This chapter is concerned with the natural concentrations of the stable isotopes of hydrogen, carbon and oxygen, with particular attention paid to those compounds relevant in the hydrological cycle. For each isotope separately, we discuss the natural fractionation effects, internationally agreed definitions, standards, and reference materials, and variations in the natural abundances.

In order to help the reader to appreciate isotopic abundance values as they occur in nature, Fig.7.1 shows some actual isotope ratios and fractionations in a choice of equilibrium systems. Surveys of some practical data of all isotopes concerned are given in the respective Sections.

Fig.7.1 Examples of isotope ratios of compounds in isotopic equilibrium and the respective isotope fractionations, as defined in Sect.3.3. As an example may serve the calculation of \( \varepsilon_{g/b} \) as \( \alpha_{g/b} - 1 \) with \( \alpha_{g/b} = 0.0111421/0.0112372 = 0.99154. \)
7.1 STABLE CARBON ISOTOPES

Table 7.1 The stable and radioactive isotopes of carbon: practical data for the natural abundance, properties, analytical techniques and standards. Further details are given in Sect. 7.1 and 8.1, and in Chapters 10 and 11.

<table>
<thead>
<tr>
<th></th>
<th>$^{12}$C</th>
<th>$^{13}$C</th>
<th>$^{14}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>stability</td>
<td>stable</td>
<td>stable</td>
<td>radioactive</td>
</tr>
<tr>
<td>natural abundance</td>
<td>0.989</td>
<td>0.011</td>
<td>&lt; 10^{-12}</td>
</tr>
<tr>
<td>natural specific activity</td>
<td>&lt; 0.25 Bq/gC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>decay mode / daughter</td>
<td>$\beta^-$ / $^{14}$N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>half-life ($T_{1/2}$)</td>
<td>5730 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>decay constant ($\lambda$)</td>
<td>$1.21 \times 10^{-4}$/a = 1/8267 a⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>max. $\beta$ energy</td>
<td>156 keV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>abundance range in hydrological cycle</td>
<td>30‰</td>
<td>0 to 10⁻¹²</td>
<td></td>
</tr>
<tr>
<td>reported as</td>
<td>$^{13}$δ or $\delta^{13}$C</td>
<td>$^{14}$A, $^{14}$a, $^{14}$δ, or $^{14}$Δ</td>
<td></td>
</tr>
<tr>
<td>in</td>
<td>‰</td>
<td>dpm/gC, Bq/gC, %, or ‰</td>
<td></td>
</tr>
<tr>
<td>instrument</td>
<td>MS</td>
<td>PGC, LSS, AMS</td>
<td></td>
</tr>
<tr>
<td>analytical medium</td>
<td>CO₂</td>
<td>CO₂, C₂H₂, CH₄, C₆H₆, graphite</td>
<td></td>
</tr>
<tr>
<td>usual standard deviation</td>
<td>0.03‰</td>
<td>1‰ to 1% at natural level</td>
<td></td>
</tr>
<tr>
<td>international standard</td>
<td>VPDB</td>
<td>Oxalic acid: Ox1, Ox2</td>
<td></td>
</tr>
<tr>
<td>with absolute value</td>
<td>0.0112372</td>
<td>13.56 dpm/gC</td>
<td></td>
</tr>
</tbody>
</table>

7.1.1 THE NATURAL ABUNDANCE

The chemical element carbon has two stable isotopes, $^{12}$C and $^{13}$C. Their abundance is about 98.9% and 1.1%, so that the $^{13}$C/$^{12}$C ratio is about 0.011 (Nier, 1950). As a result of several fractionation processes, kinetic as well as equilibrium, the isotope ratio shows a natural variation of almost 100‰.
Stable Isotopes of Hydrogen, Carbon and Oxygen

Fig. 7.2 General view of $^{13}$C/$^{12}$C variations in natural compounds. The ranges are indicative for the materials shown.

Fig. 7.2 presents a broad survey of natural abundances of various compounds, at the low-$^{13}$C end bacterial methane (marsh-gas), at the high end the bicarbonate fraction of groundwater under special conditions. In the carbonic acid system variations up to 30‰ are normally observed. Wider variations occur in systems in which carbon oxidation or reduction reactions take place, such as the CO$_2$ (carbonate) – CH$_4$ (methane) or the CO$_2$ – (CH$_2$O)$_x$ (carbohydrate) systems.

### 7.1.2 CARBON ISOTOPE FRACTIONATIONS

It will later be shown that the presence of dissolved inorganic carbon (DIC) in sea-, ground-, and surface water presents the possibility of studying gas-water exchange processes and of measuring water transport rates in oceans and in the ground. In connection with studying these phenomena, the stable and radioactive isotopes of carbon and their interactions pay an important contribution, often together with the water chemistry.
In nature equilibrium carbon isotope effects occur specifically between the phases CO\(_2\) – H\(_2\)O – H\(_2\)CO\(_3\) – CaCO\(_3\). Values for the fractionations involved only depend on temperature and are obtained from laboratory experiments. A survey is presented in Fig.7.3 and Table 7.2.

The kinetic fractionation of specific interest is that during carbon dioxide assimilation, i.e. the CO\(_2\) uptake by plants. The relatively large fractionation (up to about \(-18\%\)) is comparable to the effect observed during absorption of CO\(_2\) by an alkaline solution. A quantitative estimate shows that the isotope effect as a result of diffusion of CO\(_2\) through air can not explain the fractionation (Sect.3.5). The resulting value of \(^{13}\alpha\) is 0.9956, so that only \(-4.4\%\) of the total assimilation fractionation in favour of \(^{12}\)C can be explained by the diffusion. The remaining \(-13.6\%\), therefore, has to be found in the surface of the liquid phase and in the subsequent biochemical process.
Table 7.2  Carbon isotope fractionation in the equilibrium system $\text{CO}_2$–HCO$_3$–CO$_3$$^-$–CaCO$_3$; $^{13}\varepsilon_{y/x}$ represents the fractionation of compound $y$ relative to compound $x$. Values for intermediate temperatures may be calculated by linear interpolation (see also Fig.7.3).

$$T = t (\degree\text{C}) + 273.15 \text{K}$$

g = gaseous CO$_2$, a = dissolved CO$_2$, b = dissolved HCO$_3^-$, c = dissolved CO$_3$$^2$ ions, s = solid calcite.

<table>
<thead>
<tr>
<th>$t$ ($\degree\text{C}$)</th>
<th>$^{13}\varepsilon_{g/b}$</th>
<th>$^{13}\varepsilon_{a/g}$</th>
<th>$^{13}\varepsilon_{a/b}$</th>
<th>$^{13}\varepsilon_{c/b}$</th>
<th>$^{13}\varepsilon_{s/b}$</th>
<th>$^{13}\varepsilon_{s/g}$</th>
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<tbody>
<tr>
<td>0</td>
<td>−10.83</td>
<td>−1.18</td>
<td>−12.00</td>
<td>−0.65</td>
<td>−0.39</td>
<td>+10.55</td>
</tr>
<tr>
<td>5</td>
<td>−10.20</td>
<td>−1.16</td>
<td>−11.35</td>
<td>−0.60</td>
<td>−0.11</td>
<td>+10.19</td>
</tr>
<tr>
<td>10</td>
<td>−9.60</td>
<td>−1.13</td>
<td>−10.72</td>
<td>−0.54</td>
<td>+0.15</td>
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</tr>
<tr>
<td>15</td>
<td>−9.02</td>
<td>−1.11</td>
<td>−10.12</td>
<td>−0.49</td>
<td>+0.41</td>
<td>+9.52</td>
</tr>
<tr>
<td>20</td>
<td>−8.46</td>
<td>−1.09</td>
<td>−9.54</td>
<td>−0.44</td>
<td>+0.66</td>
<td>+9.20</td>
</tr>
<tr>
<td>25</td>
<td>−7.92</td>
<td>−1.06</td>
<td>−8.97</td>
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<td>+0.91</td>
<td>+8.86</td>
</tr>
<tr>
<td>30</td>
<td>−7.39</td>
<td>−1.04</td>
<td>−8.42</td>
<td>−0.34</td>
<td>+1.14</td>
<td>+8.60</td>
</tr>
<tr>
<td>35</td>
<td>−6.88</td>
<td>−1.02</td>
<td>−7.90</td>
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<td>+1.37</td>
<td>+8.31</td>
</tr>
<tr>
<td>40</td>
<td>−6.39</td>
<td>−1.00</td>
<td>−7.39</td>
<td>−0.25</td>
<td>+1.59</td>
<td>+8.03</td>
</tr>
</tbody>
</table>

1) Mook et al., 1974

$$^{13}\varepsilon_{g/b} = -9483/T + 23.89 \%$$

2) Vogel et al., 1970

$$^{13}\varepsilon_{a/g} = -373/T + 0.19 \%$$

3) From 1) and 2)

$$^{13}\varepsilon_{a/b} = -9866/T + 24.12 \%$$

4) Thode et al., 1965 and 1)

$$^{13}\varepsilon_{c/b} = -867/T + 2.52 \%$$

5) Our evaluation of the original data from Rubinson & Clayton, 1969

and Emrich et al., 1970

$$^{13}\varepsilon_{s/b} = -4232/T + 15.10 \%$$

6) From 1) and 5)

$$^{13}\varepsilon_{s/g} = +5380/T - 9.15 \%$$

Another kinetic process occurring in the soil is the bacterial decomposition of organic matter to form methane (CH$_4$). Here the largest fractionation amounts to about −55%. In this process CO$_2$ is simultaneously produced with a fractionation of +25%, resulting in a $^{13}\delta$ value of about 0%.

A special problem is the kinetic fractionation during uptake and release of CO$_2$ by seawater. This fractionation is included in calculations on global $^{13}$C modelling.

First we have to emphasise that the difference in isotopic composition between, for instance, gaseous CO$_2$ and the dissolved inorganic carbon content of water can not be addressed by *isotope fractionation between CO$_2$ and DIC*.
Isotope fractionation is the phenomenon that, due to an isotope exchange process, a difference between the isotopic composition of two compounds occurs, while seawater carbon consists of 3 fractions, i.e. dissolved CO$_2$ (H$_2$CO$_3$ is hardly present), dissolved HCO$_3^-$, and dissolved CO$_3^{2-}$. All these fractions are fractionated isotopically with respect to each other. The $^{13}$R value of DIC is:

$$^{13}R_{DIC} = \frac{[CO_2aq]^{^{13}R_{CO_2aq}} + [HCO_3^-]^{^{13}R_{HCO_3}} + [CO_3^{2-}]^{^{13}R_{CO_3}}}{[CO_2aq] + [HCO_3^-] + [CO_3^{2-}]}$$

or in terms of the respective fractionations:

$$^{13}R_{DIC} = \frac{a \cdot ^{13}\alpha_{a/b} + b + c \cdot ^{13}\alpha_{c/b}}{C_T}^{^{13}R_b} \quad (7.7)$$
or in terms of $\delta$ values:

$$
^{13}\delta_{\text{DIC}} = \frac{a \cdot ^{13}\alpha_{a/b} + b + c \cdot ^{13}\alpha_{c/b}}{C_T} \cdot ^{13}\delta_b + \frac{a \cdot ^{13}\varepsilon_{a/b} + c \cdot ^{13}\varepsilon_{c/b}}{C_T}
$$

(7.8)

where the brackets indicate the respective concentrations, which are also denoted by $a$ (acid), $b$ (bicarbonate), and $c$ (carbonate ions), so that $a + b + c = C_T$. The $\alpha$ values are given in Table 7.2. The chemical fractions are quantitatively treated in Chapter 9.

Originally $^{13}\varepsilon_k$ values for the uptake of CO$_2$ by seawater of about $-15\%$ were assumed, based on experimental results of CO$_2$ absorption by an alkaline solution (Baertschi, 1952). However, Siegenthaler & Münich (1981) have reasoned that this effect does not apply to the dissolving action of seawater. Calculations by these authors as well as by Inoue & Sugimura (1985) and Wanninkhof (1985) have shown the kinetic fractionation during CO$_2$ uptake to be

$$
^{13}\varepsilon_k \text{ (air \Rightarrow sea)} = ^{13}\varepsilon_k \text{ (atm.CO}_2\text{ to CO}_2\text{ taken up)} = -2.0 \pm 0.2\%
$$

This value was confirmed by experiments of the last author ($-2.4 \pm 0.8\%$). We have to remind the reader that these $^{13}\varepsilon_k$ values as well as those below are for kinetic fractionations and do not refer to Table 7.2.

The kinetic fractionation during CO$_2$ release by the ocean reported by Siegenthaler & Münich (1981) needs a correction (Mook, 1986). By application of the most recent equilibrium fractionations of Table 7.2 the equilibrium fractionation ($^{13}\alpha_{a/DIC}$) for dissolved CO$_2$ with respect to total dissolved carbon at 20 °C is 0.99055. This fractionation factor is also determined by the chemical composition of seawater, which adds to the overall temperature dependence.

At 20 °C the respective relative concentrations in seawater at pH = 8.20 are: CO$_2$(aq)/$C_T = 0.006$, HCO$_3^-$/$C_T = 0.893$ and CO$_3^{2-}$/CO$_2$ = 0.102 where $C_T$ is the total inorganic carbon concentration. By incorporation of the CO$_2$ + OH$^-$ reaction (0.9995), the resulting $^{13}\delta$ value is $-10.1$ to $-10.6\%$, depending on whether the hydration of CO$_2$ to H$_2$O is to be included.

According to Inoue & Sugimura (1985) the value is about $-10\%$, so that we can conclude to a fractionation of released CO$_2$ with respect to DIC of:

$$
^{13}\varepsilon_k \text{ (sea \Rightarrow air)} = ^{13}\varepsilon_k \text{ (DIC rel. to CO}_2\text{ released)} = -10.3 \pm 0.3\%
$$

Figure 7.4 represents a review of equilibrium and kinetic fractionations relative to gaseous CO$_2$ (left-hand scale) and the actual $^{13}\delta$ values based on $^{13}\delta$ (atm.CO$_2$) $= -7.0\%$ (right-hand scale). It is obvious that the isotopic compositions of CO$_2$ released and taken up by the ocean are equal, as is required by the condition of stationary state of isotopic equilibrium between ocean and atmosphere.
7.1.3 REPORTING $^{13}$C VARIATIONS AND THE $^{13}$C STANDARD

As described in Sect. 4.1, isotopic compositions expressed as $^{13}\delta$ values are related to those of specific reference materials. By international agreement PDB was used as the primary carbon reference (standard) material. PDB (Pee Dee Belemnite) was the carbonate from a certain (marine) belemnite found in the Cretaceous Pee Dee formation of North America. This material was the original standard sample used in the early days in Chicago and at CalTech, but has long been exhausted. The US National Bureau of Standards therefore distributed another (marine) limestone of which $^{13}\delta$ had been accurately established in relation to PDB. This first standard available to the community, Solenhofen limestone NBS20, was analysed by Craig (1957) and consecutively defined as:

$$^{13}\delta_{\text{NBS20}/\text{PDB}} = -1.06\%$$

In this way the PDB scale was indirectly established. Meanwhile NBS20 is considered to be no longer reliable, probably because of improper storage, and has been replaced by another limestone, NBS19, of which the $^{13}\delta$ value has been compared by a number of laboratories with the previous standard. Based on this comparison an IAEA panel in 1983 (Gonfiantini, 1984) adopted this new standard to define the new VPDB (Vienna PDB) scale as:

$$^{13}\delta_{\text{NBS19}/\text{VPDB}} = +1.95\%$$

(7.9)

The absolute $^{13}$C/$^{12}$C ratio of PDB was originally reported as 0.0112372 (Craig, 1957), whereas a slightly different value of 0.011183 ($\pm 0.1\%$) was reported by Zhang and Li (1987). The distinction between PDB and VPDB has been made for formal reasons, but the difference is negligibly small (< 0.01%).

Henceforth all $^{13}\delta$ values are reported relative to VPDB, unless stated otherwise.

More details on measurement and calculation procedures are given in Chapter 11. A survey of other reference samples is given in Table 11.2.

7.1.4 SURVEY OF NATURAL $^{13}$C VARIATIONS

In the other volumes certain aspects of natural $^{13}\delta$ variations will be discussed in more detail. Here we will restrict ourselves to a general survey, particularly with regard to the hydrological cycle (Fig. 7.5).

7.1.4.1 ATMOSPHERIC CO$_2$

The least depleted atmospheric CO$_2$ had originally $^{13}\delta$ values near $-7\%$. Since the 19th century this value has undergone relatively large changes. In general, high values are observed in
Stable Isotopes of Hydrogen, Carbon and Oxygen

Fig. 7.5  Schematic survey of $^{13}\delta$ variations in nature, especially of compounds relevant in the hydrological cycle.
oceanic air far removed from continental influences and occurs in combination with minimal CO$_2$ concentrations. More negative $^{13}\delta$ values are found in continental air and are due to an admixture of CO$_2$ of biospheric and anthropogenic origin ($^{13}\delta \approx -25\%$), in part from the decay of plant material, in part from the combustion of fossil fuels (Keeling, 1958; Mook et al., 1983).

### 7.1.4.2 Seawater and Marine Carbonate

Atmospheric CO$_2$ appears to be nearly in isotopic equilibrium with the oceanic dissolved bicarbonate. The $^{13}\delta$(HCO$_3^-$) values in the ocean are about +1 to +1.5\%, in agreement with the equilibrium fractionation $\varepsilon_{g/b}$ at temperatures between 15 and 20 °C (Table 7.2). According to the fractionation $\varepsilon_{a/b}$ we should expect calcite slowly precipitating in equilibrium with oceanic bicarbonate to have $^{13}\delta$ values of +2.0 to +2.5\%. This is indeed the normal range found for recent marine carbonates. Mook and Vogel (1968) observed this isotopic equilibrium between marine to brackish-water shells and dissolved bicarbonate in the water.

### 7.1.4.3 Vegetation and Soil CO$_2$

Plant carbon has a lower $^{13}$C content than the atmospheric CO$_2$ from which it was formed. The fractionation which occurs during CO$_2$ uptake and photosynthesis depends on the type of plant and the climatic and ecological conditions. The dominant modes of photosynthesis give rise to strongly differing degrees of fractionation (Lerman, 1972; Throughton, 1972). The Hatch-Slack photosynthetic pathway ($C_4$) results in $^{13}\delta$ figures of −10 to −15\% and is primarily represented by certain grains and desert grasses (sugar reed, corn). In temperate climates most plants employ the Calvin mechanism ($C_3$), producing $^{13}\delta$ values in the range of −26 ± 3\%. A third type of metabolism, the Crassulacean Acid Metabolism (CAM) produces a large spread of $^{13}\delta$ values around −17\% (Deines, 1980).

The CO$_2$ content of the soil atmosphere can be orders of magnitude larger than that of the free atmosphere. The additional CO$_2$ is formed in the soil by decay of plant remains and by root respiration and consequently has $^{13}\delta$ values centring around −25\% in temperate climates where Calvin plants dominate.

### 7.1.4.4 Fossil Fuel

As complicated biogeochemical processes are involved in the degradation of terrestrial and marine plant material ultimately into coal, oil, and natural gas, the range of $^{13}\delta$ values of these fossil fuels is larger, extending to more negative values, especially of biogenic methane (Fig.7.5). The global average of CO$_2$ from the combustion of these fuels is estimated to be about −27\%.
7.1.4.5 GLOBAL CARBON CYCLE

Biospheric carbon has a direct influence on $^{13}\delta$ of atmospheric CO$_2$. The large uptake of CO$_2$ by the global biosphere during summer and the equal release of CO$_2$ during winter causes a seasonal variation in the atmospheric CO$_2$ concentration as well as in $^{13}\delta$. The simple mixing of CO$_2$ from these two components, atmospheric CO$_2$ (atm) and biospheric CO$_2$ (bio) is represented by the equation (cf. Eqs.4.13 and 4.15):

$$
(^{13}\delta_{\text{atm}} + \Delta^{13}\delta)(C_{\text{atm}} + \Delta C_{\text{bio}}) = ^{13}\delta_{\text{atm}} C_{\text{atm}} + ^{13}\delta_{\text{bio}} \Delta C_{\text{bio}}
$$

(7.10)

where C stands for the CO$_2$ concentration, $\Delta C$ for the biospheric addition, and $\Delta^{13}\delta$ for the variation in the $\delta$ value.

- CO$_2$ concentration (ppm)
- $^{13}\delta_{VPDB}$ (%)

**Fig.7.6** Trends of the concentration and $^{13}\delta$ of atmospheric CO$_2$ of air samples collected by C.D.Keeling on top of the Mauna Loa volcano at the Island of Hawaii and at the South Pole. The seasonal variations have been removed from the original data (Roeloffzen et al., 1991). The dates refer to 1 January of each year.
Numerically this comes to a periodic (seasonal) variation of
\[
\Delta^{13}\delta = \frac{13\delta_{\text{bio}} - 13\delta_{\text{atm}}}{C_{\text{atm}} + \Delta C_{\text{bio}}} = \frac{-25 + 7.85}{353} \approx -0.05\%_{\text{o}} \text{ per ppm of CO}_2 \quad (7.11)
\]
Superimposed on this phenomenon is the gradual increase in the concentration and the accompanying decrease in $^{13}\delta$ by the emission of fossil-fuel CO$_2$. The trends are shown in Fig.7.6 and can be approximated by:
\[
\frac{\Delta^{13}\delta}{\Delta C_{\text{CO}_2}} = -0.015\%_{\text{o}} / \text{ppm} \text{ or } \Delta^{13}\delta = -0.025\%_{\text{o}} / \text{year} \quad (7.12)
\]
at a CO$_2$ concentration of 353 ppm and $^{13}\delta = -7.85\%_{\text{o}}$ over the Northern Hemisphere, valid for 01/01/1990.

The smaller $\%_{\text{o}}$/ppm value of Eq.7.12 compared to Eq.7.11 shows that the long-term trend is not due to simple addition and mixing of additional CO$_2$ in the atmosphere. The large oceanic DIC reservoir is levelling out the purely atmospheric mixing effect through isotope exchange.

### 7.1.4.6 Groundwater and Riverwater

Soil CO$_2$ is important in establishing the dissolved inorganic carbon content of groundwater. After dissolution of this CO$_2$ the infiltrating rain water is able to dissolve the soil limestone:
\[
\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (7.13)
\]
(Fig.7.7). Because limestone generally is of marine origin ($^{13}\delta \approx +1\%_{\text{o}}$), this process results in $^{13}\delta$ of the dissolved bicarbonate of about $-11$ to $-12\%_{\text{o}}$ (in temperate climates).

In the soil the HCO$_3^-$ first formed exchanges with the often present excess of gaseous CO$_2$, ultimately resulting in $^{13}\delta(\text{HCO}_3^-) = ^{13}\delta(\text{soil CO}_2) + ^{13}\delta_{\text{b/g}} \approx -25\%_{\text{o}} + 9\%_{\text{o}} = -16\%_{\text{o}}$ (Fig.7.5). Consequently, $^{13}\delta(\text{HCO}_3^-)$ values significantly outside the range of $-11$ to $-12\%_{\text{o}}$ are observed in soil water as well as in fresh surface water such as rivers and lakes. In surface waters such as lakes $^{13}C$ enrichment of dissolved inorganic carbon can be caused by isotope exchange with atmospheric CO$_2$ ($^{13}\delta \approx -7.5\%_{\text{o}}$), ultimately resulting in values of $^{13}\delta + ^{13}\delta_{\text{b/g}} = -7.5\%_{\text{o}} + 9\%_{\text{o}} = +1.5\%_{\text{o}}$, identical to oceanic values. Consequently, freshwater carbonate minerals may have "marine" $^{13}\delta$ values. In these cases the marine character of the carbonate is to be determined by $^{18}\delta$ (Sect.7.3).

In addition to HCO$_3^-$, natural waters contain variable concentrations of CO$_2$ with the effect that the $^{13}\delta$ value of DIC is lower than that of the bicarbonate fraction alone: in groundwater (Vogel and Ehhalt, 1963), and in stream and river waters derived from groundwater (Fig.7.8) the $^{13}\delta$(DIC) values are generally in the range of $-12$ to $-15\%_{\text{o}}$. 

100
Fig. 7.7 Schematic representation of the formation of dissolved inorganic carbon in groundwater from soil carbonate and soil CO$_2$. This is the main process responsible for the carbonate content of groundwater and the consecutive components of the water cycle. Generally, dissolved bicarbonate is by far the largest component. The $\%$ values referring to the respective $^{13}\delta$ have been kept simple for the sake of clarity. DIC is the dissolved inorganic carbon content of the water, i.e. HCO$_3^-$, CO$_2$(aq) and CO$_3^{2-}$.

7.2 Stable Oxygen Isotopes

7.2.1 The Natural Abundance

The chemical element oxygen has three stable isotopes, $^{16}$O, $^{17}$O and $^{18}$O, with abundances of 99.76, 0.035 and 0.2%, respectively (Nier, 1950). Observation of $^{17}$O concentrations provides little information on the hydrological cycle in the strict sense above that which can be gained from the more abundant and, consequently, more accurately measurable $^{18}$O variations (Sect.3.7). We shall, therefore, focus our attention here on the $^{18}$O/$^{16}$O ratio ($\approx 0.0020$).

Values of $^{18}\delta$ show natural variations within a range of almost 100‰ (Fig.7.9). $^{18}$O is often enriched in (saline) lakes subjected to a high degree of evaporation, while high-altitude and cold-climate precipitation, especially in the Antarctic, is low in $^{18}$O. Generally in the hydrological cycle in temperate climates we are confronted with a range of $^{18}\delta$ not exceeding 30‰.
Fig. 7.8 A three-year observation of the isotopic composition of water from the N.W. European rivers Rhine and Meuse (Mook, 1970):

A. $^{13}\delta$ values of the dissolved bicarbonate fraction, showing normal values during winter and relatively high values in summer, probably because of isotopic exchange of the surface water bicarbonate with atmospheric $\text{CO}_2$.

B. $^{18}\delta$ values, where the river Meuse is showing the average value and the seasonal variations of $^{18}\delta$ in the precipitation: high values in summer, low during winter; during early spring and summer the Rhine receives meltwater from the Swiss Alps with relatively low $^{18}\delta$ because of the high-altitude precipitation.
Table 7.3  The stable isotopes of oxygen: practical data for the natural abundance, properties, analytical techniques and standards. Further details are given in Sect.7.2, and in Chapters 10 and 11.

MS=mass spectrometry

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<th>(^{18}\text{O})</th>
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</tr>
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<td>abundance range</td>
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<td>(^{17}\delta) or (^{17}\delta)O</td>
<td>(^{18}\delta) or (^{18}\delta)O</td>
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</tr>
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<td>analytical medium</td>
<td>O(_2)</td>
<td>CO(_2) or O(_2)</td>
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</tr>
<tr>
<td>usual standard deviation</td>
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<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>international standard</td>
<td>.</td>
<td>VSMOW for water VPDB for carbonate etc</td>
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</tr>
<tr>
<td>with absolute value</td>
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<td>VSMOW: 0.0020052 VPDB: 0.0020672</td>
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7.2.2  OXYGEN ISOTOPE FRACTIONATIONS

The isotope effects to be discussed are within the system H\(_2\)O (vapour) – H\(_2\)O (liquid) – CaCO\(_3\). The equilibrium fractionation values have been determined by laboratory experiments. Fig.7.1 shows some actual isotope ratios. Fig.7.10 and Table 7.4 present a survey of the temperature dependent equilibrium isotope effects.

Equilibrium fractionations determined in the laboratory are also found in nature. The most striking observation is that the carbonate shells of many molluscs appear to have been formed in isotopic equilibrium with seawater. The palaeotemperature scale as presented by Eq.7.18 was presented by Epstein et al. (1953) (cf. Friedman & O’Neil, 1977). This relation is deduced from \(^{18}\text{O}\) measurements on carbonate laid down by marine shell animals at known temperatures and water isotopic compositions. These data lost the original interpretation of the temperature dependence of the \(\alpha_{\text{iso}}\) by the later realisation that the major oceanic palaeotemperature effect is the change in \(^{18}\delta\) of seawater –and, consequently of carbonate formed in this water- by the formation viz. melting of enormous ice caps on the poles during or after ice ages.
Kinetic effects are observed during the evaporation of ocean water, as oceanic vapour is isotopically lighter than would result from equilibrium fractionation alone. The natural isotope effect for oxygen ($\approx -12‰$) is smaller than could be brought about by fractionation by diffusion. Laboratory measurements resulted in $^{18}\varepsilon_d = -27.3 \pm 0.7‰$ (Merlivat, 1978) and $^{18}\varepsilon_d = -27.2 \pm 0.5‰$ (unpubl.). These experimental values are again smaller than results from Eq.(3.35) (-31.3‰), which may be explained by the water molecules forming clusters of
Fig. 7.10 Temperature dependent equilibrium fractionations for oxygen isotopes of water vapour (v), gaseous CO$_2$ (g), and solid calcite (s) with respect to liquid water (l).

larger mass in the vapour phase. Furthermore, evaporation of ocean water includes sea spray by which water droplets evaporate completely without fractionation, thus reducing the natural isotope effect.
Table 7.4 Oxygen isotope fractionation in the equilibrium system CO₂-H₂O-CaCO₃; \( ^{18} \epsilon_{y/x} \) represents the fractionation of compound y relative to compound x, and is approximately equal to \( \delta_y - \delta_x \). Values for intermediate temperatures may be calculated by linear interpolation (Fig. 7.9). \( T = t \, (°C) + 273.15 \, K \)

\[ l = \text{liquid H}_2\text{O}, \quad v = \text{H}_2\text{O vapour}, \quad i = \text{ice}, \quad g = \text{gaseous CO}_2, \quad l_g = \text{CO}_2(g) \] isotopic equilibrium with H₂O (l) at 25°C, \( sg = \text{CO}_2(g) \) from CaCO₃ (s) by 95% H₃PO₄ at 25°C.

<table>
<thead>
<tr>
<th>( ^{18} \epsilon_{v/l} )</th>
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<th>( ^{18} \epsilon_{g/l} )</th>
<th>( ^{18} \epsilon_{g/lg} )</th>
<th>( ^{18} \epsilon_{sg/lg} )</th>
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<td>( ^{18} \epsilon_{g/lg} )</td>
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<tr>
<td>( ^{18} \epsilon_{v/l} )</td>
<td>( ^{18} \epsilon_{s/l} )</td>
<td>( ^{18} \epsilon_{g/l} )</td>
<td>( ^{18} \epsilon_{g/lg} )</td>
<td>( ^{18} \epsilon_{sg/lg} )</td>
</tr>
</tbody>
</table>

1\) Majoube, 1971:

\[ \ln^{18} \alpha_{v/l} = -1137/T^2 + 0.4156/T + 0.0020667 \] (7.14a)

\[ 1/T \text{ adjustment:} \quad ^{18} \epsilon_{v/l} = -7 \, 356/T + 15.38\% \] (7.14b)

Values at higher temperatures can be obtained from Horita and Wesolowski, 1994

The fractionation between vapour and liquid water is independent of the NaCl concentration of the solution, contrary to some other salts (Friedman and O'Neil, 1977)

2\) From 3\) and 5\) and Friedman and O'Neil, 1971

\[ ^{18} \epsilon_{v/l} = 19 \, 668/T - 37.32\% \] (7.15)

3\) Brenninkmeijer et al., 1983

\[ ^{18} \epsilon_{g/l} = 17 \, 604/T - 17.89\% \] (7.16)

4\) From 3\), where \( l_g \) is obtained from \( l \) by applying the \( ^{18} \epsilon_{g/l} \) value at 25°C (concluded by an IAEA panel to be +41.2\%)

\[ ^{18} \epsilon_{g/lg} = 16 \, 909/T - 56.71\% \] (7.17)

This fractionation is independent of the salt content of the solution

5\) Epstein et al., 1953, 1976: \( t(°C) = 16.5 - 4.3(^{18} \delta_s - ^{18} \delta_w) + 0.14(^{18} \delta_s - ^{18} \delta_w)^2 \) (7.18)

where \( ^{18} \delta \) refers CO₂ prepared from solid carbonate with 95% H₃PO₄ at 25°C and \( ^{18} \delta_w \) to CO₂ in isotopic equilibrium with water at 25°C, both relative to VPDB-CO₂

\[ ^{18} \epsilon_{s/l} = + 10.25\% \]

\[ ^{18} \epsilon_{g/lg} = 19 \, 082/T - 65.88\% \] (7.19)

Majoube, 1971: \( ^{18} \epsilon_{v/l} = + 3.5\% \) (0°C); \( ^{18} \epsilon_{v/l} = + 15.2\% \) (0°C); \( ^{18} \epsilon_{v/l} = + 16.6\% \) (-10°C)
7.2.3 REPORTING $^{18}$O VARIATIONS AND THE $^{18}$O STANDARDS

Originally $^{18}$O/$^{16}$O of an arbitrary water sample was (indirectly, via a local laboratory reference sample) compared to that of average seawater. This Standard Mean Ocean Water in reality never existed. Measurements on water samples from all oceans by Epstein and Mayeda (1953) were averaged and referred to a truly existing reference sample, NBS1, that time available at the US National Bureau of Standards (NBS). In this way the isotope water standard, SMOW, became indirectly defined by Craig (1961a) as:

$$^{18}\delta_{\text{NBS1}/\text{SMOW}} = -7.94\%$$

The International Atomic Energy Agency (IAEA), Section of Isotope Hydrology, in Vienna, Austria and the US National Institute of Standards and Technology (NIST, the former NBS) have now available for distribution batches of well preserved standard mean ocean water for use as a standard for $^{18}$O as well as for $^2$H. This standard material, VSMOW, prepared by H.Craig to equal the former SMOW as closely as possible both for $^{18}\delta$ and $^2\delta$, has been decided by an IAEA panel in 1976 to replace the original SMOW in fixing the zero point of the $^{18}\delta$ scale. All water samples are to be referred to this standard.

From an extensive laboratory intercomparison it became clear that the difference between the early SMOW and the present VSMOW is very small (IAEA, 1978), probably:

$$^{18}\delta_{\text{SMOW}/\text{VSMOW}} = +0.05\%$$ (7.20)

At present two standard materials are available for reporting $^{18}\delta$ values, one for water samples, one for carbonates. This situation arises from the practical fact that neither the isotope measurements on water nor those on carbonates are performed on the original material itself, but are made on gaseous CO$_2$ reacted with or derived from the sample.

The laboratory analysis of $^{18}$O/$^{16}$O in water is performed by equilibrating a water sample with CO$_2$ of known isotopic composition at 25°C (Sect.10.2.1), followed by mass spectrometric analysis of this equilibrated CO$_2$ (Sect.11.1). This equilibration is generally carried out on batches of water samples, consisting of the unknown samples (x) and the standard or one or more reference samples. After the correction discussed in Sect.11.2.3.4 is made, it is irrelevant whether the water samples themselves are being related or the CO$_2$ samples obtained after equilibration, provided sample and standard are treated under equal condition:

$$^{18}\delta_x / \text{VSMOW} = ^{18}\delta_{xg} / \text{VSMOWg}$$ (7.21)

where g refers to the equilibrated and analysed CO$_2$.

The absolute $^{18}$O/$^{16}$O ratio of VSMOW is reported as $(2005.2 \pm 0.45) \times 10^{-6}$ (Baertschi, 1976). Reference and intercomparison samples are available from the IAEA and the NIST. A survey of the data is given in Table 11.2. In order to overcome small analytical errors, some laboratories prefer to fix their VSMOW scale by two extreme points (Sect.11.2.3.5). Using
this procedure, the sample $^{18}\delta$ is located on a linear $\delta$ scale between VSMOW (0‰) and SLAP (Standard Light Antarctic Precipitation) with a defined value of

$$^{18}\delta_{\text{SLAP/VSMOW}} = -55.5\%$$  \hspace{1cm} (7.22)

$^{18}\delta$ values of carbonates are given with reference to the same PDB calcite used for $^{13}\text{C}$ (Sect.7.1.3). The zero point of this PDB scale was fixed by means of the NBS20 reference sample (Solenhofen limestone) which originally was defined as (Craig, 1957):

$$^{18}\delta_{\text{NBS20/PDB}} = -4.14\%$$

The absolute $^{18}\text{O}/^{16}\text{O}$ ratio of PDB-CO$_2$ was originally reported as 0.0020790 (Craig, 1957). This value, however, does not agree with Baertschi's ratio for VSMOW and the accurately measured difference between the two standards (Fig.7.10). At present a value of 0.0020672 is considered to be more realistic (Table 11.1).

Recently, samples from NBS20 do not always show the above value. Probably because of exchange with atmospheric vapour due to improper storage, the $^{18}\delta$ value may have shifted to close to $-4.4\%$. Therefore, a new set of carbonate reference materials has been introduced by the IAEA where NBS19 replaces NBS20. The VPDB (Vienna PDB) scale has now been defined by using NBS19:

$$^{18}\delta_{\text{NBS19/VPDB}} = -2.20\%$$  \hspace{1cm} (7.23)

The carbonate itself is not analysed for $^{18}\delta$ but rather the CO$_2$ prepared according to a standard procedure which involves treatment in vacuum with 95% (or 100%) orthophosphoric acid at 25°C. If samples and reference are treated and corrected similarly,

$$^{18}\delta_x/\text{VPDB} = ^{18}\delta_{xg}/\text{VPDBg}$$  \hspace{1cm} (7.24)

where g refers to the prepared and analysed CO$_2$, so that neither the fractionation between the carbonate and the CO$_2$ prepared from it (Table 7.4) nor the reaction temperature need to be known.

The relations between the VPDB, VPDB-CO$_2$ (VPBDg), VSMOW and VSMOW-CO$_2$ (VSMOWg) scales are derived from the equations given in Table 7.4, according to Eq.7.24:

$$^{18}\delta_x/\text{VSMOW} = 1.03086^{18}\delta_x/\text{VPDB} + 30.86\%$$  \hspace{1cm} (7.25)

$$^{18}\delta_x/\text{VSMOW} = 1.04143^{18}\delta_x/\text{VPDBg} + 41.43\%$$  \hspace{1cm} (7.26)

$$^{18}\delta_x/\text{VSMOWg} = 1.00027^{18}\delta_x/\text{VPDBg} + 0.27\%$$  \hspace{1cm} (7.27)

The relations are visualised in Fig.7.11. These are of interest in isotope studies on silicates, oxides, carbonates, organic matter, and their correlation with water.
Fig. 7.11 Relations between $^{18}$O reference and intercomparison samples with respect to VPDB and VSMOW (IAEA, 1986). VPDB–CO$_2$ refers to CO$_2$ prepared from hypothetical VPDB by treatment with H$_3$PO$_4$ (95%) at 25°C, VSMOW–CO$_2$ to CO$_2$ equilibrated with VSMOW at 25°C. The vertical scale is indicative and not entirely proportional to real numbers.

$\Delta_1$ : Difference between VPDB–CO$_2$ and SMOW–CO$_2$ ($-0.22‰$) (Craig and Gordon, 1965; Mook, 1968) plus the difference between SMOW(CO$_2$) and VSMOW(CO$_2$) ($-0.05‰$) (Eq. 7.20)

$D_c$ : defined value of NBS19 relative to VPDB (Eq. 7.24)

$\Delta_2 = D_c - \Delta_1$

$\alpha_1$ : according to Friedman and O'Neil (1977)

$\alpha_2$ : average of 3 independent methods applied by 4 different laboratories
\( \Delta_3 : \) from \( \alpha_2, \alpha_1 \), and \( \Delta_1 \); 1.03086 is the exact figure quoted by Friedman and O'Neil (1977), in agreement with \( \alpha_2 = 1.04115 \) (Brenninkmeijer et al., 1983).

\( \Delta_4 : \) from \( \Delta_3 \) and \( \alpha_1 \)

The conversion equations are in general:

\[
\delta^{18}_\text{lower} = \alpha_i \delta^{18}_\text{upper} + \epsilon_i
\]

(7.28)

where \( \alpha_i = \Delta, D, \) or \( \alpha \), and "lower" and "upper" refer to the levels in the scheme.

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Henceforth, all \( \delta^{18} \) values of carbonates are reported relative to VPDB, \( \delta^{18} \) of gaseous (atmospheric) CO\(_2\) relative to VPDB–CO\(_2\), and all \( \delta^{18} \) values of water relative to VSMOW, unless stated otherwise.

More details on the measurement and calculation procedures are given in Chapter 11.

7.2.4 SURVEY OF NATURAL \( \delta^{18} \) VARIATIONS

\( \delta^{18} \) variations throughout the hydrologic cycle will be discussed in detail in the other volumes. Here we present only a broad survey (Fig.7.12).

7.2.4.1 SEAWATER

The oceans form the largest global water reservoir. The \( \delta^{18} \) content in the surface layer is rather uniform, varying between +0.5 and -0.5‰ (Epstein & Mayeda, 1953). Only in tropical and polar regions larger deviations are observed. In tropical regions more positive values are caused by strong evaporation: \( \delta^{18} \) of water in the Mediterranean amounts to +2‰ (\( \delta^{2} = +10\% \)). In polar regions more negative values originate from water melting from isotopically light snow and ice.

If ocean water were evaporating under equilibrium conditions, the vapour resulting would be 8 to 10‰ depleted in \( \delta^{18} \), depending on temperature. However, oceanic vapour appears to have an average \( \delta^{18} \) value of -12 to -13‰, which must partly be due to kinetic fractionation. The relative humidity of the air and the evaporation temperature influence the amount of non-equilibrium fractionation occurring (see Volume 2 on Precipitation).

7.2.4.2 PRECIPITATION

The transformation of atmospheric water vapour to precipitation depends on so many climatological and local factors, that the \( \delta^{18} \) variations in precipitation over the globe are very large. As a general rule \( \delta^{18} \) becomes more negative the further the rain is removed from the
Fig. 7.12 Schematic survey of natural $^{18}\delta$ variations in nature, especially relevant in the hydrological cycle. The marine vapour gradually becomes depleted in $^{18}$O during the transport to higher latitudes (Fig. 7.13). Evaporation of surface water may cause the water to become enriched in $^{18}$O. Finally the formation of solid carbonate results in a shift in $^{18}\delta$ depending on temperature (cf. Fig. 7.5).

main source of the vapour in the equatorial regions. In the Arctic and Antarctic, $^{18}\delta$ of the ice can be as low as -50‰. This gradual $^{18}$O depletion model is schematically shown in Fig. 7.13.
Chapter 7

Fig. 7.13  Schematic representation of the gradual depletion in $^{18}$O of atmospheric water vapour and the condensing precipitation, the further the vapour and precipitation process are removed from the main source of the vapour: the tropical marine belt. At lower temperatures the isotope fractionation between water vapour and liquid water is larger, counteracting but loosing from the Rayleigh depletion process (cf. Fig. 7.7 and 7.12).

In Volume 2 the various effects will be discussed in detail, causing regional and temporal variations on $^{18}$O of precipitation.

We can distinguish between:

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112
1) **latitudinal effect** with lower $^{18}\delta$ values at increasing latitude

2) **continental effect** with more negative $^{18}\delta$ values for precipitation the more inland

3) **altitude effect** with decreasing $^{18}\delta$ in precipitation at higher altitude

4) **seasonal effect** (in regions with temperate climate) with more negative $^{18}\delta$ values during winter

5) **amount effect** with more negative $^{18}\delta$ values in rain during heavy storms.

### 7.2.4.3 SURFACE WATER

In Fig. 7.8 some data are shown on $^{18}\delta$ variations in riverwater. The seasonal variation with relatively high values in summer is characteristic for precipitation in temperate regions. The basis of both curves represents the average $^{18}\delta$ values of precipitation and groundwater in the recharge areas, i.e. N.W.Europe (Meuse) and Switzerland/S.Germany (Rhine), the latter with a large transport of relatively isotopically light meltwater in spring.

Evaporation, especially in tropical and semi-arid regions, causes $^{18}\text{O}$ enrichment in surface waters. This results, for instance, in $^{18}\delta$ of the river Nile to be +3 to +4‰, and of certain lakes as high as +20‰ (Sect.4.4.5 and 7.5).

### 7.2.5 CLIMATIC VARIATIONS

The slow precipitation of calcium carbonate is a process during which carbonate and water are in isotopic equilibrium, as was pointed out earlier. The $^{18}\text{O}$ content of the carbonate is, therefore, primarily determined by that of the water. The second determining factor is the temperature, as is indicated in Fig.7.10. Consequently we can in principle deduce the water temperature from $^{18}\delta$ of carbonate samples in marine sediment cores, provided $^{18}\delta$ of the water is known ($\approx 0\%$). This was originally believed to be the basis of the $^{18}\text{O}$ palaeothermometry of fossil marine shells (Epstein et al., 1953).

The present-day opinions assume a varying $^{18}\delta$ of the surface ocean water during glacial/interglacial transitions (Emiliani, 1971; Olausson, 1981), due to varying amounts of accumulated ice with low $^{18}\delta$ as polar ice caps. As a realistic order of magnitude, an estimated amount of $5.10^5$ km$^3$ of ice ($= V_{\text{ice}}$) laid down especially on the northern polar ice cap during the last ice age with an average $^{18}\delta$ value of $-20\%$ changes the $^{18}\delta$ value (at present = 0‰) of the $10^7$ km$^3$ of ocean water ($= V_{\text{ocean}}$) by $+1\%$, as is simply deduced from the mass balance:

$$V_{\text{present ocean}}^{18}\delta_{\text{present seawater}} = V_{\text{ice-age ocean}}^{18}\delta_{\text{ice-age seawater}} + V_{\text{ice caps}}^{18}\delta_{\text{ice}} \quad (7.29)$$

Another spectacular application of isotope variations in nature is the deduction of climatic changes in the past from $^{18}\text{O}/^{16}\text{O}$ or $^{2}\text{H}/^{1}\text{H}$ ratios in polar ice cores. If the process of gradual
isotope depletion of precipitation is studied in detail as a function of latitude and thus of air temperature, a relation can be derived (Volume 2) which comes to the temperature dependence:

$$\frac{d^{18}\delta}{dt} \approx +0.7 \% / ^\circ C$$

(Dansgaard, 1964; Van der Straaten and Mook, 1983). By this relation it is possible to translate isotope variations into climatic variations during geologic times. Records have been obtained on ice cores from Greenland and the Antarctic, showing the alternation of low-\(^{18}\delta\) (or low-\(^{2}\delta\)) and high-\(^{18}\delta\) (or high-\(^{2}\delta\)) periods, respectively cold and warm periods (Eq.7.30).

**Fig.7.14** Palaeotemperature records represented by \(^{18}\delta\) variations in time in the CaCO\(_3\) fraction from foraminifera shells in deep-sea core sediments (left), in glacier ice of a Northern Greenland glacier (at Summit), and in glacier ice of an Antarctic ice core (at Vostok), respectively from left to right (figure modified from Lorius and Oeschger, 1994). In each record the left side indicates the lower temperatures, for instance, at 20 000 years BP each curve shows the most recent glacial maximum. The upper 10 000 years contain the present warm interglacial, the Holocene.
7.3 RELATION BETWEEN $^{13}$C AND $^{18}$O VARIATIONS IN H$_2$O, HCO$_3^-$, AND CO$_3^{2-}$

Differences and the relations between the various natural water-carbonate systems can nicely be displayed by considering both $^{18}$δ of the water and $^{13}$δ of the dissolved bicarbonate. Fig.7.15 is a schematic representation of three waters of realistic isotopic composition, each provided with the temperature dependent range of calcite precipitated under equilibrium conditions. This figure essentially is a combined graph of Figs.7.5 and 7.12.

From an isotopic point of view, the 4 common types of water are:

1) **Seawater**, with $^{18}$δ values around 0‰ (by definition) at present; the carbonate range is that of recent marine carbonates. Because of changing glacial and interglacial periods the $^{18}$δ of ocean water varied in the past. Also the $^{18}$δ values of marine limestone have increased during the course of geological time, while the $^{13}$δ values have essentially remained the same (Veizer & Hoefs, 1976).

2) **Ground- and river water**, with an arbitrarily chosen value of $^{18}$δ. In freshwater bicarbonate $^{13}$δ generally is around -11 to -12‰. The isotopic compositions of freshwater carbonates derived from this water may result from the known equilibrium fractionations (Tables 6.2 and 6.4), in a similar way as is indicated for marine carbonate.

3) **Stagnant surface or lake water** can be subjected to processes altering the isotopic composition. Provided the water has a sufficient residence time in the basin, isotope exchange will cause the $^{13}$C content to reach isotopic equilibrium with atmospheric CO$_2$. Then $^{13}$δ equals that in the ocean. Carbonate $^{13}$δ and $^{18}$δ are related to, respectively, HCO$_3^-$ and H$_2$O as indicated for the marine values. The $^{18}$O content of the water, especially in warmer climates, will change towards less negative or even positive values due to evaporation.

4) **Estuarine water** has intermediate values of $^{13}$δ(HCO$_3^-$) or $^{13}$δ(DIC) and $^{18}$δ(H$_2$O), depending on the degree of mixing of the river- and seawater. The latter behaves conservatively, i.e. is only determined by the mixing ratio; $^{13}$δ(DIC) also depends on the DIC values of the mixing components. Therefore, the mixing line is generally not straight. The relation with $^{13}$δ of the bicarbonate fraction is even more complicated, as the dissociation equilibria change with pH (even the pH does not at all behave conservatively) (Sect.9.5.4).
Fig. 7.15  Relation between the natural variations of $^{13}\delta$(HCO$_3^-$ and CaCO$_3$) and $^{18}\delta$(H$_2$O and CaCO$_3$). The graph is essentially a combination of Figs. 7.5 and 7.12. Estuarine mixing only results in a straight line between the river and sea values of $^{13}\delta_{\text{DIC}}$, if C$_T$ of the components is equal. Because this is rarely the case, the relation between the two members mostly is observed as a slightly curved line. Additionally, $^{13}\delta$(HCO$_3^-$) in estuaries is not subject to conservative mixing, because the mixing process rearranges the carbonate fractions (Sect. 9.5.4). Depending on the residence times of the water at the surface, evaporation and isotope exchange changes the isotopic composition to higher $\delta$ values.
7.4 STABLE HYDROGEN ISOTOPES

7.4.1 THE NATURAL ABUNDANCE

The chemical element hydrogen consists of two stable isotopes, $^1$H and $^2$H (D or Deuterium), with an abundance of about 99.985 and 0.015% and an isotope ratio $^{2}$H/$^{1}$H ≈ 0.00015 (Urey et al., 1932). This isotope ratio has a natural variation of about 250‰, higher than the $^{13}$O and $^{18}$O variations, because of the relatively larger mass differences between the isotopes (Fig.7.16).

As with $^{18}$O, high $^2$H concentrations are observed in strongly evaporated surface waters, while low $^2$H contents are found in polar ice. Variations of about 250‰ are present in the part of the hydrological cycle to be discussed here.

7.4.2 HYDROGEN ISOTOPE FRACTIONATIONS

The most important hydrogen isotope fractionation is that between the liquid and the vapour phases of water. Under equilibrium conditions water vapour is isotopically lighter (contains less $^2$H) than liquid water by amounts given in Table 7.6. Fig.7.3 shows some actual isotope ratios of equilibrium systems and the matching $^{2}$δ values. The fractionation by diffusion of H$_2$O through air ($^{2}$δ$_d$) varies between $-22.9 \pm 1.7$‰ (Merlivat, 1978) and $-20.4 \pm 1.4$‰. (unpubl.), slightly more than the value calculated from Eq.3.34 ($-16.3$‰) (cf. Sect. 7.3.2).
7.4.3 REPORTING $^2$H VARIATIONS AND THE $^2$H STANDARD

VSMOW is the standard for $^2$H/$^1$H as it is for $^{18}$O/$^{16}$O ratios. Values for the absolute $^2$H/$^1$H ratio of VSMOW and SLAP are reported to be $(155.76 \pm 0.07) \times 10^{-6}$ and $(89.02 \pm 0.05) \times 10^{-6}$, respectively, by Hagemann et al. (1970), $(155.75 \pm 0.08) \times 10^{-6}$ and $(89.12 \pm 0.07) \times 10^{-6}$ by De Wit et al. (1980), and $(155.60 \pm 0.12) \times 10^{-6}$ and $(88.88 \pm 0.18) \times 10^{-6}$ by Tse et al. (1980).

### Table 7.5

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<td>natural abundance</td>
<td>0.99985</td>
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<td>stable</td>
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<td>natural specific activity</td>
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<td>$\beta^-$ / $^3$He</td>
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<td>half-life ($T_{1/2}$)</td>
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<td>max. $\beta$ energy</td>
<td></td>
<td>18 keV</td>
<td></td>
</tr>
<tr>
<td>abundance range in hydrological cycle</td>
<td>250‰</td>
<td>0 to $10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>reported as in</td>
<td>$^2$$\delta$ or $^3$$\delta$H or $\delta$D</td>
<td>$^3$A</td>
<td></td>
</tr>
<tr>
<td>instrument</td>
<td>MS</td>
<td>PGC, LSS</td>
<td></td>
</tr>
<tr>
<td>analytical medium</td>
<td>$H_2$</td>
<td>$H_2O$, $C_2H_6$, $C_6H_6$</td>
<td></td>
</tr>
<tr>
<td>usual standard deviation</td>
<td>0.5‰</td>
<td>$\geq 1%$ at high level</td>
<td></td>
</tr>
<tr>
<td>international standard</td>
<td>VSMOW</td>
<td>NBS-SRM 4361</td>
<td></td>
</tr>
<tr>
<td>with absolute value</td>
<td>$^2$H/$^1$H = 0.00015575</td>
<td>$^3$H/$^1$H = 6600 TU</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>or = 0.780 Bq/g $H_2O$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>as of Jan.1, 1988</td>
<td></td>
</tr>
</tbody>
</table>
The average $^2\delta$ value of the secondary standard SLAP on the VSMOW scale (Sect. 7.2.3) consequently is $-428.2 \pm 0.1\%$. Based on these data the $^2\delta$ value has been defined as:

$$^2\delta_{\text{SLAP}/\text{VSMOW}} = -428.0\%$$  \hspace{1cm} (7.33)

No significant difference in $^2\delta$ has been detected between the original SMOW standard and VSMOW (IAEA, 1978).

### Table 7.6

Hydrogen isotope fractionation in the equilibrium system liquid water ($l$), water vapour ($v$), and ice ($i$); $\varepsilon_y / \varepsilon_x$ represents the fractionation of compound $y$ relative to compound $x$ and is approximately equal to $^2\delta(y) - ^2\delta(x)$. Values for intermediate temperatures may be obtained by linear interpolation; $T = t (^\circ C) + 273.15 \, K$.

<table>
<thead>
<tr>
<th>$t$ (^{\circ} C$</th>
<th>$^2\varepsilon_{v/l}^1$</th>
<th>$^{18}\varepsilon_{v/l}$</th>
<th>$^2\varepsilon_{v/l} / ^{18}\varepsilon_{v/l}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-101.0$</td>
<td>$-11.55$</td>
<td>$8.7$</td>
</tr>
<tr>
<td>5</td>
<td>$-94.8$</td>
<td>$-11.07$</td>
<td>$8.5^5$</td>
</tr>
<tr>
<td>10</td>
<td>$-89.0$</td>
<td>$-10.60$</td>
<td>$8.4$</td>
</tr>
<tr>
<td>15</td>
<td>$-83.5$</td>
<td>$-10.15$</td>
<td>$8.2^5$</td>
</tr>
<tr>
<td>20</td>
<td>$-78.4$</td>
<td>$-9.71$</td>
<td>$8.1$</td>
</tr>
<tr>
<td>25</td>
<td>$-73.5$</td>
<td>$-9.29$</td>
<td>$7.9$</td>
</tr>
<tr>
<td>30</td>
<td>$-68.9$</td>
<td>$-8.89$</td>
<td>$7.7^5$</td>
</tr>
<tr>
<td>35</td>
<td>$-64.6$</td>
<td>$-8.49$</td>
<td>$7.6$</td>
</tr>
<tr>
<td>40</td>
<td>$-60.6$</td>
<td>$-8.11$</td>
<td>$7.4$</td>
</tr>
</tbody>
</table>

1) Majoube, 1971  \hspace{1cm} \ln^2 \alpha = -24.844/T^2 + 76.248/T - 0.052612  \hspace{1cm} (7.31a)

1/T adjustment  \hspace{1cm} \varepsilon_{v/l}^2 = -85.626/T + 213.4\% \hspace{1cm} (7.31b)

Values at higher temperatures can be obtained from Horita and Wesolowski (1994)

2) The ratios between the fractionations for $^{18}\text{O}$ and $^2\text{H}$ at the liquid–vapour equilibrium are obtained from Majoube (1971).

Majoube, 1971  \hspace{1cm} \varepsilon_{v/l} = +19.3\% (at 0\(^{\circ} C\))  \hspace{1cm} (7.32)

Reference and intercomparison water samples are available from the IAEA (Table 11.3). The $^2\text{H}$ contents of hydrogen-containing samples are determined by completely converting them to hydrogen gas. Therefore, fundamental problems of isotope fractionation during sample preparation, as with $^{18}\text{O}$, do not occur; however, the analyses are more troublesome (Sect. 10).
Henceforth all $^2\delta$ values will be reported relative to VSMOW.

More details on the measurement and calculation procedures, and on isotope reference samples are given in Chapter 10.

7.4.4 SURVEY OF NATURAL $^2\text{H}$ VARIATIONS

From the foregoing it is evident that some correlation should exist between $^2\text{H}$ and $^{18}\text{O}$ fractionation effects. Therefore, in natural waters a relation between $^2\delta$ and $^{18}\delta$ values is to be expected. Indeed, the $^2\delta$ and $^{18}\delta$ variations in precipitation, ice, most groundwaters and non-evaporated surface waters have appeared to be closely related. Therefore, the qualitative discussion given in Sect.7.2.4 for $^{18}\delta$ applies to $^2\delta$ equally well. The next section is devoted to this relation.

7.5 RELATION BETWEEN $^2\text{H}$ AND $^{18}\text{O}$ VARIATIONS IN WATER

If we simply assume that evaporation and condensation in nature occur in isotopic equilibrium, the relation between the $^2\delta$ and $^{18}\delta$ values of natural waters is determined by both equilibrium fractionations $^2\varepsilon_{v/l}$ and $^{18}\varepsilon_{v/l}$. In Table 7.6 the ratio of these factors is presented for the temperature range of $0 - 40^\circ\text{C}$.

Craig (1961b) and Dansgaard (1964) found a relation between the $^2\delta$ and $^{18}\delta$ values of precipitation from various parts of the world:

$$^2\delta = 8^{18}\delta + 10 \text{‰}$$  \hspace{1cm} (7.34)

This relation, shown in Fig.7.17 has become known as the Global Meteoric Water Line (GMWL) and is characterised by a slope of 8 and a certain intercept with the $^2\text{H}$ axis (= the $^2\delta$ value at $^{18}\delta = 0 \text{‰}$). The general relation is of the MWL is:

$$^2\delta = s^{18}\delta + d$$  \hspace{1cm} (7.35)

where the slope $s = 8$, as is explained by the ratio between the equilibrium isotope fractionations of hydrogen and oxygen for the rain condensation process (Table 7.6); d is referred to as the deuterium excess (d-excess), the intercept with the $^2\delta$ axis. In several regions of the world as well as during certain periods of the year and even certain storms the $^2\delta$ value is different from 10 ‰, depending on the humidity and temperature conditions in the evaporation region.

The isotopic composition of water vapour over seawater with $^2\delta = ^{18}\delta = 0 \text{‰}$ vs VSMOW is somewhat lighter than would follow from isotopic equilibrium with the water: the evaporation
Fig. 7.17  Relation between natural variations of $\delta^{18}O$ and $\delta^2H$ ocean water, atmospheric vapour and precipitation. The black round represents the hypothetical value of water vapour in isotopic equilibrium with ocean water, black square the observed isotopic composition of equatorial marine vapour, originated from the more realistic non-equilibrium fractionation. Marine vapour gradually condenses into precipitation (hatched arrow) with a positive fractionation, leaving the vapour progressively depleted in $^{18}O$ and $^2H$ (grey arrow) (cf. Fig. 7.13).

is a non-equilibrium (partly kinetic) process. However, from the observed vapour composition onward the vapour and precipitation remain in isotopic equilibrium, because the formation of precipitation is likely to occur from saturated vapour (i.e. vapour in physical equilibrium with water). Consequently the $\delta^{18}O$ and $\delta^2H$ values both move along the meteoric water line (Eq. 7.33).
Fig. 7.18  Relation between $^{18}\delta$ and $^2\delta$ for estuarine mixing and for evaporating surface water. Because the evaporation is a non-equilibrium process, isotope fractionations involved are not necessarily related by a factor of 8, as is the equilibrium condensation process, the basis for the meteoric water line (Fig. 7.17). As in the preceding figure, the arrows indicate the direction of change of the isotopic composition of the escaping vapour and of the remaining evaporated water.
In Volume 3 (Surface Water) certain circumstances will be discussed leading to deviations from the common MWL. For instance, larger values of d are occasionally observed.

Apart from this, deviations occur in evaporating surface waters, showing slopes of 4 to 5 rather than 8. If $^2\delta_o$ and $^{18}\delta_o$ denote the original isotopic composition of an arbitrary surface water, the $\delta$ values after evaporation are related by:

$$^2\delta - ^2\delta_o \approx 4.5 \left( ^{18}\delta - ^{18}\delta_o \right) \quad \text{or} \quad \Delta^2\delta \approx 4.5 \Delta^{18}\delta$$

(Fig.7.18). The release of relatively low-$\delta$ water vapour to the air results in an increase in $\delta$ of the remaining water, as illustrated by the model of Sect.4.4.5, here for $^2\delta$ as well as $^{18}\delta$. 
