Chapter 2

TERMINOLOGY, STANDARDS AND MASS SPECTROMETRY

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Chapter 2

TERMINOLOGY, STANDARDS AND MASS SPECTROMETRY

2.1 Overview

Most of the accepted terms and symbols used in stable isotope geochemistry are precise and were developed by the earliest workers who gave the matter considerable thought. Arguably, some of the terms could be improved, and some recent workers have unilaterally coined new symbols and expressions for reasons known only to themselves. Unfortunately this practice has caused considerable confusion among new workers and more and more improper usage is finding its way into the literature and into oral presentations. In this text the terms established by the founders of our discipline will be used, both in homage to them and because these terms are, for the most part, logical and grammatically correct. In Table 2.1 a number of terms and phrases are presented that are considered to be mistakes, with the reasons why they are unacceptable, and recommended alternatives. All examples were culled from the literature. Although some of these common mistakes can be seductive in their simplicity, they should be avoided, in part to preserve the historical purity of the discipline but, most importantly, because they are indeed mistakes and not simply a matter of style.

In this chapter, the nomenclature commonly used in stable isotope geochemistry is developed, the mysterious and arcane standardization protocols and reference standards are explained and the principles of the mass spectrometer are presented.

2.2 Isotopes, Isotopologues, Isotopomers, and Mass Isotopomers

Most definitions of the word isotope include something to the extent 'one of two or more forms of an element' due to differing numbers of neutrons. Or 'one of two or more atoms having the same atomic number but different mass numbers'. However these definitions fail to describe monoisotopic elements such as fluorine. A better definition might be 'a particular form of an element defined by a specific number of neutrons' or 'a variety an element with a fixed number of neutrons". In applications to natural processes, we are obviously not concerned with monoisotopic elements, so perhaps both definitions are equally valid.

All stable isotope studies report the stable isotope composition of a particular element in a molecule or compound. For example, we measure the carbon isotope composition of CO₂ or calcite, and the hydrogen isotope composition of water. According to recommendations made in 1994 by the International Union of Pure and Applied Chemistry (IUPAC), isotopologues are molecules that differ from one another only in isotopic composition. It is therefore appropriate to talk about the different 'isotopologues' of water, but not the different 'isotopes' of water because water doesn't have isotopes – its constituent elements H and O do. Writing about 'water isotopes' may sound short and concise, but it is wrong. Just as petrologists don't talk about 'rock isotopes', so hydrologists should avoid talking about ‘water isotopes’.

Isotopologues can have the same or different masses. For example, $^{12}\text{C}^{17}\text{O}$ has the same mass as $^{13}\text{C}^{16}\text{O}$. Although they have the same mass, they are distinctly different isotopologues of carbon monoxide. The word isotopologue, when used with care, is the
appropriate term to describe molecules that are encountered in stable isotope geochemistry and will be employed frequently in this text.

**Isotopomers** (contraction of isotopic isomers) are isotopologues that differ from one another only in the positions or locations of the isotopic elements. Studies of isotopomers is common in pharmaceutical and biochemical research, where the position of atoms provides important information about metabolic processes. Isotopomers always comprise the same number of each isotope and thus **always have the same mass**. They differ from one another in the positions or locations of the isotopic elements and thus the connection to isomerism. Two different isotopic forms of acetaldehyde provide an example of isotopomers: CH$_2$DCH=O and CH$_3$CD=O. They have the same isotopic composition, but the D atom is bonded to the methyl group carbon in the first case and to the carboxyl carbon in the second. Isotopic forms of nitrous oxide (15N$_2$O and 14N$_2$NO), and ozone (16O$_2$18O and 18O$_2$16O) are among the few isotopomers studied by stable isotope geochemists (e.g., Michalski and Bhattacharya, 2009). In mass spectrometry, the expression mass isotopomer, normally an organic compound, is used to describe a family of isotopologues that **have the same mass**. Because mass isotopomers are collected simultaneously on the same collectors of a mass spectrometer, they pose a problem in isotopic analysis. The molecules 13C$_1$6O and 12C$_1$7O are mass isotopomers that each have mass 29.

### 2.2.1 'Isotope' vs. 'Isotopic'

These two words appear to be used randomly and interchangeably because the proper use of one or the other is not immediately clear. My mentor, Jim O’Neil, was confronted with this dilemma as a U.S.G.S. employee. He consulted the Technical Reports Unit at the USGS for guidance. After some research, it was decided that ‘isotope’ is used when modified and ‘isotopic’ is used as a stand-alone adjective. One therefore should write “The oxygen isotope composition of . . .” and “The isotopic composition of . . .”. In the first case, ‘oxygen’ modifies ‘isotope’ and in the second ‘isotopic’ stands alone.

### 2.3 The Delta Value

Relative differences in isotopic ratios can be determined far more precisely than absolute isotopic ratios. McKinney et al. (1950) introduced the delta ($\delta$) notation to report stable isotope data for all materials except certain extraterrestrial materials whose isotopic ratios and variations are occasionally so large that absolute ratios are used in publications (see Chapter 13). The delta value is given by

$$\delta = \left( \frac{R_x - R_{std}}{R_{std}} \right) \times 1000 \tag{2.1a}$$

---

$^1$ Some people have suggested that the ‘× 1000’ part of the definition of delta should be left out. The delta numbers would then be very small, and they would be reported in per mil (‰), percent (%) or per meg (ppm), with the actual δ value being multiplied by 1,000, 100 or 10$^6$, respectively. There is some sense to this argument, but the 50+ years of defining the delta with the ×1000 part has worked wonderfully, and as the saying goes ‘if it ain’t broke, don’t fix it’.
or equivalently
\[
\delta = \left( \frac{R_x}{R_{\text{std}}} - 1 \right) \times 1000
\]

2.1b

where \( R \) is the ratio of the abundance of the heavy to light isotope, \( x \) denotes the sample, and \( \text{std} \) is an abbreviation for standard. For the elements, hydrogen, carbon, nitrogen, oxygen, sulfur, silicon and chlorine, \( R \) is given by \( ^2\text{H}/^1\text{H} \) (or \( \text{D}/\text{H} \)), \( ^{13}\text{C}/^{12}\text{C} \), \( ^{15}\text{N}/^{14}\text{N} \), \( ^{18}\text{O}/^{16}\text{O} \) (and \( ^{17}\text{O}/^{16}\text{O} \)), \( ^{34}\text{S}/^{32}\text{S} \) (and \( ^{33}\text{S}/^{32}\text{S} \), \( ^{36}\text{S}/^{32}\text{S} \)), \( ^{30}\text{Si}/^{28}\text{Si} \) (and \( ^{29}\text{Si}/^{28}\text{Si} \)), and \( ^{37}\text{Cl}/^{35}\text{Cl} \), respectively. The notation \( ^2\text{H}/^1\text{H} \) is strictly correct for hydrogen isotope ratios (Coplen, 1994) and is used almost exclusively in the hydrological literature, but, for historical reasons, \( \text{D}/\text{H} \) is routinely used by many workers in geological studies.

Delta values are reported in per mil, or parts per thousand, and the symbol for per mil is \( \% \). A positive \( \delta \) value means that the ratio of heavy to light isotope is higher in the sample than it is in the standard, and a negative \( \delta \) value has the opposite meaning. A sample with a \( \delta^{18}\text{O} \) value of \(+19.7\% \) has an \( ^{18}\text{O}/^{16}\text{O} \) ratio that is 19.7 per mil, or 1.97 per cent, higher than that of the standard. Similarly, a negative \( \delta\text{D} \) value of \(-65.2\% \) means that the \( \text{D}/\text{H} \) ratio of the sample is 65.2 per mil or 6.52 per cent lower than that of the standard. The \( \delta \) value is computed from the intensities of ion signals measured in the

\textbf{Table 2.1. Common Mistakes in Terminology and Phraseology}

<table>
<thead>
<tr>
<th>Mistake</th>
<th>Recommended Expressions</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>referring to the symbol ( \delta ) as ‘del’</td>
<td>Since the time of the early Greeks, the name of this symbol has been and remains \textit{delta}.</td>
<td>The word \textit{del} describes either of two things in mathematics and science: an operator (( \nabla )) or the partial derivative (( \partial )).</td>
</tr>
<tr>
<td>( \delta^{13}\text{C} ) composition</td>
<td>( \delta^{13}\text{C} ) value; carbon isotope composition</td>
<td>( \delta^{13}\text{C} ) values are numbers and a \textit{composition of numbers} has no meaning.</td>
</tr>
<tr>
<td>Isotopically depleted water</td>
<td>( ^{18}\text{O} ) (or ( \text{D} )) depleted water</td>
<td>A given sample of water is neither depleted nor enriched in isotopes.</td>
</tr>
<tr>
<td>Stable water isotopes have been widely used as tracers. . .</td>
<td>Stable O and H isotope ratios in water have been used. . .</td>
<td>Only elements have isotopes. It is the H and O that has the isotopes, not ( \text{H}_2\text{O} ).</td>
</tr>
<tr>
<td>heavy (light) ( \delta^{18}\text{O} ) values</td>
<td>high (low) ( \delta^{18}\text{O} ) values</td>
<td>As numbers, ( \delta )-values can be high or low, positive or negative, but not heavy or light.</td>
</tr>
<tr>
<td>Isotopically negative</td>
<td>relatively low ( \delta ) values</td>
<td>Isotopic ratios are not negative or positive; they are lower or higher than those of the standards.</td>
</tr>
<tr>
<td>depleted ( \delta^{13}\text{C} ) value</td>
<td>low ( \delta^{13}\text{C} ) value (relative to another) isotopically heavy (light) carbonates (relatively) ( ^{18}\text{O} )-rich or ( ^{13}\text{C} )-poor carbonates</td>
<td>( \delta^{13}\text{C} ) values are numbers and, as such, they cannot be depleted or enriched. The words \textit{enrich} and \textit{deplete} are overused and much abused. These words should be reserved for describing a \textit{process} that changes the content of the heavy isotope of the element in some substance.</td>
</tr>
<tr>
<td>enriched (depleted) carbonates. enriched (depleted) compositions depleted carbon reservoir</td>
<td>low ( \delta^{13}\text{C} ) value (relative to another) isotopically heavy (light) carbonates reservoir of (isotopically) light carbon</td>
<td></td>
</tr>
<tr>
<td>oxygen isotopes in chert; inferred from carbon isotopes; isotopes of soil water</td>
<td>oxygen isotope \textit{ratio (composition) of chert; inferred from carbon isotope measurements; isotopic composition of soil water}</td>
<td>Such written mistakes are a carryover from loose oral communication.</td>
</tr>
</tbody>
</table>
The isotopic composition of the water was $\delta^{18}O = -4.3\%$.  

- The $\delta^{18}O$ value of the water was $-4.3\%$.  

A matter of redundancy.

<table>
<thead>
<tr>
<th>The isotopic value changed.</th>
<th>The isotopic composition changed. The $\delta^{18}O$ value changed.</th>
<th>The phrase <em>isotopic value</em> is ambiguous. R?, $\delta$? Which element?</th>
</tr>
</thead>
<tbody>
<tr>
<td>The isotopic signature of the rock was $\delta^{18}O = 5.7%$.</td>
<td>The $\delta^{18}O$ value of the rock was 5.7%. Thus this rock has the oxygen isotope signature of the mantle.</td>
<td>The word <em>signature</em> should be used to describe the isotopic composition of a significant reservoir like the mantle, the ocean, or a major part of the system being studied, not to the isotopic composition of ordinary samples.</td>
</tr>
<tr>
<td>$\delta^{15}$, $\delta^{18}$, $\delta^{13}$, etc.; $\delta^{15}$, $\delta^{18}$, $\delta^{13}$, etc.; $\delta^{15}$, $\delta^{18}$, $\delta^{13}$, etc.</td>
<td>$\delta^{15}N$, $\delta^{18}O$, $\delta^{13}C$, etc.</td>
<td>Introduction of new symbols that save one character of space is unnecessary at best and confusing at worst.</td>
</tr>
<tr>
<td>Sulfur was measured</td>
<td>the sulfur <em>isotope composition</em> was measured</td>
<td>Misleading because the sulfur <em>content</em> of a rock or mineral may be understood.</td>
</tr>
<tr>
<td>The $^{13}C$ content of...</td>
<td>The $^{13}C/^{12}C$ ratio of...</td>
<td>$^{13}C$ content refers to how much $^{13}C$ there is in a rock. A sample of coal has a lot of $^{13}C$ (high $^{13}C$ content) but a low $^{13}C/^{12}C$ ratio compared to most materials.</td>
</tr>
<tr>
<td>In general the water isotopes are valuable proxies of temperature variations in high latitudes</td>
<td>In general the <em>isotopologues</em> of water are valuable proxies of temperature variations in high latitudes</td>
<td>Water does not have isotopes. It is composed of H and O that have multiple isotopes.</td>
</tr>
<tr>
<td>... using data assimilation of water-isotope ratios ...</td>
<td>Same as above</td>
<td>Just as it would be wrong to say “using data of fish-isotope ratios” so it is wrong to say ‘water-isotope ratios’.</td>
</tr>
</tbody>
</table>

mass spectrometer (see section 2.8). Mass spectrometric analyses of pure gases other than H$_2$ are *reproducible* to $\pm 0.01\%$ or better. Excellent reproducibility like this does not necessarily represent the precision of an actual sample because errors can be introduced from the collection and chemical preparation procedures employed. To get a true precision of $\pm 0.01\%$ requires extreme care. Reporting a precision for an analysis based on the precision obtained on the measurement of the gas in a mass spectrometer will always result in a precision that is higher than the actual precision of the overall analysis and should be avoided. Oxygen isotope compositions are reported using the symbol $\delta^{18}O$, those of carbon by $\delta^{13}C$, and so forth. The symbol $\delta$ is the lower case Greek letter *delta* and is commonly used in many disciplines to express a difference. The unrelated symbol $\partial$ (*del*) crept into the parlance of stable isotope geochemistry about 20-30 years ago, presumably as some kind of abbreviation for the correct word *delta*$.^2$ This incorrect usage should be abandoned because the word del has been used for centuries to denote the symbol $\partial$, the partial derivative sign and is not the greek letter 'delta'.

The delta notation provides a very convenient means to express the small relative differences in isotopic ratios between samples and standards that are measured by isotope ratio mass spectrometry. The effective precision of a stable isotope measurement is much higher than is immediately apparent from the stated precision of a $\delta$ value, which in the best case is $\pm 0.01\%$. For example, the absolute $^{18}O/^{16}O$ ratio of one of the international reference standards SMOW is $(2005.20\pm0.45)\times10^{-6}$. This ratio was

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$^2$I first encountered students using $\partial$ in place of $\delta$ because the symbol took only one stroke of a keyboard (on a Mac) instead of two for the $\delta$. Needless to say, this was not a convincing reason to abandon the correct notation.
determined by comparing the isotopic value of a sample of SMOW to synthetic mixtures of pure D_2^{18}O and H_2^{16}O (Baertschi, 1976b), and is known to five significant figures, or to four parts in 10^5. The \(^{18}\text{O}/^{16}\text{O}\) ratio of a gas whose \(\delta^{18}\text{O}\) value is +2.06‰ relative to SMOW (\(\delta^{18}\text{O}\) of SMOW = 0.00‰ by definition) is 0.00200933, the value obtained by substituting 2.06 in equation 2.1

\[
2.06 = \frac{^{18}\text{O}/^{16}\text{O}}{\text{sample}} - 2005.20 \times 10^{-6} 
\times 1000,
\]

A \(\delta^{18}\text{O}\) value of +2.05‰ corresponds to an absolute ratio of 0.002009311, different from a \(\delta^{18}\text{O}\) value of +2.06‰ by ±0.00000002. Obviously, given the uncertainties in the absolute value of our reference, the absolute ratio is not known anywhere near the calculated precision. Nevertheless, by accepting a value for the absolute \(^{18}\text{O}/^{16}\text{O}\) ratio of a reference standard (SMOW in this case), we can determine relative differences in the \(^{18}\text{O}/^{16}\text{O}\) ratios of two substances at the remarkable level of two parts in the eighth decimal place! The ability to determine relative differences in small isotopic ratios at this level of precision makes stable isotope measurements among the most precise attainable in all of geochemistry.

The delta scale leads to some interesting peculiarities which fortunately, for the most part, can be ignored. Consider the oxygen isotope composition of a gas, given by

\[
\delta^{18}\text{O} = \left( \left( \frac{^{18}\text{O}/^{16}\text{O}}{\text{sample}} \right) - 1 \right) \times 1000
\]

If we have a sample with no \(^{18}\text{O}\), then the \(^{18}\text{O}/^{16}\text{O}\) ratio of the sample is 0, and the \(\delta\)\(\delta^{18}\text{O}\) value is -1000‰. The isotope scale 'bottoms out' at -1000‰. At the other extreme, a sample containing only \(^{18}\text{O}\) has a \(^{18}\text{O}/^{16}\text{O}\) ratio of ∞, and the \(\delta^{18}\text{O}\) value is ∞‰. The \(\delta\) value of a mixture of two materials can be approximated by taking the average of the two delta values of the unmixed materials in their relative proportions, and in practice, this works well, although mathematically it is not correct. Just consider mixing equal proportions of pure H_2^{18}O and pure H_2^{16}O. The mixture has a composition of H_1^{16}O_2^{18}O, with a \(\delta^{18}\text{O}\) value of 497753‰, but if we were just to take the average of the two endmember delta values (-1000 and ∞‰), the answer would not be correct. Fortunately, the rare isotope is generally in low concentrations, so that for most geological applications we can use delta values additively because the denominator (the common isotope) has a fraction close to 1.

Isotopic compositions of samples are measured relative to the isotopic composition of a reference gas, the **working standard**, in a mass spectrometer. To convert the \(\delta\) value of sample X from one scale (reference standard A – the working gas \(\delta\) value) to another scale (reference standard B – the international standard \(\delta\) value), the following equation is used:
This simple calculation, analogous to converting temperatures on the Celsius scale to temperatures on the Fahrenheit scale, is made in every stable isotope laboratory in the world\textsuperscript{3}. Laboratory working standards are calibrated relative to international reference standards, precious materials which are distributed to qualified workers by the International Atomic Energy Agency (IAEA) or the National Institute of Standards and Technology (NIST). In most stable isotope laboratories there are supplies of gases like CO\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2}, etc. contained in metal or glass tubes and tanks that are fitted with appropriate valves to allow aliquots of the gases to be taken for use as working standards or for calibration purposes. The $\delta$ values of the gases are well known from repeated measurements relative to the values of primary or secondary reference standards, which are analyzed sparingly.

Suppose that the CO\textsubscript{2} working standard (WS) used in a given mass spectrometer has a $\delta^{13}$C value of +4.75‰ relative to the international standard PDB ($\delta_{WS-PDB}$). When an unknown sample is analyzed in the mass spectrometer, the difference in the isotopic composition of the sample and the working standard is measured. If sample X has a $\delta^{13}$C value of $-22.32$‰ relative to WS ($\delta_{X-WS}$), the $\delta^{13}$C value of X on the PDB scale is

$$4.75 - 22.32 + 0.001(4.75)(-22.32) = -17.68$$. \hfill 2.5

That is, $\delta$ values are converted from the working standard of the mass spectrometer to PDB, or to any international reference standard, by simply adding a scaling term $10^{-3}(\delta_{X-WS})(\delta_{WS-PDB})$ to the sum of the two delta values $\delta_{X-WS}$ and $\delta_{WS-PDB}$. Another equation (essentially the same equation rearranged in a slightly different format) frequently used to calculate a scale change like this has, for the case above, the form

$$1.00475(-22.32) + 4.75 = -17.68$$. \hfill 2.6

The difference of 4.75‰ between the isotopic composition of the working standard and PDB must be added to the measured raw value (-22.32), but only after the raw value has been corrected for scale expansion, equivalent in this case to a multiplicative factor of 1.00475 (equal to $1 + 0.001 \times \delta_{WS-PDB}$). Note that there is a contraction or expansion of scales involved in these calculations and this term is directly related to the magnitude of the difference in $\delta$ values between the two standards. The size of $\delta$ values changes from one scale to another. When converting between scales, one must apply both an additive and multiplicative factor to the raw data. If the $\delta$ value of a working standard is 12.34‰, the multiplicative factor is 1.01234 \textit{(i.e.,} $1 + 0.001 \times \delta$\textit{)} and the additive factor is 12.34. If the $\delta$ value of another working standard is $-6.78$‰, the multiplicative factor is 0.99322 ($1 + 0.001 \times -6.78$), which in this case contracts the scale, and the additive factor is $-6.78$. The application of this equation is familiar to many geochemists analyzing carbonates. There are two references scales for oxygen, the SMOW and PDB scale. The value of

\textsuperscript{3} Certainly, many workers are not aware that such calculations are being made, as the conversion equations are hidden in the software packages provided with their mass spectrometers.
PDB on the SMOW scale (or VPDB on the VSMOW scale) is $30.91\%$. In order to convert a $\delta^{18}O$ value from the SMOW to PDB scale the equation

$$\delta^{18}O_{\text{SMOW}} = 1.03091 \times \delta^{18}O_{\text{PDB}} + 30.91$$

is used.

In order to reduce the size of the multiplicative factor, international reference standards are prepared with isotopic compositions that are as close as possible to the range of isotopic compositions of natural materials expected to be analyzed by most workers. In the same vein, a researcher can choose working standards whose isotopic compositions are close to those of the materials most commonly met in the research at hand. If given the choice, it would be better to have a working gas with a higher delta value (higher proportion of rare isotope) than the sample gas to minimize extrapolation. The practice of having similar reference and sample gas compositions results in only small improvements in precision, but is a worthwhile practice in any case.

Over the years, stable isotope geochemists have tacitly developed a certain uniformity in the presentation of their data. Some notations used in the past have all but disappeared in the modern literature, but are noted for the sake of completeness. In the early literature you will see the expressions $\delta(O^{18}/O^{16})$, $\delta^{18}O$, $\delta(D/H)$, and so forth, but these strictly more correct notations soon gave way to the simpler expressions $\delta^{18}O$ and $\delta D$. Prior to the mid-1970s the mass number was always written as a right superscript of the symbol of the element as in $O^{18}$, $C^{14}$, $U^{235}$, etc. It is for this reason that one usually hears the element name (or symbol) and number spoken in that order, as in “C-14 dating”, “Sr-90 contamination”, or “delta O-18 values”. Subsequently, IUPAC officially changed the order in which mass number and symbol are written to allow oxidation states and other identifying marks to be written to the right of the element symbol. In the early literature, $\delta D$ and $\delta^{13}C$ values were often given in per cent rather than in per mil.

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**Box 2.1 Why $^{12}C$ is the official reference mass for atomic mass units?**

Prior to the 1970s, two conventions were used for determining relative atomic masses. Physicists related their mass spectrometric determinations to the mass of $^{16}O$, the most abundant isotope of oxygen, and chemists used the weighted mass of all three isotopes of oxygen $^{16}O$, $^{17}O$, and $^{18}O$. At an international congress devoted to standardization of scientific weights and measures, the redoubtable A.O. Nier proposed a solution to these disparate conventions whose negative consequences were becoming serious. He suggested that the carbon-12 isotope ($^{12}C$) be the reference for the atomic mass unit (amu). By definition, its mass would be *exactly* 12 amu, a convention that would be acceptable to the physicists. By adopting this convention, the average mass for oxygen (the weighted sum of the three naturally occurring isotopes) becomes 15.9994 amu, a number close enough to 16 to satisfy the chemists.
2.4 The Fractionation Factor $\alpha$

The isotopic fractionation factor between two substances A and B is defined as

$$\alpha_{A-B} = \frac{R_A}{R_B}$$  \hspace{1cm} 2.8.

The $\alpha$ value is the ratio of the ratios for the rare to heavy isotope in any two substances A and B. In terms of $\delta$ values this expression becomes

$$\alpha_{A-B} = \frac{1 + \frac{\delta_A}{1000}}{1 + \frac{\delta_B}{1000}} = \frac{1000 + \delta_A}{1000 + \delta_B}$$  \hspace{1cm} 2.9.

The $\alpha$ value is a measure of the isotope fractionation between any two phases and is extremely important in terms of understanding equilibrium isotope exchange. This concept is the foundation of our field, where the early practitioners realized that the enrichment of the heavy isotope in one phase relative to coexisting phase in isotopic equilibrium is a function almost exclusively of temperature. Isotope exchange reactions are considered in terms of equilibrium thermodynamics in which isotopes of a single element are exchanged between two substances until equilibrium is reached. (Kinetic reactions that do not reach equilibrium are important for understanding the mechanisms of chemical reactions or mineral formation, but should not be considered in terms of the equilibrium fractionation factor $\alpha$). The chemical makeup of reactants and products in an isotope exchange reaction are identical. For the general case of an isotope exchange reaction between substances A and B, where the subscripts 1 and 2 refer to molecules totally substituted by the light and heavy isotope, respectively and $a$ and $b$ refer to the coefficients necessary to balance the reaction, we have

$$aA_1 + bB_2 = aA_2 + bB_1$$  \hspace{1cm} 2.10a.

An example of such a reaction is given by

$$^{12}\text{CH}_4 + ^{13}\text{CO}_2 = ^{13}\text{CH}_4 + ^{12}\text{CO}_2$$  \hspace{1cm} 2.10b.

In a real system, there would be only one methane phase and one CO$_2$ phase, nevertheless it is thermodynamically valid to consider the components $^{12}$CH$_4$ and $^{13}$CH$_4$ as making up the CH$_4$ phase. The equilibrium constant for equation 2.10a the above reaction is written in the usual way

$$K = \frac{(A_2)^a(B_1)^y}{(A_1)^a(B_2)^y} = \frac{(A_2/A_1)^a}{(B_2/B_1)^y}$$  \hspace{1cm} 2.11.

The terms in parentheses are activities but, in practice, ratios are normally used. The difference between concentrations and ratios of isotopologues is normally negligible (i.e.
the activity coefficient $\gamma \sim 1$), so that substituting ratio for activities is valid. For the reaction given by equation 2.10b, the equilibrium constant is

$$K = \frac{\left(\frac{^{13}CH_4}{^{12}CH_4}\right)^{^{12}CO_2}}{\left(\frac{^{12}CH_4}{^{13}CH_4}\right)^{^{13}CO_2}} = \frac{\left(\frac{^{13}CH_4}{^{12}CH_4}\right)}{\left(\frac{^{13}CO_2}{^{12}CO_2}\right)}$$

2.12.

Finally, because the reaction is written with the hydrogen (in methane) and oxygen (in CO$_2$) as having the same value in the numerators and denominators (we are considering their isotopic composition fixed), equation 2.12 becomes simply

$$K = \frac{\left(\frac{^{13}C/^{12}C}_{\text{methane}}\right)^{^{12}CO_2}}{\left(\frac{^{13}C/^{12}C}_{\text{CO}_2}\right)}$$

2.13,

which is identical to the $\alpha$ value.

If the isotopes are randomly distributed over all possible sites or positions in substances A and B, the fractionation factor ($\alpha$) is related to the equilibrium constant ($K$) for isotope exchange reactions in the following way:

$$\alpha = K^{1/n}$$

2.14

where $n$ is the number of atoms exchanged, normally 1 as in the example above. For the isotope exchange reaction between CO$_2$ and SiO$_2$, we have

$$K = \alpha = \frac{\left(\frac{^{18}O/^{16}O}_{\text{CO}_2}\right)}{\left(\frac{^{18}O/^{16}O}_{\text{SiO}_2}\right)}$$

2.15.

Values of $\alpha$ are normally very close to unity, typically 1.00$\chi$, and the fractionation is often considered informally to be equal to $\chi$. As a true thermodynamic equilibrium constant, $\alpha$ is a function of temperature$^4$, so values of $\alpha$ are meaningful only when temperature is specified. For example, the sulfur isotope fractionation between sphalerite (ZnS) and galena (PbS) is 1.00360 at 200°C. It is accepted parlance to state that, at 200°C, (1) the sphalerite-galena fractionation is 3.60 per mil, or (2) sphalerite concentrates $^{34}$S by 3.60 per mil relative to galena$^5$. It is common to report the difference in the isotopic composition as

$^4$ Chemical thermodynamic reactions are a function of both temperature and pressure. Because the volume change for the isotope exchange reactions 2.10a is extremely small, pressure can be ignored except in extreme cases. See Horita et al. (2002).

$^5$ Note that the difference of 3.60‰ is only correct if the $\delta^{34}$S value of the galena is 0.
\[ \Delta_{A-B} = \delta_A - \delta_B \]

\( \Delta \) is the upper case symbol for the Greek letter delta and is frequently expressed orally as “big delta” or “cap delta”.

### 2.5 1000\( \ln \alpha \), \( \Delta \), and the \( \varepsilon \) Value

For the \( ^{34}\text{S}/^{32}\text{S} \) example mentioned above, if the \( \delta^{34}\text{S} \) values of sphalerite and galena are 3.6‰ and 0.0‰, respectively, then \( \alpha = 1.0036 \) and the difference between the \( \delta^{34}\text{S} \) values of sphalerite and galena is 3.6‰. It is a useful mathematical fact that 1000\( \ln(1.00X) \) is approximately equal to \( X \). For our sphalerite-galena example, 1000\( \ln \alpha = 3.594 \). That is, 1000\( \ln \alpha \) is the fractionation between sphalerite and galena. It is close the difference in the isotopic composition of the two phases, and is independent on their actual isotopic composition. It is sometimes called the **per mil fractionation**, but this terminology is strictly not correct because \( \alpha \) is unitless. This logarithmic function has added theoretical significance. For perfect gases, \( \ln \alpha \) varies as \( 1/T^2 \) and \( 1/T \) in the high and low temperature regions, respectively. As in any expressions or calculations in thermodynamics, \( T \) is absolute temperature in kelvins.

The fractionation expressed as 1000\( \ln \alpha \) is of prime importance in stable isotope geochemistry. This quantity is very well approximated by the \( \Delta \) value, but it is important to realize that the two are not exactly the same:

\[ \Delta_{A-B} = \delta_A - \delta_B \approx 1000\ln \alpha_{A-B} \]

That is, merely subtracting \( \delta \) values is a good approximation to the per mil fractionation given by 1000\( \ln \alpha \) and identical to it within the limits of analytical error **when the individual values of \( \delta_A \) and \( \delta_B \) as well as \( \Delta_{A-B} \) are less than about 10‰**. As the numbers in Table 2.2 indicate however, the differences between \( \Delta_{A-B} \) and 1000\( \ln \alpha \) become significant when the fractionations or the \( \delta \) values are greater than 10. For all fractionations that are assumed to be at thermodynamic equilibrium, 1000\( \ln \alpha \) should be reported. Reporting the differences in delta values is valid when non-equilibrium fractionations are being studied, such as in biological processes. A few authors have used the symbol \( \varepsilon \) to designate an isotopic fractionation and define it as \( \varepsilon = (\alpha - 1)1000 \). Again, for small values of \( \varepsilon \), this function is almost identical to 1000\( \ln \alpha \) (Table 2.2). It is recommended that \( \varepsilon \) not be used for equilibrium reactions. Instead \( \varepsilon \) is more commonly used in kinetic, non-equilibrium processes, where the isotopic composition of two phases can be measured, but because they are out of chemical equilibrium, do not follow the rules of classical thermodynamics.

**Table 2.2. Comparison between values obtained using different expressions for isotopic fractionations.**

<table>
<thead>
<tr>
<th>( \delta_A )</th>
<th>( \delta_B )</th>
<th>( \alpha )</th>
<th>( \Delta_{A-B} )</th>
<th>( \varepsilon_{A-B} )</th>
<th>10^3( \ln \alpha_{A-B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>1.00100</td>
<td>1.00</td>
<td>1.00</td>
<td>1.000</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0</td>
<td>1.00500</td>
<td>5.00</td>
<td>5.00</td>
<td>4.988</td>
</tr>
<tr>
<td>10.0</td>
<td>5.0</td>
<td>1.00498</td>
<td>5.00</td>
<td>4.98</td>
<td>4.963</td>
</tr>
</tbody>
</table>
The $\alpha$ function is an integral part of a variety of analytical techniques. For example, the $\delta^{18}O$ value of a sample of liquid ($l$) water is determined by equilibrating the water with a small amount of $CO_2$ gas at a constant temperature and then measuring the oxygen isotope composition of the equilibrated $CO_2$ gas in a mass spectrometer. At 25°C, the fractionation factor $\alpha$ between $CO_2$(gas) and $H_2O$ is 1.04120. This is approximately equivalent to stating that $CO_2$ is 40.37‰ ($10^3 \ln \alpha = 40.37\%$) heavier than the water with which it was equilibrated, but the actual $\delta^{18}O$ value of the water is not equal to the $\delta^{18}O$ value of $CO_2$ - 40.37‰. The $\delta^{18}O$ value of $CO_2$ in equilibrium with $H_2O$ is determined using equation 2.9.

As another example, the isotopic compositions of carbon and oxygen in carbonates are determined by reacting the carbonates with 100% phosphoric acid and measuring the $CO_2$ that is released during the decarbonation reaction. All of the carbon is released during this procedure and the $\delta^{13}C$ value of the $CO_2$ gas is identical to the $\delta^{13}C$ value of the original carbonate. Only 2/3 of the oxygen in the carbonate is transferred to the $CO_2$ gas. There is a temperature dependent isotopic fractionation between the oxygen in the evolved $CO_2$ and the oxygen in the original carbonate. To a first-approximation, as long as the temperature of acid dissolution reaction is held constant, the fractionation between the carbonate and liberated $CO_2$ is constant. This provides us with the so-called acid fractionation factor, $\alpha$ for $CO_2$ liberated from a carbonate sample. If we know the $\alpha$ value between evolved $CO_2$ gas and carbonate at the reaction temperature, we can calculate the $\delta^{18}O$ value of the carbonate itself. At 25°C, $\alpha$(CO$_2$-calcite) for the phosphoric acid reaction is 1.01025. That is, the liberated $CO_2$ is about 10‰ heavier than the calcite. From equation 2.9, we have

$$\alpha = 1.01025 = \frac{1000 + \delta_{CO_2}}{1000 + \delta_{calcite}}$$ 2.18.

If the $\delta^{18}O$ value of the calcite is -6.78‰, then the liberated $CO_2$ gas will have a $\delta^{18}O$ value of 3.40‰. Interestingly, this $\alpha$ value is not the same as the equilibrium fractionation between $CO_2$ and calcite. At 25°C, the equilibrium $\alpha$(CO$_2$-calcite) value is 1.01258. The 1.01025 value is an empirical determination of the fractionation between a calcite sample and the $CO_2$ liberated in a non-equilibrium, but repeatable, fractionation that occurs during acid dissolution. It would probably be more correct to use $\epsilon$ for this equation, because the fractionation is not the same as the equilibrium $\alpha$ value for $CO_2$ and calcite.
2.6 Reference Standards

Very precise comparisons of isotopic compositions of materials can be determined in a given laboratory, but to allow for accurate intercomparisons of data obtained in different laboratories, an internationally accepted set of reference standards is available to all workers in the field. The measured isotopic composition of any substance should be the same in all laboratories after calibrations have been made with these international reference standards. Beginning in the 1970s, committees of stable isotope geochemists convened periodically in Vienna to select standard materials and to establish protocols for calibrating mass spectrometer analyses and presenting stable isotope data (Coplen and Clayton, 1973; Coplen et al., 1983; Hut, 1987; Coplen, 1996). These reference materials (Appendix 1) are available from the National Institute for Standards and Technology (NIST) in Gaithersburg, Maryland and from the International Atomic Energy Agency (IAEA) in Vienna. International reference standards are in limited supply and are not intended for use as working standards. They are provided in small quantities to allow workers to establish larger supplies of secondary reference materials (solids, liquids and gases) that in turn can be used on a daily basis as working standards, for calibrating extraction techniques, and so on.

The history of stable isotope reference materials is long and complex and unfortunately has led to considerable confusion. The early Chicago group reported $\delta^{13}C$ and $\delta^{18}O$ values of carbonates relative to the carbon and oxygen isotope compositions of a powdered specimen of *Belemnitella americana* from the Upper Cretaceous PeeDee formation of South Carolina. They called this calcite standard PDB (*PeeDee* *Belemnite*). When the original supply of this material became exhausted, another sample was prepared and named PDB II, a standard that was later replaced by PDB III. In each case the new standard was carefully calibrated against the isotopic composition of the original sample of PDB. Despite the fact that the original supply of PDB is exhausted, PDB remains the standard used in reporting all carbon isotope analyses and most of the oxygen isotope analyses of low-temperature carbonates. Secondary standards have been developed with isotopic compositions that are calibrated to the original PDB.

The Chicago group also created an Mean Ocean Water by taking the average ocean water samples collected at depths ranging from 500 and 2000 meters, with the goal of creating a sample that was representative of the average oxygen isotope composition of the ocean (Epstein and Mayeda, 1953). Each ocean has a slightly different $\delta^{18}O$ and $\delta D$ value (Table 2.3). In order to standardize the average ocean water value, Harmon Craig compared the $\delta^{18}O$ and $\delta D$ values of these ocean waters to the National Bureau of Standards Potomac River water (NBS-1). He coined the term Standard Mean Ocean Water, or SMOW as the average of the different ocean waters, with $\delta$ values defined in terms of NBS1 by the following relationships:

\[
\frac{D}{H} \text{(SMOW)} = 1.050 \frac{D}{H} \text{(NBS-1)} \\
\frac{^{18}O}{^{16}O} \text{(SMOW)} = 1.008 \frac{^{18}O}{^{16}O} \text{(NBS-1)}
\]

This allowed workers everywhere to standardize their 'ocean water' values to the widely distributed NBS-1 (Fig. 2.1). Ultimately an actual water standard with $\delta D$ and $\delta^{18}O$ values equal to the defined SMOW was made by mixing waters with different isotopic compositions.
compositions. This physical sample is called VSMOW (or V-SMOW), where the V is an abbreviation for 'Vienna', the headquarters for the International Atomic Energy Agency that distributes the standard. Unfortunately the original VSMOW has been used up, and a second standard VSMOW2 was made by the IAEA Isotope Hydrology Laboratory in 2006. It is thought to be essentially identical to the original VSMOW (except perhaps for its $\delta^{17}$O value) and is available for distribution through the IAEA. Many other accepted standards are available from the IAEA, so that standardization procedures are now relatively routine and stable isotope analyses made anywhere in the world are, for the most part, easily comparable.

Table 2.3. $\delta^{18}$O and $\delta^D$ values of the average deep water samples from the different oceans.

<table>
<thead>
<tr>
<th>Location (sample)</th>
<th>$\delta^D$‰</th>
<th>$\delta^{18}$O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic</td>
<td>-0.7</td>
<td>+0.14</td>
</tr>
<tr>
<td>Pacific</td>
<td>+0.9</td>
<td>+0.04</td>
</tr>
<tr>
<td>Indian</td>
<td>+0.1</td>
<td>-0.07</td>
</tr>
<tr>
<td>NBS-1</td>
<td>-47.60</td>
<td>-7.94</td>
</tr>
</tbody>
</table>

A further complication has developed because of the use of non-quantitative techniques for determining stable isotope ratios. Carbon and nitrogen isotope analyses of organic matter, and to a lesser extent sulfur isotope analyses, are now made almost exclusively using an elemental analyzer. This methodology consists of combusting organic matter (or S-bearing phase) in a helium stream and excess oxygen gas. The C is converted to $CO_2$, N is converted to $N_2$ and S is converted to $SO_2$. The gases are separated in a gas chromatograph using He as a carrier gas and measured in 'continuous flow mode' in the mass spectrometer (see section 2.7.2 for a discussion of continuous flow mass spectrometry). Unfortunately, the measured isotopic composition is often not the same as the actual composition of the sample due to a number of factors, including incomplete reaction, contamination from other C and N sources in the organic matter and fractionation at the open split. Many laboratories and the IAEA have developed standards that can be used to compare the isotopic compositions of specific isotopic compounds, including cellulose, benzoic acid and caffeine. An outline of the reference materials for selected elements is given below.

2.6.1 Hydrogen

In much of the early literature on the abundance of deuterium in natural materials, a sample of Lake Michigan water was used as a reference standard. The $\delta D$ value of the Lake Michigan standard is $-42.4$‰ on the modern VSMOW scale. Today, all hydrogen isotope analyses are reported relative to VSMOW, a logical geochemical reference material because ocean water is by far the largest terrestrial reservoir of water. By definition, the $\delta D$ value of VSMOW is equal to zero. VSMOW has a D/H ratio that is higher than the ratios of most other materials on Earth, an interesting geochemical fact in itself. Thus most $\delta D$ values of natural materials on our planet are negative on this scale in
contrast to δD values of extraterrestrial substances which can be extremely positive for reasons explained in Chapter 13.

SMOW was originally defined relative to NBS-1 (Fig. 2.1) by equation 2.19. A physical sample of water with an isotopic composition equal to SMOW was made by Harmon Craig and Ray Weiss, who distilled a large sample of ocean water (Fig. 2.2 and Fig. 2.3) and adjusted its hydrogen and oxygen isotope compositions to match SMOW by carefully adding appropriate amounts of other waters of different isotopic compositions. This was the original VSMOW sample. By definition, it has a δD value ≡ 0‰ on the VSMOW scale. Practitioners in the field should realize that data presented in older literature using the SMOW reference are identical to those using the VSMOW or VSMOW2 reference. No additional corrections are needed in order to compare data reported relative to either reference. In other words, the δD and δ18O values of SMOW and VSMOW are identical6.

All hydrogen isotope ratios are measured using H₂ gas in the mass spectrometer and H₂O gas with laser spectroscopy7 (Table 2.4). The raw δD value of a sample whose D/H ratio is quite different, say 20-30‰ or more from that of the working standard, will generally be very slightly different when measured on different mass spectrometers. The factor most responsible for this effect is the inevitable production of the ion H₃⁺ (the same mass 3 as DH⁺) in the source of the mass spectrometer (or non-linearities in the case of laser spectroscopy). In order to resolve this problem, an isotopically light natural water from Antarctica was selected as an additional reference standard for use in determining the stretching factor for individual mass spectrometers (see Appendix 2 for further discussion). The stretching factor is especially important for hydrogen isotope measurements because the variation in δD values of natural materials are about ten times larger than variations in any other element. This standard was given the acronym SLAP (Standard Light Antarctic Precipitation) and has a δD value of −428‰ on the basis of a comparison study made in many of the major stable isotope laboratories in the world in the 1970s. (SLAP2 has a δD value of −427.5±0.3‰). In order to calibrate a machine for

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6 see https://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf for details of VSMOW2
7 See sections 2.7 and 2.8 for methodological details
**Table 2.4.** Gases commonly measured in conventional gas source isotope ratio mass spectrometers.

<table>
<thead>
<tr>
<th>Element</th>
<th>Gas</th>
<th>Masses of Isotopologues Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>2, 3 (interference from H₃⁺)</td>
</tr>
<tr>
<td></td>
<td>H₂O (g)</td>
<td>(H₂O, HDO in laser spectroscopy systems)</td>
</tr>
<tr>
<td>Carbon</td>
<td>CO₂</td>
<td>44, 45</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>28, 29 (and 30 for artificially enriched samples)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>CO₂</td>
<td>44, 46</td>
</tr>
<tr>
<td></td>
<td>O₂ (fluorination)</td>
<td>32, (33), 34</td>
</tr>
<tr>
<td></td>
<td>CO (pyrolysis)</td>
<td>28, 30</td>
</tr>
<tr>
<td></td>
<td>H₂O (g)</td>
<td>(H₂¹⁶O, H₂¹⁸O in laser spectroscopy systems)</td>
</tr>
<tr>
<td>Sulfur</td>
<td>SO₂</td>
<td>64, 66</td>
</tr>
<tr>
<td></td>
<td>SF₆</td>
<td>146, (147), 148, (150)</td>
</tr>
<tr>
<td>Silicon</td>
<td>SiF₄</td>
<td>85, 86, 87</td>
</tr>
<tr>
<td>Chlorine</td>
<td>CH₃Cl</td>
<td>50, 52</td>
</tr>
</tbody>
</table>
\(\delta D\) determinations, hydrogen isotope analyses of both SMOW and SLAP are analyzed relative to the working standard, and the difference obtained multiplied by a factor so that \(\delta D_{\text{SLAP-SMOW}} = -428‰\) (Coplen, 1988).

Absolute ratios of D/H determined for both SMOW and SLAP and the absolute ratio of \(^{18}O/^{16}O\) and \(^{17}O/^{16}O\) determined for SMOW are given in Table 2.5. The absolute values were determined by mixing waters that were extremely pure samples of \(^1\text{H}_2^{16}\text{O}, \(^1\text{H}_2^{18}\text{O},\ \)\(D_2^{16}\text{O}\) and \(\text{H}_2^{17}\text{O}\). It is very difficult to prepare water that has no deuterium or \(^{18}\text{O}\) and \(^{17}\text{O}\) in it, but the best job possible was done at the time the determination was made. By careful mixing, the D/H and \(^{18}O/^{16}O\) ratios of these synthetic waters were known, but with significant uncertainty. SMOW and SLAP were then measured relative to the isotopic compositions of these waters to derive their absolute D/H and \(^{18}O/^{16}O\) ratios. While it is desirable to have reliable determinations of the absolute ratios of these standards, keep in mind that knowledge of the absolute ratios is not necessary to conduct research in stable isotope geochemistry and is not used in determining stable isotope ratios on a mass spectrometer.

Table 2.5. Determinations of the absolute ratios of the isotope ratios of selected elements and internationally accepted standards.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Standard</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/H</td>
<td>SMOW</td>
<td>(155.76 \pm 0.05) x 10^{-6}</td>
<td>(Hagemann et al., 1970)</td>
</tr>
<tr>
<td>D/H</td>
<td>SMOW</td>
<td>(155.75 \pm 0.08) x 10^{-6}</td>
<td>(de Wit et al., 1980)</td>
</tr>
<tr>
<td>D/H</td>
<td>SMOW</td>
<td>(155.60 \pm 0.12) x 10^{-6}</td>
<td>(Tse et al., 1980)</td>
</tr>
<tr>
<td>(^{13}\text{C}/^{12}\text{C})</td>
<td>PDB</td>
<td>(11179 \pm 20) x 10^{-6}</td>
<td>(Zhang et al., 1990)</td>
</tr>
<tr>
<td>(^{15}\text{N}/^{14}\text{N})</td>
<td>AIR</td>
<td>(3670 \pm 40) x 10^{-6}</td>
<td>(Junk and Svec, 1958)</td>
</tr>
<tr>
<td>(^{17}\text{O}/^{16}\text{O})</td>
<td>SMOW</td>
<td>(379.9 \pm 0.8) x 10^{-6}</td>
<td>(Li et al., 1988)</td>
</tr>
<tr>
<td>(^{18}\text{O}/^{16}\text{O})</td>
<td>SMOW</td>
<td>(2005.20 \pm 0.45) x 10^{-6}</td>
<td>(Baertschi, 1976a)</td>
</tr>
<tr>
<td>(^{33}\text{S}/^{32}\text{S})</td>
<td>VCDT</td>
<td>(78.77 \pm 0.03) x 10^{-4}</td>
<td>(Ding et al., 2001)</td>
</tr>
<tr>
<td>(^{34}\text{S}/^{32}\text{S})</td>
<td>VCDT</td>
<td>(441.626 \pm 0.039) x 10^{-4}</td>
<td>(Ding et al., 2001)</td>
</tr>
<tr>
<td>(^{29}\text{Si}/^{28}\text{Si})</td>
<td>NBS-28</td>
<td>(508.1 \pm 0.1) x 10^{-4}</td>
<td>(De Bièvre et al., 1994)</td>
</tr>
<tr>
<td>(^{30}\text{Si}/^{28}\text{Si})</td>
<td>NBS-28</td>
<td>(335.3 \pm 0.7) x 10^{-4}</td>
<td>(De Bièvre et al., 1994)</td>
</tr>
<tr>
<td>(^{37}\text{Cl}/^{35}\text{Cl})</td>
<td>SMO (ISL 354)</td>
<td>0.31977 \pm 0.00009</td>
<td>(Xiao et al., 2002)</td>
</tr>
</tbody>
</table>

Fig. 2.3. The original container of VSMOW. From https://en.wikipedia.org/wiki/Vienna_Standard_Mean_Ocean_Water.
2.6.2 Carbon

Carbon isotope ratios are reported relative to the PDB standard described above and, by definition, the $\delta^{13}C$ value of PDB is zero. The calculated $^{13}C/^{12}C$ ratio for VPDB is given in Table 2.5. Several secondary carbonate standards (e.g. Carrara marble and Solenhofen limestone) were measured relative to PDB in the early years and these standards are still in use in some older laboratories. The international isotope reference standard NBS-19 (and most recently IAEA-603) is now the accepted means of calibrating to the PDB scale. NBS-19 was originally the TS (Toilet Seat) limestone working standard used in the laboratory of Irving Friedman and colleagues at the U.S. Geological Survey (Friedman et al., 1982). It has a $\delta^{13}C$ value of +1.95‰ relative to PDB and VPDB. In other words, the $\delta^{13}C$ value of NBS-19 $\equiv +1.95‰$ on the VPDB scale. Unfortunately, NBS-19 is now out of stock, and a new calcite standard IAEA-603, a sample of the Carrara marble is available with a $\delta^{13}C$ value of +2.46‰ ± 0.01 on the VPDB scale\(^8\). Other IAEA carbon isotope standards include oil, graphite and caffeine.

As in the case for SMOW, it is recommended to append the letter V to the acronym PDB.

Carbon isotope geochemistry has remained a very active discipline since its inception, and many thousands of carbon isotope analyses are reported every year. The carbon analyzed is present in a variety of substances including the various carbonate minerals, organic matter in sediments, organic matter in meteorites, petroleum products, collagen extracted from plant material, graphite, carbonate in the apatite of bones and teeth, carbon present in trace quantities in rocks (e.g., basalts) and minerals (e.g., goethite) and in archaeological and anthropological specimens. There are major differences in the extraction techniques used for these various carbonaceous materials and the errors assigned to an analysis depend on the complexities of the extraction method employed. In almost all cases, however, the carbon is put into the form of CO$_2$ for mass spectrometric analysis (Table 2.4), and therefore can be compared to the CO$_2$ liberated from one of the IAEA standards calibrated to PDB.

2.6.3 Nitrogen

Nitrogen isotope values are measured using N$_2$ gas in the mass spectrometer. The reference standard for nitrogen isotope analyses is atmospheric nitrogen and is called AIR. The $\delta^{15}N$ value of atmospheric nitrogen is almost constant everywhere on Earth and is 0‰ by definition (Mariotti, 1983). The $^{15}N/^{14}N$ ratio of air is given in Table 2.5. One N$_2$ gas standard called NSVEC ($\delta^{15}N = -2.8‰$ vs AIR) is distributed by IAEA. Several other solid standards (nitrates) are also available from IAEA. Any laboratory can produce their own nitrogen reference by purifying air. Oxygen is removed by combusting the air sample with Cu metal, but contaminant Ar in the product can interfere with the nitrogen isotope analyses\(^9\).

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\(^8\) For details, see: https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/ Stable_Isotopes/13C18and7Li/IAEA-603/RM603_Reference_Sheet_2016-08-16.pdf

\(^9\) Note that V-AIR has not yet been proposed.
2.6.4 Oxygen

Two international reference standards are used to report variations in oxygen isotope ratios, VPDB and VSMOW. SMOW was originally defined in terms of NBS-1

\[
\frac{^{18}O}{^{16}O}_{\text{SMOW}} = 1.008 \left(\frac{^{18}O}{^{16}O}_{\text{NBS-1}}\right)
\]

SMOW has a \( \delta^{18}O \) value of 8.00‰ relative to NBS-1, and NBS-1 has a \( \delta^{18}O \) value of -7.94‰ versus SMOW. As with hydrogen, a stretching factor should be applied to oxygen isotope analyses and this factor is calibrated by analyzing VSMOW whose \( \delta^{18}O \equiv 0\% \) and SLAP (Standard Light Antarctic Precipitation) whose \( \delta^{18}O = -55.5\% \) (See Appendix 2). By calibrating in this manner, analyses of water reported on the VSMOW scale are reliable. The stretching factor is much smaller for oxygen isotope analyses than for hydrogen isotope analyses and is often ignored.

Use of the PDB standard for reporting oxygen isotope compositions is restricted to analyses of carbonates of low-temperature origin (oceanic, lacustrine, or pedogenic) in studies of paleoclimate, paleoceanography and carbonate diagenesis. As mentioned above, oxygen isotope compositions of carbonates are determined by analyses of CO₂ generated from them by reaction with 100% H₃PO₄ at a fixed temperature. It is emphasized that the PDB standard is the solid carbonate, not the acid-liberated CO₂ that is actually introduced to the mass spectrometer. The \( \delta^{18}O \) of PDB is 0‰ on the VPDB scale by definition and analysis of NBS-19 is the accepted means of relating oxygen isotope analyses to VPDB. The \( \delta^{18}O \) value of NBS-19 is \( \equiv -2.20\% \) on the VPDB scale. Additional international secondary reference standards for carbonates are available (Appendix 1), and relating analyses to PDB no longer poses any ambiguities.

Because the \( \delta^{18}O \) value of VPDB is 30.91‰ higher than VSMOW (on the VSMOW scale), the conversion between VSMOW and VPDB scales is given by equation 2.7. There is a difference of 0.28‰ (Fig. 6.1) between CO₂ in equilibrium with VSMOW (\( \alpha_{\text{CO}_2-H_2O} = 1.04120 \)) at 25°C and CO₂ liberated from PDB at 25°C (\( \alpha_{\text{CO}_2-CaCO_3} = 1.01025 \)) and all these values were used in deriving equation 2.7 (See Chapter 6 for further explanation). Marine carbonates have \( \delta^{18}O \) values near zero on the VPDB scale, while ocean waters have \( \delta^{18}O \) values near zero on the VSMOW scale. As a result of this relationship, it is not uncommon to see the two scales mixed in published reports, with data for carbonates reported on the VPDB scale and data for waters reported on the VSMOW scale. If their \( \delta^{18}O \) values were replotted on the same scale, however, they would be approximately 30‰ apart! Care must be taken not to mix scales when presenting oxygen isotope data.

Traditionally, the \( ^{17}O/^{16}O \) ratios of terrestrial materials are not measured, because they provide no additional information than the \( ^{18}O/^{16}O \) ratios alone. The \( ^{17}O/^{16}O \) ratio correlates well with the \( ^{18}O/^{16}O \) ratio by the equation

\[
\left(\frac{^{17}O}{^{16}O}\right) = \left(\frac{^{18}O}{^{16}O}\right)^\lambda
\]

where the lambda (\( \lambda \)) is an empirical best fit of -0.527 for solids and 0.528 for waters. Recently, it has been recognized that there are small departures in the \( \delta^{17}O \) values.
predicted by equation 2.22 (Luz and Barkan, 2010; Pack and Herwartz, 2014), so that high precision $\delta^{17}O$ studies have relevance and are beginning to be made on a more routine basis. The $\delta^{17}O$ value of VSMOW is by definition 0‰.

Oxygen isotope measurements are made on one of several gases. Generally, samples are converted to or equilibrated with $CO_2$, which is analyzed in the mass spectrometer. $O_2$ is routinely used for analyses of silicates which are fluorinated to produce $O_2$ gas. Analysis of $O_2$ is required for $\delta^{17}O$ analyses. Finally, oxygen from organic matter is frequently analyzed as CO by reaction with carbon at very high temperatures.

### 2.6.5 Sulfur

Sulfur has four stable isotopes $^{32}S$, $^{33}S$, $^{34}S$ and $^{36}S$ (Chapter 10). Like the triple oxygen isotope system, to a first approximation the four isotopes of sulfur fractionate in predictable proportions, so that measuring all four isotopes is redundant. (In some cases multiple sulfur isotopes can provide important information about low temperature processes – e.g., Farquhar and Wing, 2003; Ono et al., 2003). In general, only the $^{34}S/^{32}S$ ratios are measured, as these are the two most abundant isotopes of sulfur. Sulfur isotope ratios are given by $\delta^{34}S$ notation. $\delta^{34}S$ values are reported relative to the CDT (Cañon Diablo Troilite) standard, a sample of meteoritic troilite (FeS) from Meteor Crater in Arizona. The $^{34}S/^{32}S$ value of CDT is given in Table 2.5. As with the other primary standards, $\delta^{34}S(CDT) \equiv 0.0‰$ by definition. Unfortunately, the CDT standard is not as homogeneous as originally thought, at least on a scale smaller than several milligrams (Beaudoin et al., 1994). The IAEA now distributes two synthetic Ag$_2$S standards with defined $\delta^{34}S$ values relative to CDT (Appendix 1). Sulfur isotope analyses are calibrated to CDT in each laboratory by analyses of these Ag$_2$S standards whose $\delta^{34}S$ values differ by 22‰. CDT now joins the ranks of PDB in the sense that they are the accepted international reference standards for reporting all sulfur and carbon isotope analyses, but neither is distributed and both are defined in terms of recommended $\delta$ values of secondary solid standards.

Sulfur analyses are made on either $SO_2$ gas or SF$_6$ gas (Table 2.4). The advantage of each is discussed in Chapter 10. The $\delta^{34}S$ values of $SO_2$ gas are determined by measuring masses 66 ($^{34}SO_2$) and 64 ($^{32}SO_2$). Unfortunately, there is an isobaric interference at mass 66 from $^{32}S^{16}O^{18}O$, which must be corrected for. This problem does not exist with SF$_6$ because F is monoisotopic, however SF$_6$ is more difficult to produce in the laboratory and requires a mass spectrometer specially configured for the high masses (Table 2.4).

### 2.6.6 Silicon

Silicon has three stable isotopes, $^{28}Si$, $^{29}Si$, and $^{30}Si$. The abundance of the major isotope $^{28}Si$ is 92.2%, while $^{29}Si$ and $^{30}Si$ have abundances of 4.6 and 3.0%, respectively. The three isotope system follows well-established mass dependent fractionation for terrestrial materials, so that there is no need to measure all three isotopes. In general, the $^{30}Si/^{28}Si$ ratios are measured, reported in terms of $\delta^{30}Si$ values. The total range of $\delta^{30}Si$ values for terrestrial materials range from ~-4 to +4‰. Silicon isotope ratios are reported relative to the NIST standard NBS 28 quartz, with a defined value $\equiv 0‰$. Si isotope ratios are measured using either gas source mass spectrometry with SiF$_4$ as the sample gas or...
using multicollector ICPMS. Each method has equivalent precision. Samples measured with gas source mass spectrometry measure the ion fragment SiF$_3^+$ at masses 85, 86 and 87.

2.6.7. Chlorine

Chlorine has two stable isotopes, $^{35}$Cl and $^{37}$Cl. Unlike the other isotope systems commonly studied, the abundance the rare isotope is very high, leading to a non-integer mass for the average atomic weight of Cl (35.453 amu). Originally analyzed as HCl ($g$) (Hoering and Parker, 1961) or CsCl on a thermal ionization mass spectrometer (Magenheim et al., 1994), Cl isotope ratios are now analyzed exclusively using CH$_3$Cl (Long et al., 1993). Seawater, with an extremely long residence time for Cl, is well mixed, and is therefore the accepted standard, defined as Standard Mean Ocean Chloride (SMOC) with a $\delta^{37}$Cl value $\equiv$ 0.0‰. Several Cl isotope standards have been made (Appendix 1), although any ocean sample has a Cl isotope composition equal to 0.0‰, unless extreme contamination has occurred. The ocean has an essentially constant Cl isotope composition, although some publications suggest that there are variations, a conclusion that I believe in general is not correct.

2.7 Isotope Ratio Mass Spectrometry

The mass spectrometer is the heart of nearly all stable isotope laboratories. Some labs are beginning to employ laser spectroscopy systems, but for the last century, most analyses have been made using a mass spectrometer. The foundations of the mass spectrometer can be traced to the Cavendish Laboratory, University of Cambridge, where noted scientists including J.J. Thomson, E. Rutherford and F.W. Aston developed some of the first mass spectrographs. By 1927, Aston had built a second generation machine that allowed for the discovery of isotopes and accurate determinations of their atomic weights. A description of Aston's early machine is discussed in detail and is worth reading (Aston, 1927). In the early to mid-20th century, most isotope ratios were determined gravimetrically, where the mass of a sample was determined using a precise density balance. The difference in the atomic weight of oxygen in air and water – the basis for the 'Dole Effect' – was determined in this way (Dole, 1936). Major improvements were made in the sensitivity and precision of mass spectrometers in the 1940's so that variations in the isotopic composition of natural materials could be measured with the necessary precision. These machines were operated by talented physicists, and extracting high-quality data required skilled practitioners. Only starting in the 1970s and 80s did the mass spectrometer manufacturers begin to offer mass spectrometers that could be used without a great deal of training and infrastructure. Today, there are a wide range of mass spectrometers available, from simple desktop units for low-precision analyses used for simple tracer experiments, to complex doubly-focusing machines that have high sensitivities and mass resolution for analyses of exotic isotopologues from natural samples. At the same time, there is a growing industry of laser spectroscopy systems in which the isotope ratios are measured based on the absorption of infrared radiation by the different isotopologues of a particular gas, such as CO$_2$, H$_2$O, CH$_4$ and N$_2$O (see section 2.8 for further details).

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10 Mass spectrographs used photographic plates to measure the position and intensity of ion beams. Mass spectrometers use electronic collectors which measure the intensity (current) of the ion beam.
2.7.1 Components of a mass spectrometer

All mass spectrometers are based on the principle of deflecting an energetic, focused ion beam in a magnetic and/or electrostatic field. The degree of deflection is a function of mass and charge. The relative intensities of the ion beams of different masses can then be used to calculate isotopologue masses or isotope ratios. The mass spectrometer consists of three primary components (Fig. 2.4): 1) the source, where a sample is ionized, accelerated to a given energy and collimated into a well-focused beam; 2) the analyzer, which acts to deflect the ion as a function of mass. It is the ‘prism’ of the system (See Criss, 1999 for a nice review); and 3) the collector assembly for measuring the relative intensities of the different ion beams. In addition, the mass spectrometer system also has an inlet system for introducing the gas into the source without...
fractionation. (see Sharp, 2014 for a detailed discussion of gas source mass spectrometers).

2.7.1.1 The ion source

The ion source both ionizes the sample gas, accelerates it to a near-constant energy and focuses the beam in the direction of the analyzer. Sample gas is admitted into the source at low pressures and a fraction of the gas is ionized (~0.1%) with an unknown but significant isotope fractionation. The ideal ion source has high ionization efficiency, a well collimated ion beam and a near-constant, or at least linear isotope source fractionation over a wide range of source pressures.

The gas source mass spectrometer uses electron impact ionization, in which a hot tungsten filament generates electrons in the ionization box. The ionization box has a filament on one side and an anode on the other, so that the electrons are accelerated towards an anode with an energy of ~90eV (Fig. 2.5). This energy is more than enough to cause the sample gas to reach its first ionization potential, which ranges from 12.08eV for O₂ to 15.58 for N₂. Interestingly, above 100eV, ionization efficiencies begin to decrease as molecules become ‘transparent’ to the electrons (de Hoffmann et al., 1996). A magnetic field is applied to the electron beam with two small permanent magnets on either side of the ionization box which causes the electrons to spiral towards the anode, thereby increasing ion efficiency. The electron impact knocks an electron off a molecule of sample gas causing it to become positively charged. The source is held at a positive electric potential of 2 and 10 kV relative to ground. The positively ionized gas is accelerated out of the ionization box by the repeller plate and towards a stack of electrostatic lenses which focus the ions into a tight beam. Each lens is at a higher potential relative to the ionization box, so that the ions reach a nearly mono-energetic value equal to the electric potential of the source relative to ground. In addition to imparting energy to the ions, the lens stack acts as a telescope, focusing the beam at the collector assembly.

While the ideal electron impact source ionizes the sample gas by removing one electron, ion fragmentation and double ionization (removal to two or more electrons) invariably occur. If the source conditions remain nearly identical for both sample and reference gas, the fragmentation problems can generally be ignored, because it
will affect both gases to the same extent. Consider CO\textsubscript{2} as an example. CO\textsubscript{2} will ionize primarily to CO\textsubscript{2}\textsuperscript{+}, but other ion fragments, such as such as CO\textsuperscript{+}, C\textsuperscript{+}, and O\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{2+}. A mass spectrum of CO\textsubscript{2} gas will show peaks at masses 12, 16, 22 (doubly ionized CO\textsubscript{2}), 28 and 44.

The ionization efficiency of an electron impact source is on the order of 0.1 to 0.15\% (for CO\textsubscript{2}), with a large and generally unknown isotope fractionation. Again, if source conditions (i.e., pressure) are kept the same both for sample and standard, this fractionation will not affect the relative isotopic ratios of reference and sample gas. How the isotope fractionation changes with source pressure is known as \textit{linearity}. Increasing the draw-out potential from the ionization box increases linearity by minimizing ion-ion interactions, but also reduces the sensitivity of the source. A tradeoff must be made between linearity and sensitivity. If gas quantities are not an issue, then the source should be focused for highly linear conditions.

\subsection{The analyzer}

The mass analyzer is the portion of the mass spectrometer where the ion beams are separated from each other on the basis of their mass. It is equivalent to a prism, which separates light according to wavelength. Most stable isotope mass spectrometers use a magnetic field to separate ions by mass, but doubly-focusing mass spectrometers also use an electrostatic lens in order to attain very high mass resolution. The effects of electric and magnetic fields on an ion beam is given by Lorentz’s law by

\begin{equation}
F = q(E + v \times B)
\end{equation}

where \(F\) is the force acting on the ion, (which determines the degree of deflection in a circular field), \(q\) is the ion charge, \(v\) is velocity and \(E\) and \(B\) are the electric and magnetic forces, respectively.

The energy imparted by the ion source is given by

\begin{equation}
qV = \frac{1}{2} mv^2
\end{equation}

where \(q\) is the charge, \(V\) is the voltage potential between the source and ground, \(m\) is the ion mass and \(v\) is the ion velocity. The force imparted by an electrostatic field, composed of two charged plates in a semi-circular arc results in a deflection of the ion beam given by

\begin{equation}
r = \frac{mv^2}{qE}
\end{equation}

where \(E\) is the electric force. All ions of equal charge traveling through a curved electrostatic field with radius \(r\) will have a constant kinetic energy (\(\frac{1}{2}mv^2\)). Higher or lower energetic ions will have a different radius of curvature and can be physically removed from the beam with proper placement of slit apertures. An electrostatic field is therefore an energy filter, imparting a constant energy to the ion beam.
A magnetic field generates a force equal to $qvB$ which imparts a centripetal force equal to $\frac{mv^2}{r}$. The radius of curvature is given by

$$r = \frac{mv}{qB}$$

Unlike an electrostatic field, where the deflection is related to $mv^2$, a magnetic field deflects ions proportional to $mv$ or momentum. The radius of singly charged particles at constant velocity is therefore related to the mass. For a constant energy ion beam, ions with a smaller mass will be deflected more than ions with a higher mass.

High resolution doubly focusing mass spectrographs have been around for close to a century (e.g., Bainbridge and Jordan, 1936). For most stable isotope studies, sufficient mass separation is achieved with a magnetic field alone. However, for very high mass resolution and when the ions are produced with variable energy, the addition of energy filtering using an electrostatic field is required. Both an ion microprobe and high resolution ICP MS require both electrostatic and magnetic field focusing.

In a magnetic sector mass spectrometer, the magnet separates ions of different masses, but also focuses the ion beam at the point of the collector assembly (Fig. 2.6). Interestingly, it is the radius of the magnetic field, and not the total arc fraction (e.g., 60° vs. 180°) that defines the degree of separation and focus (Nier, 1940). An ion beam leaving the source will necessarily have some degree of divergence. As shown in Fig. 2.6a, the beam will enter the magnetic field and be deflected in such a way as to be refocused on a plane perpendicular to the arc of the magnetic field that includes the ion source and the point of refocusing. Beam divergence also occurs perpendicular to the plane defined by the ion path (the z direction). It has been shown that if the beam crosses the fringing field (edge) of a magnetic field non-perpendicular to the edge of the magnet, the beam will be deflected perpendicular to the median plane (in a vertical direction in a flat-lying magnetic arc – 26.5° angle in Fig. 2.6b). By adjusting the angle of the fringing field, the beam can be deflected – and thereby focused – in a vertical plane at the point of

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11 Commercially available mass spectrometers use 60° or 90° sector field with comparable results.
the collector assembly. The angle between the beam and magnet edge is a function of the arc and the path lengths on either side of the magnet. If properly designed, the deflection that occurs upon entering the magnet causes the beam to become parallel to the magnetic plates, and during the exit deflection, the beam is deflected to focus at the focal plane of the ion beam (e.g., at the collector).

2.7.1.3. Collector assembly

The final component of the gas source mass spectrometer is the collector assembly. The early machines were mass spectrographs, in which the ion beams were focused on photographic plates. The intensity and position of the exposed images gave the position and abundance of the isotopologues. The accuracy attained with photographic film was so high that Francis Aston in 1937 was able to determine the atomic weights of over twenty isotopes to better than 0.008 amu of today’s accepted value (when corrected for different scales) (Aston, 1937). All modern mass spectrometers use electronic detectors to measure the intensity (current) of an ion beam. Positive ions enter a collector which acts as an electron source for charge compensation. Neutralization of the collectors generates an extremely small electric current. The current (total charge per unit time) is related to the intensity of the ion beam. Current is related to voltage by Ohm’s law

\[ V = IR \]

where \( V \) is voltage, \( I \) is current and \( R \) is resistance. By using a very large resistor (10\(^8\) to 10\(^{12}\) \(\Omega\)), a high voltage can be generated from a very small current. A voltage-to-frequency converter is then employed to give a signal that is related to the beam strength. When multiple beams from different isotopologues are collected simultaneously, each collector is fitted with appropriate resistors so that the output voltage (current) of each ion beam are close to the same. For example, the relative abundance of the isotopologues of CO\(_2\) are roughly the following: \(^{12}\text{C}^{16}\text{O}^{16}\text{O} - 0.984\); \(^{13}\text{C}^{16}\text{O}^{16}\text{O} - 0.011\); \(^{12}\text{C}^{18}\text{O}^{16}\text{O} - 0.004\). Voltages for these three beams will be similar if resistors of \(1 \times 10^8\Omega\), \(1 \times 10^{10}\Omega\) and \(3 \times 10^{10}\Omega\) are used for masses 44, 45 and 46, respectively.

For most applications in gas source mass spectrometry, Faraday collectors are used to measure beam intensity. Positive ions are neutralized in the collector and draw an electron for charge compensation. Ideally, the collector acts as a perfect black body surface for reception of the ions. Reflection of ions is minimized by coating the inside of the collector with soft carbon. Some sputtering of the ions occurs, generating secondary electrons. The loss of such an electron would negate the charge contribution from a positive

![Fig. 2.7. Schematic of a Faraday collector. The ion beam passes through a narrow slit a and is neutralized in the collector, generating a current. A charged electrode b prevents secondary electrons generated in the collector cup from exiting the assembly.](image-url)
ion. Collectors are therefore manufactured as deep wells with narrow entrance slits to prevent the loss of secondary electrons. The collector consists of a narrow slit to prevent the introduction of stray ions and a charged electrode at the entrance to the collector to help prevent the secondary ions produced in the collector from escaping back through the entrance slit (Fig. 2.7). Multiple collectors are generally used in order to simultaneously measure the intensities of all relevant isotopologues of a given gas. In this way, electronic drift in the system is minimized. Instrumental designs include either multiple narrow detectors positioned for analysis of a single gas type or ‘universal collectors’, in which several wide cups are paired with a narrow cup. The multiple, narrow collector design is unquestionably superior to the universal collector system, but it can be costly, and flexibility is limited because the positioning of the collectors is generally fixed. For users wishing to be able to analyze multiple gases on a single instrument, the number of collectors required can be quite high. The universal collector design is simple and less costly, but inherently runs the risk of having a greater loss of secondary electrons or reflected ions and the possibility of stray ions entering the cup. In practice, by comparing standard and sample, these effects are minimized.

2.7.1.4 Dual inlet mass spectrometer inlet system

In gas source mass spectrometry, a dynamic inlet system is used. Gas continuously bleeds into the source, is partially ionized, and the excess non-ionized gas is pumped away. A dynamic inlet system avoids the problems of drift due to preferential ionization of one isotopologue relative to another by continuously streaming fresh sample gas into the source. Source pressures must be kept low to avoid molecular collisions in the flight tube which would otherwise broaden the well-focused beam. Therefore some method of pressure reduction is required between the gas reservoir and the source. Whereas the gas pressure in the sample reservoir is on the order of $10^2$-$10^3$ mbar, pressures are reduced to $10^{-4}$ bars in the ionization chamber and $10^{-6}$ to $10^{-8}$ bars in the flight tube. The pressure drop from sample volume to source could be accomplished by having a pinhole orifice between the gas volume and the source, but such a geometry causes an isotopic fractionation, with the lighter isotopologues preferentially passing through the orifice due to their higher translational velocities (Graham's Law). To eliminate this fractionation, gas source mass spectrometers are equipped with a capillary inlet system. A long (~1 m) 0.1mm I.D. capillary is connected to the gas volume adjusted to between 10-100 mbar pressure. At the other end – the interface with the high vacuum of the mass spectrometer – the capillary is crimped, so that the pressure drops to $10^{-4}$ bar in the source. The light molecules will preferentially pass through the crimp, but because the mean free path of individual molecules in the capillaries is a fraction of the capillaries’ internal diameter (~$10^{-7}$ m), the gas migrates along the capillary into the mass spectrometer under viscous flow conditions. Like leaves floating on a swift moving stream, the random motion of individual molecules is overwhelmed by the overall flow direction of the gas through the capillary into the mass spectrometer. Using this type of geometry, there is no fractionation in the capillary inlet system as long as the pressure in the capillary is kept in the 10-100 mbar range.
High precision is achieved by rapidly switching between sample and reference gas using a system of changeover valves ('switching block' in Fig. 2.4). First described by Murphey (1947) and then McKinney et al. (1950), two identical capillary systems feed through a system of four change-over valves so that either the reference gas or the sample gas enters the mass spectrometer. Gas always flows through the two capillaries to achieve steady state flow. The switching valves change the flow path between the source and a waste pump. Switching between reference and sample gas can be accomplished rapidly, so that the intensities of all ion beams for the sample and reference gas can be compared almost simultaneously. This rapid switching minimizes any errors associated with drifting electronics. In order to keep conditions in the source as similar as possible, both reference and sample gas are adjusted to be nearly the same pressure. This was originally accomplished using mercury pistons, but is now done using flexible steel bellows controlled by stepping motors ('bellows' in Fig. 2.4).

2.7.2 Gas Chromatograph Isotope Ratio Mass Spectrometry (GC-IRMS)

In recent years, the continuous flow method of gas introduction has revolutionized isotope ratio mass spectrometry and opened up a panoply of research avenues (Matthews and Hayes, 1978). In place of analyzing gas using the dual inlet method of measurement, samples of gas are entrained in a He stream, purified in a gas...
chromatograph and (with or without first oxidizing or reducing the gas by passage through an oven) introduced directly into the source of the mass spectrometer. Initial applications of the GC were mainly to purify the gas. Early online applications included the now routine high temperature combustion of very small C and/or N-bearing samples in an elemental analyzer or equivalent oxidation furnace (Fig. 2.8). Another important application is compound specific analysis of organic molecules (Hayes et al., 1989). Organic species are separated on a GC column and oxidized (or reduced) sequentially before being analyzed in the mass spectrometer. A simple example would be the analysis of a natural gas sample. The gas consists of methane (CH₄), ethane (C₂H₆), propane (C₃H₈), etc. The lighter alkanes pass through the GC column faster than heavier ones, and with a judicious choice of GC columns, flow rates, temperatures, etc, it is possible to get a quantitative separation of the different alkanes. The methane exits the GC column first and is carried by the He stream through a copper oxide furnace where it is oxidized to CO₂ and introduced into the mass spectrometer. The δ¹³C value of the methane-derived CO₂ is determined as it flows into the source. Ethane and higher alkanes follow sequentially, allowing for the δ¹³C values of each species to be determined. The range of isotopic variations within a single sedimentary organic sample can often exceed the total variation of different bulk samples (Freeman et al., 1990). This information has been used extensively for paleoclimate reconstruction, ecology and metabolic studies.

GC-IRMS (Gas Chromatography- Isotope Ratio Mass Spectrometry) technology has been modified so that it can be used in place of conventional extraction techniques for almost every material that has been analyzed conventionally. The advantages of GC-IRMS is that gases can be purified easily and efficiently, analysis is extremely rapid, and sample sizes are reduced by several orders of magnitude. Systems that combine gas chromatography and continuous flow technology continue to find important applications in the earth and biological sciences. Recent improvements in analyses of water and carbonates effectively replace analytical methods that have been in use with only minor modification for over half a century. There is a slight loss of precision relative to the traditional dual inlet system, although the gap is reduced every year.

2.7.3 Gases measured in isotope ratio mass spectrometry

Gases that are commonly introduced into isotope ratios mass spectrometers and masses of the isotopologues measured are given in Table 2.4. Hydrogen isotope ratios are almost always determined from the 3/2 ratios of H₂. Carbon isotope ratios are almost always determined from 45/44 ratios of CO₂ gas. Nitrogen isotope ratios are determined from 29/28 and 30/28 ratios of N₂. Because the concentration of ¹⁵N¹⁵N is negligible in nature, measurements are made of mass 30 only when materials artificially enriched in ¹⁵N are being studied. Oxygen isotope ratios are most commonly determined from measurements of 46/44 ratios of CO₂ but, more and more frequently, the gases CO and O₂ are being used. ¹⁸O/¹⁶O ratios are determined from the 30/28 mass ratio of CO and the 34/32 mass ratio of O₂. ¹⁷O/¹⁶O ratios are determined from 33/32 ratios of O₂. CO is the gas of choice for emerging pyrolysis applications.

As discussed in section 2.6.5., sulfur isotope ratios can be measured on either SO₂ or SF₆. SO₂ is easily produced from most samples and can be analyzed in most mass spectrometers, but has a number of disadvantages, most notably, it quickly dirts the source of the mass spectrometer (see section 10.2). This problem is reduced significantly
in continuous flow systems where only minor amounts of SO2 are introduced into the mass spectrometer. SF6 is cleaner and allows for the rare isotope ratios to be measured, but it is difficult to produce and requires a large-radius mass spectrometer especially configured for SF6.

Silicon isotope ratios are measured on SiF4 gas. The fragment SiF3+ is analyzed because it is the major isobar produced in the source. Masses 85 (28SiF3+), 86 (29SiF3+) and 87 (30SiF3+) are analyzed. Chlorine isotope ratios are made using CH3Cl. Masses 50 (CH335Cl) and 52 (CH337Cl) are analyzed. Many normal triple collector assemblies are not quite configured correctly for simultaneous analysis of masses 50 and 52, so that mass spectrometers must be fitted with special collectors for CH3Cl analysis.

2.7.4 Relations between measured and desired isotopic ratios

The relationship between intensities of measured gasses in a mass spectrometer and the actual isotopic ratio of a given element is different for each gas. A few of the salient points pertinent to the analyses of three gases (H2, N2, and CO2) will be made here to gain an appreciation of this important aspect of isotope ratio mass spectrometry.

After experimenting with various hydrogen containing gases, Irving Friedman (1953) concluded that diatomic hydrogen was the most suitable for determination of hydrogen isotope ratios and H2 remains the gas of choice to this day. Isotopic analysis of hydrogen poses a unique analytical problem. One of the ionic fragments produced in the source of the mass spectrometer is H3+ which has the same mass 3 as HD+. Collection of this ion results in an apparent 3/2 ratio that is higher than the true HD/HH ratio. The production of H3+ is proportional to the pressure of hydrogen gas in the source because this ion is produced by the reaction H2 + H2+ \rightarrow H3+ + H. The H3+ contribution to mass 3 can be minimized, but not eliminated, by using a high accelerating voltage and a low gas pressure. The contribution of H3+ is evaluated by measuring the 3/2 ratio as a function of source pressure, a procedure that is done routinely on modern mass spectrometers. The correlation is linear on most modern machines (at low pressures, less H3+ is produced). Once the relationship between pressure and contribution of H3+ is determined, a correction algorithm can be applied that removes the mass 3 contribution from the H3+ ion (i.e., extrapolate back to zero pressure).

Nitrogen isotope analysis is relatively straightforward. Measurements are made of two isotopologues of molecular nitrogen whose masses are 28 and 29. The isotopologue with mass 28 consists solely of 14N14N while that of mass 29 is a sum of the two possible orientations of 15N and 14N atoms in the molecule, 15N14N and 14N15N. The desired mass ratio is then obtained from the relatively simple relation12:

\[
\frac{29}{28} \approx 2 \times \frac{15N}{14N} \tag{2.28}
\]

12 The actual relationship is \( \frac{29}{29+28} = 2 \times \frac{15}{14} \) or \( \frac{29}{28} = \frac{2 \times 15}{14} \). If the 15/14 ratio is 3670 \times 10^{-6}, the actual stochastic 29/28 ratio is 7367 \times 10^{-6}, whereas equation 2.28 gives a 29/28 ratio of 7340 \times 10^{-6}.
Chapter 2. Terminology, Standards and Mass Spectrometry

The molecular mass ratio 29/28 is twice the atomic mass ratio of 15/14 and is the one used to determine nitrogen isotope ratios. This same mathematical correction is used for CO₂ as well.

The nine isotopologues of CO₂ that are measured on a mass spectrometer are given in Table 2.7. An additional 5 are included when mass 47 is measured in 'clumped isotope' studies (see section 6.7). Deconvolution of the three masses 44, 45 and 46 to ^13C/^12C and ^18O/^16O ratios can be made assuming that the relationship between ^17O/^16O and ^18O/^16O ratios (equation 2.2) is valid. Given that (^17O/^16O) ∼ (^18O/^16O)^0.5, the three masses 44, 45 and 46 of CO₂ can be used to determine both ^13C/^12C and ^18O/^16O ratios (Craig, 1957; Santrock et al., 1985). The 46/44 ratio measured in the mass spectrometer is close to the ^18O/^16O ratio, because ^12C^16O^18O makes up >99.7% of the total isotopologues at mass 46. On the other hand, the ^13C/^12C ratio of CO₂ gas is not the same as the 45/44 ratio because the ^12C^17O^16O isotopologue is on the order of 7% of the total mass 45 isobar. For δ¹³C analyses, the common '¹⁷O correction' must be made. The δ¹⁷O value of the CO₂ sample is estimated from the measured δ¹⁸O value and the relationship between ^17O/^16O and ^18O/^16O (equation 2.2). The ^12C¹⁷O¹⁶O contribution to mass 45 is then subtracted from the total 45 isobar intensity in order to obtain the contribution of just ^13C¹⁶O₂.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Isotopologue</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>^18O¹²C¹⁶O</td>
</tr>
<tr>
<td>45</td>
<td>^16O¹³C¹⁰O, ^1^5O¹²C¹⁶O, ^1^6O¹²C¹⁷O</td>
</tr>
<tr>
<td>46</td>
<td>^1²O¹²C¹⁰O, ^1⁶O¹³C¹⁷O, ^1⁷O¹²C¹⁷O, ^1⁸O¹²C¹⁶O, ^1⁶O¹²C¹⁸O</td>
</tr>
<tr>
<td>47</td>
<td>^1³O¹³C¹⁰O, ^1²O¹⁵C¹⁰O, ^1⁷O¹³C¹¹O, ^1⁷O¹²C¹⁸O, ^1⁸O¹²C¹⁷O</td>
</tr>
<tr>
<td>48</td>
<td>^1⁶O¹²C¹⁵O, ^1⁸O¹³C¹⁷O, ^1⁷O¹³C¹⁸O</td>
</tr>
<tr>
<td>49</td>
<td>^1⁸O¹³C¹⁸O</td>
</tr>
</tbody>
</table>

2.8 Laser absorption mass spectroscopy

In recent years, laser absorption spectroscopy has been modified for use in stable isotope analysis. This method involves measuring the absorption of electromagnetic radiation (generally infrared) generated by a laser at a frequency specific to the absorption of a single isotopologue of a gas molecule (Fig. 2.9). There are a large number of absorption bands for any molecule that has a dipole¹³, and bands are chosen in the frequency range of the laser which are close to one another without any interferences from other absorption lines. Absorption is directly related to concentration following Beer-Lambert law, given by

$$ I = I_o \exp(-\sigma Cl) $$  \hspace{1cm} 2.29,

where \( I_o \) and \( I \) are the intensity of the electromagnetic radiation entering and leaving the chamber containing the gas, \( C \) is the concentration of the absorber, \( l \) is the sample path length and \( \sigma \) is the absorption cross section at the appropriate wavelength. The laser light

¹³ A dipole has a permanent bond polarization – two atoms with different electronegativity. O₂ and N₂ consist of two atoms with the same electronegativity and have no dipole.
is directed through the input mirror (with most being reflected back to the laser) and reflects back and forth between two parallel mirrors. The intensity of the reflecting light is measured by a photo-sensitive detector behind the output mirror. The concentration of a molecular species is determined from the $I/I_0$ value.

Several systems are now commercially available that take advantage of low-cost tunable diode lasers. Two distinct methods are employed. The first, called off axis cavity output spectroscopy, measures changes in intensity of the laser beam as it scans across the wavelength of interest (Baer et al., 2002). By having the beam reflect multiple times between the two mirrors in the sample cavity, it is possible to achieve path lengths of several km, thereby drastically increasing the degree of absorption (Fig. 2.10). The second method, called cavity ring-down laser absorption spectroscopy, measures changes in the intensity of the reflecting beam as a function of time. A pulse of laser light charges the cavity and the laser is quickly shut off. The rate of decay (the ‘ring-down’ time) of the laser beam (on the order of several microseconds) is a function of the concentration of the absorbing species. The higher the concentration, the more rapid the ring-down time. Each method has certain advantages and disadvantages, and at present, it appears that the precision of the two systems are more-or-less equivalent (Johnson et al., 2011).

The tunable diode laser systems are used primarily for H and O isotope ratios of water and C and O isotope ratios of CO$_2$, carbon from methane, and N and O in N$_2$O (Baer et al., 2002; Crosson et al., 2002; Lis et al., 2008; Brand et al., 2009). Analyses can only be made on gases which are transferred into the laser cavity in a carrier gas, either N$_2$ or dry air. Precision is only slightly lower than that attainable from conventional mass spectrometry. At low concentrations of water vapor, serious analytical bias is observed, however. Care must be taken to avoid interferences from contaminant gases (Brand et al., 2009). For all of the commercially available laser systems, the sample flows through the chamber continuously throughout the measurement, although efforts to introduce a small
amount of gas into the cavity in a static mode has met with success (Berryman et al., 2011).

The future outlook for laser spectroscopy systems is quite favorable. Simultaneous analyses of both D/H and 18O/16O ratios are possible because the absorption bands of 1H216O, 1H2H16O, and 1H218O are all distinct and large enough for accurate analysis, and recently manufacturers have added 17O to the total analysis (although non-linearity problems persist). Similarly, analyses of N2O and CO2 may allow for isotopologues of the rare isotopes to be measured with far greater ease than by traditional mass spectrometry methods. Ono et al. (2014) have successfully developed a laser absorption spectroscopy system that is able to measure the isotopic composition of the rare methane isotopologue 13CH3D. Laser spectroscopy systems have also been used for measuring the rare ‘clumped’ isotope 13C16O18O (mass 47) and 17O/16O ratios in CO2 gas (Sakai et al., 2017) The ability to measure rare isotopologues and separate the contributions of different same-mass isotopologues (e.g., 13CH4 and 12CH3D) suggests exciting applications yet to come. It is doubtful that the laser systems will supplant the gas source methods entirely, although for routine analyses, the cost of the instruments are far lower than for gas source mass spectrometers and the off-line preparation of samples such as water is virtually eliminated. The laser systems are compact and easily deployable to the field. It is likely that continued advancements to the laser systems will be made, resulting in lowered price and greater versatility.

Fig. 2.10. Different configurations for laser absorption spectroscopy. Off axis cavity spectroscopy (top) causes the laser beam to reflect between two parallel mirrors multiple times before being analyzed at the detector, thereby increasing the effective cavity length (Baer et al., 2002). The second method (bottom) is the cavity ringdown laser, in which the cavity is charged with ‘light’ which reflects between several mirrors. The light source is switched off and the rate at which the light intensity decays (rings down) is measured by a detector, which allows a fraction of the radiation to pass through the mirror to the detector. The rate of decay (ringdown rate) is a function of the concentration of the absorbing gas in the cavity (Crosson et al., 2002).
REFERENCES


