

Chapter 2

The Isotopes of Hydrogen and Oxygen

Hydrogen and oxygen have a number of isotopes, both stable and radioactive. The major isotope of hydrogen with a mass of 1, (^1H), occurs in the hydrosphere at a mass abundance of 99.985%. It is accompanied by about 0.015% of the heavy isotope ^2H whose particular name is Deuterium, designated D in the older literature. An even heavier isotope of mass 3 (^3H), named Tritium, is unstable to β decay with a half-life of 12.43 years; this is the value usually accepted even though more recent measurements suggest the value of $T_{1/2} = 12.23$ years (Lucas and Unterweger, 2000). As this half-life is compatible with the holdup time in many subsurface reservoirs, Tritium is also widely used in hydrologic studies as a tracer.

The most abundant oxygen isotope, ^{16}O , whose mean mass abundance in the hydrosphere is given as 99.762%, is accompanied by a number of stable and radioactive isotopes. The radioactive oxygen isotopes ^{14}O , ^{15}O , ^{19}O and ^{20}O all have half-lives of only seconds and are thus too shortlived to be of any significance in the study of the hydrologic cycle. However, the two stable heavy isotopes of oxygen, ^{17}O and ^{18}O , whose average abundances are 0.0379% and 0.200%, respectively, are the powerhouses of isotope hydrology.

Given the five stable isotopes of hydrogen and oxygen, one will have nine isotopic water molecules (termed isotopologues in the recent literature) ranging from a mass of 18 for $^1\text{H}_2^{16}\text{O}$ to mass 22 for $^2\text{H}_2^{18}\text{O}$. Assuming statistical distribution of the isotopic species in water, the abundances shown in Table 2.1 are proposed. It is clear that one is concerned mainly with the molecules $^1\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}_2^{17}\text{O}$, $^1\text{H}_2^{18}\text{O}$ and, of course, $^1\text{H}_2^{16}\text{O}$. The doubly labeled molecules $^1\text{H}^2\text{H}^{17}\text{O}$, $^1\text{H}^2\text{H}^{18}\text{O}$ and $^2\text{H}_2^{16}\text{O}$ and even more so the triply substituted molecules $^2\text{H}_2^{18}\text{O}$ and $^2\text{H}_2^{17}\text{O}$ can be disregarded at the level of natural abundance of these isotopes.

Table 2.1. Isotopic water species and their relative abundance.*

Mass	Molecule	Rel.Abundance
18	$^1\text{H}_2^{16}\text{O}$	0.99731
19	$^1\text{H}^2\text{H}^{16}\text{O}$	3.146×10^{-4}
19	$^1\text{H}_2^{17}\text{O}$	$3,789 \times 10^{-4}$
20	$^1\text{H}^2\text{H}^{17}\text{O}$	1.122×10^{-7}
20	$^2\text{H}_2^{16}\text{O}$	2.245×10^{-8}
20	$^1\text{H}_2^{18}\text{O}$	2.000×10^{-3}
21	$^2\text{H}^{17}\text{O}$	—negligible
21	$^1\text{H}^2\text{H}^{18}\text{O}$	6.116×10^{-7}
22	$^2\text{H}_2^{18}\text{O}$	—negligible

(* Assuming equilibration during disproportionation reactions)

{Note that the abundance of molecules which are singly substituted by Deuterium, e.g. $^1\text{H}^2\text{HO}$, is twice that of the product of the atomic abundances}. As given by Coplen *et al.* (2002).

Because of the measurement procedure by mass spectrometry, one often uses isotope (abundance) ratios, R , rather than the conventional concentration units, C . $R = N_i/N_j$ where N_i and N_j are the numbers of the rare and common isotope species, respectively. For the case of low natural abundances of the heavy isotope (so that the number of double-labelled molecules such as $^2\text{H}_2\text{O}$ is low) this practically equals the atom-% of the two isotopes.

The concentration of the isotopic molecules, C , is defined as:

$$C = (\text{number of isotopic molecules})/(\text{total number of molecules}),$$

and this is related to the isotope ratio as follows: $C = R/(1 + R)$.

One uses a superscript before the symbols to refer to the isotope under consideration while the molecule involved follows in parenthesis. Thus, for example, $^{18}\text{R}(\text{H}_2\text{O})_v$ stands for the ratio of $[\text{H}_2^{18}\text{O}]/[\text{H}_2^{16}\text{O}]$ in water vapour, while $C(\text{H}_2^{18}\text{O})_v$, the concentration of H_2^{18}O , is given by the ratio of $[\text{H}_2^{18}\text{O}]/\Sigma$ [all isotopic water molecules] which can also be written as $C(\text{H}_2^{18}\text{O}) = [\text{H}_2^{18}\text{O}]/[\text{H}_2\text{O}]$, recalling that H or O without any mass assignment signifies the total amount of that element. In the case of natural waters where the abundances of the “heavy” isotopes are small, these two scales do not differ in a significant way.

Even though these isotopes are stable and not subject to radioactive decay, they can be products or reactants in nuclear reactions initiated by natural radioactivity or by cosmic radiations. Moreover, hydrogen is accreted from the solar wind with isotopic abundances quite different from the terrestrial ones. However, these interactions are believed to be of only

Table 2.2. Properties of isotopic water molecules.

	$^*H_2^{18}O$	$^2H_2^*O$	$^1H^2H^*O$
Density [g.ml ⁻¹ at 30 °C] ^b	1.107845	1.10323	1.04945 ^a
Temperature at maximum density [°C] ^b	4.305	11.24	
Boiling point [°C] ^c	100.14	101.42	
Melting point [°C] ^b	0.28	3.81	
Self-diffusion coefficient through liquid water [D.10 ³ (cm ² .s ⁻¹ at 25°C)] ^d	2.66	2.34	
Molecular diffusivity through air relative to the diffusivity of $^*H_2^*O$] ^e	0.9723		0.9755

Legend:

- * — element at natural abundance
- a — estimate by interpolation
- b — (Steckel and Szapiro, 1963)
- c — (Szapiro and Steckel, 1967; Zieborak, 1966)
- d — (Wang *et al.*, 1953)
- e — (Merlivat, 1978)

minor consequence for the average terrestrial abundance, which can be considered invariant to a first approximation.

The observed variability in the isotopic abundance within the hydrologic cycle, and in other materials in the lithosphere or biosphere, which range about $\pm 50\%$ around the mean ^{18}O abundance and from $+300\%$ to -500% in the case of Deuterium (2H), are the result of isotope fractionation processes within the system, to be discussed in the following chapters. Throughout the hydrological cycle, the phase transitions of water between ice, liquid and vapour are the most important processes to be reckoned with.

Some properties of the isotopic molecules of water are shown in Table 2.2.

The ratio of densities of $H_2^{18}O/H_2O^*$ and $^2H_2O/H_2O^*$ is close to $d_{30}^{30} = 1.12653$ and 1.108018 , respectively. These values are close to the mass ratios of 1.1110 and 1.1117 . The good agreement is the result of the fact that inter-atomic distances are almost invariant under isotopic substitution. The molecules $^1H^2H^{16}O$ and $H_2^{17}O$ have properties in between those of the heavy and light water molecules.

2.1. Measurement techniques

Mass is the most immediately discernible difference between the stable isotopic species. Thus it is only natural that in the beginning (following the

discovery of the stable isotopes of hydrogen and oxygen in the 1930s), the analytical method used for measuring isotope abundance variations in water was based on the density difference between heavy and light water. These measurements were brought to a state of great refinement, so that differences in specific gravity of the order of 0.1γ (one part in 10^7) were detected (Kirschenbaum, 1951). The detection limits by the specific gravity measurements are equivalent to the changes of 0.093 mmol% and 0.083 mmol% for Deuterium and Oxygen-18, respectively. This is well within the range of the natural variability. However, as the density of a given water sample is a function of both the Deuterium and Oxygen-18 content, it was necessary to make allowance for this; for example, by normalising either the oxygen or hydrogen content of the sample.

A number of other analytical methods, which are in use for the analysis of enriched isotopic samples, have also been used at natural abundance levels. Among these methods are the determination of the Deuterium or Oxygen-17 content by n.m.r. and by spectroscopic methods. Indeed the discovery of Oxygen-18 in natural materials by Giauque and Johnston in 1929 was based on the interpretation of the spectrum of atmospheric oxygen, and the first natural abundance determination of Deuterium by H. C. Urey (Urey *et al.*, 1932) was made by measuring the intensity of Balmer lines in the spectrum of hydrogen gas. An additional possible tool is by means of specific nuclear reactions involving one or the other of the heavy isotopes. As an example, the use of the reaction $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$ was proposed for determining the ^{18}O abundance based on the radiation counting. These methods have the advantage of enabling a (chemically) non-destructive test.

None of all these methods, however, was developed to an extent that would enable the determination of abundances at a sensitivity commensurate with natural variability and, thus, be applicable as routine tools in hydrological studies. Only recently, laser absorption spectroscopy is being developed as an attractive alternative for analysis of isotopic abundances at natural levels (Kerstel and Meijer, 2005).

Mass spectrometry is the most directly applicable tool for isotope analysis. However, in the 1940s, the achievable reproducibility of the measurement of the isotope ratio of $^{18}\text{O}/^{16}\text{O}$, for example, was barely 10^{-4} and thus not satisfactory for natural abundance variations, which require a resolution of $5 \cdot 10^{-5}$ or better for observing variations in the oceanic domain. The main reason for the noise in the measurements was long-term instrumental instabilities. This shortcoming was skilfully overcome in the Nier-McKinney mass spectrometer (Nier, 1947; McKinney *et al.*, 1950). This

mass spectrometer (MS) was designed specifically for the measurement of small differences in isotope abundance by means of a double inlet (for close comparison between sample and standard) and a double or triple collector so that a direct measurement of the isotope ratio is made. Except for some early attempts at introducing the water directly into the MS (which necessitated a heated and specially treated tube in order to minimize the adsorption and decomposition of the water molecules), one uses more inert gases as carriers of the isotopic signature. The commonly used gas for the measurement of the Deuterium content of the waters is hydrogen gas (H_2), whereas carbon dioxide (CO_2) is preferred for the measurement of oxygen isotopic abundance.

The mass-spectrometric measurement of the hydrogen gas is based on the simultaneous collection of the ion currents for masses 2 and 3. The ion current for mass 2 (I_2) accounts for the ion ($^1\text{H}_2$)⁺; the ion current for mass 3 (I_3) account for the ions ($^1\text{H}^2\text{H}$)⁺ and ($^1\text{H}_3$)⁺; to correct for the presence of the ion ($^1\text{H}_3$)⁺ readings are extrapolated to zero pressure in the MS to yield the corrected ion current I_3^* .

It is to be noted that for statistical reasons, the atom ratio of the two hydrogen isotopes, $R(3/2)_{\text{H}_2}$, is given by the equation $I_3^*/I_2 = 2 \times R(3/2)_{\text{H}_2}$.

The mass-spectrometric measurement of the CO_2 gas entails the masses 44, 45, 46 and 47.

- The ion current for mass 44 (I_{44}) accounts for the ion ($^{12}\text{C}^{16}\text{O}_2$)⁺
- The ion current for mass 45 (I_{45}) accounts for the ions ($^{13}\text{C}^{16}\text{O}_2$)⁺ and ($^{12}\text{C}^{16}\text{O}^{17}\text{O}$)⁺
- The ion current for mass 46 (I_{46}) accounts for the ions ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$)⁺ and ($^{13}\text{C}^{16}\text{O}^{17}\text{O}$)⁺
- The ion current for mass 47 (I_{47}) accounts for the ion ($^{13}\text{C}^{17}\text{O}^{18}\text{O}$)⁺ .

The corrected ion current which represents the ^{16}O component (I_{16}^*) is the sum of I_{44} and I_{45} after correction for the contribution of the ion ($^{12}\text{C}^{16}\text{O}^{17}\text{O}$)⁺ based on the Bigeleisen rule of $\Delta(^{18}\text{O}) \approx 2\Delta(^{17}\text{O})$ (Bigeleisen, 1962).

The corrected ion current which represents the heavy oxygen isotope (I_{18}^*) is the sum of I_{46} and I_{47} . Usually, I_{47} is not measured and its amount is estimated according to the contribution of the ^{13}C atom based on the ratio of I_{45}/I_{46} . The atom ratio of the isotopes $^{18}\text{O}/^{16}\text{O}$ is then given by the equation:

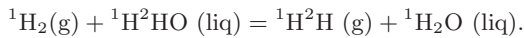
$$I_{18}^*/I_{16}^* = 2 \times R(18/16)_{\text{CO}_2}.$$

The procedures for preparing the samples of water for analyses (i.e. the conversion to CO_2 and H_2 respectively) is described in Box 2.1. Some special features of analysis of saline waters are described in Box 2.2. Lately, the use of carbon monoxide (CO) and oxygen gas is becoming more prevalent, using online conversion techniques. The measurement of the rarer isotope ^{17}O will be described in Box 2.4.

Box 2.1. Procedure for preparing water samples for MS analysis.

2.1a. Procedures for analysis of the hydrogen isotope abundance:

- (1) Classically, water vapour is obtained by the distillation of water from the sample, followed by decomposition of the vapour over hot metal, e.g. Uranium, Cobalt or Zinc. Assuming no fractionation during distillation, then $^2\text{R}(\text{H}_2) \sim ^2\text{R}(\text{H}_2\text{O})$. For problems encountered in the case of saline waters, consult Box 2.2.
- (2) By equilibration with hydrogen gas over a catalyst at a well-defined temperature, to attain equilibrium according to the reaction:

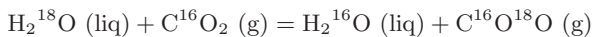


In this case, $^2\text{R}(\text{H}_2) = ^2\alpha^*(\text{T.Sal}).^2\text{R}(\text{H}_2\text{O})$ after correction for the Deuterium introduced by the hydrogen gas, where $^2\alpha^*$ is the equilibrium fractionation factor for the Hydrogen-Water exchange reaction. Note that α^* is a function of both temperature and the salinity.

Note that the isotope abundance will be given in the concentration scale in the case of preparation 1 and in the activity scale for case no. 2.

2.1b. Procedures for measuring the $^{18}\text{O}/^{16}\text{O}$ ratio in water by conversion to CO_2 gas:

- (1) Usually by equilibration with CO_2 (acid catalysed) according to the equation:

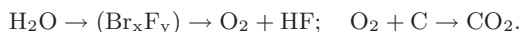


After correcting for the isotopes introduced by the CO_2 gas, we have:

$$^{18}\text{R}(\text{CO}_2) = ^{18}\alpha^*(\text{T,Sal}) \cdot ^{18}\text{R}(\text{H}_2\text{O})$$

where $^{18}\alpha^*$ is the equilibrium fractionation factor for the CO_2 -Water exchange;

- (2) Decomposition and synthesis by the following sequence of reactions:



In this case, $^{18}\text{R}(\text{CO}_2) \approx ^{18}\text{R}(\text{H}_2\text{O})$ on the concentration scale.

Box 2.2. The isotope salt effects and the analysis of saline waters.

The fundamental feature of stable oxygen and hydrogen isotopes ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) in saline waters is that the thermodynamic activity ratios of these isotopes differ from their composition ratios, which is known as the “isotope salt effects.” The isotope salt effect, first described by Taube (1954), results from the interactions between dissolved electrolyte ions and water molecules (e.g. hydration of ions) which change the activity of isotopic water molecules. The isotope salt effect can be rigorously defined in terms of thermodynamics (Horita *et al.*, 1993), as in Eq. (1):

$$\Gamma = \frac{R_{\text{activity}}}{R_{\text{composition}}} = \frac{a(\text{HDO})/a(\text{H}_2\text{O})}{X(\text{HDO})/X(\text{H}_2\text{O})}$$

or

$$\frac{a(\text{H}_2^{18}\text{O})/a(\text{H}_2^{16}\text{O})}{X(\text{H}_2^{18}\text{O})/X(\text{H}_2^{16}\text{O})} = \frac{\gamma(\text{HDO})}{\gamma(\text{H}_2\text{O})} \quad \text{or} \quad \frac{\gamma(\text{H}_2^{18}\text{O})}{\gamma(\text{H}_2^{16}\text{O})} \quad (1)$$

where a , X , and γ denote the activity, mole fraction, and activity coefficient of isotopic water molecules, respectively. The R stands for $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$. From the relation $R = 1 + 10^{-3}\delta$, we obtain,

$$10^3 \ln \Gamma \cong \delta_{\text{activity}} - \delta_{\text{composition}} \quad (2)$$

At any given temperature, the magnitude of the isotope salt effects is practically linear with the molality (mol/kg H_2O), and the oxygen and hydrogen isotope salt effects in chloride-type brines at 20–25°C can be expressed as a sum of the effects by individual electrolyte components (Sofer and Gat, 1972, 1975; Horita, 1989), as in Eq. (3):

$$\begin{aligned} 10^3 \ln \Gamma(\text{D/H}) &= 2.2m \text{ NaCl} + 2.5m \text{ KCl} + 5.1m \text{ MgCl}_2 + 6.1m \text{ CaCl}_2 \\ 10^3 \ln \Gamma(^{18}\text{O}/^{16}\text{O}) &= 0.16m \text{ KCl} - 1.11m \text{ MgCl}_2 - 0.47m \text{ CaCl}_2 \end{aligned} \quad (3)$$

where m is the molality (mol/kg H_2O). Horita *et al.* (1993, 1995) extended experimental determinations of the isotope salt effects to elevated temperatures.

For isotopic fractionation processes between brines and other phases (vapor, gas, minerals) and dissolved species, the isotope activity ratio should be used. For processes in which isotopic water molecules behave conservatively (e.g. mixing of different water bodies, dissolution-precipitation of evaporite deposits), the isotope composition ratio is the unit of choice. However, even in such cases the isotope activity ratio is equally useful, because the magnitude of the isotope salt effects is practically linear with the concentration of dissolved salts. For more in-depth discussion and examples for geochemical implications of the isotope salt effects, see Horita *et al.* (1993b).

The isotopic compositions of saline waters have traditionally been determined by the same methods which have been used for fresh waters; metal- (Zn, U, Cr. . .) reduction for $\delta^2\text{H}$ and CO_2 –water equilibration methods for $\delta^{18}\text{O}$ values.

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Box 2.2. (Continued)

It should be noted that the former method yields the $\delta^2\text{H}$ composition values, but that the latter method the $\delta^{18}\text{O}$ activity ratio. In addition to this discrepancy between the two analytical methods, several problems are encountered in the isotopic analysis of brines due to dissolved salts, e.g. incomplete reduction of water in brines to H_2 , sluggish isotope equilibration between CO_2 and brines, etc. (Horita, 1989). The former problem, particularly, resulted in poor $\delta^2\text{H}$ values of hypersaline brines from the Dead Sea. Using the H_2 -water equilibration method for obtaining the $\delta^2\text{H}$ activity ratio (Horita, 1988) and the azeotropic distillation method after the removal of alkaline-metal cations for obtaining the composition ratio (Horita and Gat, 1988), it was possible to determine directly both $\delta^2\text{H}$ values for a suite of Dead Sea brines (Horita and Gat, 1989). These results show that the $\delta^2\text{H}$ composition values of Dead Sea brine from the literature are systematically (up to ca. 10‰) lower than the new set of data. In addition, the new data of $\delta^2\text{H}$ varies linearly with $\delta^{18}\text{O}$ activity values as expected for evaporative water bodies. The directly measured $^2\text{H}/^1\text{H}$ isotope salt effects ($10^3/\ln\Gamma$) for the Dead Sea brines of salinity $\sigma_{25} = 232.2$ ($m\text{NaCl}=1.95$, $m\text{KCl}=0.15$, $m\text{MgCl}_2 = 2.00$, and $m\text{CaCl}_2 = 0.49$) is +17.8‰, which is in excellent agreement with that calculated from the experimentally determined Eq. (3). A small (+1.2‰) hydrogen isotope salt effect was detected even for a suite of seawaters (Shank *et al.*, 1995).

The H_2 — water equilibration method is a preferred method for $\delta^2\text{H}$ measurements of brines because of (a) high precision and accuracy, (b) yielding the isotope activity ratio, and (c) high throughputs by automation (Horita *et al.*, 1989).

Using the differential MS measurements, reproducibilities of better than $2 \cdot 10^{-5}$ for the $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios were achieved. The preparation of the sample for mass spectrometric analysis, rather than the MS measurement itself, is often the weakest link in the analysis.

The differential measurement technique obviously requires a reference, with which the measurements of the different samples are compared. Following some early arbitrarily chosen standards, such as the NBS-1 reference standard (a sample of Potomac River water), Craig in 1961 suggested the mean ocean water composition as a natural standard for the measurement of the water isotopes, in view of the pre-dominance of ocean water in the hydrosphere. However, even though the differences in isotopic composition among the various oceanic water masses are relatively small (of the order of 1‰ in ^{18}O abundance), a virtual “standard mean ocean water” (SMOW) was defined relative to the NBS-1 standard as follows

(Craig, 1961):

$$R(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} \equiv 1.008 \cdot R(^{18}\text{O}/^{16}\text{O})_{\text{NBS-1}};$$

$$R(^2\text{H}/^1\text{H})_{\text{SMOW}} \equiv 1.050 \cdot R(^2\text{H}/^1\text{H})_{\text{NBS-1}}.$$

Later, an actual water sample which can be measured and whose isotopic composition matches that of the defined SMOW was made up and deposited at the International Atomic Energy Agency (IAEA) in Vienna. Nowadays, all measurements of the isotope abundance in water are reported in comparison to this VSMOW reference standard. In view of the relatively large range of the isotopic compositions in the hydrologic cycle, which often exceeds the linearity of the mass spectrometers, a number of secondary standards have been prepared for operational reasons and their assigned values are shown in Table 2.3. In this table are also shown standards for these isotopic species and of other elements in substances other than in water itself.

Due to this measurement procedure, the isotopic abundances are reported, in practice, as δ values, i.e. the relative deviations with respect to the standard value, as defined as below:

$$\delta = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}} = (R_{\text{sample}} / R_{\text{standard}}) - 1.$$

Applied to the deuterium–hydrogen pair, the notations of either $^2\delta$ or $\delta(^2\text{H})$ is used. The equivalent notation for the pair of isotopes of ^{18}O and ^{16}O is $^{18}\delta$ or $\delta(^{18}\text{O})$. In older literature, ^2H was referred to as D (short for Deuterium) and the notation δD was used.

Table 2.3. Standards used for calibrating the δ -measurements.

Name of Standard	Isotope/substance	assigned δ -value ‰
VSMOW	^{18}O in water	$^{18}\delta = 0$ [vs SMOW]
VSMOW	^2H in water	$^2\delta = 0$ [vs SMOW]
GISP	^{18}O in water	$^{18}\delta = -24.79$ [vs SMOW]
GISP	^2H in water	$^2\delta = -189.7$ [vs SMOW]
SLAP	^{18}O in water	$^{18}\delta = -55.50$ [vs SMOW]
SLAP	^2H in water	$^2\delta = -428.0$ [vs SMOW]
PDB	^{18}O in CO_2	$^{18}\delta = 0$ [vs PDB]
...	...	$^{18}\delta = +30.6$ [vs SMOW]
PDB	^{13}C in CO_2	$^{13}\delta = 0$ [vs PDB]
NBS19	^{18}O in CO_2	$^{18}\delta = -2.20$ [vs PDB]
NBS19	^{13}C in CO_2	$^{13}\delta = +1.95$ [vs PDB]
N_2 in air	^{15}N	$^{15}\delta = 0$ [vs air Nitrogen]

Since δ is usually a small number, it is given in permil (‰), equivalent to a factor of 10^{-3} . Unless stated otherwise, the δ values of the water isotopes are given relative to the VSMOW standard.

During routine measurements, a reproducibility of $\sigma = \pm 0.1\text{‰}$ for the Oxygen-18 isotope and $\sigma = \pm 1\text{‰}$ in the case of Deuterium can be achieved.

A number of absolute abundance measurements of VSMOW were made, albeit at a precision which falls short of that of the differential measurements. Lately, with improvements in the absolute isotope ratio measurements by the Avogadro project, a measurement of the ^{18}O abundance at a reproducibility level of 10^{-5} is underway, based on O_2 as the measurement gas rather than the conventionally used CO_2 , as described in Box 2.3.

Box 2.3. The absolute calibration of the delta scale.

In addition to the aesthetically unsatisfactory situation of having a standard (or standards) whose isotope abundance is inadequately known and which is inherently unstable in time (in the case of the water standard) or possibly not quite homogenous (in the case of a mineral standard), there are recurring practical problems that invite an absolute measurement of the isotope abundance. One of the problems relates to the wide range of isotopic values in the water cycle which requires the use of at least two reference standards to bracket the isotopic value of the measured samples, since a linear extrapolation of the mass-spectrometric measurements may not be appropriate and, actually differ from machine to machine. Indeed, two reference standards, namely VSMOW and SLAP which differ by about 55.5‰ in $\delta^{18}\text{O}$, are provided by the IAEA. Unless a reliable calibration of both these reference standards is available, one is faced by two or more incompatible δ -scales: one based on a linear interpolation between the standards and another based on an extrapolation of measurements from one standard assuming ideal linear MS performance. An even more serious problem arises when isotope ratios between different chemical species are to be compared. This applies, in particular, to the determination of isotopic fractionation between co-existing phases such as water and carbonates, silicates, phosphates, etc. For the differential ratio measurements it is then necessary to convert the oxygen in the different materials into a common gas to be measured, where every conversion procedure potentially introduces some isotope fractionation. Neither the equilibrium fractionation factors nor the fractionation introduced by incomplete conversions are adequately known. The common use of semi-empirical correction factors in these procedures introduces uncertainties that are one to two orders of magnitude larger than the reproducibility of the mass-spectrometric measurements. It is only an absolute measurement of the isotope ratio that would enable one to control the reliability of the conversion procedures, especially for the case when data from different laboratories and procedures are to be matched. The measurement of the absolute isotope ratio of $^2\text{H}/^1\text{H}$ in VSMOW was attempted by comparing these to a synthetic mixture

(Continued)

Box 2.3. (Continued)

of the isotopes, at a reproducibility of $2 \cdot 10^4$ (Hagemann *et al.*, 1970). For many other “reference materials” and other isotopic species there are no absolute isotope ratio determinations and their comparison to SMOW and other standards depends on estimates of the isotope fractionation between the different co-existing materials. However, recently, the isotope abundance measurements have been much improved and reproducibilities of 10^{-4} to 10^{-5} can be obtained for the measurement of absolute ratios of oxygen isotopes in O_2 gas. Since fluorination techniques can produce O_2 gas from water, carbonates, sulfates, silicates and phosphates at close to 100% yield, thus being free of fractionation effects, it has been suggested that atmospheric O_2 gas from areas of either sources or sinks of oxygen be used as a primary standard for the oxygen isotopes. Following the accurate calibration of such a standard by means of synthetic mixtures of the isotopes concerned, a comparison can then be made between CO_2 produced by conversion of the standard to CO_2 with the CO_2 produced in each case by the accepted analytical procedures, i.e. H_2O-CO_2 equilibration, acid decomposition of carbonates, etc (Gat and DeBievre, 2002).

2.2. The natural abundance of isotopes of oxygen and hydrogen

The two Boato diagrams (Figs. 2.1 and 2.2) show the range of the abundance of the heavy isotopes in natural materials (Boato, 1961). $\delta^{18}O$ values span a range of $\pm 50\%$ around SMOW, with most of this range pertaining to the waters of the hydrologic cycle. The range of δ^2H values is considerably larger. In the water cycle, the meteoric waters, i.e. the precipitation and water derived directly from precipitation are relatively depleted in the heavy isotopes, whereas surface water exposed to evaporation and water in geothermal systems fall on the enriched side of the scale.

The average of the present hydrosphere is estimated at $\delta(^{18}O) = -0.64\%$. The value of the primordial water, i.e. that water first condensed over the primitive earth and still possibly present deep down under the earth’s surface, has been of great interest. The value suggested is $\delta^{18}O = +5\%$ and $\delta^2H = -55\%$ and is based on the isotopic composition of old rocks formed at high temperatures (so that no isotope fractionation can be expected) and on the value of water in magmatic exhalation. The evolution in the δ value of the hydrogen isotopes from the primordial to the present day hydrosphere is explained by the slow but preferential loss to space of 1H atoms from the exosphere. In the case of the Oxygen-18, the loss of heavy oxygen can be accounted for by the deposition of carbonates

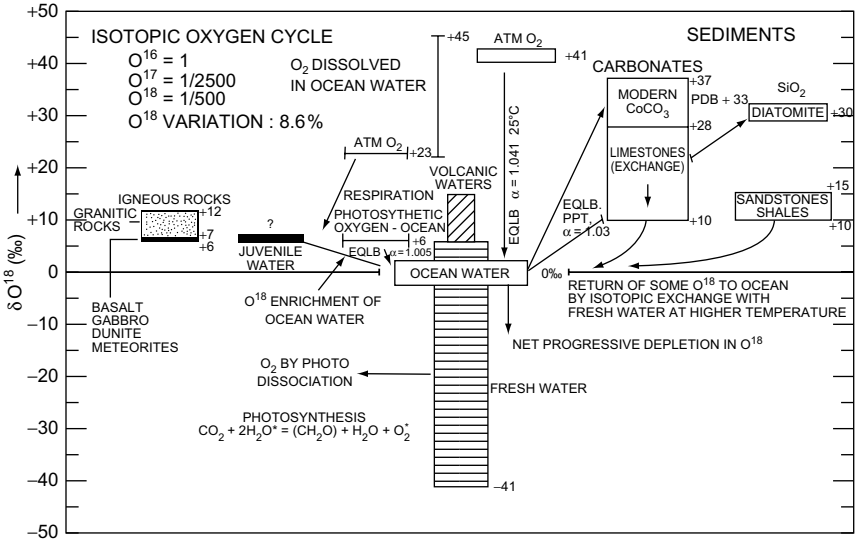


Fig. 2.1.

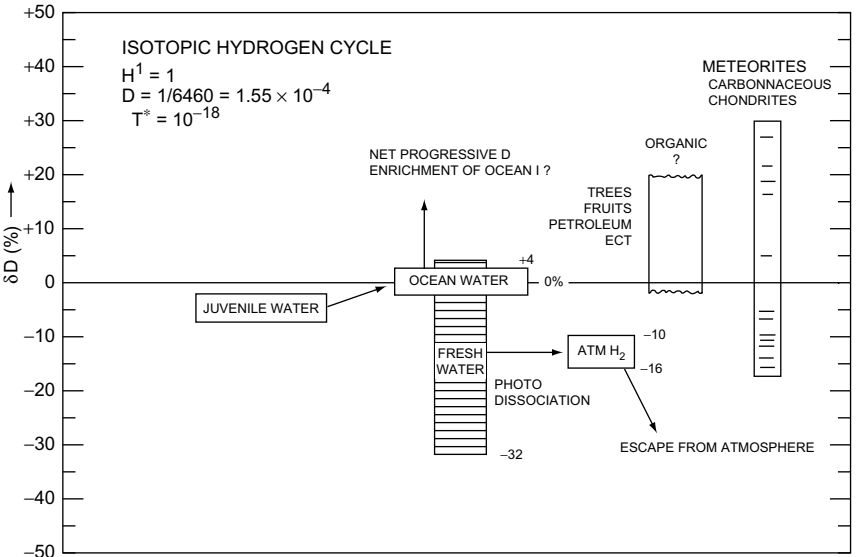


Fig. 2.2.

Box 2.4. Oxygen-17 Labelled Water.

Classical equilibrium isotope fractionation theory (Bigeleisen, 1962) predicts that the isotopic changes of the Oxygen-17 labelled molecules would be about one half that of the equivalent ones labelled by Oxygen-18. The prevalent measurement techniques for Oxygen-17, namely by NMR or Mass Spectrometry on CO₂ (where the molecule ¹³C¹⁶O₂ of mass 45 masks the changes in abundance of the sought after molecule ¹²C¹⁶O¹⁷O), were not sensitive enough to detect any deviations from such a relationship within the hydrologic cycle. However, it was shown that extra-terrestrial abundances of ¹⁷O in meteorites differed markedly from the expected ones (Clayton, 1993). Moreover, measurements of the isotopic composition of stratospheric oxygen and CO₂ (cf. Thiemans *et al.*, 1995) established an anomalously large enrichment of the ¹⁷O-labelled molecules of oxygen and ozone; this was shown to be the result of a mass-independent fractionation by photochemical reactions in the upper atmosphere.

In order to exploit this isotopic tracer pulse for studies of the mixing and incorporation of the high altitude oxygen in the terrestrial geochemical cycles (Luz *et al.*, 1999), the Oxygen-17 analytic procedures had to be improved. This was achieved by using Oxygen gas for the measurement in the MS, which was produced from the water by electrolysis (Meijer and Li, 1998) or by a fluorination technique, with CoF₃ as the fluorination agent. Barkan and Luz (2005) perfected this procedure to obtain a precision of 0.01‰ to 0.03‰ for both δ¹⁷O and δ¹⁸O. Using this method, they determined the fractionation factor ¹⁷α and ¹⁸α for the liquid/vapour equilibrium and found the ratio of ln¹⁷α/ln¹⁸α to be constant with a value of 0.529 ± 0.001 over the temperature range of 11.4° to 41.5°C. Moreover, a large suite of samples of meteoric waters followed a similar relationship. However, the relationship between the fractionation effects of the diffusion of the isotopic water molecules through air during the evaporation of water followed a smaller slope of 0.518, so that these two effects can be distinguished by measuring both the ¹⁷O and ¹⁸O isotopes. Examples of use of this methodology is found in Landais *et al.* (2008).

and other sedimentary minerals (which are relatively enriched in the heavy isotope) from the world ocean over the geologic time span.

The ¹⁷O abundance is estimated at about 37.4 × 10⁻³. By and large, the variability in ¹⁷O mimics that of ¹⁸O at about one half the amount of change, since most of the isotope fractionation occurs in a mass-dependent fashion. However, there is mounting evidence that some mass-independent fractionation takes place during photochemical interactions in the higher atmosphere. The case of the ¹⁷O labeled waters is discussed in Box 2.4.