variation—this is the case for H, Li, B, C, N, O, Si, and S—and may be greatly different from that of the best measurement material.

With the proliferation of microprobe techniques for isotope measurements, large variations in isotopic composition have been found in source materials over distances of the order of 1 to 1000 μm [9]. Such data are excluded from this compilation, as are data from extraterrestrial materials and from elements exhibiting isotope variation caused by radioactivity.

Although the data presented in this report may allow reduction in the uncertainty in atomic weight of a material, the reader is warned that when critical work is undertaken, such as assessment of individual properties, samples with accurately known isotope abundances should be obtained or suitable measurements made.

VARIATIONS IN ISOTOPIC COMPOSITION OF SELECTED ELEMENTS

Hydrogen $_1$H $A_r(H) = 1.007\ 94(7)$

Isotope	Atomic mass	Mole fraction in VSMOW [2,10]
^{1}H	1.007 825 0319(6) u	0.999 844 26(5)
^{2}H	2.014 101 7779(6) u	0.000 155 74(5)

Since 1993, the Commission has recommended [11] that stable H relative isotope ratios be reported relative to the International Atomic Energy Agency (IAEA) reference water VSMOW [also distributed by the National Institute of Standards and Technology (NIST) as RM 8535], which is assigned a $\delta(^2H)$ value of 0 ‰ on a scale normalized by assigning a value of –428 ‰ to IAEA reference water SLAP (NIST RM 8537). One water (GISP), 1 oil (NBS 22), 1 biotite (NBS 30), 1 polyethylene foil (PEF1, renamed IAEA-CH-7), and 3 natural gases (NGS1, NGS2, and NGS3) are secondary reference materials distributed by IAEA and/or NIST (Fig. 1) [12]. In addition, IAEA distributes two reference waters enriched in ^{2}H for medical and biological tracer studies [13]. Compilations of H isotope-ratio variations and isotope-fractionation factors have been published [14–18]. Sometimes $\delta(^2H)$ is designated δD in the literature.

Variations in the $\delta(^2H)$ values of surface waters, ground waters, and glacial ice generally are concordant with variations in $\delta(^{18}O)$ values and are caused primarily by evaporation and condensation processes. In meteoric waters (waters that originate as precipitation), $\delta(^2H)$ values range from –495 ‰ in Antarctic ice [19] to +129 ‰ in evaporated lakes in equatorial regions [20]. An unusual occurrence of water from a well in the Lacq natural gas field in France yielded $\delta(^2H)$ values as high as +375 ‰ [21]; a small amount of the water equilibrated at near-ambient temperature with a much larger amount of H_2S with a $\delta(^2H)$ value of –430 ‰. Agricultural food products contain meteoric waters with a range
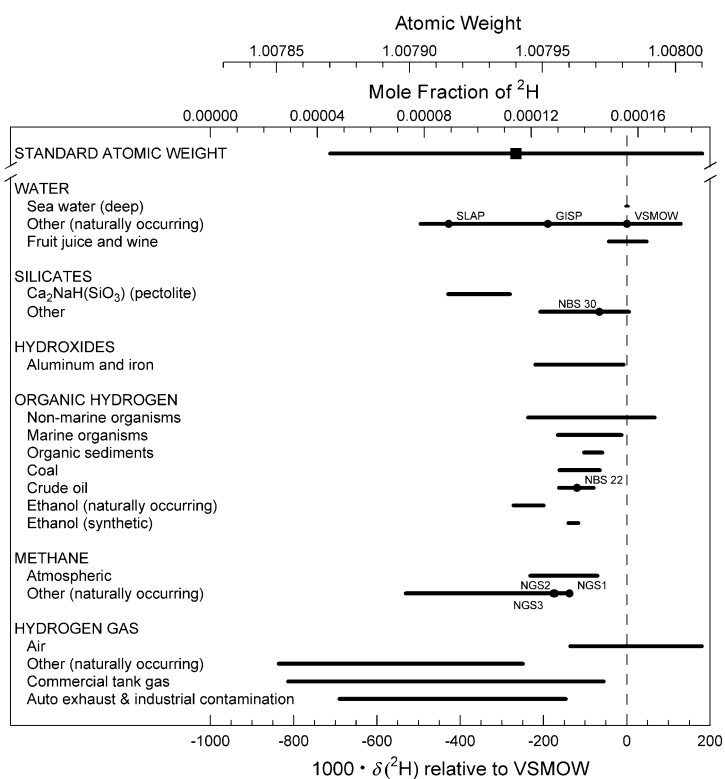
Fig. 1 Hydrogen isotopic composition and atomic weight of selected hydrogen-bearing materials [25]. The $\delta(^2H)$ scale and ^2H mole-fraction scale were matched using the data of Hagemann et al. [10]; therefore, the uncertainty in placement of the atomic-weight scale and the ^2H mole-fraction scale relative to the $\delta(^2H)$ scale is equivalent to ±0.3 ‰.

of $\delta(^2H)$ values, which may be reflected in tissues and fluids of birds and other animals consuming this food. The H isotope fractionation between plants and water in the local environment water is dependent upon evapotranspiration and species-specific variations during metabolic or biochemical processes. For example, citrus trees found in subtropical climates may undergo extensive evaporation, resulting in ^2H enrichment in cellular water—thus, ^2H of orange juice, for example, may be enriched by as much as 40 ‰ relative to local meteoric water [22]. Commercial compressed tank H_2 produced by electrolysis is variable in isotopic composition, but commonly it is only slightly depleted in ^2H relative to source water [e.g., $\delta(^2H) = -56$ ‰] [25]. H_2 produced as a by-product in petrochemical plants is depleted in ^2H, and its $\delta(^2H)$ value is as low as −813 ‰ [25].

The lowest $\delta(^2H)$ value found for a material of natural terrestrial origin reported in the literature is −836 ‰ (Fig. 1), for gaseous H_2 in natural gas from a Kansas (USA) well [23]. For this sample, $A_r(H) = 1.007\ 851$ and the mole fraction of ^2H is 0.000 0255. The highest $\delta(^2H)$ value reported for a material of natural terrestrial origin is +180 ‰ for atmospheric H_2 [24]. For this sample, $A_r(H) = 1.008\ 010$ and the mole fraction of ^2H is 0.000 1838.

Lithium $_3$**Li** A_r**(Li) = 6.941(2)**

Isotope	Atomic mass	Mole fraction in L-SVEC Li_2CO_3 [2,26]
^{6}Li	6.015 1223(5) u	0.075 91(20)
^{7}Li	7.016 0041(5) u	0.924 09(20)

The basis for relative abundance measurements of Li isotopes is IAEA isotopic reference material L-SVEC (NIST RM 8545) Li_2CO_3 with an assigned $\delta(^7Li)$ value of 0 ‰. In accordance with the recommendation of IUPAC [27], $\delta(^7Li)$ values are reported herein, though $\delta(^6Li)$ values commonly are found in the literature. Two additional Li_2CO_3 reference materials are available from the Institute of Reference Materials and Measurements (IRMM) in Geel, Belgium. IRMM–015 is highly depleted in ^{7}Li, and IRMM–016 is essentially identical in isotopic composition to L-SVEC [26].

Sea water is approximately homogeneous in Li isotopic composition with a $\delta(^7Li)$ value of about +33 ‰ (Fig. 2). Lithium is supplied to the ocean primarily from two sources: (1) high-temperature (>250 ℃) basalt-ocean-water reactions [28] and (2) river input of weathering continental crust. Removal processes of lithium from the ocean include (1) low-temperature (<250 ℃) alteration of oceanic crust in which basalts take up lithium; (2) biogenic carbonate production—marine carbonates contain 2 mg/kg lithium on average; (3) biogenic opal and chert production—Quaternary radiolarian and diatomaceous oozes contain about 30 mg/kg Li; and (4) diagenesis of clay minerals and authigenic clay mineral production, which may be the most important sink for lithium [29].

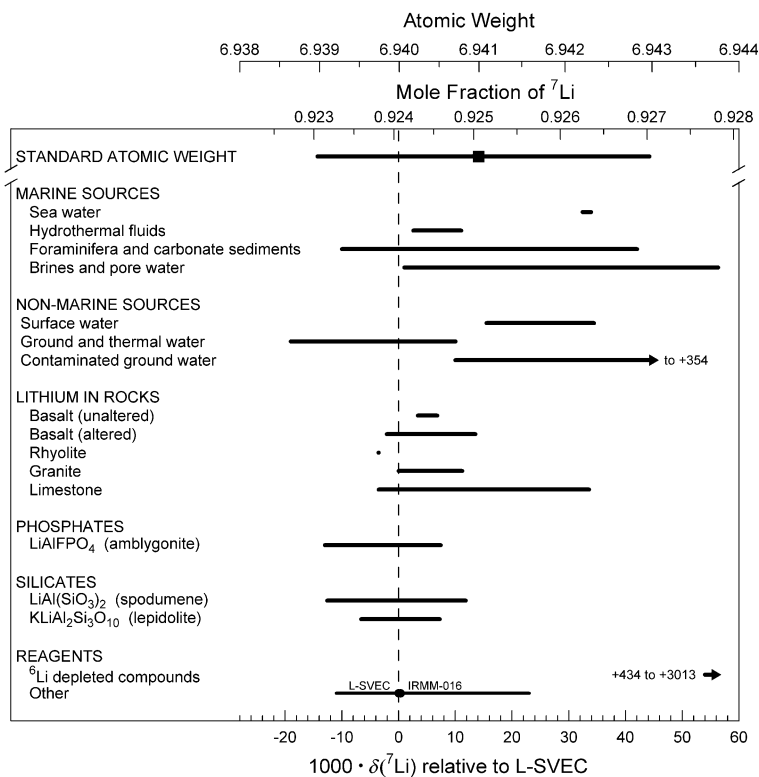**Fig. 2** Lithium isotopic composition and atomic weight of selected lithium-bearing materials [25]. The $\delta(^7Li)$ scale and ^{7}Li mole-fraction scale were matched using the data of Qi et al. [26]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{7}Li mole-fraction scale relative to the $\delta(^7Li)$ scale is equivalent to ±3 ‰.

Of the chemical elements discussed in this report, Li is particularly unusual because large amounts of Li have been isotopically fractionated by removal of ^{6}Li for use in hydrogen bombs. The remaining Li is substantially enriched in ^{7}Li, and some of this material has found its way into laboratory reagents and into the environment. An analysis of 39 laboratory reagents [30] showed a range in $\delta(^7$Li) of –11 to +3013 ‰. For the most enriched in ^{7}Li, A_r(Li) = 6.9959 and the mole fraction of ^{7}Li is 0.9799. Values of $\delta(^7$Li) as high as +354 ‰ have been measured in ground water from a carbonate aquifer underlying West Valley Creek in Pennsylvania (USA), down-gradient from a Li processing plant [25].

The lowest ^{7}Li content reported in a material of natural terrestrial origin is Li dissolved in ground water from a coastal aquifer in South Carolina (USA) with $\delta(^7$Li) = –19 ‰ [25]. For this sample, A_r(Li) = 6.9387 and the mole fraction of ^{7}Li is 0.9227. The highest ^{7}Li abundance reported in a material of natural terrestrial origin [$\delta(^7$Li) = +56.3 ‰] is found in pore water from a marine core [31]. For this sample, A_r(Li) = 6.9438 and the mole fraction of ^{7}Li is 0.9278.

Boron $_5$B A_r(B) = 10.811(7)

Isotope	Atomic mass	Mole fraction in NIST SRM 951 boric acid [2,32]
^{10}B	10.012 9371(3) u	0.198 27(13)
^{11}B	11.009 3055(4) u	0.801 73(13)

The basis for the relative abundance measurement of B isotopes is NIST SRM 951 boric acid, which is assigned a $\delta(^{11}$B) value of 0 ‰. A second reference material, IRMM–011 boric acid, is identical (within measurement error) in isotopic composition to SRM 951. Two boric acid reference materials (IRMM–610 and SRM 952) depleted in ^{11}B are available [33,34]. Three waters and five rocks are secondary reference materials to be distributed by IAEA (B-1 through B-8 in Fig. 3) [35].

Bassett [36] compiled and critically evaluated B isotope measurements prior to 1990. B isotope ratios have large variations (>90 ‰) in the terrestrial environment (Fig. 3). Not included in Fig. 3 is a $\delta(^{11}$B) value of –59 ‰ for a steam condensate from a fumarole at Larderello, Italy [37], because analytical results could not be reproduced. In solution, coexisting boric acid is enriched in ^{11}B by 40 ‰ relative to neutral borate ions; consequently, B isotope fractionation can occur during precipitation and adsorption. B isotopes are fractionated during precipitation of salts from brines; precipitated salts are depleted in ^{11}B, thus enriching the remaining brine in ^{11}B [38]. B isotopes are fractionated by 30–40 ‰ by preferential adsorption of ^{10}B of dissolved B on clay minerals [39].

The material of natural terrestrial origin with the lowest reported ^{11}B content in Fig. 3 is kornerupine [(Mg,Fe^{2+})$_4$(Al,Fe^{3+})$_6$(SiO$_4$,BO$_4$)$_5$(O,OH)$_2$] from Antarctica with $\delta(^{11}$B) = –34.2 ‰ [40]. For this specimen, A_r(B) = 10.8062 and the mole fraction of ^{11}B is 0.7961. The Victorian volcanic-crater lakes of southeastern Australia are the materials of natural terrestrial origin most enriched in ^{11}B (Fig. 3), with $\delta(^{11}$B) values as positive as +59.2 ‰ [41]. For this sample, A_r(B) = 10.8207 and the mole fraction of ^{11}B is 0.8107.

Nonmarine evaporite deposits in California (USA) and Turkey yield large quantities of commercial B-bearing products, including laboratory reagents. These deposits are substantially depleted in ^{11}B relative to sea water; nonmarine B evaporites range in $\delta(^{11}$B) between –31 ‰ and +7 ‰ (Fig. 3).
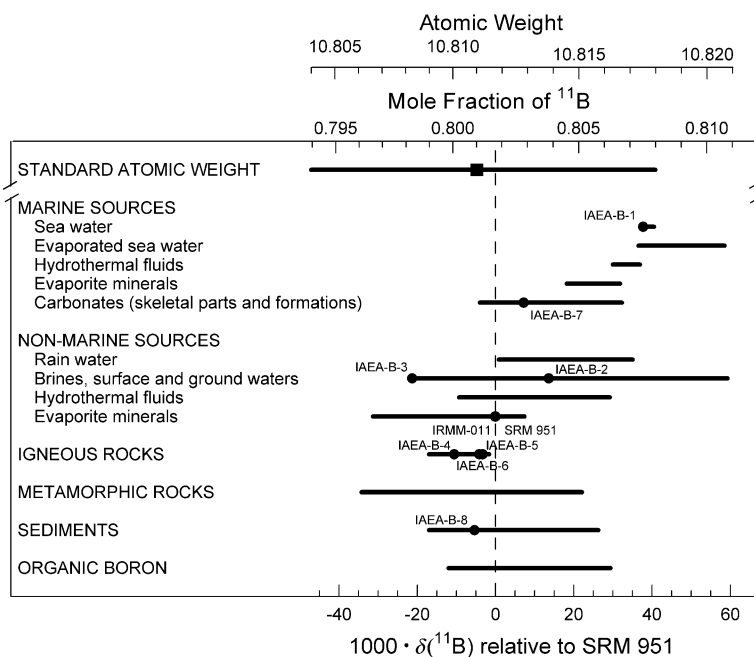
Fig. 3 Boron isotopic composition and atomic weight of selected boron-bearing compounds [25]. The $\delta(^{11}B)$ scale and ^{11}B mole-fraction scale were matched using the data of Catanzaro et al. [32]; therefore, the uncertainty in the placement of the atomic-weight scale and the ^{11}B mole-fraction scale relative to the $\delta(^{11}B)$ scale is equivalent to ±0.8 ‰.

Carbon $_6$C $A_r(C) = 12.0107(8)$

Isotope	Atomic mass	Mole fraction in VPDB [2,42]
^{12}C	12 u (exactly)	0.988 944(28)
^{13}C	13.003 354 838(5) u	0.011 056(28)

Beginning in the 1950s, isotope-abundance measurements of C isotopes were expressed relative to Peedee belemnite (PDB), which was assigned a $\delta(^{13}C)$ value of 0 ‰. Because the supply of PDB is exhausted, IUPAC recommended in 1993 [11,43] that $\delta(^{13}C)$ values be reported relative to VPDB (Vienna PDB) by assigning a $\delta(^{13}C)$ value of +1.95 ‰ on the VPDB scale to IAEA reference material NBS 19 $CaCO_3$. Various carbonates, several CO_2 gases, 3 natural gases, 1 sugar, and 1 oil are secondary reference materials distributed by IAEA and/or NIST (see Fig. 4) [12,25]. Reference materials in a subset of these are variably enriched in ^{13}C and intended for use mainly in medical and biological tracer studies [13].

Useful compilations of C isotope variations and isotope-fractionation mechanisms have been published [16–18,25]. C occurs primarily in three reservoirs on Earth, sedimentary organic matter, the biosphere, and sedimentary carbonates, the latter having $\delta(^{13}C)$ values near 0 ‰. Sedimentary carbonates with unusually low ^{13}C concentrations tend to be associated with organic matter or hydrocarbons. These reservoirs differ in isotopic composition because of different isotope-fractionation mechanisms. Kinetic isotope fractionation associated with photosynthesis preferentially enriches plant material in ^{12}C. This enrichment gives rise to organic sediments, coal, and crude oil with $\delta(^{13}C)$ values near –25 ‰ (Fig. 4). The predominant mechanism by which plants assimilate carbon is the C3 metabolic process (Fig. 4), which generally results in $\delta(^{13}C)$ of plants between –34 and –24 ‰. A second metabolic pathway (C4) utilized by plants in hot, dry, sunny environments (e.g., maize, sugar cane, and sorghum) yields more
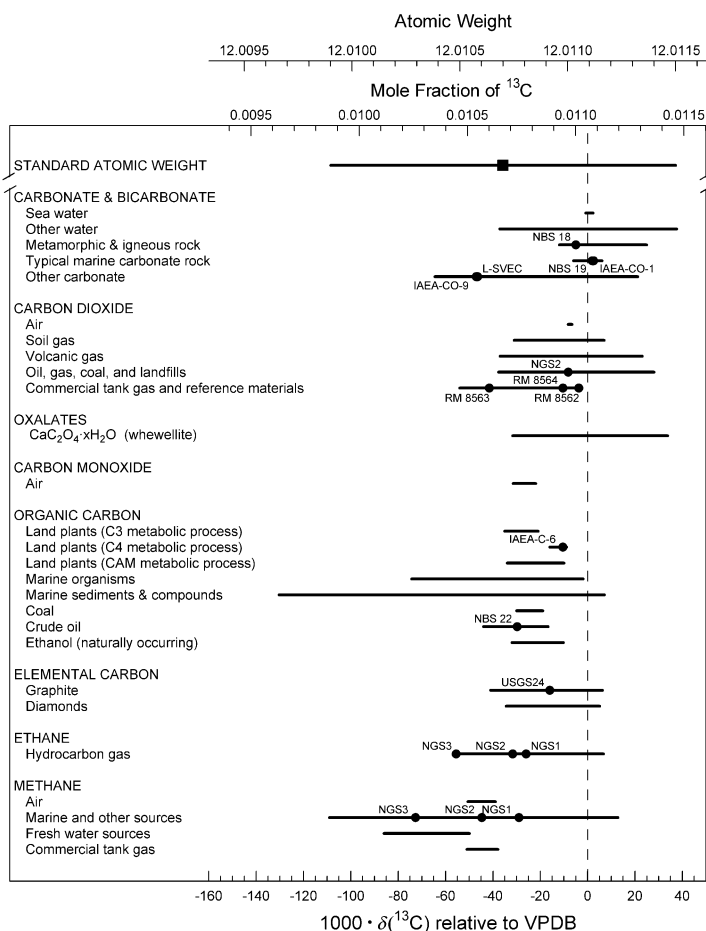
Fig. 4 Carbon isotopic composition and atomic weight of selected carbon-bearing materials [25]. The $\delta(^{13}C)$ scale and ^{13}C mole-fraction scale were matched using the data of Chang and Li [42]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{13}C mole-fraction scale relative to the $\delta(^{13}C)$ scale is equivalent to ±2.5 ‰.

positive $\delta(^{13}C)$ values ranging between –16 and –9 ‰. Animals commonly will have $\delta(^{13}C)$ values within 2 ‰ of their food supply; thus, C isotope-ratio analysis of animal tissues and fluids provides information on diet.

Although the variation in $\delta(^{13}C)$ of ocean water is small (Fig. 4), reported values in deep-sea pore waters range as high as +37.5 ‰ [44], which is the most positive $\delta(^{13}C)$ value of any C-bearing material of natural terrestrial origin in the literature. For this sample, $A_r(C) = 12.011\ 50$ and the mole fraction of ^{13}C is 0.011 466. The lowest $\delta(^{13}C)$ value (–130.3 ‰) reported in the literature for a material of natural terrestrial origin is for crocetane (2,6,11,15-tetramethylhexadecane), produced at cold seeps of the eastern Aleutian subduction zone [45]. The value of $A_r(C)$ of this material is 12.009 66, and the mole fraction of ^{13}C is 0.009 629.

Nitrogen $_7$N $A_r(N) = 14.0067(2)$

Isotope	Atomic mass	Mole fraction in N_2 in air [2,46]
^{14}N	14.003 074 0074(18) u	0.996 337(4)
^{15}N	15.000 108 973(12) u	0.003 663(4)

The primary reference material for relative abundance measurements of N isotopes is atmospheric N_2, which is homogeneous with respect to analytical uncertainties [47] and is assigned a $\delta(^{15}N)$ value of 0 ‰ (Fig. 5). Various ammonium sulfates, several potassium nitrates, 2 ureas, and 1 tank of purified N_2 gas are secondary reference materials distributed by IAEA and/or NIST [12,13,48]. Some of these materials are highly enriched in ^{15}N and intended for use mainly in medical and biological tracer studies.

Compilations of N isotopic variations and isotope-fractionation mechanisms have been published [49–52]. The ranges of isotopic composition and corresponding $A_r(N)$ of naturally occurring materials

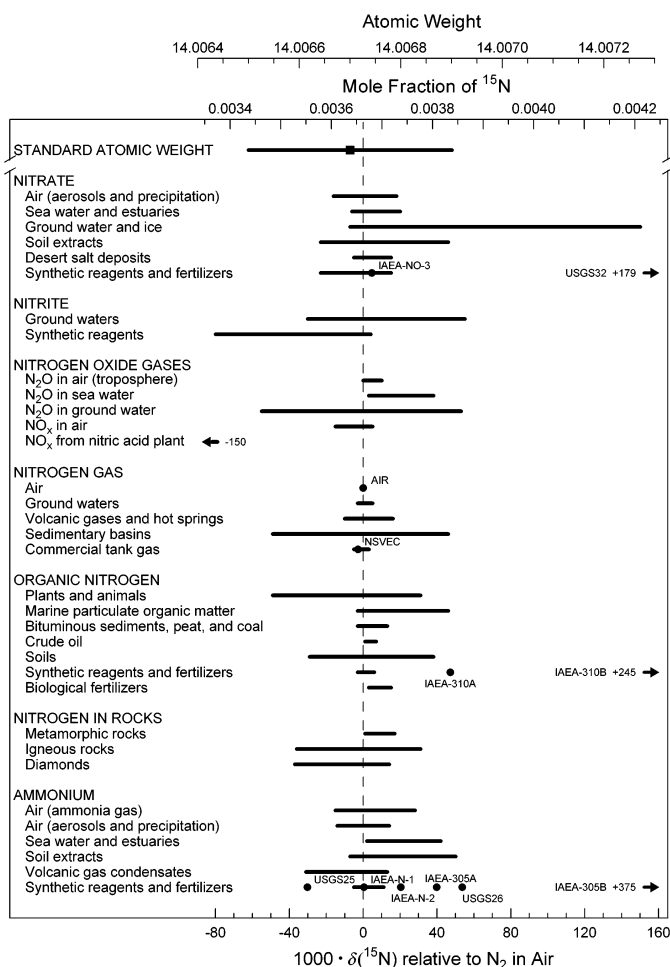**Fig. 5** Nitrogen isotopic composition and atomic weight of selected nitrogen-bearing materials [25]. The $\delta(^{15}N)$ scale and ^{15}N mole-fraction scale were matched using the data of Junk and Svec [46]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{15}N mole-fraction scale relative to the $\delta(^{15}N)$ scale is equivalent to ±1.1 ‰.

and reference materials are shown in Fig. 5. An early report of very positive $\delta(^{15}N)$ values in uranium ores [53] is not included because its results were not confirmed [54].

Atmospheric N_2 is the dominant N component in the combined atmosphere–biosphere–hydrosphere portion of the Earth, so the bulk $\delta(^{15}N)$ value of accessible N at the Earth's surface is close to 0 ‰. However, N isotopes are strongly fractionated by a variety of chemical and physical processes, so common materials have variable isotope ratios. The mole fraction of ^{15}N in the majority (>99 %) of N-bearing materials likely to be encountered in terrestrial materials ranges from 0.003 61 to 0.003 74; corresponding $\delta(^{15}N)$ values range from –15 to +20 ‰; corresponding values for $A_r(N)$ are 14.006 67 and 14.007 10. The isotopic composition of N in the deep Earth (hence, the bulk value for the whole Earth) is not well known.

N with atomic-weight values substantially different from the reference value occurs in the environment as a result of both kinetic and equilibrium isotope fractionation associated with biologic and nonbiologic processes. For example, residual inorganic aqueous N species may be relatively enriched in ^{15}N during assimilation by plants, oxidation of ammonium to nitrate (nitrification), reduction of nitrate to N gases (denitrification), or volatilization of ammonia from ammonium-bearing solutions. Microbial N fixation and organic N mineralization, however, commonly have relatively minor effects. Some of the highest $\delta(^{15}N)$ values found in the literature (>+20 ‰) are in nitrate and ammonium separated from ground waters and soils that may have experienced several such processes. The highest $\delta(^{15}N)$ value found in the literature (+150 ‰) for a material of natural terrestrial origin is for nitrate in Antarctic ice, where partial evaporation of HNO_3 may have caused isotope fractionation [55]; the corresponding $A_r(N) = 14.007\ 27$, and the mole fraction of ^{15}N is 0.004 210. N substantially depleted in ^{15}N is found in precipitation and in some soils, plants, and natural gases. Some of the lowest $\delta(^{15}N)$ values reported (<–20 ‰) for materials of natural terrestrial origin are in soil nitrate from the Dry Valley region of Antarctica, where the dominant source of N may be precipitation with low ^{15}N content [56]. The lowest value of a natural biologic sample in the literature (–49 ‰) is for epibenthic algae from a saline pond in the same region of Antarctica, and may be due to a combination of low ^{15}N content in the nutrient source plus isotope fractionation during assimilation [56]. Slightly lower $\delta(^{15}N)$ values were reported for N_2O from ground water undergoing denitrification [57], and the lowest $\delta(^{15}N)$ value is –55 ‰. For this sample, $A_r(N) = 14.006\ 53$ and the mole fraction of ^{15}N is 0.003 462. KNO_2 reagents have $\delta(^{15}N)$ values as negative as –80 ‰ [25]; corresponding $A_r(N) = 14.006\ 43$, and the mole fraction of ^{15}N is 0.003 371.

Recent studies have rapidly expanded the limits for several of the subcategories of natural terrestrial materials, and it would not be surprising if the extreme values were exceeded in the future. It should be noted that large quantities of reagents and fertilizers manufactured and distributed for experimental purposes have ^{15}N mole fractions ranging from at least 0.000 016 to 0.99 [58,59].

Oxygen $\quad\quad _8O \quad\quad\quad A_r(O) = 15.9994(3)$

Isotope	Atomic mass	Mole fraction in VSMOW [2,60,61]
^{16}O	15.994 914 6223(25) u	0.997 6206(5)
^{17}O	16.999 131 50(22) u	0.000 3790(9)
^{18}O	17.999 1604(9) u	0.002 0004(5)

Relative oxygen isotope ratios are based on $n(^{18}O)/n(^{16}O)$ measurements. Since 1993, the Commission has recommended that oxygen isotope ratios be reported relative to the reference water VSMOW (NIST RM 8535) or relative to VPDB [defined by adopting a $\delta(^{18}O)$ value of –2.2 ‰ exactly for NBS 19 $CaCO_3$] on a scale normalized (Fig. 6) such that the $\delta(^{18}O)$ of SLAP reference water (NIST RM 8537) is –55.5 ‰ exactly relative to VSMOW [11]. Marine carbonates commonly are expressed relative to the VPDB scale [11], which differs by about 30 ‰ from the VSMOW scale (Fig. 6). O-bearing gases com-
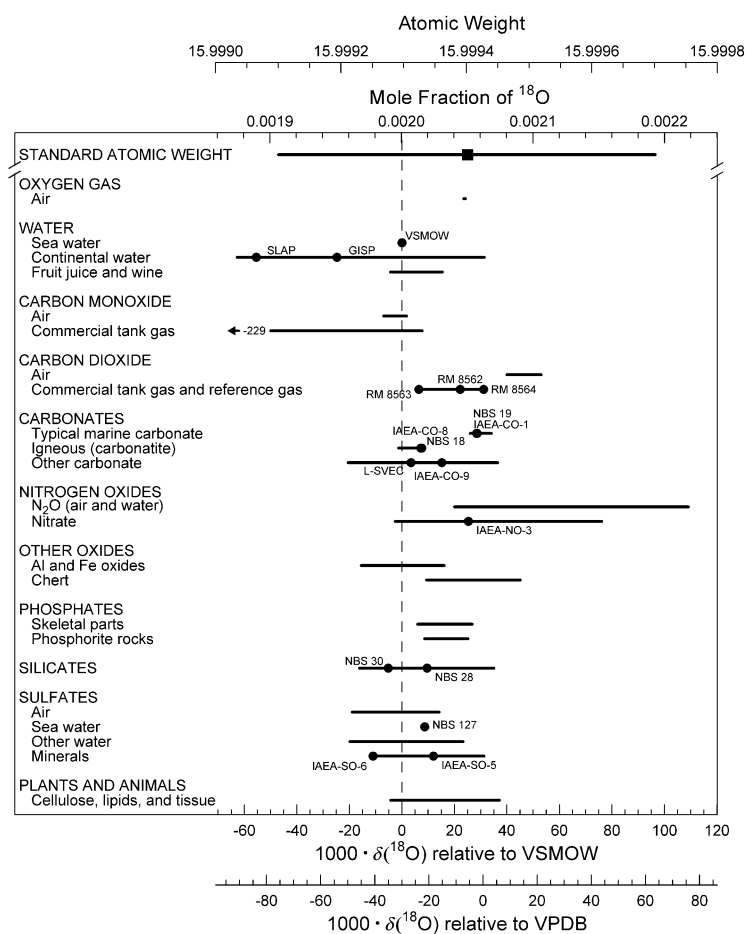
Fig. 6 Oxygen isotopic composition and atomic weight of selected oxygen-bearing materials [25]. The $\delta(^{18}O)$ scale and ^{18}O mole-fraction scale were matched using the data of Li et al. [60] and Baertschi [61]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{18}O mole-fraction scale relative to the $\delta(^{18}O)$ scale is equivalent to ±0.3 ‰.

monly are expressed relative to atmospheric O_2. Various carbonates, 1 silica sand, 1 sulfate, 3 CO_2 gases, and 1 biotite are secondary reference materials distributed by IAEA and/or NIST (Fig. 6) [12]. In addition, IAEA distributes several reference materials for medical and biological tracer studies [13].

Compilations of oxygen isotopic variations and isotope-fractionation mechanisms have been published [16–18,25,62]. As shown in Fig. 6, the $\delta(^{18}O)$ of atmospheric O_2 is constant within the uncertainty of analytical measurement [63]. Variations in the $\delta(^{18}O)$ values of terrestrial waters generally are concordant with $\delta(^2H)$ variations and are caused primarily by evaporation and condensation processes. The $\delta(^{18}O)$ of plants and animals reflects the $\delta(^{18}O)$ of meteoric water in their environment. In natural waters, $\delta(^{17}O)$ variations, based on $n(^{17}O)/n(^{16}O)$ measurements relative to VSMOW, were found to be 0.5281 ± 0.0015 times variation in $\delta(^{18}O)$ [64]. The $\delta(^{18}O)$ of bulk Earth is well represented by mid-ocean ridge basalts (+5.7 ± 0.5 ‰), which cover much of the ocean floor [65].

Mass-independent $\delta(^{17}O)$ and $\delta(^{18}O)$ isotopic variation has been observed in atmospheric O_3, O_2, N_2O, H_2O_2, CO, and CO_2 [66,67] and is attributed to discrimination between symmetric and asymmetric isotopic species during photochemical reaction [68]. Bao et al. [69] report $\delta(^{17}O)$ and $\delta(^{18}O)$ values of +11.1 ‰ and +12.5 ‰ for sulfate in sand crystals from Scotts Bluff, Nebraska (USA), a

+4.6 ‰ enrichment in [17]O relative to the expected mass-dependent value. This is the first sulfate deposit on the Earth's surface reported to be enriched in [17]O. [17]O enrichments in excess of 20 ‰ relative to mass-dependent values have been reported for nitrate from the Atacama Desert, Chile [25].

The lowest $\delta(^{18}O)$ value found in the literature for a naturally occurring material is –62.8 ‰ for Antarctic precipitation [70]. For this sample, the corresponding $A_r(O) = 15.999\ 04$ and the mole fraction of [18]O is 0.001 875. The highest $\delta(^{18}O)$ found in the literature for a terrestrial material of natural origin is +109 ‰, found in marine N_2O [71]. For this sample, $A_r(O) = 15.999\ 76$ and the mole fraction of [18]O is 0.002 218.

## Magnesium	$_{12}$Mg	$A_r(Mg) = 24.3050(6)$

Isotope	Atomic mass	Mole fraction in NIST SRM 980 Mg metal [2,72]
[24]Mg	23.985 041 87(26) u	0.789 92(25)
[25]Mg	24.985 837 00(26) u	0.100 03(9)
[26]Mg	25.982 593 00(26) u	0.110 05(19)

Relative Mg isotope ratios are based on $n(^{26}Mg)/n(^{24}Mg)$ measurements and are expressed relative to NIST SRM 980 Mg metal, which is assigned a $\delta(^{26}Mg)$ value of 0 ‰, exactly.

Daughtry et al. [73] measured carbonates where dolomitization had occurred and reported variations as large as 50 ‰. Catanzaro and Murphy [74] measured 60 natural samples including carbonates, evaporites, hydroxides, silicates, oxides, biological materials, and sea water using thermal emission mass spectrometry. Within their analytical uncertainty for $\delta(^{26}Mg)$ of ±2.2 ‰ (2σ uncertainty), they observed no isotopic variation. They attributed the variations seen by Daughtry et al. [73] to the fact that "those workers apparently did not control their analyses as strictly as necessary." Using a multiple collector inductively coupled plasma mass spectrometer, Chang et al. [75] analyzed sea water, foraminifera, and SRM 980 Mg metal, and found variations spanning 4.5 ‰ (Fig. 7). Four sea water samples were indistinguishable (+2.55 ± 0.12 ‰) in isotopic composition and have the highest [26]Mg content in the literature for a material of natural terrestrial origin (Fig. 7). For these samples, the corresponding $A_r(Mg) = 24.3055$ and the mole fraction of [26]Mg is 0.1103. Marine foraminifera were depleted in [26]Mg by 1.7 to 4.5 ‰ relative to sea water, consistent with a kinetic isotope fractionation of 1.8 to 2.5 ‰ during precipitation of calcite. The sample of natural terrestrial origin with the lowest [26]Mg content is a foraminifera with a $\delta(^{26}Mg)$ value of –1.95 ‰ [75]. This value is consistent with the

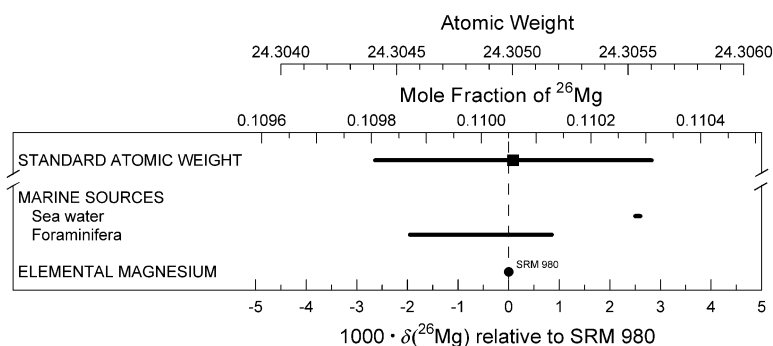**Fig. 7** Magnesium isotopic composition and atomic weight of selected magnesium-bearing materials [25]. The $\delta(^{26}Mg)$ scale and the [26]Mg mole-fraction scale were matched using the data of Catanzaro et al. [72]; therefore, the uncertainty in placement of the atomic-weight scale and the [26]Mg mole-fraction scale relative to the $\delta(^{26}Mg)$ scale is equivalent to ±2.1 ‰.

results of a cave study by Galy et al. [76], which indicates that calcite is depleted in ^{26}Mg relative to water from which it is precipitating. For this sample, the corresponding A_r(Mg) = 24.3046 and the mole fraction of ^{26}Mg is 0.1099.

Silicon $\quad _{14}$Si $\qquad A_r$(Si) = 28.0855(3)

Isotope	Atomic mass	Mole fraction in NBS 28 SiO$_2$ [25,77]
^{28}Si	27.976 926 49(22) u	0.922 223(9)
^{29}Si	28.976 494 68(22) u	0.046 853(6)
^{30}Si	29.973 770 18(22) u	0.030 924(7)

Relative Si isotope ratios are based on $n(^{30}$Si)$/n(^{28}$Si) measurements and are expressed relative to NIST NBS 28 silica sand, which is assigned a $\delta(^{30}$Si) value of 0 ‰. Three other isotopic reference materials are available: NIST SRM 990 elemental Si, IRMM–017 elemental Si, and IRMM–018 SiO$_2$ (Fig. 8). These three reference materials have been used primarily for absolute isotope-abundance measurements.

The most comprehensive report on Si isotope variations is Ding et al. [78]. Other useful compilations of Si isotope variations and isotope-fractionation factors include Hoefs [15] and Douthitt [79]. Si does not have multiple redox states, and isotope-fractionation factors are not large. Low-temperature reactions involving, for instance, opaline sinter, biogenic opal, and clay minerals, produce the largest isotope fractionations (a few per mill). Extremes in the stable isotopic composition of naturally occurring Si-bearing materials are shown in Fig. 8. An anomalous $\delta(^{30}$Si) value of –11.2 ‰ for a kaolin sample [80] is not included in Fig. 8. Excluding that value, the lowest $\delta(^{30}$Si) value reported for a sample of natural terrestrial origin is –3.7 ‰, from biogenic sponge spicules [79]. For this sample, the corresponding A_r(Si) = 28.085 22 and the mole fraction of ^{30}Si is 0.030 816. The highest $\delta(^{30}$Si) found in

Fig. 8 Silicon isotopic composition and atomic weight of selected silicon-bearing materials [25]. The $\delta(^{30}$Si) scale and ^{30}Si mole-fraction scale were matched using the data of De Bièvre et al. [77] and a $\delta(^{30}$Si) value for IRMM–017 of –1.3 ‰ relative to NBS 28 [25]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{30}Si mole-fraction scale relative to the $\delta(^{30}$Si) scale is equivalent to ±0.23 ‰.

the literature for a sample of natural terrestrial origin is +3.4 ‰, from silicified algal matter in sediments [80]. For this sample, $A_r(Si) = 28.085\,78$ and the mole fraction of ^{30}Si is 0.031 023.

Sulfur $_{16}S$ $A_r(S) = 32.065(5)$

Isotope	Atomic mass	Mole fraction in VCDT [81]
^{32}S	31.972 070 73(15) u	0.950 3957(90)
^{33}S	32.971 458 54(15) u	0.007 4865(12)
^{34}S	33.967 866 87(14) u	0.041 9719(87)
^{36}S	35.967 080 88(25) u	0.000 1459(21)

Relative S isotope ratios are based on $n(^{34}S)/n(^{32}S)$ measurements. The historical reference material for these measurements, CDT troilite (FeS) from the Cañon Diablo meteorite, varies in $\delta(^{34}S)$ by as much as 0.4 ‰ [82]. Consequently, an advisory committee of IAEA recommended in 1993 that the Ag_2S reference material IAEA-S-1 (previously known as NZ-1) be assigned a $\delta(^{34}S)$ value of –0.3 ‰ exactly, thereby establishing a VCDT (Vienna CDT) scale (Fig. 9). An elemental sulfur, 1 sphalerite, and various barium sulfates and silver sulfides are reference materials distributed internationally by IAEA and/or NIST [12].

Although most isotope fractionation of S isotopes is mass-dependent, mass-independent isotopic variation has been observed in sulfate and sulfide rock [83,84]. Rumble et al. [84] report values for

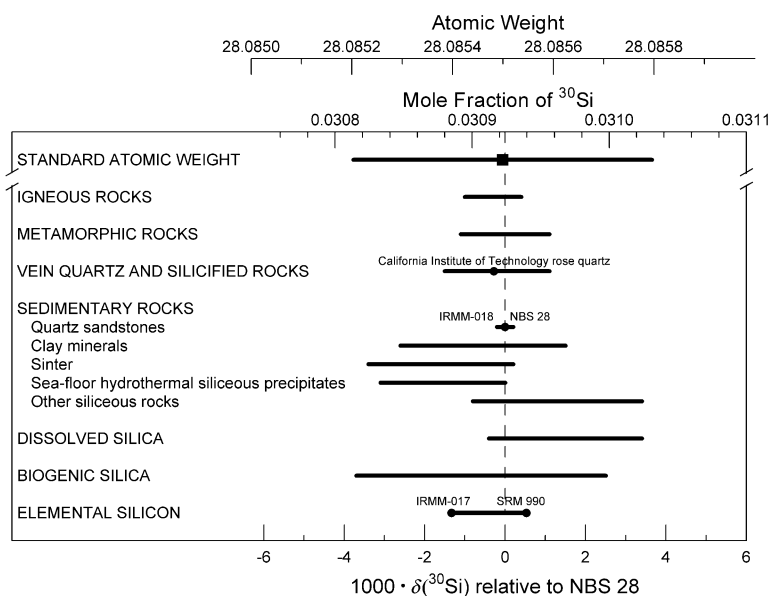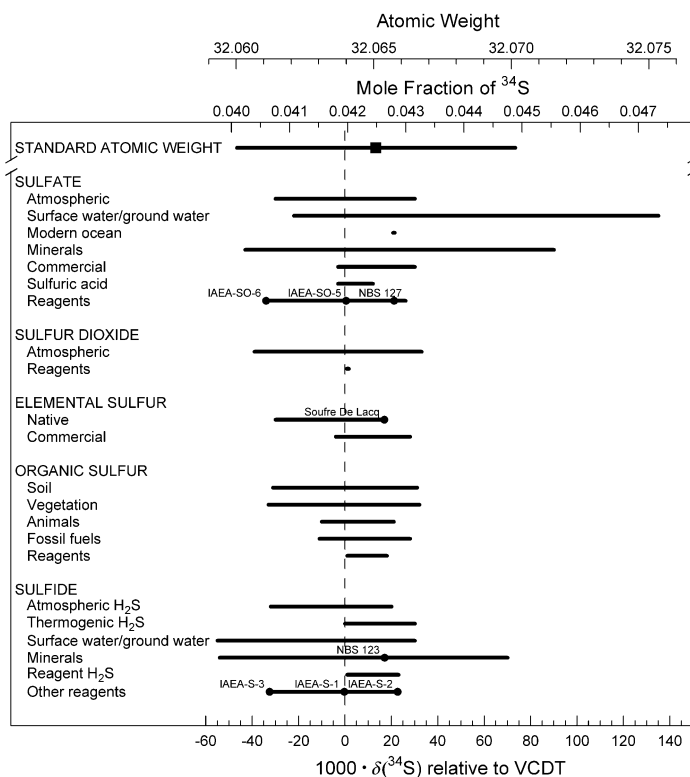**Fig. 9** Sulfur isotopic composition and atomic weight of selected sulfur-bearing materials [25]. The $\delta(^{34}S)$ scale and ^{34}S mole-fraction scale were matched using the data of Ding et al. [81]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{34}S mole-fraction scale relative to the $\delta(^{34}S)$ scale is equivalent to ±0.2 ‰.

$\delta(^{33}S)$ of between –2 and +7 ‰ in excess of mass-dependent values for black shale with an age of 2.5 Ga.

The dominant mechanism of terrestrial S isotope fractionation is low-temperature bacterial sulfate reduction, whereby $^{32}SO_4{}^{2-}$ may react up to 1.07 times faster than $^{34}SO_4{}^{2-}$ [85]. As reduction proceeds, unreacted sulfate and product sulfide not mixed with earlier produced sulfide can acquire highly positive $\delta(^{34}S)$ values. The highest value in the literature for a sample of natural terrestrial origin is +135 ‰ from dissolved sulfate in pore fluids in deep ocean sediments undergoing bacterial reduction at elevated temperature off the coast of Washington state (USA) [86]. For this value, $A_r(S) = 32.075$ and the mole fraction of ^{34}S is 0.0473.

Very negative $\delta(^{34}S)$ values were found for biogenic H_2S and metal sulfides in environments where the fraction of sulfate reduction was small, e.g., –50 ‰ for biogenic HS⁻ in spring waters and boreholes [85], pyrite in some Deep Sea Drilling Project sediment cores [87], pyrite concretions in sedimentary rocks [86], and hydrotroilite in river sediments [88]. The most negative $\delta(^{34}S)$ value reported for a material of natural terrestrial origin is –55 ‰ for HS⁻ under ice cover in a sewage treatment lagoon [25]. For this sample, $A_r(S) = 32.059$ and the mole fraction of ^{34}S is 0.0398.

In a database of over 13 000 natural samples, the bulk of the oxidized forms were found to have $\delta(^{34}S)$ values between +5 and +25 ‰, whereas the corresponding range for reduced forms was –5 to +15 ‰ [89]. Although the total variation in terrestrial $\delta(^{34}S)$ values extends from –55 to +135 ‰, most commercial S comes ultimately from two reservoirs, lower crustal sulfide (mean ~+2 ‰) and oceanic sulfate (variable over geological time from +10 to +25 ‰). Some 40 laboratory reagents were found to have $\delta(^{34}S)$ values ranging from –4 to +26 ‰, with a peak in the distribution near 0 ‰ [25]. Unfortunately, a working list with manufacturer and catalog number could prove misleading because $BaSO_4$ from the same manufacturer and catalog number was found to have $\delta(^{34}S)$ values of –2.7 ‰ and +11.5 ‰ when purchased in 1973 and 1985, respectively.

Chlorine	$_{17}$Cl	$A_r(Cl) = 35.453(2)$
Isotope	Atomic mass	Mole fraction in SMOC [2,90,91]
^{35}Cl	34.968 852 71(4) u	0.757 79(46)
^{37}Cl	36.965 902 60(5) u	0.242 21(46)

Most relative abundance measurements of Cl isotopes (Fig. 10) have been expressed relative to sea water chloride (SMOC or standard mean ocean chloride), which is thought to be isotopically homogeneous to within approximately ±0.15 ‰ by some investigators [92]. One isotopic reference material, NIST SRM 975 NaCl, is the basis of the absolute isotope-ratio determination of Cl [90]. Using a $\delta(^{37}Cl)$ value of +0.43 ‰ for SRM 975 relative to sea water chloride [91], the absolute isotope abundances of sea water chloride can be calculated, as listed above. Because the supply of SRM 975 is exhausted, it has been replaced by SRM 975a, which is depleted in ^{37}Cl by 0.23 ‰ relative to SRM 975 [25]. Xiao et al. [93], report $\delta(^{37}Cl)$ values as high as +0.94 ‰ for sea water from the Central Indian Ridge. Their results indicate that SMOC should be defined in terms of an internationally distributed homogeneous chlorine isotopic reference material and not random samples of sea water. Xiao et al. [91] purified NaCl from sea water for distribution as a new chlorine isotopic reference material, named ISL 354. IAEA will distribute this reference material, and it can serve as the anchor of the SMOC scale. Its $\delta(^{37}Cl)$ value is +0.05 ± 0.02 ‰ relative to sea water chloride [91].

Discussions of Cl isotopic variations and isotope-fractionation mechanisms have been published [94,95]. Cl isotopes are fractionated at low temperatures by molecular diffusion and ion filtration in ground water systems and by chloride mineral precipitation. Isotope fractionation in hydrothermal fluids may be caused by high-temperature equilibrium isotope exchange. Isotope fractionation during biochemical reaction has been observed during degradation of anthropogenic organic compounds.
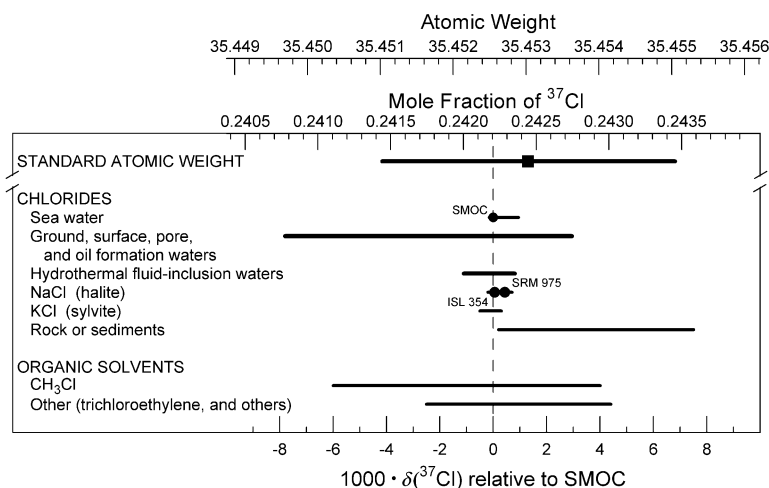
Fig. 10 Chlorine isotopic composition and atomic weight of selected chlorine-bearing materials [25]. The $\delta(^{37}Cl)$ scale and the ^{37}Cl mole-fraction scale were matched using the data of Shields et al. [90] and Long et al. [91]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{37}Cl mole-fraction scale relative to the $\delta(^{37}Cl)$ scale is equivalent to ±2.5 ‰.

The range of $\delta(^{37}Cl)$ of naturally occurring samples is about 16 ‰ (Fig. 10). The data of Vengosh et al. [96] are not used because these data have not been reproduced and the samples were analyzed without standard chemical preparation techniques. Chlorinated solvents have a range of $\delta(^{37}Cl)$ values between −6 ‰ for methyl chloride [97] and +4.4 ‰ for trichloroethylene [98]. Chlorinated solvents are increasingly being found in ground waters, and it should not be surprising if these extreme values are exceeded in the future. The lowest $\delta(^{37}Cl)$ value (−7.7 ‰) for a naturally occurring terrestrial material was reported for pore water from the Nankai subduction zone [99]. This low value is attributed to formation of clays that preferentially incorporate ^{37}Cl into their structure, enriching pore waters in ^{35}Cl. The corresponding $A_r(Cl)$ is 35.4497, and mole fraction of ^{37}Cl is 0.240 77. The most positive reported $\delta(^{37}Cl)$ value for a sample of natural terrestrial origin is +7.5 ‰, for Cl in smectite from a Costa Rica Rift ocean drill hole [100]; enrichment in ^{37}Cl was attributed to stronger bonding of Cl in solid phases relative to the aqueous solution. The corresponding $A_r(Cl)$ is 35.4553, and the mole fraction of ^{37}Cl is 0.243 56.

Calcium $_{20}$Ca $A_r(Ca) = 40.078(4)$

Isotope	Atomic mass	Mole fraction in NIST SRM 915a $CaCO_3$ [2,25,101]
^{40}Ca	39.962 5912(3) u	0.969 41(6)
^{42}Ca	41.958 6183(4) u	0.006 47(3)
^{43}Ca	42.958 7668(5) u	0.001 35(2)
^{44}Ca	43.955 4811(9) u	0.020 86(4)
^{46}Ca	45.953 6927(25) u	0.000 04(1)
^{48}Ca	47.952 533(4) u	0.001 87(1)

Ca isotope ratios have been based on $n(^{44}Ca)/n(^{40}Ca)$ measurements and are expressed relative to NIST SRM 915a $CaCO_3$ herein [25], which is assigned a $\delta(^{44}Ca)$ value of 0 ‰ exactly. Laboratories have expressed $\delta(^{44}Ca)$ values relative to various materials, including sea water [102], a laboratory $CaCO_3$ [103], and NIST SRM 915a $CaCO_3$ [104]. ^{40}Ca may be a poor choice for the denominator in this isotope ratio because it is a product of ^{40}K radioactive decay; thus, the mole fraction of ^{40}Ca will vary with the age and K/Ca ratio of a material.
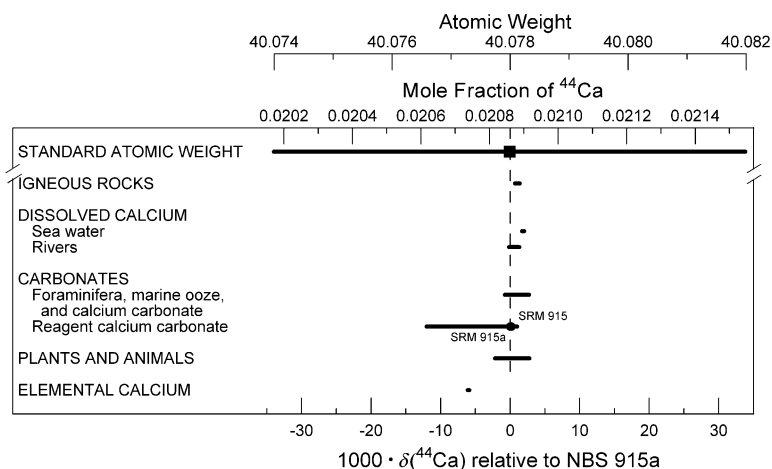
Fig. 11 Calcium isotopic composition and atomic weight of selected calcium-bearing materials [25]. The $\delta(^{44}Ca)$ scale and the ^{44}Ca mole-fraction scale were matched using the data of Moore et al. [101] and the determination by DePaolo that NBS 915a is depleted in ^{44}Ca relative to NBS 915 by 0.17 ‰ [25]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{44}Ca mole-fraction scale relative to the $\delta(^{44}Ca)$ scale is equivalent to ±2 ‰.

Ca isotope ratios span a range of about 5 ‰ (Fig. 11) as a result of isotope fractionation in natural materials of terrestrial origin. Biologically induced Ca isotope fractionation in the fixation of Ca affects the distribution of Ca isotopes in the terrestrial Ca cycle. As dissolved Ca in sea water is incorporated into foraminifera, ^{40}Ca preferentially is fixed, increasing the $\delta(^{44}Ca)$ of sea water. Thus, the $\delta(^{44}Ca)$ of most biological samples is lower than that of sea water. In a survey of numerous materials, Skulan and DePaolo [105] found that Ca from bone and shell is depleted in ^{44}Ca relative to Ca of soft tissue from the same organism and relative to source (dietary) Ca. The lowest $\delta(^{44}Ca)$ value (–2.17 ‰) in a sample of natural terrestrial origin was found in a cougar bone [105]. For this sample, $A_r(Ca) = 40.0778$ and the mole fraction of ^{44}Ca is 0.020 82. The highest ^{44}Ca content [$\delta(^{44}Ca) = +2.76$ ‰] in a sample of natural terrestrial origin was found in egg white [105]. For this sample, $A_r(Ca) = 40.0784$, and the mole fraction of ^{44}Ca is 0.020 92.

Ca reagents can be found that are highly depleted in ^{44}Ca because elemental Ca can be prepared by an evaporation–distillation process [106]. Russell et al. [106] found a range in $\delta(^{44}Ca)$ between –12 ‰ and +1.5 ‰ for Ca metal, $CaCO_3$, and CaF_2.

Chromium $\quad_{24}$Cr $\qquad A_r(Cr) = 51.9961(6)$

Isotope	Atomic mass	Mole fraction in NIST SRM 979 $Cr(NO_3)_3$ [2,107]
^{50}Cr	49.946 0495(14) u	0.043 452(85)
^{52}Cr	51.940 5115(15) u	0.837 895(117)
^{53}Cr	52.940 6534(15) u	0.095 006(110)
^{54}Cr	53.938 8846(15) u	0.023 647(48)

Relative Cr isotope ratios are based on $n(^{53}Cr)/n(^{52}Cr)$ measurements and are expressed relative to NIST SRM 979 $Cr(NO_3)_3$ herein, which is assigned a $\delta(^{53}Cr)$ value of 0 ‰ exactly. Cr isotope ratios span a range of about 6 ‰ (Fig. 12). Previous work by Ball (1996) is not included in this report because there may have been analytical problems during isotopic measurements [25].
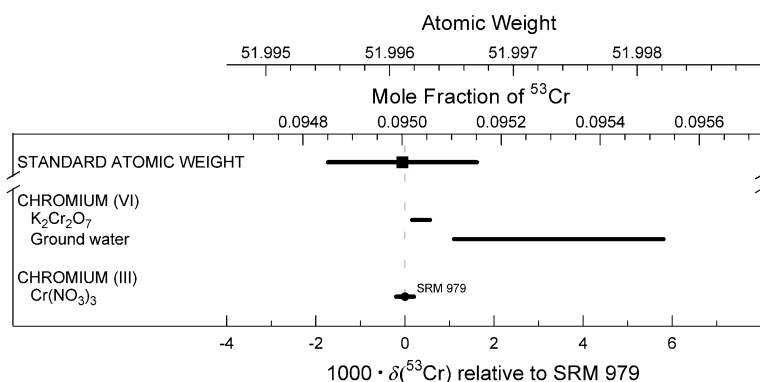
Fig. 12 Chromium isotopic composition and atomic weight of selected chromium-bearing materials [25]. The $\delta(^{53}Cr)$ scale and the ^{53}Cr mole-fraction scale were matched using data of Shields et al. [107] and Rosman and Taylor [2]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{53}Cr mole-fraction scale relative to the $\delta(^{53}Cr)$ scale is equivalent to ±1.2 ‰.

Cr isotope ratios of reagent $K_2Cr_2O_7$, Cr (VI) plating solution, and Cr (VI) in ground water have been reported [108]. The $\delta(^{53}Cr)$ of reagent $K_2Cr_2O_7$ and plating solution is near 0 ‰. However, Cr (VI) contaminated ground water shows a large variation in Cr isotopic composition (+1.1 to +5.8 ‰) [108]. This large variation is attributed to preferential abiotic reaction during reduction of ^{52}Cr by about 3.5 ‰, based on experimental studies [108]. The $\delta(^{53}Cr)$ value of +5.8 ‰ is the most positive for a material of natural terrestrial origin; for this material, $A_r(Cr) = 51.9982$ and the mole fraction of ^{53}Cr is 0.095 53. For the lowest ^{53}Cr content sample of natural terrestrial origin [$\delta(^{53}Cr) = 0$ ‰], $A_r(Cr) = 51.9961$ and the mole fraction of ^{53}Cr is 0.095 01.

Iron (Ferrum)	$_{26}$**Fe**	$A_r(Fe) = 55.845(2)$
Isotope	Atomic mass	Mole fraction in IRMM–014 elemental Fe [2,109]
^{54}Fe	53.939 6147(14) u	0.058 45(23)
^{56}Fe	55.934 9418(15) u	0.917 54(24)
^{57}Fe	56.935 3983(15) u	0.021 191(65)
^{58}Fe	57.933 2801(15) u	0.002 819(27)

Relative Fe isotope ratios are based on $n(^{56}Fe)/n(^{54}Fe)$ measurements and can be expressed relative to IRMM–014 elemental Fe, which is assigned a $\delta(^{56}Fe)$ value of 0 ‰ exactly. Fe can act as an electron acceptor under anaerobic conditions and as an electron donor under both anaerobic and aerobic conditions. Thus, there is the potential for kinetic fractionation of Fe isotopes during metabolic reactions. The $n(^{57}Fe)/n(^{56}Fe)$ abundance ratio of ground water from a toxic waste site in South Carolina (USA) (JP–4 jet fuel spill) in a microbially mediated anaerobic zone was about 0.5 % greater than $n(^{57}Fe)/n(^{56}Fe)$ of 0.5 N HCl leachates of aquifer sediment and was substantially greater than $n(^{57}Fe)/n(^{56}Fe)$ of ground water from the up-gradient aerobic zone [110]. A recent summary of the variation in isotope abundances of Fe in natural materials and discussion of Fe isotope fractionation is given in Anbar [111]. The variation in $\delta(^{56}Fe)$ is greater than 3 ‰ (Fig. 13). Large variations were reported by Dixon et al. [112], but they are not used herein because they contain internal inconsistencies among the isotope ratios according to Beard and Johnson [113].

The $\delta(^{56}Fe)$ of Fe in blood from 10 human males ranged from –2.9 to –2.5 ‰ [114]. The sample with a value of –2.9 ‰ has the lowest $\delta(^{56}Fe)$ value in a naturally occurring terrestrial material. For this
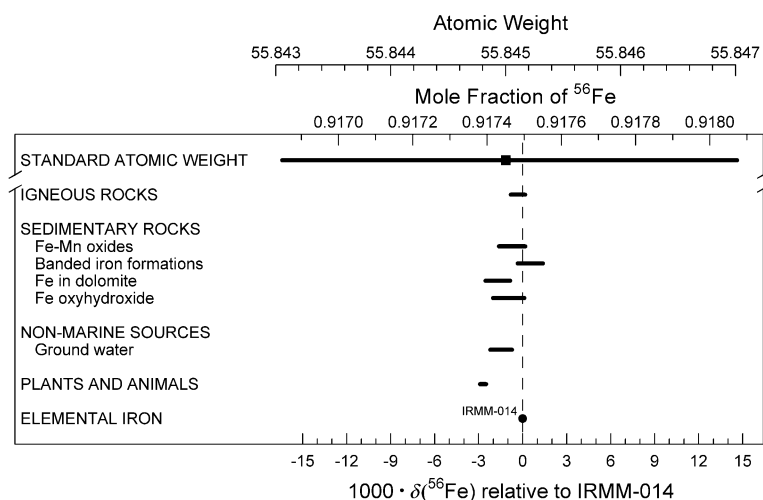
Fig. 13 Iron isotopic composition and atomic weight of selected iron-bearing materials [25]. The $\delta(^{56}\text{Fe})$ scale and the ^{56}Fe mole-fraction scale were matched using data of Taylor et al. [109] and Rosman and Taylor [2]; therefore, the uncertainty in placement of the atomic-weight scale and the ^{56}Fe mole-fraction scale relative to the $\delta(^{56}\text{Fe})$ scale is equivalent to ±4.3 ‰.

sample, $A_r(\text{Fe}) = 55.844\ 77$ and the mole fraction of ^{56}Fe is 0.917 42. The highest reported $\delta(^{56}\text{Fe})$ value in a naturally occurring terrestrial sample is +1.36 ‰, found in a Proterozoic banded iron formation [115]. For this sample, $A_r(\text{Fe}) = 55.845\ 32$ and the mole fraction of ^{56}Fe is 0.917 60.

Copper (Cuprum) $_{29}$Cu $A_r(\text{Cu}) = 63.546(3)$

Isotope	Atomic mass	Mole fraction in NIST SRM 976 elemental Cu [2,116]
^{63}Cu	62.929 6007(15) u	0.691 74(20)
^{65}Cu	64.927 7938(19) u	0.308 26(20)

The basis for relative abundance measurements of Cu isotopes is the NIST SRM 976 elemental Cu, with a $\delta(^{65}\text{Cu})$ value of 0 ‰. Cu isotope ratios in natural materials span more than 14 ‰ (Fig. 14). Isotope-fractionation mechanisms and isotopic variations are discussed by Shields et al. [117]. Development of multiple collector plasma source mass spectrometry [118] has made isotopic analysis of Cu much easier and improved analytical precision substantially [119,120].

Specimens of atacamite [CuCl$_2$·3Cu(OH)$_2$] from Atacama, Chile, have been analyzed by both Shields et al. [117] and Gale et al. [121]. Shields et al. determined a $\delta(^{65}\text{Cu})$ value of –1.65 ‰, whereas Gale et al. measured –7.65 ‰ for their specimen. Therefore, these samples and values need to be scrutinized in light of developing technology. The $\delta(^{65}\text{Cu})$ value of –7.65 ‰ is the lowest for a material of natural terrestrial origin. For this sample, $A_r(\text{Cu}) = 63.542$ and the mole fraction of ^{65}Cu is 0.3066. The highest reported $\delta(^{65}\text{Cu})$ value in a naturally occurring terrestrial sample is +9.0 ‰, found in a sample of aurichalcite (Zn, Cu carbonate) from Globe, Arizona (USA) [117]. For this sample, $A_r(\text{Cu}) = 63.549$ and the mole fraction of ^{65}Cu is 0.3102.
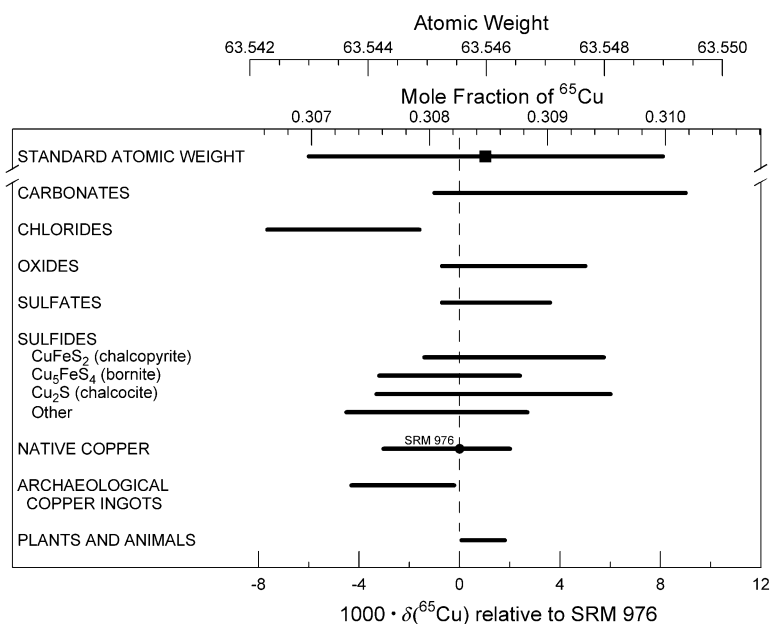
Fig. 14 Copper isotopic composition and atomic weight of selected copper-bearing materials [25]. The $\delta(^{65}Cu)$ scale and the ^{65}Cu mole-fraction scale were matched using data of Shields et al. [116] and Rosman and Taylor [2]; therefore, uncertainty in placement of the atomic-weight scale and the ^{65}Cu mole-fraction scale relative to the $\delta(^{65}Cu)$ scale is equivalent to ±0.9 ‰.

Zinc $_{30}$Zn $A_r(Zn) = 65.409(4)$

Isotope	Atomic mass	Mole fraction in a naturally occurring sample [2,122]
^{64}Zn	63.929 1461(18) u	0.4863(20)
^{66}Zn	65.926 0364(17) u	0.2790(9)
^{67}Zn	66.927 1305(17) u	0.0410(4)
^{68}Zn	67.924 8473(17) u	0.1875(17)
^{70}Zn	69.925 325(4) u	0.0062(1)

Rosman [122] has determined the absolute isotope abundances of Zn. The advent of multiple collector plasma source mass spectrometry [118] has improved the analytical precision of the isotopic analysis of Zn [119]. Maréchal et al. [119] reported $n(^{66}Zn)/n(^{64}Zn)$ ratios for Zn-bearing materials and expressed their results as $\delta(^{66}Zn)$ values relative to JMC (Johnson Matthey) 3–0749 L solution because there are no internationally distributed isotopic reference materials for Zn. The full range in naturally occurring materials is about 1 ‰ [119]. The material with the lowest ^{66}Zn content is ZnS from the Lau Basin, Pacific Ocean, with a $\delta(^{66}Zn)$ value of –0.19 ‰ [119]. The material with the highest reported ^{66}Zn content is a mussel with a $\delta(^{66}Zn)$ value of +0.82 ‰ [119].

Selenium $_{34}$**Se** A_r(**Se**) = 78.96(3)

Isotope	Atomic mass	Mole fraction in a naturally occurring sample [2,123]
^{74}Se	73.922 4767(16) u	0.008 89(3)
^{76}Se	75.919 2143(16) u	0.093 66(18)
^{77}Se	76.919 9148(16) u	0.076 35(10)
^{78}Se	77.917 3097(16) u	0.237 72(20)
^{80}Se	79.916 5221(20) u	0.496 07(17)
^{82}Se	81.916 7003(22) u	0.087 31(10)

Few measurements are available of variations in the isotopic composition of terrestrial Se. Furthermore, absolute abundance determinations have not been made for any specimen used in relative abundance investigations. The published maximum range of δ(^{82}Se) values (based on n(^{82}Se)/n(^{76}Se) measurements) in naturally occurring terrestrial materials is 16 ‰ [124]. Se is analogous to S in that bacterial redox reactions have been identified in nature and substantial kinetic isotope effects have been realized during laboratory SeO$_4$$^{2-}$ and SeO$_3$$^{2-}$ reductions [124–129]. If a k_{76}/k_{82} value of 1.018 (average for laboratory studies) existed during reduction of SeO$_3$$^{2-}$ containing Se with A_r(Se) = 78.963, the initial Se^0 product would have an A_r(Se) = 78.948.

Molybdenum $_{42}$**Mo** A_r(**Mo**) = 95.94(2)

Isotope	Atomic mass	Mole fraction in a naturally occurring sample [2,130]
^{92}Mo	91.906 810(4) u	0.148 362(148)
^{94}Mo	93.905 0867(20) u	0.092 466(92)
^{95}Mo	94.905 8406(20) u	0.159 201(159)
^{96}Mo	95.904 6780(20) u	0.166 756(167)
^{97}Mo	96.906 0201(20) u	0.095 551(96)
^{98}Mo	97.905 4069(20) u	0.241 329(241)
^{100}Mo	99.907 476(6) u	0.096 335(96)

Moore and others [130] have determined the absolute isotope abundances of Mo; however, absolute isotope-abundance determinations have not been made for any specimen used in relative isotope-abundance investigations. Multiple collector plasma source mass spectrometry [118] has improved the analytical precision of the isotopic analysis of Mo and demonstrated natural isotopic variation. The material with the highest n(^{98}Mo)/n(^{95}Mo) ratio is ocean water, which is homogeneous in isotopic composition within ±0.1 ‰, and Siebert et al. [131] have recommended that the Mo isotope scale be anchored by assigning a δ(^{98}Mo) value of 0 ‰ to ocean water because no internationally distributed isotopic reference material is available for Mo. The material with the lowest n(^{98}Mo)/n(^{95}Mo) ratio is the crust of a ferromanganese deep-sea nodule with a δ(^{98}Mo) value of –3.1 ‰ relative to Mo in ocean water [131]. The reported isotopic variation is within the atomic-weight uncertainty.

Palladium $_{46}$**Pd** $A_r(Pd) = 106.42(1)$

Isotope	Atomic mass	Mole fraction in a sample from Sudbury, Ontario [2,132]
[102]Pd	101.905 607(3) u	0.0102(1)
[104]Pd	103.904 034(5) u	0.1114(8)
[105]Pd	104.905 083(5) u	0.2233(8)
[106]Pd	105.903 484(5) u	0.2733(3)
[108]Pd	107.903 895(4) u	0.2646(9)
[110]Pd	109.905 153(12) u	0.1172(9)

Shima et al. [132] analyzed samples from Sudbury, Ontario, Canada (containing a mass fraction of 0.25 mg/kg Pd) and from the western Bushveld Igneous Complex in South Africa at Lonrho (containing a mass fraction of 7.7 mg/kg Pd). Although Shima et al. found no variation in isotopic composition in these terrestrial samples, Mermelengas et al. [133] reported evidence of isotope fractionation in a precious metal concentrate from the Atok mine in South Africa. A concentrate from a second mine, also from the Bushveld Complex, was not isotopically fractionated. Rosman et al. [134] reanalyzed these samples together with another four mineral concentrates and one highly refined sample of palladium metal (Table 1).

Table 1 Isotope fractionation of naturally occurring palladium-bearing samples.

Location	Mass fraction Pd in percent	Isotope fractionation, in ‰/mass unit (relative to reagent Pd[a])	
		Mermelengas et al. [133]	Rosman et al. [134]
Atok mine	13.3	+3.8 ± 0.3[b]	+3.6 ± 0.2[b]
Merensky reef	3–4	−0.2 ± 0.3[b]	+0.1 ± 0.2
Union section	0.6		+0.1 ± 0.2
Amandelbult section	2.4		+0.2 ± 0.2
Rustenburg section, code R	3		+0.2 ± 0.3
Rustenburg section, code C	20		+0.1 ± 0.1
Code 84/85, unknown section[c]	99.99		+0.1 ± 0.2

[a]Same reagent used in both studies.
[b]Average of two measurements.
[c]Probably South Africa.

Rosman et al. [134] confirmed that palladium samples with higher atomic weights are present in the Atok mine, which is located in the eastern part of the Bushveld complex. No enrichment was found in other samples, which all come from the western part of the Bushveld Complex. Rosman et al. concluded that isotope fractionation in the Atok mine sample was produced by natural geochemical processes rather than by industrial processing or purification.

Tellurium $_{52}$**Te** $A_r(\text{Te}) = 127.60(3)$

Isotope	Atomic mass	Mole fraction in a naturally occurring sample [2,135]
^{120}Te	119.904 026(11) u	0.000 96(1)
^{122}Te	121.903 0558(29) u	0.026 03(1)
^{123}Te	122.904 2711(20) u	0.009 08(1)
^{124}Te	123.902 8188(16) u	0.048 16(2)
^{125}Te	124.904 4241(20) u	0.071 39(2)
^{126}Te	125.903 3049(20) u	0.189 52(4)
^{128}Te	127.904 4615(19) u	0.316 87(4)
^{130}Te	129.906 2229(21) u	0.337 99(3)

Few determinations of Te isotopic composition in materials of natural terrestrial origin have been performed [135,136]. Furthermore, absolute isotope-ratio measurements have not been conducted on a specimen used in relative isotope-ratio investigations. The reported maximum range of $\delta(^{130}\text{Te})$ values, which are based on $n(^{130}\text{Te})/n(^{122}\text{Te})$ measurements, is 4 ‰, the ranges being similar for natural telluride minerals, native Te, and commercial K_2TeO_3 [136]. A kinetic isotope effect k_{122}/k_{130}, as high as 1.008, has been obtained during TeO_3^{2-} reduction. If tellurite (TeO_3^{2-}) with $A_r(\text{Te}) = 127.603$ were reduced with this k_{122}/k_{130} value, the initial Te^0 product would have $A_r(\text{Te}) = 127.58$. By analogy with S and Se, the natural variation in Te isotope abundances, because of mass fractionation, probably is higher than reported here.

In contrast to mass fractionation effects, highly anomalous Te isotope abundances have been found near the Oklo natural fission reactor in Gabon [137,138]. Thus, $A_r(\text{Te})$ is highly variable and this variability is dependent upon many factors, such as the amount of fissiogenic Te present, neutron capture reactions involving Te nuclei, and the migration (retention) of precursor nuclei. For example, the range reported for the ratio n(fission product ^{125,128,130}Te)/n(primordial Te) for Zone 9 at Oklo was 81 to 190 [138]. The maximum corresponds to a mole fraction of ^{130}Te of about 0.8 as compared to 0.34 found for the "normal" abundance. Fission product Te isotopes increase $A_r(\text{Te})$, so that $A_r(\text{Te})$ is greater than 129.

Thallium $_{81}$**Tl** $A_r(\text{Tl}) = 204.3833(2)$

Isotope	Atomic mass	Mole fraction in NIST SRM 997 elemental Tl [2,139]
^{203}Tl	202.972 329(3) u	0.295 24(9)
^{205}Tl	204.974 412(3) u	0.704 76(9)

The basis for relative isotope-ratio measurements of Tl is the NIST isotopic reference material SRM 997 elemental Tl metal, with an assigned $\delta(^{205}\text{Tl})$ value of 0 ‰. Development of multiple collector inductively coupled plasma mass spectrometry has improved Tl isotope-ratio measurements substantially; isotope ratios can be determined with a 1-σ standard deviation of better than ±0.05 ‰ [140]. The range in $\delta(^{205}\text{Tl})$ of natural terrestrial materials is 1.6 ‰ (Fig. 15). The $\delta(^{205}\text{Tl})$ of igneous rocks ranges from –0.18 ‰ to +0.35 ‰, based on analysis of seven terrestrial samples [140]. The lowest ^{205}Tl content in the literature of a material of natural terrestrial origin [$\delta(^{205}\text{Tl})$ = –0.18 ‰] is found in a volcanic rhyolite in the East Rift Zone of Iceland [140]. For this sample, the mole fraction of ^{205}Tl is 0.704 72 and $A_r(\text{Tl}) = 204.383\ 24$. The $\delta(^{205}\text{Tl})$ values of crusts of ferromanganese deep-sea nodules range from +0.33 to +1.43 ‰ [140,141]. High $\delta(^{205}\text{Tl})$ values (+1.31 to +1.43 ‰) were found in ferromanganese crusts of samples collected from the Southern Atlantic Ocean, the Indian Ocean, and the central Pacific Ocean [141]. The value of +1.43 ‰ is the highest $\delta(^{205}\text{Tl})$ value in the literature of a material of natural terrestrial origin. For this sample, the mole fraction of ^{205}Tl is 0.705 06 and $A_r(\text{Tl}) = 204.383\ 91$.
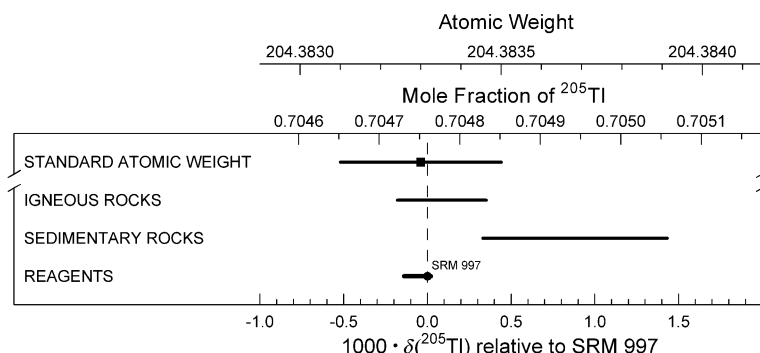
Fig. 15 Thallium isotopic composition and atomic weight of selected thallium-bearing materials [25]. The $\delta(^{205}Tl)$ scale and the ^{205}Tl mole-fraction scale were matched using the data of Dunstan et al. [139] and Rosman and Taylor [2]; therefore, uncertainty in placement of the atomic-weight scale and the ^{205}Tl mole-fraction scale relative to the $\delta(^{205}Tl)$ scale is equivalent to ±0.4 ‰.

The range in atomic weight of Tl in materials of natural terrestrial origin (204.383 24 to 204.383 91) extends outside the limits of the standard atomic weight (204.3833 ± 0.0002). In future meetings, CAWIA may consider expanding the atomic-weight uncertainty of Tl or consider adding a footnote *g* to Tl in the Table of Standard Atomic Weights to indicate that "geological specimens are known in which the element has an isotopic composition outside the limits for normal material."

SUMMARY AND CONCLUSIONS

The standard atomic weights and their uncertainties tabulated by the IUPAC Commission on Atomic Weights and Isotopic Abundances are intended to apply to most normal terrestrial materials and laboratory reagents. The minimum and maximum concentrations of a selected isotope in naturally occurring terrestrial materials for selected chemical elements reviewed in this report are given below:

Isotope	Minimum mole fraction	Maximum mole fraction
^{2}H	0.000 0255	0.000 1838
^{7}Li	0.9227	0.9278
^{11}B	0.7961	0.8107
^{13}C	0.009 629	0.011 466
^{15}N	0.003 462	0.004 210
^{18}O	0.001 875	0.002 218
^{26}Mg	0.1099	0.1103
^{30}Si	0.030 816	0.031 023
^{34}S	0.0398	0.0473
^{37}Cl	0.240 77	0.243 56
^{44}Ca	0.020 82	0.020 92
^{53}Cr	0.095 01	0.095 53
^{56}Fe	0.917 42	0.917 60
^{65}Cu	0.3066	0.3102
^{205}Tl	0.704 72	0.705 06

The numerical values above have uncertainties that depend upon the uncertainties of the absolute isotope abundance measurements of reference materials of the elements. Because there are no internationally distributed isotopic reference materials for the elements zinc, selenium, molybdenum, palla-

dium, and tellurium, ranges in isotopic composition are not listed for these elements even though ranges may be measurable with state-of-the-art mass spectrometry. Two chemical elements, chromium and thallium, have isotope-abundance variations in materials of natural terrestrial origin that may exceed atomic-weight uncertainties.

Preparation of isotopic reference materials for the elements zinc, selenium, molybdenum, palladium, and tellurium would improve comparability of isotope-ratio measurements among laboratories. In addition, IUPAC may consider preparation of guidelines for reporting relative isotope-abundance ratios of iron and calcium with respect to existing reference materials, such as IRMM-014 elemental iron and SRM 915a calcium carbonate.

ACKNOWLEDGMENTS

REFERENCES

1. T. B. Coplen. *Pure Appl. Chem.* **73**, 667–683 (2001).
2. K. J. R. Rosman and P. D. P. Taylor. *Pure Appl. Chem.* **70**, 217–235 (1998).
3. H. S. Peiser, N. E. Holden, P. De Bièvre, I. L. Barnes, R. Hagemann, J. R. de Laeter, T. J. Murphy, E. Roth, M. Shima, H. G. Thode. *Pure Appl. Chem.* **56**, 695–768 (1984).
4. J. R. de Laeter, J. K. Böhlke, P. De Bièvre, H. Hidaka, H. S. Peiser, K. J. R. Rosman, P. D. P. Taylor. "The Atomic Weights of the Elements, Review 2000", *Pure Appl. Chem.* (2003). In press.
5. G. Audi and A. H. Wapstra. *Nucl. Phys.* **A565**, 1–65 (1993).
6. International Organization for Standardization. *ISO–31–0, Quantities and Units, Part 0, General Principles, Subclause 2.3.3*, Geneva, International Organization for Standardization (1992).
7. T.-L. Chang, M.-T. Zhao, W. Li, J. Wang, Q.-Y. Qian. *Int. J. Mass Spectrom.* **208**, 113–118 (2001).
8. M. E. Wieser and J. R. de Laeter. *Int. J. Mass Spectrom.* **197**, 253–261 (2000).
9. M. A. McKibben and C. S. Eldridge. "S isotopic effects in sulfur transformation: SHRIMP microanalysis of $\delta^{34}S$ zoning in pyrite from sedimentary and hydrothermal settings", Paper 101 of ACS Division of Geochemistry, 208th ACS National Meeting, 21–25 August 1994, Washington, DC (1994).
10. R. Hagemann, G. Nief, E. Roth. *Tellus* **22**, 712–715 (1970).
11. T. B. Coplen. *Pure Appl. Chem.* **66**, 273–276 (1994).
12. R. Gonfiantini, W. Stichler, K. Rozanski. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, pp. 13–29, International Atomic Energy Agency, Vienna, IAEA-TEC-DOC-825 (1995).
13. R. M. Parr and S. A. Clements. *Intercomparison of Enriched Stable Isotope Reference Materials for Medical and Biological Studies*, Vienna, International Atomic Energy Agency, NAHRES-5 (1991).
14. I. Friedman and J. R. O'Neil. *Handbook of Geochemistry II–1,* K. H. Wedepohl (Ed.), pp. 1B1–1B8, Springer-Verlag, Berlin (1978).

15. J. Hoefs. *Stable Isotope Geochemistry* 3rd ed., Springer-Verlag, New York (1987).

16. I. Friedman and J. R. O'Neil. U.S. Geological Survey Professional Paper 440–KK, *Data of Geochemistry*, 6th ed., Chapter KK (1977).

17. R. E. Criss. *Principles of Stable Isotope Distribution*, Oxford University Press, Oxford (1999).

18. J. W. Valley and D. R. Cole (Eds.). *Stable Isotope Geochemistry*, Mineralogical Society of America, *Rev. Mineral. Geochem.* **43**, 662 (2001).

19. J. Jouzel, C. Lorius, J. R. Petit, C. Genthon, N. I. Barkov, V. M. Kotlyakov, V. M. Petrov. *Nature* **329**, 403–408 (1987).

20. J. Ch. Fontes and R. Gonfiantini. *Earth Planet. Sci. Lett.* **3**, 258–266 (1967).

21. E. Roth. *Compt. Rend. Acad. Sci., Paris* **242**, 3097–3100 (1956).

22. G. J. Martin, C. Guillou, M. L. Martin, M.-T. Cabanis, J. Aerny. *J. Agric. Food Chem.* **36**, 316–322 (1988).

23. R. M. Coveney, Jr., E. D. Goebel, E. J. Zeller, G. A. M. Dreschhoff, E. E. Angino. *Bull. Am. Assoc. Pet. Geol.* **71**, 39–48 (1987).

24. B. Gonsior, I. Friedman, G. Lindenmayr. *Tellus* **18**, 256–261 (1966).

25. T. B. Coplen, J. A. Hopple, J. K. Böhlke, H. S. Peiser, S. E. Rieder, H. R. Krouse, K. J. R. Rosman, T. Ding, R. D. Vocke, Jr., K. M. Révész, A. Lamberty, P. Taylor, P. De Bièvre. "Compilation of minimum and maximum isotope ratios of selected elements in naturally occurring terrestrial materials and reagents", U.S. Geological Survey Water-Resources Investigations Report 01-4222 (2002).

26. H. P. Qi, P. D. P. Taylor, M. Berglund, P. De Bièvre. *Int. J. Mass Spectrom. Ion Proc.* **171**, 263–268 (1997).

27. T. B. Coplen. *Pure Appl. Chem.* **68**, 2339–2359 (1996).

28. J. M. Edmond, C. Measures, R. E. McDuff, L. H. Chan, R. Collier, B. Grant, L. I. Gordon, J. B. Corliss. *Earth Planet. Sci. Lett.* **46**, 1–18 (1979).

29. L.-H. Chan, J. M. Edmond, G. Thompson, K. Gillis. *Earth Planet. Sci. Lett.* **108**, 151–160 (1992).

30. H. P. Qi, T. B. Coplen, Q. Zh. Wang, Y. H. Wang. *Anal. Chem.* **69**, 4076–4078 (1997).

31. C.-F. You and L.-H. Chan. *Geochim. Cosmochim. Acta* **60**, 909–915 (1996).

32. E. J. Catanzaro, C. E. Champion, E. L. Garner, G. Marinenko, K. M. Sappenfield, W. R. Shields. *NBS Special Publication 260-17*, U.S. Printing Office, Washington, DC (1970).

33. IRMM, *Certificate, spike isotopic reference material IRMM-610*, Institute for Reference Materials and Measurements, Geel, Belgium (2001).

34. NIST, *Certificate of Analysis, Standard Reference Material 952 Enriched Boric Acid Standard*, National Institute Standards and Technology, Gaithersburg, Maryland (1999).

35. S. Tonarini, M. Pennisi, A. Adorni-Braccesi, A. Dini, G. Ferrara, R. Gonfiantini, M. Gröning, M. Wiedenbeck. "Intercomparison of boron stable isotope measurements", Geostandards Newsletter. In press.

36. R. L. Bassett. *Appl. Geochem.* **5**, 541–554 (1990).

37. U. S. Klötzli. *Chem. Geol.* **101**, 111–122 (1992).

38. A. Vengosh, A. Starinsky, Y. Kolodny, A. R. Chivas, M. Raab. *Geology* **20**, 799–802 (1992).

39. H. P. Schwarcz, E. K. Agyei, C. C. McMullen. *Earth Planet. Sci. Lett.* **6**, 1–5 (1969).

40. G. Wang and Y. K. Xiao. *Rock Miner. Anal.* **19**, 169–172 (2000).

41. A. Vengosh, A. R. Chivas, M. T. McCulloch, A. Starinsky, Y. Kolodny. *Geochim. Cosmochim. Acta* **55**, 2591–2606 (1991).

42. T. L. Chang and W. Li. *Chin. Sci. Bull.* **35**, 290–296 (1990).

43. IUPAC Commission on Atomic Weights and Isotopic Abundances. *Pure Appl. Chem.* **66**, 2423–2444 (1994).

44. G. E. Claypool, C. N. Threlkeld, P. N. Mankiewicz, M. A. Arthur, T. F. Anderson. *Initial Reports of the Deep Sea Drilling Project* **84**, 683–691 (1995).

45. M. Elvert, E. Suess, J. Greinert, M. J. Whiticar. "Archaea mediating anaerobic methane oxidation in deep-sea sediments at cold seeps of the eastern Aleutian subduction zone", *Org. Geochem.* **31**, 1175–1187 (2000).

46. G. Junk and H. J. Svec. *Geochim. Cosmochim. Acta* **14**, 234–243 (1958).

47. A. Mariotti. *Nature* **303**, 685–687 (1983).

48. J. K. Böhlke and T. B. Coplen. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, pp. 51–66, International Atomic Energy Agency, Vienna, TECDOC-825 (1995).

49. R. Létolle. In *Handbook of Environmental Isotope Geochemistry*, *Volume 1, The Terrestrial Environment, A*, P. Fritz and J. Ch. Fontes (Eds.), pp. 407–433, Elsevier, Amsterdam (1980).

50. T. H. E. Heaton. *Chem. Geol.* **59**, 87–102 (1986).

51. H. Hübner. In *Handbook of Environmental Isotope Geochemistry, Vol. 2, The Terrestrial Environment, B*, P. Fritz and J. Ch. Fontes (Eds.), pp. 361–425, Elsevier, Amsterdam (1986).

52. N. J. P. Owens. *Adv. Mar. Biol.* **24**, 389–451 (1987).

53. W. C. White and H. Yagoda. *Science* **111**, 307–308 (1950).

54. F. Wlotzka. In *Handbook of Geochemistry II–1*, K. H. Wedepohl (Ed.), pp. 7B1–7B9, Springer-Verlag, Berlin (1972).

55. H. D. Freyer, K. Kobel, R. J. Delmas, D. Kley, M. R. Legrand. *Tellus* **48B**, 93–105 (1996).

56. E. Wada, R. Shibata, T. Torii. *Nature* **292**, 327–329 (1981).

57. J. K. Böhlke, R. L. Smith, K. M. Revesz, T. Yoshinari. *EOS, Trans. Am. Geophys. Union* **81**, S186 (2000).

58. R. D. Hauck and J. M. Bremner. *Adv. Agron.* **28**, 219–266 (1976).

59. C. Van Kessel and J. P. Roskoski. *Plant Soil* **111**, 17–23 (1988).

60. W. Li, B. Ni, D. Jin, T. L. Chang. *Kexue Tongbao* **33**, 1610–1613 (1988).

61. P. Baertschi. *Earth Planet. Sci. Lett.* **31**, 341–344 (1976).

62. H.-L. Schmidt, R. A. Werner, A. Roßmann. *Phytochem.* **58**, 9–32 (2001).

63. M. Dole, G. A. Lange, D. P. Rudd, D. A. Zaukelies. *Geochim. Cosmochim. Acta* **6**, 65–78 (1954).

64. H. A. J. Meijer and W. J. Li. *Isot. Environ. Health Stud.* **34**, 349–369 (1998).

65. T. K. Kyser. In *Stable Isotopes in High Temperature Geological Processes, Reviews of Mineralogy*, Vol. 16, J. W. Valley, H. P. Taylor, Jr., J. R. O'Neil (Eds.), pp. 141–164, Mineralogical Society of America, Washington, DC (1986).

66. M. H. Thiemens, T. L. Jackson, C. A. M. Brenninkmeijer. *Geophys. Res. Lett.* **22**, 255–257 (1995).

67. M. H. Thiemens. *Science* **293**, 226 (2001).

68. Y. Q. Gao and R. A. Marcus. *Science* **293**, 259–263 (2001).

69. H. Bao, M. H. Thiemens, J. Farquhar, D. A. Campbell, C. C.-H. Lee, K. Heine, D. B. Loope. *Nature* **406**, 176–178 (2000).

70. L. Aldaz and S. Deutsch. *Earth Planet. Sci. Lett.* **3**, 267–274 (1967).

71. T. Yoshinari, M. A. Altabet, S. W. A. Naqvi, L. Codispoti, A. Jayakumar, M. Kuhland, A. Devol. *Mar. Chem.* **56**, 253–264 (1997).

72. E. J. Catanzaro, T. J. Murphy, E. L. Garner, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **70A**, 453–458 (1966).

73. A. C. Daughtry, D. Perry, M. Williams. *Geochim. Cosmochim. Acta* **26**, 857–866 (1962).

74. E. J. Catanzaro and T. J. Murphy. *J. Geophys. Res.* **71**, 1271–1274 (1966).

75. V. T.-C. Chang, A. Galy, R. K. O'Nions. In Eleventh Annual V. M. Goldschmidt Conference, Abstract 3426: LPI Contribution No. 1088, Lunar and Planetary Institute, Houston (CD-ROM) (2001).

76. A. Galy, M. Bar-Matthews, L. Halicz, R. K. O'Nions. Cambridge Publications, *J. Conf. Abstr.* **5** (2), 422 (2000).

77. P. De Bièvre, S. Valkiers, H. S. Peiser. *J. Res. Natl. Inst. Stand. Technol.* **99**, 201–202 (1994).

78. T. Ding, S. Jiang, D. Wan, Y. Li, J. Li, H. Song, Z. Liu, X. Yao. *Silicon Isotope Geochemistry*, Geological Publishing House, Beijing, China (1996).
79. C. B. Douthitt. *Geochim. Cosmochim. Acta* **46**, 1449–1458 (1982).
80. T. Ding, D. Wan, J. Li, S. Jiang, H. Song, Y. Li, Z. Li. *Kuangchang Dizhi (Mineral Deposits)* **7**, 90–95 (1988).
81. T. Ding, S. Valkiers, H. Kipphardt, P. De Bièvre, P. D. P. Taylor, R. Gonfiantini, H. R. Krouse. *Geochim. Cosmochim. Acta* **65**, 2433–2437 (2001).
82. G. Beaudoin, B. E. Taylor, D. Rumble III, M. Thiemens. *Geochim. Cosmochim. Acta* **58**, 4253–4255 (1994).
83. J. Farquhar, H. Bao, M. Thiemens. *Science* **289**, 756–758 (2000).
84. D. Rumble, A. Bekker, J. Farquhar, H. D. Holland, G. Hu, S. Maruyama, S. Ono, H. Ohmoto, M. Rosing, Y. Ueno, P. Wang, B. A. Wing. *EOS, Transactions of the American Geophysical Union, Spring Meeting Supplement Abstract V41A-02*, **83**, S373 (2002).
85. K. U. Weyer, H. R. Krouse, W. C. Horwood. In *Isotope Hydrology 1978,* Vol. 1, pp. 251–264, International Atomic Energy Agency, Vienna (1979).
86. M. D. Rudnicki, H. Elderfield, B. Spiro. *Geochim. Cosmochim. Acta* **65**, 777–789 (2001).
87. H. R. Krouse, H. M. Brown, R. B. Farquharson. *Can. J. Earth Sci.* **14**, 787–793 (1977).
88. N. V. Veselovsky, A. L. Rabinovitch, V. S. Putintseva. *Gidrokhim. Mater.* **51**, 112–119 (1969).
89. H. Nielsen. In *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*, H. R. Krouse and V. A. Grinenko (Eds.), pp. 65–67, John Wiley, New York (1991).
90. W. R. Shields, T. J. Murphy, E. L. Garner, V. H. Dibeler. *J. Am. Chem. Soc.* **84**, 1519–1522 (1962).
91. Y. Xiao, Y. Zhou, Q. Wang, H. Wei, W. Liu, C. J. Eastoe. *Chem. Geol.* **182**, 655–661 (2002).
92. R. S. Kaufmann, A. Long, D. J. Campbell. *Am. Assoc. Petrol. Geol. Bull.* **72**, 839–844 (1988).
93. Y. K. Xiao, Y. M. Zhou, W. G. Liu, A. S. Hong, Q. Z. Wang, H. Z. Wei, P. V. Shirodkar. "The character of chlorine isotopic compositions in ocean water (in Chinese)", *Geol. Rev.* **48** (suppl.). In press.
94. D. E. Desaulniers, R. S. Kaufmann, J. A. Cherry, H. W. Bentley. *Geochim. Cosmochim. Acta* **50**, 1757–1764 (1986).
95. R. S. Kaufmann, S. K. Frape, R. H. McNutt, C. Eastoe. *Appl. Geochem.* **8**, 403–408 (1993).
96. A. Vengosh, A. R. Chivas, M. T. McCulloch. *Chem. Geol.* **79**, 333–343 (1989).
97. N. Tanaka and D. Rye. *Nature* **23**, 707 (1991).
98. R. Aravena, S. K. Frape, B. J. Moore, E. M. Van Warmerdam, R. J. Drimmie. In *Isotopes in Water Resources Management*, pp. 31–42, International Atomic Energy Agency, Vienna (1996).
99. B. Ransom, A. J. Spivack, M. Kastner. *Geology* **23**, 715–718 (1995).
100. A. J. Magenheim, A. J. Spivack, P. J. Michael, J. M. Gieskes. *Earth Planet. Sci. Lett.* **131**, 427–432 (1995).
101. L. J. Moore and L. A. Machlan. *Anal. Chem.* **44**, 2291–2296 (1972).
102. P. Zhu and D. Macdougall. *Geochim. Cosmochim. Acta* **62**, 1691–1698 (1998).
103. J. Skulan, D. J. DePaolo, T. L. Owens. *Geochim. Cosmochim. Acta* **61**, 2505–2510 (1997).
104. L. Halicz, A. Galy, N. S. Belshaw, R. K. O'Nions. *J. Anal. Atom. Spectrom.* **14**, 1835–1838 (1999).
105. J. Skulan and D. J. DePaolo. *Proc. Natl. Acad. Sci. U.S.A.* **96**, 13709–13713 (1999).
106. W. A. Russell, D. A. Papanastassiou, T. A. Tombrello. *Geochim. Cosmochim. Acta* **42**, 1075–1090 (1978).
107. W. R. Shields, T. J. Murphy, E. J. Catanzaro, E. L. Garner. *J. Res. Nat. Bur. Stand. (U.S.)* **70A**, 193–197 (1966).
108. A. S. Ellis, T. M. Johnson, T. D. Bullen. *Science* **295**, 2060–2062 (2002).
109. P. D. P. Taylor, R. Maeck, P. De Bièvre. *Int. J. Mass Spectrom. Ion Proc.* **121**, 111–125 (1992).
110. T. D. Bullen and P. M. McMahon. *EOS, Trans. Amer. Geophys. Union* **78**, S173 (1997).
111. A. D. Anbar. *EOS, Trans. Am. Geophys. Union* **82**, 173–179 (2001).

112. P. R. Dixon, D. R. Janecky, R. E. Perrin, D. J. Rokop, P. L. Unkefer, W. D. Spall. In *Water-Rock Interaction*, *Vol. 2, Moderate and High Temperature Environments*, Y. K. Kharaka and A. S. Maest (Eds.), pp. 915–918, A. A. Balkema, Rotterdam, Netherlands (1992).

113. B. L. Beard and C. M. Johnson. *Geochim. Cosmochim. Acta* **63**, 1653–1660 (1999).

114. T. Walczyk. *Fresenius' J. Anal. Chem.* **370**, 444–453 (2001).

115. B. L. Beard, C. M. Johnson, L. Cox, H. Sun, K. H. Nealson, C. Aguilar. *Science* **285**, 1889–1892 (1999).

116. W. R. Shields, T. J. Murphy, E. L. Garner. *J. Res. Natl. Bur. Stand. (U.S.)* **68A**, 593–599 (1964).

117. W. R. Shields, S. S. Goldich, E. L. Garner, T. J. Murphy. *J. Geophys. Res.* **70**, 479–491 (1965).

118. J. A. Walder and P. A. Freedman. *J. Anal. Atom. Spectrom.* **7**, 571–575 (1992).

119. C. N. Maréchal, P. Télouk, F. Albarède. *Chem. Geol.* **156**, 251–273 (1999).

120. X. K. Zhu, R. K. O'Nions, Y. Guo, N. S. Belshaw, D. Rickard. *Chem. Geol.* **163**, 139–149 (2000).

121. N. H. Gale, A. P. Woodhead, Z. A. Stos-Gale, A. Walder, I. Bowen. *Int. J. Mass Spectrom.* **184**, 1–9 (1999).

122. K. J. R. Rosman. *Geochim. Cosmochim. Acta* **36**, 801–819 (1972).

123. M. Wachsmann and K. G. Heumann. *Adv. Mass Spectrom.* **11B**, 1828–1829 (1989).

124. H. R. Krouse and H. G. Thode. *Can. J. Chem.* **40**, 367–375 (1962).

125. C. E. Rees and H. G. Thode. *Can. J. Chem.* **44**, 419–427 (1966).

126. K. Rashid and H. R. Krouse. *Can. J. Chem.* **63**, 3195–3199 (1985).

127. T. M. Johnson, M. J. Herbel, T. D. Bullen, P. T. Zawislanski. *Geochim. Cosmochim. Acta* **63**, 2775–2783 (1999).

128. M. J. Herbel, T. M. Johnson, R. S. Oremland, T. D. Bullen. *Geochem. Cosmochim. Acta* **64**, 3701–3709 (2000).

129. T. M. Johnson, T. D. Bullen, P. T. Zawislanski. *Environ. Sci. Technol.* **34**, 2075–2079 (2000).

130. L. J. Moore, L. A. Machlan, W. R. Shields, E. L. Garner. *Anal. Chem.* **46**, 1082–1089 (1974).

131. C. Siebert, T. F. Nägler, F. von Blankenburg, J. D. Kramers. *EOS, Trans. Am. Geophys. Union* **82**, F1324–F1325 (2001).

132. M. Shima, C. Rees, H. G. Thode. *Can. J. Phys.* **56**, 1333–1339 (1978).

133. N. Mermelengas, K. J. R. Rosman, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Phys.* **37**, 1–11 (1981).

134. K. J. R. Rosman, J. R. de Laeter, N. Kempt. *Int. J. Mass Spectrom. Ion Proc.* **93**, 107–114 (1989).

135. C. L. Smith, K. J. R. Rosman, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Phys.* **28**, 7–17 (1978).

136. M. R. Smithers and H. R. Krouse. *Can. J. Chem.* **46**, 583–591 (1968).

137. R. D. Loss, J. R. de Laeter, K. J. R. Rosman, T. M. Benjamin, D. B. Curtis, A. J. Gancarz, J. E. Delmore, W. J. Maeck. *Earth Planet. Sci. Lett.* **89**, 193–206 (1988).

138. R. D. Loss, K. J. R. Rosman, J. R. de Laeter, D. B. Curtis, T. M. Benjamin, A. J. Gancarz, W. J. Maeck, J. E. Delmore. *Chem. Geol.* **76**, 71–84 (1989).

139. L. P. Dunstan, J. W. Gramlich, I. L. Barnes, W. C. Purdy. *J. Res. Natl. Bur. Stand. (U.S.)* **85**, 1–10 (1980).

140. M. Rehkämper and A. N. Halliday. *Geochem. Cosmochim. Acta* **63**, 935–944 (1999).

141. M. Rehkämper, M. Frank, A. N. Halliday, J. R. Hein. European Union of Geosciences, 11th Biannual Symposium, Strasbourg, France, Book of Abstracts, p. 689 (2001).