

## IUPAC Technical Report

Willi A. Brand\*, Tyler B. Coplen, Jochen Vogl, Martin Rosner and Thomas Prohaska

# Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report)<sup>1</sup>

**Abstract:** Since the early 1950s, the number of international measurement standards for anchoring stable isotope delta scales has mushroomed from 3 to more than 30, expanding to more than 25 chemical elements. With the development of new instrumentation, along with new and improved measurement procedures for studying naturally occurring isotopic abundance variations in natural and technical samples, the number of internationally distributed, secondary isotopic reference materials *with a specified delta value* has blossomed in the last six decades to more than 150 materials. More than half of these isotopic reference materials were produced for isotope-delta measurements of seven elements: H, Li, B, C, N, O, and S. The number of isotopic reference materials for other, heavier elements has grown considerably over the last decade. Nevertheless, even primary international measurement standards for isotope-delta measurements are still needed for some elements, including Mg, Fe, Te, Sb, Mo, and Ge. It is recommended that authors publish the delta values of internationally distributed, secondary isotopic reference materials that were used for anchoring their measurement results to the respective primary stable isotope scale.

**Keywords:** delta notation; delta values; geochemistry; inductively coupled plasma (ICP) mass spectrometry; isotopes; IUPAC Inorganic Chemistry Division; mass spectrometry; reference materials.

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\*Corresponding author: **Willi A. Brand**, Max-Planck Institute for Biogeochemistry, Jena, Germany, e-mail: wbrand@bgc-jena.mpg.de

**Tyler B. Coplen:** U.S. Geological Survey, Reston, VA, USA

**Jochen Vogl:** BAM Federal Institute for Materials Research and Testing, Berlin, Germany

**Martin Rosner:** IsoAnalysis UG, Berlin, Germany

**Thomas Prohaska:** University of Natural Resources and Life Sciences, Vienna, Tulln, Austria

## 1 Introduction

Reference materials for use in differential measurements of stable isotope-number ratio (often shortened to “isotope ratio”) determination have been used since the early 1950s. They emerged from the few laboratories that started performing isotopic measurement, mostly in the geosciences. Locally produced isotopic reference materials were disseminated to new research groups to enable results traceable to a common origin. The carbon and oxygen isotopic reference material PDB (Peedee belemnite) [1] is a good example. The raw carbonate material (Cretaceous belemnite guards) was initially sampled by Heinz Lowenstam and Harold Urey during a field trip to the Peedee formation in South Carolina [2]. By analyzing relative oxygen-18 abundances, they discovered to their disappointment that the material was relatively uniform in oxygen isotopic abundance. However, this uniformity is exactly what is needed for stable isotopic reference materials. Consequently, they collected a substantial amount of material and milled it until it was finely ground. This material was used for years as a reference material for stable carbon and oxygen isotopes in carbonate samples.

In the early 1950s, stable isotope mass spectrometers were not available commercially. These instruments were constructed in university laboratories, and a substantial effort went into the design and maintenance of these manually operated instruments. As isotope-ratio mass spectrometry (IRMS) spread into hydrology, biology, and other fields, computer-controlled instruments became available commercially in the late 1970s

and early 1980s. While the routine performance of mass spectrometers continued improving, it became evident that the existing isotopic reference materials in use were not optimal for the task. PDB was comprised of microscopic chunks of calcite belemnite rostra, which were grown by the animal over a span of several years. During growth, water temperature changed throughout the seasons, which was reflected by variations in the oxygen isotopic composition within the rostrum [2]. Hence, on a microscopic scale, PDB was not sufficiently homogeneous. Additionally, the original supply was fully satisfactory for a few laboratories, but as the number of stable isotope applications and laboratories grew, isotopic reference materials were soon in short supply. PDB was exhausted by the end of the 1970s. Consequently, a larger effort was made that finally led to the replacement of PDB in the early 1980s [3–5]. Both new carbon and oxygen scales were termed the “VPDB” (Vienna PDB) scale, in recognition of the leading role and efforts of the International Atomic Energy Agency (IAEA) in Vienna, Austria. The scale origins were defined through fixed offsets from NBS 19, a calcite material with agreed-upon isotopic compositions.

## 2 Notation

In general, in stable isotopic abundance measurements, the isotope-number ratio of an unknown sample is compared to a sample with well-known and/or agreed-upon properties. [Often, only isotopic homogeneity is well established; in (relative) delta measurements, the “absolute” abundances themselves are less relevant]. Because the differences in isotope-number ratios usually are very small, of the order of  $10^{-3}$  or even smaller, the delta notation [6–8] is used for conveniently and accurately expressing such small differences.

The relative difference of isotope ratios (also called relative isotope-ratio or in short isotope-delta values) have been reported with the short-hand notation  $\delta^{i/j}E$ , see below. The isotope-delta value is obtained from isotope number-ratios  $R(^iE, ^jE)_p$

$$R(^iE, ^jE)_p = \frac{N(^iE)_p}{N(^jE)_p},$$

where  $^iE$  denotes the higher (superscript  $i$ ) and  $^jE$  the lower (superscript  $j$ ) atomic mass number of element  $E$ . The subscript  $P$  denotes the substance used to determine the respective values. It is customary to use a more practical short-hand notation  $R^{(i/jE)}_p$  instead.

$$\delta(^iE, ^jE)_{P,Ref} = \frac{R(^iE, ^jE)_p - R(^iE, ^jE)_{Ref}}{R(^iE, ^jE)_{Ref}}.$$

The relative difference of isotope ratios (isotope-delta values) is obtained by the relation where Ref indicates a reference material. A more convenient short-hand notation is used as follows:

$$\delta(^{i/j}E) = \delta^{i/j}E = \frac{{}^{i/j}R_p - {}^{i/j}R_{Ref}}{{}^{i/j}R_{Ref}}.$$

It is obvious from the short-hand notation that a correct interpretation of  $\delta^{(i/jE)}$  requires knowledge of the various propositions displayed in the defining relations presented above. Isotope-delta values are small numbers and therefore frequently presented in multiples of  $10^{-3}$  or per mil (symbol ‰) (see also Coplen [7] and Wieser et al. [9]).

Isotope delta is a traditional notation in the geological sciences and has been adopted in many other areas. Reporting of isotope values using isotope-number ratios may still be preferred for a number of elements. The international conventions of scientific symbols suggest clear demarcation of the quantity symbol and the accompanying qualifying contextual information. This demarcation is commonly achieved with the use of subscripts or parentheses [10–12]. Thus, the carbon-isotope delta of the material X against material Y

could be written as  $\delta^{(13/12)}_{X,Y}$ . However, to avoid clutter in mathematical expressions, publications in the last 60 years have traditionally opted for the simplified shorter form of notation by omitting the brackets and the denominator isotope where possible, e.g.,  $\delta^{13}\text{C}_V$ . While we follow this traditional short form, the omission of the qualifying brackets throughout this manuscript does not constitute an IUPAC recommendation of such practice; it merely employs a particular notation widely used and understood in the addressed science community.

### 3 Primary and secondary isotopic reference materials and the “*IT Principle*”

The delta notation allows small differences in number ratios to be expressed unambiguously beyond the precise knowledge of “absolute” isotopic abundances in the element. Best-measurement results are obtained when a sample and a reference material are similar in their chemical and physical properties, including their isotopic compositions. During measurement, small differences are not likely to be subject to systematic instrumental or preparatory bias; hence, one can measure these with the best accuracy. Moreover, sample and reference materials need to be processed in the same manner through the same sample preparation/conversion system that generates the analyte, which is introduced into the mass spectrometer (often a simple gas such as  $\text{CO}_2$  or  $\text{H}_2$ ). The procedure has been coined the “*IT Principle*” (IT = **I**dentical **T**reatment [13, 14]). It has been in practical use since the 1950s as a general guideline for making stable isotopic measurements. As an example, the measurement standard NBS 19, a pure natural calcite powder of uniform, defined grain size [3], anchors both the stable oxygen and stable carbon isotopic composition scales. This material can be used to compare results with other calcite samples, using, for example, an acid digestion preparation or a high-temperature reaction to release  $\text{CO}_2$  for subsequent isotopic analysis. However, during such a preparation the isotopic composition of the material may be altered. The  $\text{CO}_2$  gas evolved from the acid reaction has only two oxygen atoms, whereas the calcite from which it emerged had three oxygen atoms attached to the carbon. Fortunately, because the materials are comparable in nature, the associated isotopic fractionation applies to the sample and to the reference material in the same quantitative fashion. Hence, the isotope relation between reference and sample remains identical.

For samples other than calcite, the situation can be substantially more difficult. For example, a difference in the mineralogy or chemical composition of carbonates can introduce different oxygen isotopic fractionations. This is the case for the oxygen isotopic determination of carbonates, such as siderite or dolomite. The specimen also could be a different chemical compound such as complex oil, or a bio-compound such as whole wood, DNA, a blood sample, or a trace gas component in an air sample, etc. The sample might contain the element being analyzed in both exchangeable and non-exchangeable compartments, such as hydrogen in keratin [15]. A specimen could contain included extraneous water or other contaminant compounds, for example, barium sulfate for oxygen isotopic analysis that could contain pore water and nitrate [16]. The physical/chemical preparation process for producing the pure measurement material can vary considerably, and this often is a significant source of isotopic fractionation and/or contamination. It would be ideal to have dedicated, well-calibrated isotopic reference materials for all types of sample compounds and matrices, but this is not possible. Instead, the practice has emerged to distinguish primary and secondary isotopic reference materials.

*Primary isotopic reference materials* for delta measurements are “international measurement standards” as defined in the International Vocabulary of Metrology, VIM3 [17]. They define the scale zero or an anchor point and, if applicable, the scale span.<sup>1</sup> These materials are assigned stable isotope values by consensus,

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<sup>1</sup> In metrology the usual aim is to produce SI-traceable results. Here, primary reference materials are those having the highest metrological quality for SI-traceable quantity values like concentrations or (*absolute*) isotopic abundances with associated uncertainty. For primary isotope reference materials defining delta scales, this is different. These materials are given without uncertainty by definition because these values have been determined by international agreement. Isotope ratios are measured *relative* to these materials. The corresponding (*absolute*) isotopic abundances cannot be measured with the required precision.

with no uncertainty when used as reference for the respective delta scale (see Coplen [7].<sup>2</sup>) No measurement uncertainty is involved in establishing the reference (zero). “No uncertainty” applies to the consensus reference value for the material as a whole; any subsampling can lead to isotopic variations, which enter the error budget.<sup>3</sup> The only remaining uncertainty arises from isotopic inhomogeneity, which is addressed during preparation of the reference materials. This uncertainty has to be considered and propagated accordingly, if accessible from the certificates or from the original literature. In many cases the heterogeneity of the reference material may be hidden in the uncertainty of the analytical measurement of the respective reference material or in the reported repeatability of the measurement of subsamples. The primary isotopic reference materials mark the end members of the respective traceability chains associated with the isotopic measurements.

*Secondary isotopic reference materials* serve to bridge the materials and chemistry gap. They are designed to be representative of a variety of typical compounds or substances that are analyzed by stable isotope laboratories. The values of secondary isotopic reference materials often are evaluated and compiled as a collaborative effort of several laboratories. These laboratories mostly are selected according to their demonstrated ability to make accurate measurements for the respective type of material; this process commonly is called value assessment. Values of secondary isotopic reference materials cannot be fixed permanently by a single certificate; their values may change as a result of new peer-reviewed, published values based on improved analytical methods and instrumentation. Improvement in value assignment has turned out to be necessary for some secondary isotopic reference materials every few years. A good example is NBS 22 oil (see Table 5). Its evaluated stable carbon isotopic composition had to be changed repeatedly because improved sample conversion procedures and a better understanding of instrumental effects led to a reduction in systematic errors.

For many isotopic reference materials, certificates are available from the respective institution. As an example, Fig. 1 depicts the top section of the NIST certificate (“Report of Investigation”) for NBS 22, Reference Material 8539 [18]. The full certificate is available from the NIST Web site ([www.nist.gov/srm/](http://www.nist.gov/srm/)). Apart from reference delta values, the certificate provides information on the origin of the material, the analytical methods used for establishing the certified values, isotopic homogeneity, recommended scaling procedures,



National Institute of Standards & Technology

## Report of Investigation

### Reference Material 8539

NBS 22 Oil

(Carbon and Hydrogen Isotopes in Oil)

This Reference Material (RM) is intended for use in developing and validating methods for measuring relative differences in carbon (C) isotope-number ratios,  $R(^{13}\text{C}/^{12}\text{C})$ , and hydrogen (H) isotope-number ratios,  $R(^2\text{H}/^1\text{H})$  [1]. Even though the values for this RM are reference values and not certified [2], its use will improve the comparability of data from different laboratories. The equivalent name for this RM as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS) is NBS 22. A unit of RM 8539 consists of one ampoule containing approximately 1 mL of oil.

Table 1. Reference Values<sup>(a)</sup> and Expanded Uncertainties for the Relative C and H Isotope-Number Ratio Differences of RM 8539

RM Number	Name	Reference Value $10^3 \delta^{13}\text{C}_{\text{VPDB-LSVEC}}^{(b)}$	Expanded Uncertainty $10^3 \delta^{13}\text{C}_{\text{VPDB-LSVEC}}^{(b)}$	Reference Value $10^3 \delta^2\text{H}_{\text{VSMOW-SLAP}}^{(c)}$	Expanded Uncertainty $10^3 \delta^2\text{H}_{\text{VSMOW-SLAP}}^{(c)}$
8539	NBS 22	-30.03	±0.09	-116.9	±0.3

Fig. 1 Part of the NIST certificate for NBS 22. The full report of investigation is available from <http://www.nist.gov/srm/> (last accessed 4/2013).

<sup>2</sup> Full article freely available at <http://onlinelibrary.wiley.com/doi/10.1002/rcm.5129/abstract>.

<sup>3</sup> This is in contrast to “absolute” isotope-ratio assessment, where also the uncertainty of the isotope-number ratio determination has to be accounted for in the certificate.

and reporting recommendations. Last, but not least, most of the relevant scientific literature concerning the respective reference material is provided.

In addition to traditional light-element stable isotopic abundance analysis (C, H, N, O, and S), accessible by gas-isotope mass spectrometry or more recently by optical (laser) absorption spectroscopy, other predominantly heavier element isotopes are being analyzed by delta measurement techniques. Their isotope-amount ratios increasingly are being measured in geochemistry, archeology, forensics, and food science, owing to improvements in mass spectrometric techniques such as TIMS (thermal ionization mass spectrometry) or SIMS (surface ionization mass spectroscopy), but mainly owing to the advent of MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) [19–21]. The latter technique is very versatile in addressing a number of isotope systems in spite of pronounced mass bias effects [22–24]. In addition, isobaric interferences need to be evaluated and corrected for accordingly. For all techniques, the chemical preparation prior to the actual measurement can be laborious and may require treatments from sample digestion to matrix separation (e.g., via ion exchange) [25–28]. If possible, the reference materials are subjected to the same procedures, thus adhering to the IT principle [13, 14]. It is a difficult task to match the matrices of the large variety of samples to be analyzed in any one laboratory with a suitable reference material and matrix. This compromises the ultimately achievable accuracy. For a discussion of the impact of matrix effects on the error budget, see, for instance, Rosner et al. [29]. A review of heavy-element stable isotopic variations in terrestrial materials has been published recently by Tanimizu et al. [30].

Within the last decade, spatially resolved isotope-ratio analysis using LA-(MC)-ICP-MS or SIMS of solid samples has become a rapidly growing field in isotope analytics. These in situ techniques require homogeneous, well-characterized compact solid reference materials or standards. However, many certified isotopic reference materials for the elements in question are salts or solutions. Solid reference materials with certified isotope-amount ratios or  $\delta$  values for position-specific isotopic analysis do not exist. The scientific community has mainly used the NIST SRM 600 glass series as a delta standard for various isotope systems in the past. However, when the sample and the NIST glass are compositionally or texturally different, this approach may be problematic (in direct violation of the IT principle [13]). Differences in instrumental mass fractionation or matrix effects during sampling and sample preparation may lead to substantial errors. To ensure accurate and traceable in situ isotope-ratio determinations, compact, isotopically homogeneous matrix standards with well-characterized  $\delta$  values are urgently needed.

We have included the newly emerging isotopic reference materials for delta scales in the set of tables presented below. However, it should be emphasized that the use of some of these materials is still at an early stage. The delta-value scales are often not widely agreed upon. Some reference materials were produced only recently and, they still need to demonstrate their merits as scale anchors or even as zero-delta materials, defining the origin of the respective delta scales. Apart from radiogenically altered elemental compositions, the terrestrial isotopic variations found in natural samples are usually small, owing to the fact that the relative mass differences are small as well. Moreover, isotopic fractionation effects via gas/liquid phase transitions are rare, and samples exhibiting enzymatically catalyzed isotopic changes in these elements still need to become more common on the laboratory shelf.

To express the small isotopic signatures, the delta equation [7] often has been given in the literature with a factor of 10 000. The defined quantity was then called epsilon ( $\epsilon$ ). However, as a coherent quantity equation, the extraneous factor should be omitted [10, 17]; the delta and epsilon equations become identical. Hence, we recommend that this use of epsilon be abandoned [7]. Instead, and in order to comply with the guidelines for the SI system, the order of magnitude can be expressed using “per meg” or “pptt” [7]. The terminology can also be changed completely to adopt the proposed urey [8] (symbol Ur) as the unit for delta, enabling one to employ the full range of prefixes permissible in the SI system. We also suggest that authors follow the agreed-upon convention that the heavy isotope should always be in the numerator and the lighter isotope in the denominator of the ratio in question [7].

In light of the role that secondary isotopic reference materials have played in the past regarding inter-laboratory comparability of data, this compilation sets out to cover comprehensively the secondary isotopic reference materials that have been used in the past for inter-laboratory comparability of data (although the



list may still omit some materials accidentally). Arbitrarily selected examples on the most prominent use of the isotope-number ratios are listed for the single elements even though this publication does not intend to be a full review of applications and cannot reflect all publications in the respective fields accordingly.

Scientific publications are made at a particular point in time, while the data presented therein should be valid for a long time. Hence, it is important and has become common practice in scientific publications to provide information about (international) reference materials used and their values measured or employed as a secondary anchor for the respective stable isotope scales. Should a new value assignment of respective material arise after the initial measurements, sample results can be recalculated based on the newly found reference value for the secondary isotopic reference material employed in that publication.

In the following, the history and currently assigned values of isotopic reference materials are provided in the form of commented tables. The isotopic abundances of the elements in naturally occurring terrestrial materials are given as coarse information only with a reduced number of digits. Full values are listed in the recent IUPAC compilations [9, 31], available from the Web site of the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) (<http://www.CIAAW.org>). In 2002, an extensive compilation of stable isotope data focusing on minimum and maximum isotope values found in natural samples was assembled by Coplen et al. [32, 33]. Only elements for which a zero-delta scale material has been produced or proposed are listed below. Thus, no information is provided for elements such as barium and tellurium.

To provide an up-to-date comprehensive overview, most isotopic reference materials that have played a significant role and/or were available to a wider scientific audience are included in the tables given below.<sup>4</sup> This also applies to materials whose supply is now exhausted or that have been superseded by newer materials for various reasons. The tables are organized according to the periodic table of the elements as appropriate for stable isotopic measurements. Isotopic reference materials are, in general, identified by their original name. If the materials are important for more than one element, comments are given for each element, accepting some redundancy of information. Delta-value assignments are provided in chronological order with a corresponding reference. In the case of multiple entries, the current delta value recommended by CIAAW (if any) is listed in bold font. Values of international measurement standards (primary isotopic reference materials) are underlined in bold font. Multiple entries emphasize the necessity to report both the reference material used for scale anchoring as well as the delta value employed in the presented study. The column “uncertainty” presents uncertainties as provided in the cited literature. These uncertainties are

**Table 1** Resource information for stable isotopic reference materials.<sup>a</sup>

Institution	URL
NIST (formerly NBS), Gaithersburg, MD (USA)	<a href="http://www.nist.gov/srm/">http://www.nist.gov/srm/</a>
IRMM, Geel (Belgium)	<a href="http://irmm.jrc.ec.europa.eu/">http://irmm.jrc.ec.europa.eu/</a>
IAEA, Vienna (Austria)	<a href="http://nucleus.iaea.org/rpst/">http://nucleus.iaea.org/rpst/</a>
USGS, Reston, VA (USA)	<a href="http://isotopes.usgs.gov/">http://isotopes.usgs.gov/</a>
OSIL (IAPSO), Havant, Hampshire (UK)	<a href="http://www.osil.co.uk/">http://www.osil.co.uk/</a>
BAM, Federal Institute for Materials Research and Testing, Berlin (Germany)	<a href="http://www.bam.de">http://www.bam.de</a>
ERM, European Reference Materials	<a href="http://www.erm-crm.org/">http://www.erm-crm.org/</a>
NRC, Ottawa, Ontario (Canada)	<a href="http://www.nrc-cnrc.gc.ca/">http://www.nrc-cnrc.gc.ca/</a>
IAGeo, Nottingham (UK)	<a href="http://www.geoanalyst.org/">http://www.geoanalyst.org/</a>
NBL (New Brunswick Laboratory), Argonne, IL (USA)	<a href="http://9zdip.w4yserver.at/products_iageo.html">http://9zdip.w4yserver.at/products_iageo.html</a>
CEA, Gif-sur-Yvette (France)	<a href="http://www.nbl.doe.gov/">http://www.nbl.doe.gov/</a>
NIM, National Institute of Metrology (China)	Materials available from <a href="http://www.eurisotop.com/">http://www.eurisotop.com/</a>
	<a href="http://en.nim.ac.cn/new-measurement-standards">http://en.nim.ac.cn/new-measurement-standards</a>
	<a href="http://www.ncrm.org.cn/English/Home/Index.aspx">http://www.ncrm.org.cn/English/Home/Index.aspx</a>

<sup>a</sup>Additional resources can be found at <http://www.rminfo.nite.go.jp/english/link/link2.html>.

<sup>4</sup> While striving for a complete set, we certainly may have missed some of the important materials.

often – especially for certified materials – expanded uncertainties ( $U$ ) of combined standard uncertainties ( $u_c$ ) with a coverage factor  $k = 2$  ( $U = k \cdot u_c$ ). Data in the scientific literature provide a larger variety of uncertainties and, in many cases, the measurement precision alone, usually expressed as 1-sigma value. The type of uncertainty is not stated in the tables. For further information, readers are recommended to consult the original literature.

### 3.1 Hydrogen

Hydrogen has two stable isotopes,  $^1\text{H}$  and  $^2\text{H}$ , with isotopic abundances of 99.98 and 0.02 %, respectively, in naturally occurring terrestrial materials. For historical reasons, the stable isotopes of hydrogen bear special names, protium and deuterium.<sup>5</sup> The latter, mass number 2 isotope, was discovered in 1931 by Harold C. Urey [51, 52], the same Nobel prize winning chemist who provided the PDB standard calcite and started the new field of isotope geochemistry in his Chicago laboratory around the middle of the last century. Water was a

**Table 2** The  $\delta^2\text{H}$  values of hydrogen isotopic reference materials.<sup>a</sup>

Description	NIST RM #	Material	$\delta^2\text{H}_{\text{VSMOW}}$	Uncertainty	References	Comment
VSMOW	8535	Water	<b>0<sup>b</sup></b>	None	[34]	Quarantined <sup>c</sup>
SLAP	8537	Water	<b>-428.5 ‰</b>	0.1	[35]	Quarantined <sup>c</sup>
			<b>-427.8 ‰</b>	0.5	[36]	
			<b>-428.8 ‰</b>	1.3	[37]	
			<b>-425.8 ‰</b>	1.0	[38]	
			<b><u>-428 ‰<sup>b</sup></u></b>	None	[34]	
SMOW		n/a	0	–	[39]	Scale discontinued [4]
VSMOW2		Water	<b>0</b>	0.3 ‰	[40]	
SLAP2		Water	<b>-427.5 ‰</b>	0.3 ‰	[40]	
GISP	8536	Water	<b>-189.7 ‰</b>	0.9 ‰	[41]	
GISP2		Water	<b>-258.3 ‰</b>	0.3 ‰	IAEA	Not yet released
NBS 1		Water	<b>-47.6 ‰</b>	n/a	[39]	Exhausted
NBS 1a		Water	<b>-183.3 ‰</b>	n/a	[39]	Exhausted
USGS45		Water	<b>-10.3 ‰</b>	0.4 ‰	[42]	
USGS46		Water	<b>-235.8 ‰</b>	0.7 ‰	[43]	
USGS47		Water	<b>-150.2 ‰</b>	0.5 ‰	[44]	
USGS48		Water	<b>-2.0 ‰</b>	0.4 ‰	[45]	
NBS 22	8539	Oil	<b>-119.2 ‰</b>	0.7 ‰	[46]	
			<b>-116.9 ‰</b>	0.8 ‰	[47]	
NBS 30	8538	Biotite	<b>-65.7 ‰</b>	0.3 ‰	[41]	
NGS1	8559	Natural gas (coal origin)	<b>-138 ‰ (CH<sub>4</sub>)</b>	~5 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	<b>-173 ‰ (CH<sub>4</sub>)</b>	~2.5 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	<b>-121 ‰ (C<sub>2</sub>H<sub>6</sub>)</b>	~7 ‰	[48]	Exhausted
NGS3	8561	Natural gas (biogenic)	<b>-176 ‰ (CH<sub>4</sub>)</b>	~1 ‰	[48]	Exhausted
IAEA-CH-7	8540	Polyethylene foil	<b>-100.3 ‰</b>	2.0 ‰	[41]	
USGS42		Human hair (Tibetan)	<b>-78.5 ‰</b>	2.3 ‰	[49, 50]	
USGS43		Human hair (Indian)	<b>-50.3 ‰</b>	2.8 ‰	[49, 50]	

<sup>a</sup>Values for hydrogen isotope deltas are supplied with one place after the decimal point. They are listed in chronological order of the cited literature. In the case of multiple entries, values recommended by the Commission of Isotopic Abundances and Atomic Weights (CIAAW) are listed in bold font; those defining a scale are underlined in bold font. The latter have no associated uncertainty (by definition).

<sup>b</sup>Exact values defining the  $\delta^2\text{H}_{\text{VSMOW-SLAP}}$  scale. Please note that both scale-defining materials, VSMOW for the scale origin and SLAP for the scale span, are given without uncertainty. These are fixed consensus values. They cannot be changed without changing the scale as well.

<sup>c</sup>Still available from the Reston Stable Isotope Laboratory of the U.S. Geological Survey.

<sup>5</sup> The  $^3\text{H}$  isotope also has a popular name, tritium. Because it is radioactive (half-life ~12.3 years), it is not listed in this compilation of stable isotopic reference materials.

prime medium of the first studies; thus, isotopic reference materials were first needed for water. Beginning in the 1950s, steam condensate from Potomac River Water (NBS 1) and snow melt water (NBS 1a) from Yellowstone, Wyoming, USA, were distributed by the U.S. National Bureau of Standards (NBS, now NIST) for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  mass-spectrometric measurements of water [53, 54]. To anchor isotope-ratio results from water samples to the major world water pool, a new (virtual) Standard Mean Ocean Water (SMOW) scale was introduced by Craig [39] in 1961. He recommended that NBS 1 reference water be assigned a  $\delta^2\text{H}$  value of  $-47.62$  ‰ relative to SMOW, the new virtual hydrogen-isotope scale, making NBS 1 the first international measurement standard for water. The first secondary measurement standard for water was NBS 1a. The supply of NBS 1 was insufficient to satisfy the expected demand. Therefore, at the request of the International Atomic Energy Agency (IAEA), H. Craig collected ocean water from the equator and  $180^\circ$  longitude, distilled it, and slightly adjusted its  $\delta^2\text{H}$  value so that it would agree with the NBS 1 definition [55]. This water reference was first assigned the name SMOW for the acronym Standard Mean Ocean Water, but it was renamed VSMOW (after Vienna-SMOW) at a 1976 IAEA's Consultants' Meeting because there could be confusion between the virtual SMOW scale defined in terms of NBS 1 reference water and the scale defined in terms of the water prepared by H. Craig. Stocks of VSMOW were divided between NIST and the IAEA. It was found that the  $\delta^2\text{H}$  of NBS 1a reference water (approximately  $-183$  ‰) was not sufficiently negative to encompass the full range of terrestrial water, and ice from the Antarctic Vostok site was obtained by the IAEA. This reference material was initially assigned the acronym SNOW, but it was later renamed with the acronym SLAP for Standard Light Antarctic Precipitation [55].

As outlined above, SMOW was introduced as a concept first, with a fixed distance from the then used NBS 1 water standard. This was before a common water standard replaced the virtual scale origin with a physically existing reference water, VSMOW [34]. Together with VSMOW, the second  $^2\text{H}$ -depleted water standard, SLAP, was introduced because it had been recognized that water, in particular, was prone to isotope-scale contraction effects, mainly owing to its surface adhesion properties. The SLAP reference water was the first case of a second (isotopically “light”) anchor point for a stable isotope scale, which has greatly improved comparability of experimental data from laboratories worldwide. This was made an official rule for all hydrogen-bearing compounds at the 37<sup>th</sup> IUPAC General Assembly in 1993 in Lisbon. The Commission on Atomic Weights and Isotopic Abundances (CAWIA)<sup>6</sup> recommended that  $\delta^2\text{H}$  values of *all* hydrogen-bearing materials be measured and expressed relative to VSMOW reference water on a scale normalized by assigning the consensus value of  $-428$  ‰ to SLAP [56, 57]. Previously, this recommendation applied only to water [34]. Authors should discontinue reporting  $\delta^2\text{H}$  values relative to SMOW [4].

For non-water samples, only a few reference materials exist at present. These include NBS 22 oil, NBS 30 biotite, and IAEA-CH-7 polyethylene foil. However, these materials do not differ substantially in their  $^2\text{H}$  abundances. Therefore, a SLAP-analog reference material is urgently needed to make use of the scaling rule for non-aqueous samples. There are relatively few organic reference materials having exchangeable hydrogen that are available from conventional suppliers of reference materials (Table 1). Two such materials are USGS42 Tibetan human hair and USGS43 Indian human hair. At present, several new materials are not yet characterized completely for hydrogen isotopic composition (IAEA-CH-3, IAEA-CH-6, IAEA-600, USGS40, USGS41). Only provisional data are available.

### 3.2 Lithium

Lithium has two stable isotopes,  $^7\text{Li}$  and  $^6\text{Li}$ , with isotopic abundances of 92.4 and 7.6 %, respectively, in naturally occurring terrestrial materials. Relative lithium isotopic ratios in geochemical and environmental studies commonly are reported as  $\delta^7\text{Li}_{\text{RM8545}}$  values relative to the internationally distributed lithium carbonate isotopic reference material NIST RM 8545 ( $\delta^7\text{Li} = 0$ ; LSVEC) in terms of  $N(^7\text{Li})/N(^6\text{Li})$  ratios. A high variability

<sup>6</sup> Now the Commission on Isotope Abundances and Atomic Weights, CIAAW (see [www.ciaaw.org](http://www.ciaaw.org)).



**Table 3** The  $\delta^7\text{Li}$  values of lithium isotopic reference materials.

Description	Material	$\delta^7\text{Li}_{\text{RM8545}}$	Uncertainty	References	Comment
NIST RM 8545 (LSVEC)	Lithium carbonate	<b>0<sup>a</sup></b>	None	[58, 59]	<sup>b</sup>
IRMM-016	Lithium carbonate	+0.35 ‰			Calc. from certificates
		-0.01 ‰	0.6 ‰	[58, 60]	Mean from GeoReM <sup>c</sup>
		-0.01 ‰	0.72 ‰	[58, 60–62]	
		+0.15 ‰	1.0 ‰	[63]	
		-0.2 ‰	0.5 ‰	[64]	
NRC NASS-5	Seawater	<b>+0.14 ‰</b>	0.2 ‰	[65]	
		+30.63 ‰	0.44 ‰	[66]	
		+30.7 ‰			Mean from GeoReM <sup>c</sup>
OSIL IAPSO	Seawater	+30.84 ‰	0.19 ‰	[66]	
		+31.1 ‰	0.3 ‰		Mean from GeoReM <sup>c</sup>
IRMM BCR-403	Seawater	+30.8 ‰	0.6 ‰		Mean from GeoReM <sup>c</sup>
NIST SRM 610	Silicate glass	+32.36 ‰	0.29 ‰	[67]	
		<b>+32.5 ‰</b>	0.02 ‰	[65]	
NIST SRM 612	Silicate glass	+35.26 ‰	0.79 ‰	[68]	
		+31.78 ‰	0.34 ‰	[67]	
		<b>+31.2 ‰</b>	0.1 ‰	[65]	
		+31.1 ‰	0.4 ‰	[69]	
		+20.5 ‰	0.1 ‰	[65]	
NIST SRM 614	Silicate glass	+20.5 ‰	0.1 ‰	[65]	
BCR-2	Silicate glass	+2.87 ‰	0.39 ‰	[66]	
		+4.08 ‰	0.1 ‰	[65]	
		+5.57 ‰	0.44 ‰	[66]	
JA-1	Andesite	+5.79 ‰	0.65 ‰	[70]	
JB-2	Basalt	+4.78 ‰	0.47 ‰	[66]	
		+4.29 ‰	0.34 ‰	[70]	
JB-3	Basalt	+3.94 ‰	0.29 ‰	[70]	
BHVO-1	Basalt	+5.0 ‰	0.35 ‰	[66]	
		+5.31 ‰	0.18 ‰	[68]	
BHVO-2	Basalt	+4.5 ‰	0.5 ‰		Mean from GeoReM <sup>c</sup>
		+4.55 ‰	0.29 ‰	[68]	
		+4.33 ‰	0.33 ‰	[62]	
		<b>+4.7 ‰</b>	0.2 ‰	[65]	

<sup>a</sup>Exact value defining the  $\delta^7\text{Li}_{\text{RM8545}}$  scale. For Li, the commonly used name is “RM 8545”. For carbon, the name “LSVEC” is more popular.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>Mean of values published in GeoReM (georem.mpch-mainz.gwdg.de/); last accessed 4/2013.

in lithium isotopic compositions of about 80 ‰ is observed in naturally occurring terrestrial materials, primarily due to the very large difference in mass between  $^6\text{Li}$  and  $^7\text{Li}$ .

Some laboratories still are reporting  $\delta^6\text{Li}$  values by using  $N(^6\text{Li})/N(^7\text{Li})$  ratios. This is confusing because (i)  $\delta^7\text{Li}$  values are opposite in sign to  $\delta^6\text{Li}$  values, (ii) the absolute values of  $\delta^7\text{Li}$  and  $\delta^6\text{Li}$  are not equal, and (iii) samples with more positive  $\delta$  values are commonly thought of as being more dense or “heavier”, but samples with more positive  $\delta^6\text{Li}$  values are less dense. To eliminate possible confusion in the reporting of relative lithium-isotope-ratio data, CIAAW has recommended that relative lithium isotopic measurements of all substances be expressed as  $\delta^7\text{Li}$  values in terms of  $N(^7\text{Li})/N(^6\text{Li})$  ratios relative to the internationally distributed lithium carbonate isotopic reference material NIST RM 8545 ( $\delta^7\text{Li} = 0$ ). Reporting of  $\delta^6\text{Li}$  values, expressed in terms of  $N(^6\text{Li})/N(^7\text{Li})$  ratios, should be discontinued. Guidelines for reporting lithium delta values were published in “Atomic weights of the elements 1995” [57].

For reporting  $\delta^7\text{Li}$  it is recommended that NIST RM 8545 lithium carbonate (LSVEC) be used, which was prepared by H. Svec, Iowa State University [59] from virgin, North Carolina ores. In comparison to average seawater, NIST RM 8545 is depleted in  $^7\text{Li}$  by about 30 ‰. Using MC-ICP-MS, repeated analysis of NIST RM 8545 standard solutions can be made with an uncertainty of  $\sim 0.2$  ‰ [66]. Due to NIST RM 8545 carbonate’s rather negative  $\delta^{13}\text{C}$  value, close to that of atmospheric methane, it frequently has been used as a carbon

stable isotopic reference material [71], and it serves as the anchor for the low isotopic abundance end of the stable carbon-isotope scale [72].

In addition to the lithium  $\delta$ -zero material (NIST RM 8545, LSVEC), three certified lithium isotopic reference materials are available. IRMM-015 and IRMM-016 are  $\text{Li}_2\text{CO}_3$  materials, and IRMM-615 is a solution made from IRMM-015 base material. While IRMM-015 and IRMM-615 are highly enriched in  $^6\text{Li}$  ( $N(^6\text{Li})/N(^7\text{Li}) = \sim 21.9$ ), IRMM-016 has a natural lithium isotopic composition very close to that of NIST RM 8545. Compared to the  $\delta^7\text{Li}_{\text{SRM8545}}$  value of +0.35 ‰ calculated from the certificates, 17 independent studies report consistent  $\delta^7\text{Li}_{\text{RM8545}}$  values between -0.8 and +0.5 ‰, with a mean of -0.01 ‰ ( $\pm 0.6$ ) for IRMM-016 (georem.mpch-mainz.gwdg.de/).

Within the last 20 years, seawater and rock reference materials, primarily, have been characterized for  $\delta^7\text{Li}_{\text{RM8545}}$  values. For seawater, a very large dataset of published  $\delta^7\text{Li}_{\text{RM8545}}$  values exists. In 2007, a data compilation for  $\delta^7\text{Li}_{\text{RM8545}}$  values of seawater was published that indicated a mean  $\delta^7\text{Li}_{\text{RM8545}}$  value of +30.8 ‰ for modern seawater (open ocean) [66]. In addition to seawater samples,  $\delta^7\text{Li}_{\text{RM8545}}$  values for the seawater reference materials NRC NASS-5 (+30.7 ‰ ( $n = 1$ )), IRMM BCR-403 (+30.8 ‰  $\pm 0.6$  ( $n = 10$ )), and the seawater salinity standard OSIL IAPSO (+31.1 ‰  $\pm 0.3$  ( $n = 4$ )) have been compiled in the GeoReM database.

For silicate reference materials, a large dataset of published  $\delta^7\text{Li}_{\text{RM8545}}$  values is available. The entire NIST SRM 61x silicate glass series was characterized by Kasemann et al. in 2005 for  $\delta^7\text{Li}_{\text{RM8545}}$  values [65]. In addition to this complete dataset of  $\delta^7\text{Li}_{\text{RM8545}}$  values, three studies published lithium-isotope data for NIST SRM 610 and 612. The reason for the high  $\delta^7\text{Li}_{\text{RM8545}}$  value published by Magna et al. [68] is unclear. Representative of the numerous rock reference materials, the basaltic BHVO materials are mentioned. In March 2013, the mean of 22 published  $\delta^7\text{Li}_{\text{RM8545}}$  values for BHVO-2 listed in the GeoReM database yielded a mean value of +4.5 ‰ ( $\pm 0.5$ ).

The consistency of published  $\delta^7\text{Li}_{\text{RM8545}}$  values for isotopic reference and quality control materials suggests an overall expanded analytical uncertainty of most lithium-isotope studies of well below 1 ‰.

### 3.3 Boron

Boron has two stable isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , with isotopic abundances of 19.8 and 80.2 ‰, respectively, in naturally occurring terrestrial materials. Following the general rule that the heavy isotope should be reported in the numerator of the respective ratio, isotopic measurements are measured relative to NIST SRM 951 and published as  $\delta^{11}\text{B}_{\text{SRM951}}$  values. Due to the large relative mass difference between the two boron isotopes and the special physicochemical behaviour of boron, the variability of boron isotopic composition of naturally occurring terrestrial materials is about 80 ‰. Owing to a high scientific interest in boron-isotope chemistry and the use of boron for nuclear applications, a large number of certified isotopic reference materials exist for boron.

NIST SRM 951 and NIST SRM 952 were both prepared at NIST within the same effort to generate certified reference materials for boron isotopic composition [82]. NIST SRM 951 was made from an original lot of pure  $\text{H}_3\text{BO}_3$  of more than 200 kg in 22 containers, which was free from impurities and largely homogeneous throughout the lot (except for one container). NIST SRM 951a is a newly bottled batch of the NIST SRM 951 material. Although not mentioned in the certificate, exactly the same values with their uncertainties have been certified. The raw material for the  $^{11}\text{B}$ -depleted NIST SRM 952 was obtained from Oak Ridge National Laboratory. To ensure sample homogeneity and absence of metallic and other impurities, the material was recrystallized twice before further characterization.

The Institute for Reference Materials and Measurements (IRMM) produced two certified boron isotopic reference materials. IRMM-011 consists of 1 g crystalline boric acid aliquots in glass vials. IRMM-610 is an aqueous solution of pure boric acid with an acid content of  $\sim 5 \text{ mmol}\cdot\text{L}^{-1}$  and boron isotopic composition, which was designed to be close to that of NIST SRM 952. The certified values have been obtained by applying the  $\text{Na}_2\text{BO}_2^+$  thermal ionization mass spectrometry (TIMS) technique and using a mass spectrometer calibrated via synthetic isotope mixtures [83]. Recently, a  $\delta^{11}\text{B}_{\text{SRM951}}$  value of -0.37 ‰ for IRMM-011 was determined using the  $\text{Na}_2\text{BO}_2^+$  method [74].

**Table 4** The  $\delta^{11}\text{B}$  values of boron isotopic reference materials.

Description	Material	$\delta^{11}\text{B}_{\text{SRM951}}$	Uncertainty	References	Comment
NIST SRM 951	Boric acid	0 <sup>a</sup>	none	[33, 73]	<sup>b</sup>
NIST SRM 951a					
IRMM-011	Boric acid	+0.16 ‰		[29]	Calc. from certificates
		-0.375 ‰		[74, 75]	
ERM-AE101	Boric acid aqueous solution	-122.96 ‰		[29, 76]	Calc. from certificates
		-123.01 ‰	0.41 ‰	[29, 76]	
ERM-AE120	Boric acid aqueous solution	-20.2 ‰	0.6 ‰	[74, 77]	
ERM-AE121	Boric acid aqueous solution	+19.9 ‰	0.6 ‰	[74, 78]	
ERM-AE122	Boric acid aqueous solution	+39.7 ‰	0.6 ‰	[74, 79]	
ERM-ED102	Boron carbide powder	-5.0 ‰			Calc. from certificates
NRC NASS-5	Seawater	+39.89 ‰			Mean from GeoReM <sup>c</sup>
OSIL IAPSO	Seawater	+39.64 ‰	0.42 ‰	[80]	
IAEA-B-1	Seawater	+38.6 ‰	1.66 ‰	[81]	
		+38.76 ‰	0.79 ‰	[29]	
IAEA-B-2	Groundwater	+13.8 ‰	0.79 ‰	[81]	
		+14.38 ‰	1.2 ‰	[29]	
IAEA-B-3	Groundwater	-21.4 ‰	0.89 ‰	[81]	
		-20.82 ‰	0.86 ‰	[29]	
IAEA-B-4	Tourmaline	-8.7 ‰	0.18 ‰	[81]	
IAEA-B-5	Basalt	-3.8 ‰	2.0 ‰	[81]	
IAEA-B-6	Obsidian	-1.8 ‰	1.5 ‰	[81]	
IAEA-B-7	Limestone	+9.7 ‰	5.9 ‰	[81]	
IAEA-B-8	Clay	-5.1 ‰	0.87 ‰	[81]	
NIST SRM 610	Silicate glass	-0.52 ‰	0.53 ‰		Mean from GeoReM <sup>c</sup>
NIST SRM 612	Silicate glass	-0.51 ‰	0.52 ‰		Mean from GeoReM <sup>c</sup>
GSJ JB-2	Basalt rock powder	+7.24 ‰	0.33 ‰		Mean from GeoReM <sup>c</sup>
GSJ JCP-1	Coral powder	+24.24 ‰			Mean from GeoReM <sup>c</sup>
NIST RM 1547	Peach leaves	+41.09 ‰	1.12 ‰	[29]	
NIST RM 8433	Corn bran	+8.3 ‰	1.69 ‰	[29]	
BCR-679	White cabbage	-23.8 ‰	1.15 ‰	[29]	

<sup>a</sup>Exact value defining the  $\delta^{11}\text{B}_{\text{SRM951}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>Mean of values published in GeoReM ([georem.mpch-mainz.gwdg.de/](http://georem.mpch-mainz.gwdg.de/)); last accessed 4/2013.

Beginning in 2001, the BAM Federal Institute of Materials and Testing (BAM) produced a number of certified boron isotopic reference materials with a large variety of isotopic compositions. Six of the BAM materials are enriched in  $^{10}\text{B}$ , one is isotopically similar to that of NIST SRM 951 (ERM-AE120), three materials are  $\delta$ -reference materials (ERM-AE120, 121, 122) with  $\delta^{11}\text{B}$  values of -20, +20, and +40 ‰, and one is a boron carbide matrix material (ERM-ED102). ERM-AE120, ERM-AE121, and ERM-AE122 are the first boron reference materials, which are certified for their  $\delta$  values.<sup>7</sup> They were produced by mixing normal boric acid either with  $^{10}\text{B}$  or with  $^{11}\text{B}$  solutions to yield specific  $\delta^{11}\text{B}$  values, covering about three-quarters of the boron isotopic variability of naturally occurring materials. To obtain the certified  $\delta^{11}\text{B}$  values listed in Table 4, results from  $\text{Na}_2\text{BO}_2^+$  TIMS measurements have been combined with those from  $\text{Cs}_2\text{BO}_2^+$  TIMS measurements and gravimetric preparation.

Apart from certified boron isotopic reference materials, numerous matrix materials are used for quality control of boron-isotope data. Here we focus on internationally recognized natural solution materials from IAEA, NRCC, and OSIL (Ocean Scientific International Ltd.), rock and glass materials from IAEA and NIST, and plant reference materials from NIST and IRMM.

<sup>7</sup> More isotopic reference materials, which are certified for their isotopic composition, but not for delta values, are available from BAM, featuring boron-10 isotopic abundances from 20 to 96 ‰; see Vogl and Rosner [74] and <https://www.webshop.bam.de>. An overview on available boron isotope reference materials is given in Vogl et al. [22].

In 2003, eight boron isotope quality control materials were produced by the Istituto di Geoscienze e Georisorse, Pisa, Italy [84] for the IAEA.<sup>8</sup> These materials (natural waters, rocks, and one glass) have recommended  $\delta^{11}\text{B}$  values, which originate from an inter-laboratory comparison study:

- IAEA-B-1 is a surface seawater sample collected from the north of Elba Island, Ligurian Sea, Italy.
- IAEA-B-2 is a groundwater sample collected from an alluvial aquifer in the lower basin of the Cecina River, Italy. After filtration, water samples were acidified with boron-free HCl and distributed in polyethylene (PE) bottles.
- IAEA-B-3 is a groundwater sample collected from an alluvial aquifer in the upper basin of the Cecina River, Italy. After filtration, water samples were acidified with boron-free HCl and distributed in PE bottles.
- IAEA-B-4 was obtained from a composite sample of euhedral crystals of black tourmaline, near San Piero in Campo, Elba Island. Prior to distribution into PE bottles, the material was ground to a grain size ranging between 5 and 40  $\mu\text{m}$  with a few larger grains of 100  $\mu\text{m}$ , mixed, and homogenized [84].
- IAEA-B-5 is a natural basalt material, originating from the Etna Volcano eruption in 1998. The material was ground to a grain size generally smaller than 5  $\mu\text{m}$  with a few grains up to 40  $\mu\text{m}$ , mixed, and homogenized [84].
- IAEA-B-6 was derived from obsidian collected on the Lipari Island. Homogenization of the material was obtained by alkali fusion [84].
- IAEA-B-7 is a marine limestone collected at Maiella (Abruzzo). The material was ground to a grain size smaller than 5  $\mu\text{m}$  and homogenized [84].
- IAEA-B-8 is a natural clay material collected from a deposit near Montelupo (Tuscany). The clay was heated for three days at 120 °C to remove water, then ground to a grain size smaller than 5  $\mu\text{m}$ , and homogenized [84].

For NIST SRM 610/612 and the natural seawaters NASS-5 and IAPSO, published  $\delta^{11}\text{B}_{\text{SRM951}}$  values are available. The latter two values are close to the global seawater mean  $\delta^{11}\text{B}_{\text{SRM951}}$  value of  $(+39.61 \pm 0.2) \text{‰}$  [85]. Plant reference materials were characterized for the first time in 2011 for their boron isotopic composition. The  $\delta^{11}\text{B}_{\text{SRM951}}$  values of  $-23.8 \text{‰}$  for cabbage (BCR-679),  $+8.3 \text{‰}$  for corn bran (NIST SRM 8433), and  $+41.1 \text{‰}$  for peach leaves point to an extreme variability of  $\delta^{11}\text{B}_{\text{SRM951}}$  values in plants.

### 3.4 Carbon

Carbon has two stable isotopes,  $^{12}\text{C}$  and  $^{13}\text{C}$ , with natural isotopic abundances of 98.9 and 1.1 %, respectively. Carbon has one long-lived radioactive isotope,  $^{14}\text{C}$ , with an isotopic abundance of  $\sim 10^{-12}$ . (Carbon-14 is constantly produced in the upper atmosphere. With a half-life of  $\sim 5700$  years, it is important for dating recent artifacts. Owing to its radioactivity, it is not considered further in this compilation.)

The  $R(^{13}\text{C}/^{12}\text{C})$  ratio, commonly abbreviated as  $^{13}\text{C}/^{12}\text{C}$ , probably is the most frequently analyzed stable isotope quantity. The corresponding primary scale (VPDB) and its history are discussed above. Today, the scale is realized through two reference materials, NBS 19 (a natural calcite [102]) and LSVEC (NIST RM 8545; lithium carbonate from natural ores [59]) with consensus  $\delta^{13}\text{C}_{\text{VPDB}}$  values of  $+1.95$  and  $-46.6 \text{‰}$ , respectively [72, 103]. The isotopic compositions differ sufficiently to encompass most naturally occurring carbon-bearing materials with the notable exception of biogenic methane, which often is depleted in  $^{13}\text{C}$  beyond that of LSVEC [104]. LSVEC lithium carbonate was prepared by H. Svec, Iowa State University [59], originally to be used as a reference material for lithium isotopic composition. The carbon isotopic composition of LSVEC happened to match that of  $\text{CH}_4$  in modern air samples. The two materials are used to apply scaling error corrections, thus allowing an improved inter-laboratory comparability of results [72, 103].

<sup>8</sup> Additional information on these materials is available at the IAEA Web site, [http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable\\_Isotopes/index.htm](http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/index.htm).

Table 5 The  $\delta^{13}\text{C}$  values of carbon isotopic reference materials.

Description	NIST RM #	Material	$\delta^{13}\text{C}_{\text{VPDB}}$	Uncertainty	References	Comment
PDB		Calcite (belemnite guard powder)	0	–	[1, 2, 86]	Scale discontinued
NBS 19	8544	Limestone	<b>+1.95 ‰<sup>a</sup></b>	none	[3, 48, 87]	Quarantined
LSVEC	8545	Lithium carbonate	–46.65 ‰	0.06 ‰	[48]	
			–46.48 ‰	0.15 ‰	[41, 71]	
			–46.53 ‰	0.12 ‰	[88]	
			–46.61 ‰	0.06 ‰	[89]	
			<b>–46.6 ‰<sup>a</sup></b>	none	[72]	
NBS 18	8543	Carbonatite	–5.04 ‰	0.06 ‰	[48]	
			–5.03 ‰	0.05 ‰	[41]	
			–5.06 ‰	0.03 ‰	[88]	
			<b>–5.01 ‰</b>	0.03 ‰	[3, 72]	
NBS 20		Solnhofen limestone	–1.08 ‰	0.06 ‰	[48]	Quarantined
			<b>–1.06 ‰</b>	0.02 ‰	[90]	
NBS 21		Graphite	–28.16 ‰	0.11 ‰	[48]	Exhausted
			–27.79 ‰		[86]	
			–28.00 ‰		[91]	
			–28.19 ‰		[92]	
			<b>–28.16 ‰</b>	0.01 ‰	[46]	
NBS 22	8539	Oil	–29.40 ‰		[91]	
			–29.73 ‰	0.09 ‰	[48]	
			–29.81 ‰		[46]	
			–29.74 ‰	0.09 ‰	[41]	
			–29.91 ‰		[93]	
			–29.99 ‰	0.05 ‰	[94]	
			<b>–30.03 ‰</b>	0.05 ‰	[72]	
NBS 23			–35.32 ‰	0.16 ‰	[48]	Discontinued
NGS1	8559	Natural gas (coal origin)	–29.0 ‰ (CH <sub>4</sub> )	0.13 ‰	[48]	Exhausted
NGS1	8559	Natural gas (coal origin)	–26.2 ‰ (C <sub>2</sub> H <sub>6</sub> )	0.35 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	–44.5 ‰ (CH <sub>4</sub> )	0.56 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	–31.7 ‰ (C <sub>2</sub> H <sub>6</sub> )	0.43 ‰	[48]	Exhausted
NGS3	8561	Natural gas (biogenic)	–72.8 ‰ (CH <sub>4</sub> )	0.21 ‰	[48]	Exhausted
CO <sub>2</sub> -Heavy	8562	Carbon dioxide	–3.76 ‰	0.03 ‰	[88]	
			<b>–3.72 ‰</b>	0.03 ‰	[72]	
CO <sub>2</sub> -Light	8563	Carbon dioxide	–41.59 ‰	0.06 ‰	[72]	
CO <sub>2</sub> (Biogenic)	8564	Carbon dioxide	–10.45 ‰	0.03 ‰	[72, 88]	
NBS 16		Carbon dioxide	–41.59 ‰	0.06 ‰	[48]	Exhausted
			<b>–41.61 ‰</b>	0.03 ‰	[90]	
NBS 17		Carbon dioxide	–4.45 ‰	0.05 ‰	[48]	Exhausted
			<b>–4.48 ‰</b>	0.02 ‰	[90]	
NARCIS II		Carbon dioxide	+1.923 ‰	0.01 ‰	[95]	
			<b>+1.923 ‰</b>	0.003 ‰	[96]	
NARCIS I		Carbon dioxide	–8.55 ‰	0.02 ‰	[95, 97]	
USGS24	8541	Graphite	–15.99 ‰	0.10 ‰	[41, 71]	
			<b>–16.05 ‰</b>	0.04 ‰	[72]	
USGS40	8573	L-glutamic acid	–26.24 ‰	0.07 ‰	[93]	
			<b>–26.39 ‰</b>	0.04 ‰	[72]	
USGS41	8574	L-glutamic acid	+37.76 ‰	0.16 ‰	[93]	
			<b>+37.63 ‰</b>	0.05 ‰	[72]	
IAEA-CO-1		Calcium carbonate	+2.48 ‰	0.03 ‰	[41, 72]	
			+2.49 ‰	0.03 ‰	[72]	
USGS42		Human hair (Tibetan)	–21.09 ‰	0.1 ‰	[50]	
USGS43		Human hair (Indian)	–21.28 ‰	0.1 ‰	[50]	
IAEA-CH-3		Cellulose	–24.72 ‰	0.04 ‰	[72]	
IAEA-CH-6	8542	Sucrose	–10.47 ‰	0.13 ‰	[48]	
			–10.43 ‰	0.13 ‰	[41]	



(Table 5 Continued)

Description	NIST RM #	Material	$\delta^{13}\text{C}_{\text{VPDB}}$	Uncertainty	References	Comment
IAEA-CH-7	8540	Polyethylene foil	-10.45 ‰	0.03 ‰	[72]	
			-31.77 ‰	0.08 ‰	[48]	
			-31.83 ‰	0.11 ‰	[41]	
			-32.15 ‰	0.05 ‰	[72]	
IAEA-CO-8		Carbonatite	-5.75 ‰	0.06 ‰	[41, 71]	
			-5.76 ‰	0.03 ‰	[72]	
IAEA-CO-9		Barium carbonate	-47.14 ‰	0.15 ‰	[88]	
			-47.12 ‰	0.15 ‰	[41, 71]	
			-47.32 ‰	0.05 ‰	[72]	
IAEA-600		Caffeine	-27.77 ‰	0.04 ‰	[72]	
IAEA-601		Benzoic acid	-28.81 ‰	0.04 ‰	[72]	
IAEA-602		Benzoic acid	-28.85 ‰	0.04 ‰	[72]	
IAEA-303A <sup>b</sup>		Sodium bicarbonate	[+91, +96] ‰	n/a	[98, 99]	95 % confidence interval
IAEA-303B <sup>b</sup>		Sodium bicarbonate	[+460, +472] ‰	n/a	[98, 99]	95 % confidence interval
IAEA-309A		UL-D-glucose	+93.9 ‰	1 ‰	[98, 100]	
IAEA-309B		UL-D-glucose	+535.3 ‰	5 ‰	[98, 100]	
IRMM-BCR 656		Ethanol (wine origin)	-26.91 ‰	0.07 ‰	[101]	
IRMM-BCR 657		Glucose	-10.76 ‰	0.04 ‰	[101]	
IRMM-BCR 660		Ethanol (wine origin)	-26.72 ‰	0.09 ‰	[101]	

<sup>a</sup>Exact values defining the  $\delta^{13}\text{C}_{\text{VPDB-LSVEC}}$  scale [72].

<sup>b</sup>Reference material IAEA-303 consists of two sodium bicarbonate reference materials (IAEA-303A and IAEA-303B), which were prepared by dissolving  $\text{NaH}^{13}\text{CO}_3$  in distilled water and assayed for total  $\text{CO}_2$  by acidification followed by manometric measurement. The ranges of isotopic compositions listed in the table were established on the basis of statistically valid results submitted by laboratories that had participated in an international inter-laboratory comparison organized by the IAEA Section of Nutritional and Health Related Environmental Studies [98].

When analyzing plant or plant-derived material (including mineral oil),  $\delta^{13}\text{C}_{\text{VPDB}}$  values mostly cluster between -25 and -30 ‰, arising from the commonly observed discrimination against  $^{13}\text{C}$  during (C-3) photosynthesis. NBS 21 graphite and NBS 22 oil are secondary reference materials that have been in use frequently for these organic materials, but the supply of NBS 21 is exhausted. The relatively large spread of delta values for NBS 22 [93, 94] reflects the analytical history of reference-value assignments, caused by mass-spectrometric cross-contamination effects (“ $\eta$ -effect”) [105], which before 2000 were largely overlooked and unaccounted for during reference-material-calibration measurements [88, 89, 106, 107]. Another larger source of error in past  $\delta^{13}\text{C}$  measurements has been an inconsistent correction procedure for the  $^{17}\text{O}$ -bearing  $\text{CO}_2$  isotopologue, representing about 7 % of the  $m/z$ -45 ion current [11, 86, 108–112]. For improving inter-laboratory comparability, IUPAC now recommends [11] that the Assonov [109] parameter set be used for the correction of the  $^{17}\text{O}$  contribution. The  $\delta^{13}\text{C}$ -table (Table 5) already has an impressive number of reference materials, which mainly reflects the frequency of this kind of analysis. However, with the ever-increasing relevance of chromatographic techniques, there is a growing need for new, well-calibrated reference materials amenable to and compatible with these techniques.

At the Beijing General Assembly in 2005, the Commission recommended that  $\delta^{13}\text{C}$  values of all carbon-bearing materials be measured and expressed relative to the VPDB scale. This scale is to be normalized by assigning consensus values of -46.6 ‰ to LSVEC lithium carbonate and +1.95 ‰ to NBS 19 calcium carbonate, and authors should clearly state so in their reports [113]. Authors are encouraged to report their measurement results for  $\delta^{13}\text{C}$  values of NBS 22 oil, USGS41 L-glutamic acid, IAEA-CH-6 sucrose, or other internationally distributed reference materials, as appropriate for the measurement method concerned, had they been analyzed with the author’s samples. This recommendation supersedes the recommendation made by the Commission in 1993 [56]. Full analytical data supporting this recommendation is found in Coplen et al. [72].

Authors should discontinue reporting their  $\delta^{13}\text{C}$  values relative to PDB [4]. The full recommendation appears in Wieser [113].

### 3.5 Nitrogen

Nitrogen has two stable isotopes,  $^{14}\text{N}$  and  $^{15}\text{N}$ , with natural isotopic abundances of 99.6 and 0.4 %, respectively. Most of the nitrogen on Earth is in the atmosphere as  $\text{N}_2$ , and its isotopic composition cannot be changed easily. This has earned the  $R(^{15}\text{N}/^{14}\text{N})$  ratio of  $\text{N}_2$  in air the status of the zero-delta point for the  $\delta^{15}\text{N}_{\text{AIR}}$  scale.

Atmospheric  $\text{N}_2$  is isotopically homogeneous within current analytical uncertainty, is the international measurement standard for  $\delta^{15}\text{N}$  measurements, and is assigned a  $\delta^{15}\text{N}$  value of zero by international agreement [114, 115, 117]. Intended for use mainly in medical and biological tracer studies, the IAEA distributes ammonium sulfate (IAEA-305A and IAEA-305B), urea (IAEA-310A and IAEA-310B), and ammonium sulfate enriched in  $^{15}\text{N}$  (IAEA-311) [98].

**Table 6** The  $\delta^{15}\text{N}$  values of nitrogen isotopic reference materials.

Description	NIST RM #	Material	$\delta^{15}\text{N}_{\text{AIR-N}_2}$	Uncertainty	References	Comment
Air- $\text{N}_2$		Air	0 <sup>a</sup>	None	[114, 115]	
NSVEC	8552	Nitrogen gas	-2.78 ‰		[116]	
			-2.78 ‰	0.04 ‰	[117]	
NBS 14		Nitrogen gas	-1.18 ‰		[116, 118]	
IAEA-N-1 <sup>b</sup>	8547	Ammonium sulfate	+0.43 ‰ <sup>c</sup>	0.07 ‰	[117]	
			+0.54 ‰	0.19 ‰	[41]	
IAEA-N-2	8548	Ammonium sulfate	+20.41 ‰	0.12 ‰	[117]	
			+20.34 ‰	0.47 ‰	[41]	
			+20.30 ‰		[118]	
IAEA-NO-3	8549	Potassium nitrate	+4.72 ‰	0.13 ‰	[117]	
			+4.61 ‰	0.19 ‰	[41]	
			+3 ‰	1 ‰	[118]	
USGS25	8550	Ammonium sulfate	-30.41 ‰	0.27 ‰	[117]	
			-30.2 ‰		[118]	
USGS26	8551	Ammonium sulfate	+53.75 ‰	0.24 ‰	[117]	
			+53.6 ‰		[118]	
USGS32	8558	Potassium nitrate	+179.9 ‰		[118]	
			+180 ‰ <sup>c</sup>	none	[117]	
USGS34	8568	Potassium nitrate	-1.8 ‰	0.1 ‰	[119]	
USGS35	8569	Sodium nitrate	+2.7 ‰	0.1 ‰	[119]	
USGS40	8573	L-glutamic acid	-4.52 ‰	0.06 ‰	[93]	
USGS41	8574	L-glutamic acid	+47.57 ‰	0.1 ‰	[93]	
USGS42		Human hair (Tibetan)	+8.05 ‰	0.1 ‰	[50]	
USGS43		Human hair (Indian)	+8.44 ‰	0.1 ‰	[50]	
IAEA-600		Caffeine	+0.91 ‰	0.09 ‰	[120]	
IAEA-305A		Ammonium sulfate	+39.79 ‰	1.09 ‰	[98]	
IAEA-305B		Ammonium sulfate	+375.3 ‰	5.60 ‰	[98]	
IAEA-310A		Urea	+47.24 ‰	3.00 ‰	[98]	
IAEA-310B		Urea	+244.63 ‰	1.73 ‰	[98]	
IAEA-311		Ammonium sulfate	+2.05 ‰ <sup>c</sup>	0.04 ‰ <sup>d</sup>	[98]	

<sup>a</sup>Primary reference defining  $\delta^{15}\text{N}_{\text{AIR-N}_2}$ -scale origin.

<sup>b</sup>IAEA-N-1 is recommended as a scale anchor for samples that need combustion as a means of sample preparation. Air- $\text{N}_2$  is difficult to produce free from Ar, which can interfere with isotopic analysis [114].

<sup>c</sup>Interim consensus values used for scale normalization.

<sup>d</sup>Value is  $^{15}\text{N}$  fraction.

To eliminate possible confusion in the reporting of the nitrogen isotope-amount ratio,  $n(^{14}\text{N})/n(^{15}\text{N})$ , the Commission recommended in 1991 at the 36<sup>th</sup> General Assembly in Hamburg that the value 272 be employed for the  $n(^{14}\text{N})/n(^{15}\text{N})$  value of  $\text{N}_2$  in air for calculating  $n(^{14}\text{N})/n(^{15}\text{N})$  values. Such quantities are atom fractions or stable isotopic abundance fractions. This recommendation derives from the fact that the Commission's 1983 Table of Isotopic Compositions rounds the originally reported Junk and Svec [121]  $n(^{14}\text{N})/n(^{15}\text{N})$  value of  $272.0 \pm 0.3$  in atmospheric nitrogen to  $(99.634 \pm 0.001)/(0.366 \pm 0.001)$ , which is  $272.22 \pm 0.75$ . The difference between 272 and 272.22 corresponds to a  $\delta^{15}\text{N}$  difference of 0.8 ‰, which is about 10 times the measurement precision of many stable isotope laboratories. When converting  $\delta^{15}\text{N}_{\text{AIR}}$  values to stable isotope-amount ratios, some authors use 272 and some use 272.22. The Commission recommends that 272 always be used in this conversion. The full recommendation appears in Coplen et al. [122].

### 3.6 Oxygen

Oxygen has three stable isotopes,  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ , with isotopic abundances of 99.76, 0.04, and 0.20 ‰, respectively, in naturally occurring terrestrial material. The ratio  $R(^{18}\text{O}/^{16}\text{O})$  is the most commonly measured isotope ratio. The choice of an oxygen-isotope scale depends on the substances measured. Three concurrent delta scales are in use: one for water ( $\delta^{18}\text{O}_{\text{VSMOW}}$ ), one for carbonates ( $\delta^{18}\text{O}_{\text{VPDB}}$ ), and one for  $\text{O}_2$  gas ( $\delta^{18}\text{O}_{\text{air-O}_2}$ ). Measurements of the respective materials can best be made using the appropriate reference material. The relations of the scales are given in the tables; however, they are not fixed permanently. Rather, with new studies or technological advances, these relations might be refined in the future. Nevertheless, the VSMOW and VPDB scales commonly are related for sample  $x$  by the quantity equation [32]

$$\delta^{18}\text{O}_{x/\text{VPDB}} = 0.97001 \delta^{18}\text{O}_{x/\text{VSMOW}} - 29.99 \text{ ‰}$$

One of the problems with barium sulfate isotopic reference materials is that they may contain inter-crystalline water, trapped during precipitation of barium sulfate. For example, Hannon et al. [16] report that heating IAEA-SO-6 barium sulfate to 600 °C reduces the yield of oxygen from  $105.0 \pm 1.2$  to  $100.0 \pm 1.0$  ‰, and the  $\delta^{18}\text{O}$  value increases from  $-11.34 \pm 0.10$  to  $-10.81 \pm 0.08$  ‰. This increase in  $\delta^{18}\text{O}$  with heating is consistent with removal of water with a  $\delta^{18}\text{O}$  value of approximately  $-19$  ‰ relative to VSMOW.

In addition to  $\delta^{18}\text{O}$ , the  $R(^{17}\text{O}/^{16}\text{O})$  ratio, or rather its deviation from the statistical, purely mass-dependent fractionation, has garnered considerable interest. For clarity, a separate table for  $\delta^{17}\text{O}$  reference materials is provided.

At the 37<sup>th</sup> IUPAC General Assembly in 1993 in Lisbon, the Commission recommended guidelines for  $\delta^{18}\text{O}$  measurements.

#### 3.6.1 Water

Relative  $N(^{18}\text{O})/N(^{16}\text{O})$  values ( $\delta^{18}\text{O}$ ) of water should be expressed relative to VSMOW water ( $\delta^{18}\text{O} = 0$ ) on a scale normalized such that the  $\delta^{18}\text{O}$  of SLAP water is  $-55.5$  ‰ exactly and so stated in the author's report.

#### 3.6.2 Carbonate

Relative  $N(^{18}\text{O})/N(^{16}\text{O})$  values ( $\delta^{18}\text{O}$ ) of carbonate should be expressed on a scale normalized such that the  $\delta^{18}\text{O}$  of SLAP reference water is  $-55.5$  ‰ exactly relative to VSMOW water, and so stated in author's report. The measured value should be expressed either relative to VPDB on a scale such that the  $\delta^{18}\text{O}$  of NBS 19 calcite is  $-2.2$  ‰ exactly, stating the value of the oxygen isotopic fractionation factor used to calculate the  $\delta^{18}\text{O}$  of the carbonate sample and NBS 19 if they are not identical, or relative to VSMOW water ( $\delta^{18}\text{O} = 0$ ),

Table 7 The  $\delta^{18}\text{O}$  values of oxygen isotopic reference materials.

Description	NIST RM #	Material	$\delta^{18}\text{O}_{\text{VSMOW}}$	Uncertainty	References	$\delta^{18}\text{O}_{\text{VPDB}}$	Uncertainty	References	Comment
VSMOW	8535	Water	0 <sup>a</sup>	None	[34]				Primary VSMOW reference (quarantined)
SLAP	8537	Water	$-55.5\text{‰}$ <sup>a</sup>	None	[34]				Primary VSMOW reference (quarantined)
NBS 19	8544	Limestone	$+28.65\text{‰}$		[88] <sup>c</sup>		$-2.19\text{‰}$ $-2.2\text{‰}$ <sup>a</sup>	[123] [87]	Primary VPDB reference (quarantined)
NBS 18	8543	Carbonatite	$+7.20\text{‰}$ $+7.20\text{‰}$	$0.03\text{‰}$	[123] [88] <sup>c</sup>		$0.03\text{‰}$ $0.22\text{‰}$ $0.17\text{‰}$ $-22.90\text{‰}$	[123] [88] [40, 124] [125]	(1) in discussion for 2 <sup>nd</sup> $^{18}\text{O}$ anchor (2) variability on grain size level [125]
Air-O <sub>2</sub>		Air	$+23.88\text{‰}$ <b><math>+23.88\text{‰}</math></b>	$0.3\text{‰}$ $0.02\text{‰}$	[32, 126] [127]				$\delta^{18}\text{O}_{\text{Air-O}_2} = 0^b$
PDB		Calcite (belemnite guard powder)						[1, 2, 86]	PDB scale discontinued [4]
SMOW		n/a	$\sim 0$	–	[39]				SMOW scale discontinued [4]
VSMOW2		Water	0	$0.02\text{‰}$	[40, 128]				
SLAP2		Water	$-55.5\text{‰}$	$0.02\text{‰}$	[40, 128]				
GISP	8536	Water	<b><math>-24.78\text{‰}</math></b>	$0.08\text{‰}$	[41]				
GISP2		Water	$-33.43\text{‰}$	$0.02\text{‰}$	IAEA				Not released yet
NBS 1		Water	<b><math>-7.91\text{‰}</math></b>	$0.04\text{‰}$	[123]				Discontinued
NBS 1a		Water	$-7.94\text{‰}$ <b><math>-24.36\text{‰}</math></b>	$0.03\text{‰}$	[39] [123]				Discontinued
USGS45		Water	$-2.24\text{‰}$	$0.01\text{‰}$	[42]				
USGS46		Water	$-29.80\text{‰}$	$0.02\text{‰}$	[43]				
USGS47		Water	$-19.80\text{‰}$	$0.02\text{‰}$	[44]				
USGS48		Water	$-2.22\text{‰}$	$0.01\text{‰}$	[45]				
IAEA-304A		Water	$+249.2\text{‰}$ $254.2\text{‰}$	n/a	[98, 99]				95 % confidence interval; exhausted
IAEA-304B		Water	$+498.9\text{‰}$ $506.1\text{‰}$	n/a	[98, 99]				95 % confidence interval; exhausted
IRMM BCR-658		Water-ethanol	$-7.19\text{‰}$	$0.04\text{‰}$	[101]				
IRMM BCR-659		Water-ethanol	$-7.18\text{‰}$	$0.02\text{‰}$	[101]				
NBS 20		Solnhofen limestone	$+26.64\text{‰}$	$0.02\text{‰}$	[90, 123]		$-4.14\text{‰}$	[90]	Discontinued
LSVEC	8545	Lithium carbonate	$+3.69\text{‰}$		[88] <sup>f</sup>		$-26.44\text{‰}$	[88]	Not recommended as a reference for $\delta^{18}\text{O}$ (material too fine, O-exchange with moisture)
IAEA-CO-1		Calcite					$-2.44\text{‰}$	[41, 71]	Exhausted

(Table 7 Continued)

Description	NIST RM #	Material	$\delta^{18}\text{O}_{\text{VSMOW}}$	Uncertainty	References	$\delta^{18}\text{O}_{\text{VPDB}}$	Uncertainty	References	Comment
IAEA-CO-8		Carbonatite				-22.67 ‰	0.19 ‰	[41, 71]	
IAEA-CO-9		Barium carbonate				-15.28 ‰	0.09 ‰	[40]	
NBS 28	8546	Silica sand (optical)	+15.04 ‰		[88] <sup>c</sup>	-15.40 ‰	0.26 ‰	[88]	
NBS 30	8538	Biotite	+9.64 ‰	0.06 ‰	[123]				
NBS 127	8557	Barium sulfate	+9.58 ‰	0.09 ‰	[41]				
IAEA-SO-5		Barium sulfate	+5.24 ‰	0.24 ‰	[41]				
IAEA-SO-6		Barium sulfate	+5.1 ‰	0.06 ‰	[123]				
OGS		Barium sulfate	+9.34 ‰	0.32 ‰	[41]				
CO <sub>2</sub> -Heavy	8562	Carbon dioxide	<b>+8.59 ‰</b>	0.26 ‰	[120]				Possibly contaminated by water [16]
CO <sub>2</sub> -Light	8563	Carbon dioxide	<b>+12.13 ‰</b>	0.33 ‰	[120]				Discontinued
CO <sub>2</sub>	8564	Carbon dioxide	<b>-11.35 ‰</b>	0.31 ‰	[120]				
(Biogenic)		Carbon dioxide	<b>+9.31 ‰</b>	0.06 ‰	[123]				
NBS 16		Carbon dioxide	+11.86 ‰		[88] <sup>c</sup>		0.22 ‰	[88]	
NBS 17		Carbon dioxide	-3.64 ‰		[88] <sup>c</sup>		0.24 ‰	[88]	
NARCIS II		Carbon dioxide	+20.52 ‰		[88] <sup>c</sup>		0.2 ‰	[88]	
NARCIS I		Carbon dioxide							
USGS32	8558	Potassium nitrate	+3.89 ‰	0.01 ‰	[90, 123]		0.01 ‰	[90, 123]	Exhausted
USGS34	8568	Potassium nitrate	+21.99 ‰	0.04 ‰	[87, 121]		0.04 ‰	[90, 123]	Exhausted
USGS35	8569	Sodium nitrate	+25.7 ‰	0.2 ‰	[119]		0.06 ‰	[95, 96]	
IAEA-NO-3	8549	Potassium nitrate	<b>+25.4 ‰</b>	0.2 ‰	[120] <sup>d</sup>		0.06 ‰	[95]	
IAEA-600		Caffeine	-27.9 ‰	0.37 ‰	[119]				
IAEA-601		Benzoic acid	<b>-27.78 ‰</b>		[120]				
IAEA-602		Benzoic acid	+57.5 ‰	0.31 ‰	[119]				
USGS42		Human hair	<b>+56.81 ‰</b>	0.2 ‰	[119]				
USGS43		Human hair	+25.6 ‰	0.2 ‰	[119]				
			<b>+25.32 ‰</b>	0.29 ‰	[120]				
			<b>-3.48 ‰</b>	0.53 ‰	[120]				
			<b>+23.14 ‰</b>	0.19 ‰	[120]				
			<b>+71.28 ‰</b>	0.36 ‰	[120]				
			<b>+8.56 ‰</b>	0.1 ‰	[50]				
			<b>+14.11 ‰</b>	0.1 ‰	[50]				

<sup>a</sup>Exact values defining the  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  scale.<sup>b</sup>Defines the origin of  $\delta^{18}\text{O}_{\text{IR-02}}$  scale. A possible inconsistency may arise from the VSMOW/SLAP values measured by Barkan and Luz [127, 129].<sup>c</sup>Calculated from data in ref. [88] and the relation between VPDB and VSMOW given on page 36 of Coplen et al. [32]. See also Werner and Brand [13].<sup>d</sup>Calculated from data in refs. [119, 120].



**Table 8** The  $\delta^{17}\text{O}$  values of oxygen isotopic reference materials.

Description	NIST RM #	Material	$\delta^{17}\text{O}_{\text{VSMOW}}$	Uncertainty	References	Comment
VSMOW	8535	Water	0 <sup>a</sup>	None	[34]	Primary VSMOW reference
SLAP	8537	Water	-29.6986 ‰ <sup>a</sup>	None	[130]	Primary VSMOW reference calculated using $\lambda = 0.528$
			-29.70 ‰		[112]	
			-29.69 ‰	0.04 ‰	[112]	
			-29.69 ‰	0.13 ‰	[112, 127]	
VSMOW2		Water	0	0.03 ‰	[40, 128]	
SLAP2		Water	-29.697 ‰	0.05 ‰	[40, 128]	
			-29.6986 ‰		[130]	Calc.
GISP	8536	Water	-13.16 ‰	0.05 ‰	[130]	
IAEA-NO-3	8549	Potassium nitrate	+13.2 ‰		[119]	
USGS34	8568	Potassium nitrate	-14.8 ‰		[119]	
USGS35	8569	Sodium nitrate	+51.5 ‰		[119]	

<sup>a</sup>Exact values defining the  $\delta^{17}\text{O}_{\text{VSMOW}}$  scale. The (calculated) SLAP and SLAP2 values are based on the accepted mass-dependent fractionation for the world water pool with  $\lambda = 0.528$  [11, 130–132].

stating the values of all isotopic fractionation factors upon which the  $\delta^{18}\text{O}$  measurement depends. If the  $\delta^{18}\text{O}$  values cannot be reported on a normalized scale (perhaps because of the lack of a capability to analyze water samples), the author's measured  $\delta^{18}\text{O}$  of NBS 18 carbonatite or other internationally distributed isotopic reference material should be reported, as appropriate, had it been analyzed with the samples.

### 3.6.3 Other substances (oxygen gas, sulfate, silicate, phosphate, etc.)

Relative  $N(^{18}\text{O})/N(^{16}\text{O})$  values ( $\delta^{18}\text{O}$ ) of all other oxygen-bearing substances should be expressed relative to VSMOW water ( $\delta^{18}\text{O} = 0$ ) on a scale normalized such that the  $\delta^{18}\text{O}$  of SLAP water is -55.5 ‰ exactly relative to VSMOW water, and so stated in the author's report. The author's report should state either the values of all isotopic fractionation factors upon which a  $\delta^{18}\text{O}$  values depends, or the author's measured  $\delta^{18}\text{O}$  of NBS 28 quartz, NBS 127 barium sulfate, USGS35 sodium nitrate, or other internationally distributed reference material had it been analyzed with the samples. If the  $\delta^{18}\text{O}$  values cannot be reported on a normalized scale (perhaps because of the lack of a capability to analyze water samples), the author's measured  $\delta^{18}\text{O}$  of NBS 18 carbonatite or other internationally distributed isotopic reference material should be reported, as appropriate, had it been analyzed with the samples.

Oxygen gas may also be analyzed relative to air- $\text{O}_2$  as a reference. Such measurements often require very high precision, which cannot be maintained relative to a water sample like VSMOW [127, 129]. Rather, values are simply measured relative to  $\text{O}_2$  gas calibrated against air- $\text{O}_2$  defining the origin of the  $\delta^{18}\text{O}_{\text{air-O}_2}$  scale [133]. Authors should discontinue reporting their  $\delta^{18}\text{O}$  values relative to SMOW and PDB [4]. The full recommendation appears in Coplen et al. [56].

## 3.7 Magnesium

Magnesium is comprised of three stable isotopes,  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ , and  $^{26}\text{Mg}$ , with isotopic abundances of 79.0, 10.0, and 11.0 %, respectively, in naturally occurring terrestrial material. The  $R(^{26}\text{Mg}/^{24}\text{Mg})$  ratio is studied more frequently, owing to the larger relative mass difference. Isotopic variations in nature extend over a  $\delta^{26/24}\text{Mg}$  range of no more than 6 ‰ [137–139], making an uncertainty of 0.1 ‰ or better desirable.

NIST SRM 980 was certified by NIST in the 1960s by synthetic isotope mixtures [134, 135]. This material served for decades as an isotopic reference material for “absolute” isotope-ratio determinations and as a zero-delta material for the  $\delta^{26/24}\text{Mg}_{\text{SRM980}}$  scale. However, in 2003, SRM 980 was demonstrated to be isotopically

**Table 9** The  $\delta^{26/24}\text{Mg}$  and  $\delta^{25/24}\text{Mg}$  values of magnesium isotopic reference materials.

Description	Material	$\delta^{25/24}\text{Mg}_{\text{DSM3}}$	Uncertainty	$\delta^{26/24}\text{Mg}_{\text{DSM3}}$	Uncertainty	References	Comment
NIST SRM 980	Elemental magnesium	– <sup>a</sup>	–	– <sup>a</sup>	–	[33, 134, 135]	<sup>b</sup> See text
DSM3 <sup>b</sup>	Nitrate solution	0	(0.07 ‰) <sup>c</sup>	0	(0.12 ‰) <sup>c</sup>	[136]	
IRMM-009	Nitrate solution (from NIST SRM 980)	–	–	–	–		See text
ERM-AE637	Nitrate solution			~+2.6 ‰			Calc. <sup>d</sup>
ERM-AE638	Nitrate solution			~+2311 ‰			Calc. <sup>d</sup>
IAPSO	Seawater	–0.44 ‰	0.03 ‰	–0.93 ‰	0.08 ‰	[137]	
JCP1	Coral	–1.05 ‰	0.03 ‰	–1.99 ‰	0.06 ‰	[137]	

<sup>a</sup>NIST SRM 980 previously was recommended as the anchor for the magnesium delta scales,  $\delta^{25/24}\text{Mg}_{\text{SRM980}}$  and  $\delta^{26/24}\text{Mg}_{\text{SRM980}}$ . However, it has been found to be isotopically inhomogeneous [136]. Currently, there are no isotopically homogeneous magnesium reference materials in sufficient quantity to provide worldwide distribution for the next several years. Such a material is needed.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>No uncertainty when used as the zero-delta material.

<sup>d</sup>Calc.: Value has been calculated from certificate data and published data.

inhomogeneous by Galy et al. [136], who found heterogeneities of ~0.35 ‰ for  $\delta^{25/24}\text{Mg}$  and ~0.69 ‰ for  $\delta^{26/24}\text{Mg}$ , both expressed as  $2\sigma_{\text{mean}}$ . These heterogeneities are still within the certified uncertainties of NIST SRM 980, but they are much too large for current isotope research, which can achieve uncertainties at the 0.1 ‰ level. Galy et al. [136] proposed two new magnesium standard solutions, DSM3 and Cambridge1, with DSM3 being recommended as a new zero-delta standard for magnesium, which is what many analysts have been doing since. The drawbacks of these materials are that neither are international reference materials nor are they publicly available in sufficient quantities to satisfy global distribution needs for the next several years. As a possible solution to this dilemma, IRMM-009, being derived from NIST SRM 980, could be used successfully as the zero-delta material for the  $\delta^{25/24}\text{Mg}_{\text{SRM980}}$  and the  $\delta^{26/24}\text{Mg}_{\text{SRM980}}$  scales, thereby avoiding the known heterogeneity issues of the solid NIST SRM 980 material. Another option could be to use the IAPSO seawater standard with  $\delta^{25/24}\text{Mg} = +0.44$  ‰ as an interim reference until a replacement for DSM3 has been found. The IAPSO seawater isotopic composition is very close to the global mean seawater delta values of  $\delta^{25/24}\text{Mg} = +0.43 \pm 0.04$  ‰ and  $\delta^{26/24}\text{Mg} = +0.82 \pm 0.06$  ‰, respectively [85]. The magnesium delta scales need to be clarified in the near future.

In 2000 and 2001, together with IRMM-009, two additional isotopic reference materials were released by IRMM, ERM-AE637 (formerly IRMM-637), and ERM-AE638 (formerly IRMM-638). ERM-AE637 has an isotopic composition in the range of terrestrial materials, and ERM-AE638 is highly enriched in  $^{26}\text{Mg}$ . Both materials have been certified using NIST SRM 980 for correcting mass fractionation and/or discrimination. The delta values have been calculated from the certified ratios, which is not very precise. They are given without certified uncertainties.

### 3.8 Silicon

Silicon has three stable isotopes,  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ , and  $^{30}\text{Si}$ , with isotopic abundances of 92.2, 4.7, and 3.1 ‰, respectively, in naturally occurring terrestrial material. While being the second most abundant element on Earth, silicon isotopes have found only limited applications. This may be due to the fact that the variation in silicon isotopic composition is small ( $\delta^{30/28}\text{Si} \sim \pm 3.5$  ‰) [144], thus requiring rather high precision and limiting a wider spread of interest. In addition, preparation of a gaseous compound like  $\text{SiF}_4$  is more cumbersome than a simple oxidation step for other elements.

More recently, MC-ICP-MS with a medium mass resolution ( $m/\Delta m > 2000$ ) has been introduced as a solution to this experimental challenge [145]. Replacing the fluorination step with a  $\text{NaOH-SiO}_2$  fusion reaction,

**Table 10** The  $\delta^{30/28}\text{Si}$  and  $\delta^{29/28}\text{Si}$  values of silicon isotopic reference materials.

Description	NIST RM #	Material	$\delta^{29/28}\text{Si}_{\text{NBS28}}$	Uncertainty	$\delta^{30/28}\text{Si}_{\text{NBS28}}$	Uncertainty	References	Comment
NBS 28	8546	Silica sand (optical)	0 <sup>a</sup>	None	0 <sup>a</sup>	None	[33]	
NIST SRM 990		Elemental silicon	+0.3 ‰		+0.5 ‰		[140]	Discontinued
IRMM-017		Elemental silicon	-0.7 ‰		-1.3 ‰		[140]	
					-1.41 ‰	0.07 ‰	[141]	
IRMM-018a		Elemental silicon	0		0		[140]	
IRMM-018		Silicon dioxide (quartz)	-0.85 ‰	0.01 ‰	-1.65 ‰	0.01 ‰	[142]	
BHVO-2		Basalt			-0.30 ‰	0.04 ‰	[143]	
					-0.27 ‰	0.08 ‰	[141]	
USGS SGR-1b		Shale			+0.01 ‰	0.04 ‰	[143]	
Diatomite					+1.22 ‰	0.03 ‰	[143]	

<sup>a</sup>Exact values defining the  $\delta^{29/28}\text{Si}_{\text{NBS28}}$  and  $\delta^{30/28}\text{Si}_{\text{NBS28}}$  scales.

silicon-isotope values can now be compared between laboratories with improved uncertainty [142]. Additionally, materials covering a wider range of isotopic compositions have been investigated [141, 142].

### 3.9 Sulfur

**Table 11** The  $\delta^{34}\text{S}$  values of sulfur isotopic reference materials.

Description	NIST RM #	Material	$\delta^{34}\text{S}_{\text{VCDT}}$	Uncertainty	References	Comment
VCDT		N/A	0	None	[146]	
CDT		Troilite	0	–	[146]	CDT scale discontinued
IAEA-S-1	8554	Silver sulfide <sup>a</sup>	-0.3 ‰ <sup>b</sup>	None	[147, 148]	Primary VCDT reference
IAEA-S-2	8555	Silver sulfide <sup>a</sup>	+22.67 ‰	0.08 ‰	[140, 149]	
			<b>+22.62 ‰</b>	0.16 ‰	[150]	
IAEA-S-3		Silver sulfide <sup>a</sup>	-32.55 ‰	0.08 ‰	[140, 149]	
			<b>-32.49 ‰</b>	0.16 ‰	[150]	
IAEA-S-4 Soufre de Lacq	8553	Elemental sulfur	<b>+16.90 ‰</b>	0.12 ‰	[151]	
IAEA-SO-5		Barium sulfate	+0.15 ‰	0.06 ‰	[152]	
			<b>+0.49 ‰</b>	0.11 ‰	[140]	
			+0.51 ‰	0.15 ‰	[153]	
IAEA-SO-6		Barium sulfate	-34.12 ‰	0.12 ‰	[152]	
			<b>-34.05 ‰</b>	0.08 ‰	[140]	
			-34.05 ‰	0.12 ‰	[153]	
NBS 122		Sphalerite	<b>+0.18 ‰</b>	0.14 ‰	[48]	Discontinued, possibly non-homogeneous
NBS 123	8556	Sphalerite	<b>+17.09 ‰</b>	0.31 ‰	[41, 123]	Discontinued
			<b>+17.44 ‰</b>	0.10 ‰	[154]	
NBS 127	8557	Barium sulfate	+20.32 ‰	0.36 ‰	[41, 123]	
			+21.17 ‰	0.12 ‰	[152]	
			+21.10 ‰	–	[140]	
			<b>+21.12 ‰</b>	0.22 ‰	[153]	
USGS42		Human hair (Tibetan)	+7.84 ‰	0.25 ‰	[50]	
USGS43		Human hair (Indian)	+10.46 ‰	0.22 ‰	[50]	

<sup>a</sup>From IAEA-S1, IAEA-S2, and IAEA-S3, the reference materials IRMM 643, IRMM 644, and IRMM 645 have been produced as nitric acid solutions. These have been used to determine absolute isotope-amount ratios.

<sup>b</sup>Exact value defining the  $\delta^{34}\text{S}_{\text{VCDT}}$  scale.

Sulfur has four stable isotopes,  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ , with isotopic abundances of 95.0, 0.75, 4.2, and 0.015 %, respectively, in naturally occurring terrestrial material. Of these, the  $R(^{34}\text{S}/^{32}\text{S})$  ratio is the most common target for stable isotope determinations. Isotopic measurements are made relative to VCDT (“Vienna Cañon Diablo

Troilite”; see below) and expressed as  $\delta^{34}\text{S}_{\text{VCDT}}$  values. The traditional measurement gas is  $\text{SO}_2$  [155, 156], which is easy to generate by combustion, but also has several drawbacks.

1.  $\text{SO}_2$  does not represent the highest oxidation state.  $\text{SO}_3$  gas is also formed during oxidation, which chemically is highly reactive. It can form solid needles at lower temperatures and vanish from a reaction stream, resulting in apparent isotopic alteration. Optimization of an intermediate stage is required to ensure that sulfur is converted quantitatively to  $\text{SO}_2$ .
2.  $\text{SO}_2$  easily dissolves in water or on water-covered surfaces, forming sulfurous acid,  $\text{H}_2\text{SO}_3$ . Likewise,  $\text{SO}_3$  generates sulfuric acid,  $\text{H}_2\text{SO}_4$  under such conditions. These acids, in turn, can damage surfaces in inlet systems and in a gas source mass spectrometer.  $\text{SO}_2$  can produce other gaseous compounds, which may interfere with the sulfur isotopic analysis.
3. In mass spectrometry, the  $\text{SO}_2$  ion current on the  $m/z$ -64 signal is comprised of  $^{34}\text{S}^{16}\text{O}^{16}\text{O}^+$ ,  $^{32}\text{S}^{18}\text{O}^{16}\text{O}^+$ , and  $^{33}\text{S}^{17}\text{O}^{16}\text{O}^+$ . To extract the pure  $^{34}\text{S}$  signature, the  $m/z$ -64 ion current needs to be corrected. This requires that the sample and reference materials have identical oxygen isotopic compositions, which can be achieved by a common combustion procedure.
4. Due to the high surface activity of  $\text{SO}_2$ , measured isotopic differences between samples often are too small, and a cross-contamination (between-sample memory) is difficult to avoid even when heating all transfer lines as well as the mass spectrometer ion source.

For establishing delta values for isotopic reference materials, it has therefore become common practice to use  $\text{SF}_6$  instead of  $\text{SO}_2$ . The chemistry is difficult to master, but the mass-spectrometric measurement is facilitated by the inertness of  $\text{SF}_6$  and by the fact that fluorine has only one stable isotope [157]. Once appropriate reference values are assigned, the respective materials can be used for scaling measured isotopic distances using isotope bracketing. More recently, sulfur isotopic information has also been obtained from MC-ICP-MS measurements, with a major advantage of a significantly reduced sample size [153, 158, 159].

The Commission wanted to eliminate possible confusion in the reporting of relative sulfur isotope-amount-ratio data. Thus, in 1995 at the 38<sup>th</sup> IUPAC General Assembly in Guildford, UK, in agreement with an IAEA Consultants' Meeting, the Commission recommended that  $\delta^{34}\text{S}$  measurements of all sulfur-bearing materials be expressed relative to VCDT. The VCDT scale is defined by assigning a  $\delta^{34}\text{S}$  value of  $-0.3\text{‰}$  exactly (relative to VCDT) to the silver sulfide reference material IAEA-S-1. This recommendation derives from the determination by Beaudoin et al. [160] that the troilite from the Cañon Diablo meteorite, CDT, is isotopically inhomogeneous, having a  $\delta^{34}\text{S}$  variability of  $0.4\text{‰}$ . Reporting of  $\delta^{34}\text{S}$  measurements relative to CDT should be discontinued. The full recommendation appears in Krouse et al. [146].

### 3.10 Chlorine

**Table 12** The  $\delta^{37}\text{Cl}$  values of chlorine isotopic reference materials.

Description	Material	$\delta^{37}\text{Cl}_{\text{SMOC}}$	Uncertainty	References	Comment
SMOC	n/a	0	None		
NIST SRM 975	Sodium chloride	$+0.43\text{‰}^a$	None	[140, 161]	<sup>b</sup> Exhausted
NIST SRM975a	Sodium chloride	$+0.2\text{‰}$	(None)	[140]	
ISL-354	Sodium chloride	$+0.05\text{‰}$	$0.02\text{‰}$	[140, 161]	

<sup>a</sup>Exact value defining the  $\delta^{37}\text{Cl}_{\text{SMOC}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Chlorine has two isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , with isotopic abundances of 75.8 and 24.2 %, respectively, in naturally occurring terrestrial material. The relative mass difference is similar to that of oxygen, and the corresponding isotope effects could be large enough for routine measurements (neglecting the differences in valence states).

This is, however, only true for some special cases, in particular when isotopic fractionations between a liquid and a gas phase are involved. Most chlorine is in the world oceans, where the signature does not change by much more than 1 ‰. Hence, high precision is a requirement for studying  $\delta^{37}\text{Cl}$  signatures in natural samples. Industrially produced organic chlorine compounds exhibit a wider range of  $\delta^{37}\text{Cl}_{\text{SMOC}}$  values (–7 to +6 ‰) [162, 163]. Only recently, a set of natural, soil-organic compounds highly depleted in  $^{37}\text{Cl}$  [164, 165] has been found with  $\delta^{37}\text{Cl}_{\text{SMOC}}$  values extending to –13 ‰. Typically, these phenolic compounds arise from enzymatically catalyzed reactions with chloro-peroxidases (CPO) [164] in forest soils.

Before approximately 2002, most delta measurements of chlorine isotopes were expressed relative to seawater chloride (SMOC for Standard Mean Ocean Chloride), which was thought to be homogeneous in chlorine isotopic composition to within approximately  $\pm 0.15$  ‰ [166]. However, the  $\delta^{37}\text{Cl}$  value of seawater chloride can vary by more than 1 ‰ depending upon geographic location of specimen [33], and seawater chloride itself cannot serve as an isotopic reference material. Xiao et al. [161] measured a  $\delta^{37}\text{Cl}$  value of +0.43 ‰ for NIST SRM 975. This value has been internationally accepted as the new anchor for the SMOC scale. As a replacement material, NIST SRM 975a has been assigned a  $\delta^{37}\text{Cl}$  value of +0.2 ‰ exactly [33]. Closer to the SMOC scale origin is ISL-354 sodium chloride, which has been produced from seawater by Y. Xiao of the Qinghai Institute of Salt Lakes [161]. ISL-354 is intended to be used in addition to NIST SRM 975a as a secondary reference material. The relation between the different reference materials and their implications for the atomic weight of chlorine has recently been investigated thoroughly by Wei et al. [167].

### 3.11 Calcium

**Table 13** The  $\delta^{44/40}\text{Ca}$  and  $\delta^{44/42}\text{Ca}$  values of calcium isotopic reference materials.

Description	Material	$\delta^{44/40}\text{Ca}_{\text{SRM915a}}$	Uncertainty	$\delta^{44/42}\text{Ca}_{\text{SRM915a}}$	Uncertainty	References	Comment
NIST SRM 915a	Calcium carbonate	0 <sup>a</sup>	None	0 <sup>a</sup>	None	[33, 168]	Exhausted <sup>b</sup>
NIST SRM 915	Calcium carbonate	+0.17 ‰	0.20 ‰	+0.085 ‰	Calc.	[32]	Exhausted
IAPSO	Seawater	+1.9 ‰	0.3 ‰	+0.88 ‰	0.11 ‰	[169]	
USGS EN-1	Shell from marine organism			+0.35 ‰	0.09 ‰	[169]	

<sup>a</sup>Exact value defining the delta scale. For some studies,  $\delta^{44/42}\text{Ca}$  measurements may be more appropriate.

<sup>b</sup>The NIST Web site states that NIST SRM 915a has been superseded by NIST SRM 915b. However, this material is not identical; no  $\delta^{44/42}\text{Ca}_{\text{SRM915a}}$  values are available.

Calcium has five naturally stable isotopes,  $^{40}\text{Ca}$ ,  $^{42}\text{Ca}$ ,  $^{43}\text{Ca}$ ,  $^{44}\text{Ca}$ , and  $^{46}\text{Ca}$ , with isotopic abundances of 96.9, 0.6, 0.1, 2.1, and 0.004 %, respectively, in naturally occurring terrestrial material. It also has one very long lived radioactive isotope,  $^{48}\text{Ca}$  (half-life  $4.4 \times 10^{19}$  years [9]), with a characteristic terrestrial isotopic composition, amounting to an isotopic abundance of 0.2 %. Terrestrial isotopic variations are largest for biological systems, whereas inorganic materials exhibit only small calcium isotopic fractionations [170]. For an orca bone, Skulan et al. [171] found a  $\delta^{44/40}\text{Ca}$  value of –3.2 ‰ relative to dissolved calcium in seawater.

NIST SRM 915a is used most often as a reference for the respective isotope ratios. Calcium isotope-amount ratios  $n(^{44}\text{Ca})/n(^{40}\text{Ca})$  commonly are measured to determine  $\delta^{44/40}\text{Ca}$  values. However,  $^{40}\text{Ca}$  may be a poor choice for the denominator in this ratio because  $^{40}\text{Ca}$  is a product of  $^{40}\text{K}$  radioactive decay; thus, the mole fraction of  $^{40}\text{Ca}$  will vary with the age and the  $N(\text{K})/N(\text{Ca})$  ratio of a material [33, 170]. In addition,  $^{40}\text{Ca}$  cannot be used in (hot-plasma) MC-ICP-MS studies due to the overwhelming  $^{40}\text{Ar}$  interference. Here, analysis of  $\delta^{44/42}\text{Ca}$  at a resolution of  $m/\Delta m > 2500$  is the only choice. By multiplying with 1.9995, these data may be converted to  $\delta^{44/40}\text{Ca}$  values [168, 172]. This technique can also be used to exclude the small radiogenic contribution in  $^{40}\text{Ca}$ . The  $\delta^{44/42}\text{Ca}$  values can be measured in this manner with an uncertainty below 0.2 ‰ [169]. For comprehensive reviews, see DePaolo [170] and Boulyga (2010) [173].



### 3.12 Chromium

**Table 14** The  $\delta^{53/52}\text{Cr}$  values of chromium isotopic reference materials.

Description	Material	$\delta^{53/52}\text{Cr}_{\text{SRM979}}$	Uncertainty	References	Comment
NIST SRM 979	Chromium(III) nitrate salt	0 <sup>a</sup>	None	[33]	<sup>b</sup>
NIST SRM 3112a	Chromium(III) nitrate solution	-0.067 ‰	0.024 ‰	[174]	
IRMM-012	Chromium(III) solution	+0.023 ‰	0.013 ‰	[174]	
IRMM-625	Chromium(III) chloride solution	> +210		[175]	

<sup>a</sup>Exact value defining the  $\delta^{53/52}\text{Cr}_{\text{SRM979}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Chromium has four stable isotopes,  $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$ , and  $^{54}\text{Cr}$ , with isotopic abundances of 4.3, 83.8, 9.5, and 2.4 %, respectively, in naturally occurring terrestrial material. Only  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$  are used for  $\delta$ -value measurements;  $^{50}\text{Cr}$  and  $^{54}\text{Cr}$  suffer from interference of  $^{50}\text{V}$  and  $^{54}\text{Fe}$ . The  $R(^{53}\text{Cr}/^{52}\text{Cr})$  ratio is about 0.113 and should, in principle, be easy to measure precisely. However, considerable difficulties due to the redox chemistry of chromium can arise during sample preparation for TIMS, limiting attainable uncertainty to about 0.1 ‰.

Usually, NIST SRM 979 serves as the  $\delta^{53/52}\text{Cr}$  reference point defining the scale origin. IRMM-012 has been made from NIST SRM 979 by dissolution of the nitrate salt in nitric acid. Variations in nature of up to +6 ‰ relative to NIST SRM 979 have been observed, most notably in groundwater samples [176]. These enrichments seem to be related to chromium(VI) compound cycling. With the newer MC-ICP-MS instrumentation, operating with a mass resolution of  $m/\Delta m \sim 10\,000$ , sample preparation is improved and results can have uncertainties as low as 0.06 ‰ [177]. Reproducibility of a local laboratory reference solution has been reported to be as low as 0.024 ‰ [174]. IRMM-625 is a  $^{53}\text{Cr}$ -enriched material (atom fraction = ~95.5 %) with  $R(^{53}\text{Cr}/^{52}\text{Cr}) = 23.95$  [175].

Chromium stable isotopic distributions have been studied in a variety of fields including geochemistry [178, 179], cosmo-chemistry [180], and nutrition [181]. In almost all cases, NIST SRM 979 has been used as a reference, either as an isotopic reference material for correcting mass fractionation or as the zero-delta material for the  $\delta^{53/52}\text{Cr}$  scale.

### 3.13 Iron

**Table 15** The  $\delta^{56/54}\text{Fe}$  values of iron isotopic reference materials.

Description	Material	$\delta^{56/54}\text{Fe}_{\text{IRMM014}}$	Uncertainty	References	Comment
IRMM-014	Elemental iron	0 <sup>a</sup>	None	[33, 182]	<sup>b</sup> Exhausted
IRMM-634	Dissolved IRMM-014				<sup>c</sup>
BHVO-1	Basalt	+0.111 ‰	0.006 ‰	[183]	

<sup>a</sup>Exact value defining the  $\delta^{56/54}\text{Fe}_{\text{IRMM014}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>Candidate for replacing IRMM-014.

Iron has four stable isotopes,  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$ , and  $^{58}\text{Fe}$ , with isotopic abundances of 5.8, 91.8, 2.1, and 0.3 %, respectively, in naturally occurring terrestrial material. Isotopic variations are usually reported on the  $R(^{56}\text{Fe}/^{54}\text{Fe})$  ratio (~15.7) relative to the elemental iron reference material IRMM-014, which has been certified with synthetic isotope mixtures. IRMM-014 generally is accepted as the zero-delta reference for the  $\delta^{56/54}\text{Fe}$  scale, but stocks of this material are now exhausted, and a replacement is urgently needed. Variations of  $\delta^{56/54}\text{Fe}_{\text{IRMM014}}$  values in natural materials range from -3.0 to + 2.5 ‰. Using TIMS, isotopic measurements can be made with an uncertainty of 0.15 ‰. Using high-resolution MC-ICP-MS with  $m/\Delta m > 9000$ , routine

measurement uncertainty for  $\delta^{56/54}\text{Fe}_{\text{IRMM014}}$  of 0.1 ‰ and below has become achievable [184, 185]. With further refinement of chemical methods, this value has been further optimized, and a routine precision of 0.03 ‰ can be obtained [183].

BHVO-1 is a Hawaiian basalt reference material from the U.S. Geological Survey (USGS) with a mole fraction of iron >12 % (as  $\text{Fe}_2\text{O}_3$ , see [http://crustal.usgs.gov/geochemical\\_reference\\_standards/basaltbhvo1.html](http://crustal.usgs.gov/geochemical_reference_standards/basaltbhvo1.html)). Iron-isotope studies are carried out in a variety of fields [186, 187]; the majority of studies focus on medical [188], nutritional [189], and biological issues.

### 3.14 Nickel

**Table 16** The  $\delta^{60/58}\text{Ni}$  values of nickel isotopic reference materials.

Description	Material	$\delta^{60/58}\text{Ni}_{\text{SRM986}}$	Uncertainty	References	Comment
NIST SRM 986	Elemental nickel	0 <sup>a</sup>	None	[33, 190]	

<sup>a</sup>Exact value defining the  $\delta^{60/58}\text{Ni}_{\text{SRM986}}$  scale.

Nickel has five stable isotopes,  $^{58}\text{Ni}$ ,  $^{60}\text{Ni}$ ,  $^{61}\text{Ni}$ ,  $^{62}\text{Ni}$ , and  $^{64}\text{Ni}$ , with isotopic abundances of 68.1, 26.2, 1.1, 3.6, and 0.9 %, respectively, in naturally occurring terrestrial material. Isotopic variation among major inorganic compartments is very small, vanishing in the measurement uncertainty of 0.1–0.2 ‰ for  $\delta^{60/58}\text{Ni}_{\text{SRM986}}$  values. As a consequence, nickel has been used rarely in stable isotope studies. The majority of reports on nickel isotopes have focused on radiogenic isotope studies [191], on nutrition studies [192], and some on mass-dependent isotopic fractionation studies [193]. Recent work on methanogen biomarkers with variations in nickel isotopic composition suggests that there is more to learn from these types of experiments [194].

Whenever  $\delta^{60/58}\text{Ni}$  (sometimes also  $\delta^{62/58}\text{Ni}$  or  $\delta^{61/58}\text{Ni}$ ) values are determined, NIST SRM 986 is used as the zero-delta material. Using high-resolution MC-ICP-MS, Gall et al. [193] recently improved measurement procedures and reached a routine  $\delta^{60/58}\text{Ni}_{\text{SRM986}}$  uncertainty of 0.07 ‰ for USGS reference materials like BHVO-2 (basalt). For a synthetic (pure) nickel-oxide powder, long-term precision (observed over one year) was improved by a factor of two (0.034 ‰), showing the role of unresolved interfering components on natural samples like BHVO-2.

### 3.15 Copper

**Table 17** The  $\delta^{65}\text{Cu}$  values of copper isotopic reference materials.

Description	Material	$\delta^{65}\text{Cu}_{\text{SRM976}}$	Uncertainty	References	Comment
NIST SRM 976	Elemental copper	0 <sup>a</sup>	None	[33]	Exhausted <sup>b</sup>
ERM-AE633	Copper nitrate solution	-0.01 ‰	0.054 ‰	[195, 196]	
ERM-AE647	Copper nitrate solution	-0.21 ‰	0.054 ‰	[195, 197]	

<sup>a</sup>Exact value defining the  $\delta^{65}\text{Cu}_{\text{SRM976}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Copper has two stable isotopes,  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , with isotopic abundances of 69.2 and 30.8 %, respectively, in naturally occurring terrestrial material. Isotopic variations are measured relative to NIST SRM 976 and reported as  $\delta^{65}\text{Cu}_{\text{SRM976}}$  values. Natural samples cover a range of roughly 16 ‰ with the most positive values found in carbonates and the most negative values in copper chlorides [32]. The preferred mass-spectrometric technique today is MC-ICP-MS at a medium mass resolution, resulting in a routine analytical uncertainty

of ~0.05 ‰ [198]. Most studies focus on geochemical topics [199] or, in special cases, on financially driven topics, such as the provenance of minerals [200].

Nearly all studies use NIST SRM 976 as the zero-delta material for the  $\delta^{65}\text{Cu}$ -scale; only in laser ablation techniques has NIST SRM 610 been used as a reference [200]. Regrettably, the supply of NIST SRM 976 is exhausted. However, this material may still be in use at some institutions. Several units of NIST SRM 976 have been dissolved by IRMM and are now offered as ERM-AE633. ERM-AE47 has been prepared by dissolving the primary material (BAM-Y001) from the BAM Federal Institute for Materials Research and Testing, which is certified for its purity. For future studies, it is recommended that both ERM-AE633 and ERM-AE647 be used in order to assign values on the  $\delta^{65}\text{Cu}_{\text{SRM976}}$  scale using the values given in Table 17.

### 3.16 Zinc

**Table 18** The  $\delta^{66/64}\text{Zn}$  and  $\delta^{68/64}\text{Zn}$  values of zinc isotopic reference materials.

Description	Material	$\delta^{68/64}\text{Zn}_{\text{IRMM-3702}}$	Uncertainty	$\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$	Uncertainty	References	Comment
IRMM-3702	Zinc solution	0 <sup>a</sup>	–	0 <sup>a</sup>	None	[201]	<sup>b</sup>
IRMM-651	Zinc solution	(–23.77 ‰)	0.52 ‰	(–12.06 ‰)	0.75 ‰	[201]	Calc. <sup>c</sup>
IM-1009	Zinc solution	(–0.91 ‰)	0.57 ‰	(–0.43 ‰)	0.75 ‰	[201]	Calc. <sup>c</sup>
JMC Lyon	Zinc metal			–0.29 ‰	0.05 ‰	[195]	Exhausted
BHVO-2	Basalt			+0.19 ‰	0.13 ‰	[195]	

<sup>a</sup>Exact values defining the  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  scales.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>Calc.: Value has been calculated from certificate data and published data.

Zinc has five stable isotopes,  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$ , and  $^{70}\text{Zn}$ , with isotopic abundances of 49.2, 27.7, 4.0, 18.4, and 0.6 %, respectively, in naturally occurring terrestrial material. Both  $R(^{68}\text{Zn}/^{64}\text{Zn})$  and  $R(^{66}\text{Zn}/^{64}\text{Zn})$  ratios routinely are used in stable isotope studies.

The natural variation of zinc isotopes has been investigated in geochemical, biological, and environmental research projects [202]. Isotopic variations in natural samples are rather small, exhibiting a range of only ~1 ‰ for  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  measurements, and because of this, the measurement precision must be very high. The first Zn-isotope studies were performed by Maréchal et al. in 1999 [198] on an early MC-ICP-MS with a mass resolution of  $m/\Delta m \sim 500$ , enabling an uncertainty of 0.05 ‰ for  $\delta^{66/64}\text{Zn}$  measurements. The authors used an in-house zinc metal (JMC 3-0749, “JMC Lyon”) from Johnson and Matthey as their first reference material. This material is now exhausted. Since 2006, the isotopic reference material IRMM-3702 has been available [201]. It should be used as the zero-delta anchor for both the  $\delta^{66/64}\text{Zn}$  and  $\delta^{68/64}\text{Zn}$  scales. In order to establish a firm bridge, a thorough re-evaluation of the isotopic ratios of the JMC material relative to IRMM-3702 has been made recently by Moeller et al. [195], establishing a  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  value of –0.29 ‰ for JMC Lyon. IRMM-651 and IM-1009 are alternative reference materials. The  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  and  $\delta^{68/64}\text{Zn}_{\text{IRMM-3702}}$  values in Table 18 are calculated from the certified isotopic abundance ratios [201].

### 3.17 Gallium

Gallium has two stable isotopes,  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$ , with isotopic abundances of 60.1 and 39.9 %, respectively, in naturally occurring terrestrial material. The standard reference material, NIST SRM 994, has been characterized using TIMS by Machlan et al. in 1986 [203, 204]. According to these authors, the  $R(^{71}\text{Ga}/^{69}\text{Ga})$  ratio is  $1.50676 \pm 0.00039$ . Gallium isotopes have been used primarily for correcting mass bias effects in ICP-MS [25, 27, 205]. NIST SRM 994 is suggested as the zero-delta material.

**Table 19** The  $\delta^{71/69}\text{Ga}$  values of gallium isotopic reference materials.

Description	Material	$\delta^{71/69}\text{Ga}_{\text{SRM994}}$	Uncertainty	References	Comment
NIST SRM 994	Elemental gallium	0 <sup>a</sup>	None	[203]	<sup>b</sup>

<sup>a</sup>Exact value defining the  $\delta^{71/69}\text{Ga}_{\text{SRM994}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

### 3.18 Germanium

Germanium has five stable isotopes,  $^{70}\text{Ge}$ ,  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$ , and  $^{76}\text{Ge}$ , with isotopic abundances of 20.6, 27.5, 7.8, 36.5, and 7.7 %, respectively, in naturally occurring terrestrial material. Stable isotope-ratio measurements using MC-ICP-MS have recently found a wider interest [206, 208–211]. While all isotopes can be used for stable isotope studies, subtle isotopic variations require an uncertainty of better than 0.1 ‰ using the  $R(^{74}\text{Ge}/^{70}\text{Ge})$  ratio; both isotopes have a relatively high abundance, and they exhibit the largest atomic mass difference. In naturally occurring terrestrial materials, the corresponding  $\delta^{74/70}\text{Ge}$  values cover an interval between  $-5$  and  $+5$  [206, 207] relative to NIST SRM 3120a, which has been proposed as the zero-delta reference by Escoube et al. [206]. The most negative  $\delta^{74/70}\text{Ge}_{\text{SRM3120a}}$  values are found in natural germanium sulfide materials [206].

**Table 20** The  $\delta^{74/70}\text{Ge}$  values of gallium isotopic reference materials.

Description	Material	$\delta^{74/70}\text{Ge}_{\text{SRM3120a}}$	Uncertainty	References	Comment
NIST SRM3120a	Elemental germanium	0 <sup>a</sup>	None	[206]	<u>Spectrometry standard</u>
BHVO-1	Basalt	+0.55 ‰	0.15 ‰		
BHVO-2	Basalt	+0.51 ‰	0.10 ‰		
–	Seawater	$\sim +2.5$ ‰	–	[206]	From Fig. 3 in [206]
–	BSE (bulk silicate Earth)	+0.59 ‰	0.18 ‰	[206]	
Ge-Spex	Solution	$-0.70$ ‰	0.06 ‰	[207]	
CLB-1	USGS coal	+1.24 ‰	0.101 ‰	[207]	

<sup>a</sup>Exact value defining the  $\delta^{74/70}\text{Ge}_{\text{SRM3120a}}$  scale; other isotope ratios are also in use.

### 3.19 Selenium

Selenium has six stable isotopes,  $^{74}\text{Se}$ ,  $^{76}\text{Se}$ ,  $^{77}\text{Se}$ ,  $^{78}\text{Se}$ ,  $^{80}\text{Se}$ , and  $^{82}\text{Se}$ , with isotopic abundances of 0.9, 9.4, 7.6, 23.8, 49.6, and 8.7 %, respectively, in naturally occurring terrestrial material. Measurements of selenium-isotope ratios began in 1989 by Wachsmann and Heumann using negative TIMS [214, 215].

Natural variations are now best measured by MC-ICP-MS using the  $^{82}\text{Se}/^{76}\text{Se}$  ratio, which exhibits a natural  $\delta^{82/76}\text{Se}$  range of almost 15 ‰ [213]. The NIST SRM 3149 reference solution (10 mg/g Se) has been proposed as the zero-delta material [212, 213, 216–218].

**Table 21** The  $\delta^{82/76}\text{Se}$  values of selenium isotopic reference materials.

Description	Material	$\delta^{82/76}\text{Se}_{\text{SRM3149}}$	Uncertainty	References	comment
NIST SRM 3149	Selenium in solution	0 <sup>a</sup>	None	[212, 213]	<sup>b</sup>

<sup>a</sup>Exact value defining the  $\delta^{82/76}\text{Se}_{\text{SRM3149}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

### 3.20 Bromine

**Table 22** The  $\delta^{81}\text{Br}$  values of bromine isotopic reference materials.

Description	Material	$\delta^{81}\text{Br}_{\text{SMOB}}$	Uncertainty	References	Comment
SMOB	n/a	0 <sup>a</sup>		[219]	
NIST SRM 977	Sodium bromide	-0.64 ‰	0.06 ‰	[220]	<sup>b</sup>

<sup>a</sup>Exact value defining the  $\delta^{81}\text{Br}_{\text{SMOB}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Bromine has two stable isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , with isotopic abundances of 50.7 and 49.3 %, respectively, in naturally occurring terrestrial material. Measurements of bromine-isotope ratios began by 1920, and since this time a variety of techniques have been developed including negative ion TIMS, positive ion TIMS, IRMS, and MC-ICP-MS [219, 221, 222]. Most investigations focus on volatile organic compounds. Standard Mean Ocean Bromine (SMOB) has been proposed as an international reference material for  $\delta^{81}\text{Br}$  measurements because variations in bromine isotopic composition of seawater bromide were not discernible [219]. Sample preparation usually involves precipitation with  $\text{Ag}^+$  solutions, followed by conversion of bromine to methyl bromide, which is measured directly using gas IRMS. As an alternative, (GC-)MC-ICP-MS has also been used for analyzing bromine isotopes [222–224]. The range of terrestrial  $\delta^{81}\text{Br}_{\text{SMOB}}$  values is not large (–0.8 to +3.3 ‰), with the largest variations found in oil-field formation waters [219, 225]. (Industrially produced brominated organic compounds can have a much larger range with  $\delta^{81}\text{Br}_{\text{SMOB}}$  values as low as –4.3 ‰ [226]). The measurement uncertainty, therefore, is critical; values of 0.06 ‰ have been achieved for seawater samples [220, 227]. A review of the techniques has been compiled recently by Cincinelli et al. [228].

SMOB itself is not available as an isotopic reference material. Instead, NIST SRM 977 could be used for anchoring the  $\delta^{81}\text{Br}_{\text{SMOB}}$  scale, using an assigned  $\delta^{81}\text{Br}_{\text{SMOB}}$  value of –0.64 ‰ for NIST SRM 977 [220]. This will become necessary as instrumentation improves and authors report variations in bromine isotopic composition of seawater bromide with geographic location.

### 3.21 Rubidium

**Table 23** The  $\delta^{87/85}\text{Rb}$  values of rubidium isotopic reference materials.

Description	Material	$\delta^{87/85}\text{Rb}_{\text{SRM984}}$	Uncertainty	References	Comment
NIST SRM 984	Rubidium chloride	0 <sup>a</sup>	None	[229]	<sup>b</sup>
IRMM-619	Rubidium nitrate solution	0	1.0 ‰	[230]	

<sup>a</sup>Exact value defining the  $\delta^{87/85}\text{Rb}_{\text{SRM984}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Rubidium has one stable isotope,  $^{85}\text{Rb}$ , accounting for 72.2 % of the terrestrial isotopic abundance, and it has one very long-lived radioactive isotope,  $^{87}\text{Rb}$ , adding to the terrestrial isotopic composition with an abundance of 27.8 %. The half-life of  $^{87}\text{Rb}$  is  $\sim 5 \times 10^{10}$  years. In both terrestrial materials and chondrites,  $\delta^{87/85}\text{Rb}$  values usually do not vary by more than 1–2 ‰, indicating a very homogenous mixture of these isotopes throughout the solar system [229, 231]. Owing to this isotopic invariability, changes in the  $R(^{87}\text{Rb}/^{85}\text{Rb})$  ratio have only rarely been studied and expressed using the delta notation. Using MC-ICP-MS, materials enriched in  $^{87}\text{Rb}$  with  $\delta^{87/85}\text{Rb}_{\text{SRM984}} > 14$  ‰ can be analyzed with an uncertainty of 0.2 ‰ or better. Owing to its radioactivity,  $^{87}\text{Rb}$  is assessed by measuring  $R(^{85}\text{Rb}/^{87}\text{Rb})$  together with  $R(^{87}\text{Sr}/^{86}\text{Sr})$  ratio in order to determine the radiogenic  $^{87}\text{Sr}$  abundance in rocks for age determination. IRMM-619 is a solution of 0.5  $\mu\text{mol}$  rubidium dissolved in a 4-mL acid solution, and it has a certified  $R(^{85}\text{Rb}/^{87}\text{Rb})$  ratio of 2.5930(20), reflecting that of terrestrial materials.



### 3.22 Strontium

**Table 24** The  $\delta^{88/86}\text{Sr}$  and  $\delta^{87/86}\text{Sr}$  values of strontium isotopic reference materials.

Description	Material	$\delta^{88/86}\text{Sr}_{\text{SRM987}}$	Uncertainty	References	$\delta^{87/86}\text{Sr}_{\text{SRM987}}$	Uncertainty	References	Comment
NIST SRM 987	Strontium carbonate	0 <sup>a</sup>	None	[232, 233]	0 <sup>a</sup>	None	[232, 233]	<sup>b</sup>
OSIL IAPSO	Seawater	+0.381 ‰	0.010 ‰	[234]	+0.177 ‰	0.021 ‰	[237]	
		+0.350 ‰	0.100 ‰	[235]				
		<b>+0.386 ‰</b>	0.005 ‰	[236]				
		+0.370 ‰	0.026 ‰	[237]				
NRC TORT-3	Lobster hepato pancreas	+0.454 ‰	0.030 ‰	[238]	-1.363 ‰	0.036 ‰	[238]	
NRC Dolt-4	Dogfish liver	+0.207 ‰	0.012 ‰	[239]	-1.377 ‰	0.018 ‰	[239]	
JB-3	Basalt	+0.31 ‰	0.02 ‰	[240]				
BHVO-2	Basalt	+0.25 ‰	0.02 ‰	[240]				
		+0.24 ‰	0.24 ‰	[241]				
BCR-2	Basalt	+0.22 ‰	0.02 ‰	[240]				
		+0.24 ‰	0.09 ‰	[241]				
W-2	Diabase	+0.24 ‰	0.03 ‰	[240]				
		+0.25 ‰	0.12 ‰	[242]				
MRG-1	Diabase	+0.25 ‰	0.01 ‰	[240]				
JA-2	Andesite	+0.19 ‰	0.02 ‰	[240]				
		+0.25 ‰	0.01 ‰					
AGV-2	Andesite	+0.28 ‰	0.01 ‰	[240]				
G-2	Granite	+0.36 ‰	0.03 ‰	[240]				
		+0.31 ‰	0.09 ‰	[241]				
		+0.35 ‰	0.11 ‰	[242]				
JG-2	Granite	-0.20 ‰	0.02 ‰	[240]				
		-0.20 ‰	0.03 ‰	[243]				
UB-N	Serpentinite	+0.54 ‰	0.03 ‰	[240]				
GBW07294	Poly-metallic nodule	+0.03 ‰	0.02 ‰	[240]				
GBW07294	Poly-metallic nodule	+0.02 ‰	0.02 ‰	[240]				
GBW07295	Poly-metallic nodule	-0.01 ‰	0.02 ‰	[240]				

<sup>a</sup>Exact value defining the  $\delta^{88/86}\text{Sr}_{\text{SRM987}}$  and  $\delta^{87/86}\text{Sr}_{\text{SRM987}}$  scales.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Strontium has four stable isotopes,  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$ , with isotopic abundances of 0.6, 9.9, 7.0, and 82.6 %, respectively, in naturally occurring terrestrial material. Best suited for stable isotope studies is the  $R(^{88}\text{Sr}/^{86}\text{Sr})$  ratio. However, the major part of strontium isotopic analysis is focused on the determination of the radiogenic  $^{87}\text{Sr}$  (see rubidium), more specifically the  $R(^{87}\text{Sr}/^{86}\text{Sr})$  ratio, commonly abbreviated as  $^{87}\text{Sr}/^{86}\text{Sr}$ , for Rb/Sr dating or studies of material origin. Stable isotopic variations of strontium are used in provenancing water [244] and food [245, 246], for studying biological migration [247] and environmental cycles [248, 249], and in archaeometry [250] and forensic science [244]. Marine calcium carbonates have been used to investigate equilibrium or kinetic isotope effects [236]. Additionally,  $\delta^{88/86}\text{Sr}_{\text{SRM}}$  values can be used as a paleo-thermometer [234] (actually studying both  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{88}\text{Sr}/^{86}\text{Sr}$  isotope pairs in order to account for the  $\delta^{88/86}\text{Sr}$  variations in natural terrestrial materials). The values found in seawater corals reflect the water temperature during coral growth with a slope of +0.033(5) ‰ per kelvin, whereas inorganic aragonite has a much smaller dependence (+0.0054(5) ‰ per kelvin) [234]. Routine measurement uncertainty for  $\delta^{88/86}\text{Sr}$  on a MC-ICP-MS is ~0.025 ‰. NIST SRM 987 is recommended for radiogenic and stable strontium-isotope studies as the zero-delta reference.

The IAPSO seawater standard has been analyzed by several groups [234–236], reporting very similar values. The most recent  $\delta^{88/86}\text{Sr}_{\text{SRM987}}$  value of 0.386 ‰ by Krabbenhoef seems to be the most precise measurement.

Recently, the first biological reference materials were characterized for their strontium isotopic composition. DOLT-4 (dogfish liver) [239] and TORT-3 (lobster hepatopancreas) [238] were characterized for their strontium isotopic composition including  $\delta^{87/86}\text{Sr}_{\text{SRM987}}$  values of  $-1.377 \pm 0.018$  and  $-1.363 \pm 0.036$  ‰, respectively.

### 3.23 Molybdenum

**Table 25** The  $\delta^{98/95}\text{Mo}$  values of molybdenum isotopic reference materials.

Description	Material	$\delta^{98/95}\text{Mo}_{\text{SRM3134}}$	Uncertainty	References	Comment
NIST SRM 3134	Solution	0 <sup>a</sup>	None	[251, 252]	<u>Spectrometry standard</u>
NIST SRM 610	Solid glass	+0.06 ‰	0.09 ‰	[252]	
NIST SRM 612	Solid glass	+0.04 ‰	0.10 ‰	[252]	
OSIL IAPSO	Seawater	+2.09 ‰	0.07 ‰	[252]	
SCP Science –PlasmaCal		-0.42 ‰	0.05 ‰	[253]	
JMC 726	Pure Mo rod	-0.45 ‰	0.06 ‰	[253]	

<sup>a</sup>Exact value defining the  $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$  scale.

Molybdenum has six stable isotopes,  $^{92}\text{Mo}$ ,  $^{94}\text{Mo}$ ,  $^{95}\text{Mo}$ ,  $^{96}\text{Mo}$ ,  $^{97}\text{Mo}$ , and  $^{98}\text{Mo}$ , with isotopic abundances of 14.5, 9.2, 15.8, 16.7, 9.6, and 24.4 %, respectively, in naturally occurring terrestrial material, and it has one radioactive isotope,  $^{100}\text{Mo}$ , with a characteristic terrestrial isotopic composition having an isotopic abundance of 9.8 % [31, 251, 254]. The half-life of  $^{100}\text{Mo}$  is  $\sim 7 \times 10^{18}$  years. Of these,  $R(^{97}\text{Mo}/^{95}\text{Mo})$  and  $R(^{98}\text{Mo}/^{95}\text{Mo})$  ratios have been used primarily for studies of small isotopic variations using delta notation ( $^{92}\text{Mo}$ ,  $^{94}\text{Mo}$ , and  $^{96}\text{Mo}$  often are not analyzed because of possible isobaric interferences from residual zirconium isotopes). In accordance with mass-dependent fractionation, the largest isotope effects are observed for  $R(^{98}\text{Mo}/^{95}\text{Mo})$  ratios. The corresponding natural  $\delta^{98/95}\text{Mo}$  isotopic variations cover a range from (-1.5 to + 3) ‰ on the  $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$  scale [253, 255].

The first determinations of stable molybdenum isotopic variations were published in 2001 by Anbar et al. [256] and Siebert et al. [257]. Although both groups used different delta notations, the  $\delta^{98/95}\text{Mo}$  value used by Siebert et al. has been accepted widely since publication. Unfortunately, no internationally accepted reference material was available, and therefore each group used its own isotopic reference material. This problem has been recognized, and recently different reference materials have been analyzed relative to each other [251, 252], including the material used as the best measurement for defining the Mo atomic weight (NIST SRM 3134) [253, 254, 258]. This material, which is an atomic spectrometry standard provided by NIST, has been proposed as an anchor point for the  $\delta^{98/95}\text{Mo}$  [251]<sup>9</sup>. Mean Ocean Molybdenum (MOMo)  $\delta^{98/95}\text{Mo}$  has been measured as  $+2.09 \pm 0.07$  ‰ relative to NIST SRM 3134 [252] by analysis of five IAPSO ampoules (four from the Atlantic and one from the Mediterranean). Another value has been given in the same paper as  $+2.34$  ‰ relative to JMC-Bern, a local reference material, thus revealing a small offset between the two reference materials employed. The scales can be converted with the relation  $\delta^{98/95}\text{Mo}_{\text{SRM 3134}} = \delta^{98/95}\text{Mo}_{\text{JMC Bern}} - 0.25$  ‰ [252].

### 3.24 Silver

Silver has two stable isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , with isotopic abundances of 51.8 and 48.2 %, respectively, in naturally occurring terrestrial material. Only a few studies involving silver stable isotopes have been published. The majority of these studies focus on radiogenic  $^{107}\text{Ag}$  ( $\beta^-$  decay of  $^{107}\text{Pd}$  with a half-life 6.5 million years) in cosmological materials [260, 261], with some studies investigating isotopic fractionation of terrestrial environmental samples [259].

<sup>9</sup> According to the NIST Web page (<http://www.nist.gov/srm/>), SRM 3134 is out of stock. Hence, a replacement for the scale defining material is necessary in the near future.

**Table 26** The  $\delta^{109/107}\text{Ag}$  values of silver isotopic reference materials.

Description	Material	$\delta^{109/107}\text{Ag}_{\text{SRM978a}}$	Uncertainty	References	Comment
NIST SRM 978a	Silver nitrate	0 <sup>a</sup>	None	[259]	<sup>b</sup>

<sup>a</sup>Exact value defining the  $\delta^{109/107}\text{Ag}_{\text{SRM978a}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

The most common delta notation is  $\delta^{107/109}\text{Ag}_{\text{SRM978a}}$  with the radiogenic isotope in the numerator in order to express the variability of this isotope directly. However, we prefer and follow the general rule to put the heavier isotope in the numerator and the lighter one in the denominator so that characterizations like “heavy” or “light” can be used without confusion [7].

Using MC-ICP-MS, a  $\delta^{109/107}\text{Ag}_{\text{SRM978a}}$  measurement uncertainty of 0.05 ‰ or better (as low as 0.01 ‰, depending upon the material) can be achieved [259, 262]. This is suitable for detecting commercial products fortified with silver by identifying variations in silver isotopic composition. Most natural samples exhibit only very small deviations from the reference NIST SRM 978a.

### 3.25 Cadmium

**Table 27** The  $\delta^{114/110}\text{Cd}$  values of cadmium isotopic reference materials.

Description	Material	$\delta^{114/110}\text{Cd}_{\text{SRM3108}}$	Uncertainty	References	Comment
NIST SRM 3108	Solution	0		[263]	<u>Spectrometry standard</u>
BAM-I012	Nitrate solution	-1.305 ‰ <sup>a</sup>	None	[33, 264, 265]	<sup>b</sup>
Cd-2211	Solid <sup>c</sup>	+0.355 ‰		[266]	Not yet available

<sup>a</sup>Exact value defining the  $\delta^{114/110}\text{Cd}_{\text{SRM3108}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>The material is a solid metal but might be sold as a solution in the future.

Cadmium has seven stable isotopes,  $^{106}\text{Cd}$ ,  $^{108}\text{Cd}$ ,  $^{110}\text{Cd}$ ,  $^{111}\text{Cd}$ ,  $^{112}\text{Cd}$ ,  $^{114}\text{Cd}$ , and  $^{116}\text{Cd}$ , with isotopic abundances 1.2, 0.9, 12.5, 12.8, 24.1, 28.7, and 7.5 %, respectively, in naturally occurring terrestrial material, and it has one radioactive isotope,  $^{113}\text{Cd}$ , with a characteristic terrestrial isotopic composition having an isotopic abundance of 12.2 %. The half-life of  $^{113}\text{Cd}$  is  $8 \times 10^{15}$  years. The most commonly measured isotope ratio is  $R(^{114}\text{Cd}/^{110}\text{Cd})$  because both isotopes have abundances greater than 10 %, and there is a substantial difference in mass between the two isotopes. Variations in  $\delta^{114/110}\text{Cd}$  values of terrestrial materials range from -3.6 ‰ to +3.4 ‰ [266]. The primary technique for analyzing cadmium isotopes is by MC-ICP-MS, where a routine  $\delta^{114/110}\text{Cd}$  uncertainty of -0.4 ‰ can be achieved [267]. For the isotopic composition of reference materials in standard solutions, uncertainty values lower than 0.07 ‰ have been reported by different laboratories [268].

BAM-I012 is a primary isotopic reference material for which “absolute” isotope-amount ratios have been determined using synthetic isotope mixtures [266]. Unfortunately, the base material is isotopically fractionated relative to the mean Earth’s crust by -1.3 ‰ [264, 269]; therefore, the scientific community is searching for a new zero-delta material. In the meantime, this criterion has been achieved with NIST SRM 3108 [263]. As NIST SRM 3108 is an atomic spectrometry standard, it is suggested that BAM-I012 be assigned a  $\delta^{114/110}\text{Cd}_{\text{SRM3108}}$  value of -1.3 ‰, which effectively retains NIST SRM 3108 as the zero-delta material.

A number of additional secondary reference materials have been in use, including “Münster Cd”, “JMC Cd Mainz”, “Alfa Cd Zürich”, and “JMC Cd Münster” [263]. Most of these local laboratory materials are not available as a general resource internationally. Pritzkow et al. [266] prepared and characterized a material named Cd-2211, which they suggested as the zero-delta material, but which is not yet commercially available. On this scale, the BAM-I012 material (named Cd-I012 herein) is listed with  $\delta^{114/110}\text{Cd}_{\text{Cd-2211}} = -1.66$  ‰.

### 3.26 Rhenium

**Table 28** The  $\delta^{187/185}\text{Re}$  values of rhenium isotopic reference materials.

Description	Material	$\delta^{187/185}\text{Re}_{\text{SRM989}}$	Uncertainty	References	Comment
NIST SRM 989	Elemental rhenium	0 <sup>a</sup>	None	[270, 271]	Exhausted <sup>b</sup>
NIST SRM 3143	Rhenium solution	+0.29 ‰	0.07 ‰	[271]	
USGS SDO-1	Shale oil	+0.21 ‰	0.13 ‰	[271]	

<sup>a</sup>Exact value defining the  $\delta^{187/185}\text{Re}_{\text{SRM989}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Rhenium has one stable isotope,  $^{185}\text{Re}$ , with an isotopic abundance of 37.4 %, and it has one radioactive isotope,  $^{187}\text{Re}$ , with a characteristic terrestrial isotopic composition with an isotopic abundance of 62.6 %. The half-life of  $^{187}\text{Re}$  is  $4.16 \times 10^{10}$  years. Using MC-ICP-MS, the isotopic composition of rhenium ( $\delta^{187/185}\text{Re}_{\text{SRM989}}$ ) can be measured relative to the NIST SRM 989 elemental rhenium with an external reproducibility of 0.04 ‰ [271]. The range in natural materials of  $\delta^{187/185}\text{Re}$  values is small, extending from 0 to 0.3 ‰ [271]. Analytical complications arise from the fact that  $^{187}\text{Re}$  is long-lived, undergoing  $\beta^-$  decay with a half-life of  $4.16 \times 10^{10}$  years [9], thereby producing its isobar,  $^{187}\text{Os}$ , which must be removed quantitatively before analysis.

The majority of rhenium-isotope measurements are for rhenium-osmium chronology in geochemistry and cosmo-chemistry [272]. For these uses and other geochemical research, however, only  $R(^{187}\text{Re}/^{186}\text{Os})$  or  $R(^{187}\text{Re}/^{188}\text{Os})$  ratios are used [273]. One application in which rhenium-isotope ratios are measured is the quantification of rhenium by isotope-dilution mass spectrometry (IDMS) [274]. For the determination of the desired isotope-amount ratios (absolute or “true” isotope ratios), an isotopic reference material such as NIST SRM 989 (or SRM 3143 with  $\delta^{187/185}\text{Re}_{\text{SRM989}} = +0.29$  ‰) is helpful. Otherwise, tabulated IUPAC data for natural rhenium may be used to make corrections for mass fractionation and/or discrimination.

### 3.27 Osmium

**Table 29** The  $\delta^{187/188}\text{Os}$  and  $\delta^{186/188}\text{Os}$  values of osmium isotopic reference materials.

Description	Material	$\delta^{187/188}\text{Os}_{\text{IAG-CRM-4}}$	Uncertainty	References	Comment
IAG-CRM-4	Osmium solution	0 <sup>a</sup>	none	[275]	<sup>b</sup>

<sup>a</sup>Exact value defining the osmium delta scales. This assignment is only tentative [275].

*Please note: The delta notation is not yet in frequent use for osmium isotopes. There is a similar expression though, ( $\gamma_{\text{Os}}$ ), which could be expressed as  $\delta_{\text{Os}}/10$ . It describes the relative difference of the  $R(^{187}\text{Os}/^{188}\text{Os})$  ratios between a sample and a chondritic reference using a numeric value equation [276]. Typical  $\gamma_{\text{Os}}$  values found in terrestrial samples range from  $-30$  to  $+30$  %. It is recommended that the quantity  $\gamma_{\text{Os}}$  be replaced by the delta notation as given in this table.*

<sup>b</sup>Certificate pending; IAGeo Ltd. International Association of Geo-analysts (<http://9zdip.w4yserver.at/index.html>; last access 4/2013).

Osmium has six stable isotopes,  $^{184}\text{Os}$ ,  $^{187}\text{Os}$ ,  $^{188}\text{Os}$ ,  $^{189}\text{Os}$ ,  $^{190}\text{Os}$ , and  $^{192}\text{Os}$ , with isotopic abundances of 0.02, 2.0, 13.2, 16.1, 26.3, and 40.8 %, respectively, in naturally occurring terrestrial material, and it has one radioactive isotope,  $^{186}\text{Os}$ , with a characteristic terrestrial isotopic composition with an isotopic abundance of 1.6 %. The half-life of  $^{186}\text{Os}$  is  $2 \times 10^{15}$  years. Due to the  $\beta^-$  decay of  $^{187}\text{Re}$  to  $^{187}\text{Os}$  and the radiogenic production of  $^{186}\text{Os}$  from  $^{190}\text{Pt}$ , the most often studied isotope ratios are  $R(^{187}\text{Os}/^{188}\text{Os})$  and  $R(^{186}\text{Os}/^{188}\text{Os})$ . These are used for dating meteorites or rhenium-bearing terrestrial minerals. In addition, the  $R(^{187}\text{Os}/^{188}\text{Os})$  ratio is used primarily to obtain information on the origin of igneous rocks, the evolution of the Earth’s crust and mantle [277], mixing scenarios [278], and climate-related processes [279].

The osmium-isotope ratios of interest have been analyzed primarily using N-TIMS [276, 280–282]. With the advent of MC-ICP-MS, the corresponding  $R(^{187}\text{Os}/^{188}\text{Os})$  and  $R(^{186}\text{Os}/^{188}\text{Os})$  ratios can now be measured

with uncertainties of 0.016 and 0.017 %, respectively [283]. Ratios of the more abundant osmium isotopes,  $R(^{192}\text{Os}/^{188}\text{Os})$  and  $R(^{189}\text{Os}/^{188}\text{Os})$ , are used mainly for normalizing other ratios of interest [275]. These ratios are considered largely invariant across most terrestrial materials. A number of reference materials have been used for osmium stable isotope studies (DTM, UMD, LOSST, and DROS) [275]; however, no reliable  $\delta^{1xx/188}\text{Os}_{\text{IAG-CRM-4}}$  values, where  $xx = 84, 87, 89, 90, \text{ or } 92$ , are yet available for these materials.

### 3.28 Platinum

**Table 30** The  $\delta^{198/194}\text{Pt}$  values of platinum isotopic reference materials.

Description	Material	$\delta^{198/194}\text{Pt}_{\text{IRMM010}}$	Un-certainty	References	Comment
IRMM-010	Elemental platinum	0 <sup>a</sup>	None	[284]	<sup>b</sup>

<sup>a</sup>Exact value defining platinum-isotope-delta scale (not in frequent use).

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

Platinum has five stable isotopes,  $^{192}\text{Pt}$ ,  $^{194}\text{Pt}$ ,  $^{195}\text{Pt}$ ,  $^{196}\text{Pt}$ , and  $^{198}\text{Pt}$ , with isotopic abundances of 0.8, 32.9, 33.8, 25.2, and 7.4 %, respectively, in naturally occurring terrestrial material, and it has one radioactive isotope,  $^{190}\text{Pt}$ , with a characteristic terrestrial isotopic composition with an isotopic abundance of 0.01 %. The half-life of  $^{190}\text{Pt}$  is  $4.5 \times 10^{11}$  years.

The first use of platinum stable isotopes measured with a double spike technique on a MC-ICP-MS was published only recently [285–287]. A delta scale has been introduced as  $\mu^{198}\text{Pt}$  with an extraneous factor of  $10^6$ , which we recommend be abandoned. Instead, in order to unify terminology and avoid inconsistencies, we suggest  $\mu^{198}\text{Pt}$  to be replaced by  $\delta^{198/194}\text{Pt}_{\text{IRMM010}}$  and values be expressed in “per meg”. No further studies on platinum isotopic variation or fractionation in natural samples have been found in the recent literature (except those related to the platinum-osmium method for mineral dating). Apparently, platinum-isotope-ratio measurements have only been made in IDMS studies for quantifying platinum concentrations in biological, environmental, and geological samples [274, 288].

### 3.29 Mercury

**Table 31** The  $\delta^{202/198}\text{Hg}$  values of mercury isotopic reference materials.

Description	Other names	Material	$\delta^{202/198}\text{Hg}_{\text{NIMS1}}$	Uncertainty	References	Comment
NRC NIMS-1	(NIST SRM 3133)	Mercury solution (prepared from NIST SRM 3133)	0 <sup>a</sup>	None	[289, 290]	
NIST SRM 3133		Mercury solution	0		[290]	
NIST SRM 2225		Elemental mercury	+4.6 ‰	1.3 ‰	[289, 291, 292]	Calc. <sup>b</sup>
NIST SRM 1641d		Mercury solution	+0.03 ‰	0.10 ‰	[290, 293]	

<sup>a</sup>Exact value defining the  $\delta^{202/198}\text{Hg}_{\text{NIMS1}}$  scale.

<sup>b</sup>Calc.: Value has been calculated from certificate data and published data.

Mercury has seven stable isotopes,  $^{196}\text{Hg}$ ,  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ , and  $^{204}\text{Hg}$ , with isotopic abundances of 0.1, 10.0, 16.9, 23.1, 13.2, 29.9, and 6.9 %, respectively, in naturally occurring terrestrial material. None of the isotopes of mercury are radiogenic, and isotopic variations largely follow mass-dependent isotopic fractionation laws, with some notable exceptions. The  $R(^{202}\text{Hg}/^{198}\text{Hg})$  ratio, with a nominal value of 2.963, can be measured with the most reliable precision [289]. Natural isotopic variations [291] encompass a  $\delta^{202/198}\text{Hg}$  range of about  $\pm 4$  ‰. The most precise method for assessing stable mercury isotopic variations today is MC-ICP-MS, which has a reported routine external precision for  $\delta^{202/198}\text{Hg}$  measurements as low as 0.08 ‰ [19, 290].

Triggered by the rapid development in MC-ICP-MS, mercury-isotope studies have increased significantly within the last decade. Mercury-isotope research is carried out in many disciplines, and a major part involves investigating isotopic fractionation in the biogeochemical mercury cycle [294–297]. Within this research, even mass-independent isotopic fractionation of mercury has been observed [298–300]. Differentiation between mass-dependent and mass-independent isotopic fractionation requires higher accuracies than usual [301]. Therefore, mercury isotopic reference materials supporting measurement uncertainties in the sub-permil range are required [23].

NIMS-1 has been certified as isotopic reference material [289] and is recommended for use as an anchor for the  $\delta^{202/198}\text{Hg}$  scale. Before NIMS-1 was certified, NIST SRM 3133 was used as a mercury isotopic reference material. However, NIST SRM 3133 was prepared and certified for quantitative analysis only, not for isotopic measurements. NIMS-1 has been made from NIST SRM 3133, and it is now specifically recommended for future mercury isotopic analysis. While both materials are listed with  $\delta^{202/198}\text{Hg}_{\text{NIMS1}} = 0$  in Table 31, the exact values may still differ slightly.

### 3.30 Thallium

**Table 32** The  $\delta^{205/203}\text{Tl}$  values of thallium isotopic reference materials.

Description	Material	$\delta^{205/203}\text{Tl}_{\text{SRM997}}$	Uncertainty	References	Comment
NIST SRM 997	Elemental thallium	0 <sup>a</sup>	none	[33]	<sup>b</sup>
ERM-AE649	Thallium nitrate solution	0	0.604 ‰	[23]	Calc. <sup>c</sup>
NRC-NASS-5	Seawater	−0.5 ‰	0.1 ‰	[302]	

<sup>a</sup>Exact value defining the  $\delta^{205/203}\text{Tl}_{\text{SRM997}}$  scale.

<sup>b</sup>Isotope-amount ratio determined using synthetic isotope mixtures.

<sup>c</sup>Calc.: Value has been calculated from certificate data and published data.

Thallium has only two stable isotopes,  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$ , with isotopic abundances of 29.5 and 70.5 %, respectively, in naturally occurring terrestrial material. The corresponding  $\delta^{205/203}\text{Tl}$  values are expressed relative to NIST SRM 997 and can be determined with an uncertainty of 0.1 ‰ using MC-ICP-MS [302]. Values of  $\delta^{205/203}\text{Tl}$  in terrestrial materials cover an interval of no more than 2 ‰ [302], which is large when considering the relative mass differences.

Before the widespread use of MC-ICP-MS, the main interest in thallium-isotope studies was the search for anomalies in the  $^{205}\text{Tl}$  abundance in meteorites due to the decay of the now-extinct  $^{205}\text{Pb}$  [303]. With the advent of MC-ICP-MS, the precisions of  $R(^{205}\text{Tl}/^{203}\text{Tl})$  ratio determinations have improved such that investigations of mass-dependent thallium stable isotopic fractionation can now be carried out [304]. In these studies,  $R(^{205}\text{Tl}/^{203}\text{Tl})$  ratios have been expressed relative to NIST SRM 997. Although  $\varepsilon$  notation is still commonly employed, it is recommended that isotopic compositions be communicated as  $\delta^{205/203}\text{Tl}_{\text{SRM 997}}$  values in publications. If desired, values can be expressed in *parts per ten thousand*, using the abbreviation pptt, with explanation of the abbreviation in a footnote. More details on this topic can be found in Coplen [7].

ERM-AE649 is a thallium nitrate solution with a  $^{205}\text{Tl}$  isotope-amount fraction (isotopic abundance) of  $0.704766(89)_{k=2}$  [305] that is indistinguishable from that of NIST SRM 997, which is  $0.704765(88)_{k=2}$  [306].

### 3.31 Lead

Lead has four stable isotopes,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ , with isotopic abundances of 1.4, 24.1, 22.1, and 52.3 %, respectively, in naturally occurring terrestrial material. Only  $^{204}\text{Pb}$  is primordial; the three heavier isotopes are radiogenic.  $^{206}\text{Pb}$  is the end member of the  $^{238}\text{U}$  decay chain and  $^{207}\text{Pb}$  that of the  $^{235}\text{U}$  chain.  $^{208}\text{Pb}$  is generated from  $^{232}\text{Th}$ . The corresponding isotope-abundance variations in naturally occurring terrestrial materials



**Table 33** The  $\delta^{208/206}\text{Pb}$  values of lead isotopic reference materials.

Description	Material	$\delta^{208/206}\text{Pb}_{\text{SRM981}}$ <sup>a</sup>	Uncertainty	References	Comment
ERM-3800	Lead solution	0 <sup>b</sup>	None	[307, 308]	Available soon <sup>c</sup>
NIST SRM 981	Elemental lead			[309]	
NIST SRM 610	Lead in glass			[310]	

<sup>a</sup>This is only one of the possible lead-isotope ratios; others include  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$ , and  $^{206}\text{Pb}/^{204}\text{Pb}$ .

<sup>b</sup>Exact value defining the  $\delta^{208/206}\text{Pb}_{\text{SRM981}}$  scale.

<sup>c</sup>Material not listed yet in the 2013 IRMM catalogue

(see [http://irmm.jrc.ec.europa.eu/reference\\_materials\\_catalogue/catalogue/Documents/rm\\_catalogue.pdf](http://irmm.jrc.ec.europa.eu/reference_materials_catalogue/catalogue/Documents/rm_catalogue.pdf); last accessed June 2013).

cover a wide range, e.g., ~100 ‰ for  $\delta^{207/206}\text{Pb}$  and ~60 ‰ for  $\delta^{208/206}\text{Pb}$ . For isotopic variations generated by mass-dependent isotopic fractionation processes, the common isotope preferred in the denominator is  $^{204}\text{Pb}$  [311]. With an isotopic abundance of only 1.4 %, mass-spectrometric measurements are rather difficult and sometimes lack the necessary measurement precision. Compared to the radiogenic abundance alterations, the mass-dependent fractionation changes are small, of the order of 1 ‰ [312]. The IRMM has made an attempt to produce calibration reference materials explicitly for lead isotope- $\delta$  measurements (“ $\delta$ -iCRM”) [307] with ERM-3800 proposed as the zero-delta material. With these materials used as references in MC-ICP-MS direct comparisons, an uncertainty between 0.01 and 0.05 ‰ has been achieved [308].

Lead is one of the most frequently studied isotope systems in geochemistry (for a review, see Faure and Mensing [277]). Based on geochemical findings and archaeological applications, lead-isotope signatures have, for instance, been used to trace the origin of archeological artifacts [313–315]. The common control reference for these studies, NIST SRM 981, has been measured by many laboratories (see Weiss et al. [316] and Baker et al. [311]). The accepted  $R(^{208}\text{Pb}/^{206}\text{Pb})$  ratio for NIST SRM 981 is 2.1681(8), and that for NIST SRM 610 has been determined as 2.1694(1) [310, 311].

Only a limited number of studies have published lead-isotope variations as  $\delta$  values, e.g., the investigation of lead isotopic fractionation during smelting and refining [312]. In this study, mass-dependent isotopic fractionation was investigated, and  $\delta^{208/206}\text{Pb}$  values reported relative to NIST SRM 981 were published. Additionally, lead-isotope ratios from a number of reference materials can be found in Baker et al. [311].

### 3.32 Uranium

Natural uranium has three isotopes,  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ , having isotopic abundances of  $54 \times 10^{-6}$ , 0.7 %, and 99.3 %, respectively, in naturally occurring terrestrial material. All three are radioactive isotopes with characteristic terrestrial isotopic compositions.  $^{234}\text{U}$  is an intermediate product of the  $^{238}\text{U}$  decay chain with a half-life

**Table 34** The  $\delta^{238/235}\text{U}$  values of common uranium isotopic reference materials.

Description	Other names	Material	$\delta^{238/235}\text{U}_{\text{SRM950A}}$	Uncertainty	References	Comment
NIST SRM 950-A		Uranium oxide	0 <sup>a</sup>	none	[317, 318]	Exhausted
NBL CRM C112-A	SRM 960, CRM 145	Natural uranium solution	+0.02 ‰	0.05 ‰	[317, 318]	
NBL CRM 129-A		Uranium oxide	-1.2 ‰			Calc. <sup>b</sup>
HU-1	“Harwell uraninite”	Uranium solution			[318]	
IRMM 184		Uranium solution	-1.15 ‰		[318, 319]	
REIMEP-18a			-0.18 ‰	0.06 ‰	[320]	
					[317, 319]	
–		Seawater	-0.41 ‰	0.02 ‰	[317]	

<sup>a</sup>Exact value defining the  $\delta^{238/235}\text{U}_{\text{SRM950A}}$  scale.

<sup>b</sup>Calc.: Value has been calculated from certificate data and published data.

of about  $2.5 \times 10^5$  years. Large natural variations are seen in the isotope-amount ratio  $n(^{234}\text{U})/n(^{238}\text{U})$  due to the relative rates of release of these isotopes from minerals [317]. The half-lives of  $^{235}\text{U}$  and  $^{238}\text{U}$  of ( $7 \times 10^8$  and  $4.6 \times 10^9$ ) years, respectively, are sufficiently long to have preserved these materials since the formation of the solar system. Uranium disequilibrium dating methods are based on the uranium activity and measurement of the corresponding radiogenic products (for more information, see the reviews by Ivanovich and Harmon [321, 322]).

For stable isotopic measurements, only the isotope-number ratio  $R(^{238}\text{U}/^{235}\text{U})$ , commonly abbreviated as  $^{238}\text{U}/^{235}\text{U}$ , is of interest. Until recently, no natural variation in this ratio with a value of 137.88 had been observed. This value recently was investigated in an inter-laboratory effort with eight participants, organized by the IRMM in Geel (see Richter et al. [323]). They found a significantly lower average ratio of 137.837. Hiess et al. [324] confirmed the basic finding and published results for a large number of terrestrial minerals. They suggest that the  $^{238}\text{U}/^{235}\text{U}$  ratio be revised to 137.818(45). With new and improved instrumentation allowing for much smaller sample sizes (MC-ICP-MS),  $\delta^{238/235}\text{U}$  variations of the order of 1 ‰ have been observed in naturally occurring terrestrial materials [317]. This variation could be a result of uranium oxidation–reduction reactions and/or to a nuclear field shift which would cause preferential separation of some uranium isotopomers [318, 325]. Delta measurements are reported relative to NIST SRM 950-A, which is the zero-delta material for the  $\delta^{238/235}\text{U}_{\text{SRM950A}}$  scale [317, 318]. Uranium in sea water differs by  $-0.41(2)$  ‰ from that of SRM 950-A [317].

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