Stable Isotope Hydrology
Deuterium and Oxygen-18 in the Water Cycle

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1981
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STABLE ISOTOPE HYDROLOGY
Deuterium and Oxygen-18
in the Water Cycle

A MONOGRAPH PREPARED UNDER THE AEGIS OF THE
IAEA/UNESCO WORKING GROUP ON
NUCLEAR TECHNIQUES IN HYDROLOGY OF THE
INTERNATIONAL HYDROLOGICAL PROGRAMME

Scientific editors: J.R. Gat, R. Gonfiantini

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1981
The Nier mass spectrometer, 1947 (by courtesy of Professor A.O. Nier).
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Chapter 1

HISTORICAL INTRODUCTION*

Early in this century it was conjectured that some elements consisted of mixtures of atoms of different weight. The term isotopes was introduced in 1913 by Soddy (1913) for nuclides which occupy the same position in the periodic table but which differ in their nuclear properties. In the same year, Thomson (1913) showed the element neon to be made up of more than one isotope.

With the advent of Aston’s mass spectrograph in 1919, the discovery of isotopes of all elements was well under way (Aston, 1919).

1.1. DISCOVERY OF THE OXYGEN ISOTOPES

The isotopes of the elements which constitute the water molecule were not discovered by means of the mass spectrogram. The existence of oxygen of mass 17 was first observed by Blackett (1925) while studying the nuclear reaction $^{14}\text{N}(\alpha,p)^{17}\text{O}$, but he did not determine whether this nuclide was stable with regard to radioactive decay. It was not until 1929 that oxygen-18 and 17 were discovered in natural materials; this was achieved within a few months by Giauque and Johnston (1929) while interpreting the adsorption bands in the spectrum of atmospheric oxygen. The authors were not able to give reliable values for the abundance of these isotopes, but estimated them to be about one part in 1250 for $^{18}\text{O}$ and about one part in 10 000 for $^{17}\text{O}$.

Chemical atomic weights had been defined in terms of natural oxygen, which was taken as 16 atomic mass units. The physical scale of atomic masses was defined in terms of $^{16}\text{O}$ as 16 atomic mass units. The discovery that natural oxygen was a mixture of isotopes meant that the two mass scales could not be identical. Further, the possibility then existed that the isotopic composition of oxygen in nature might be variable and that the chemical scale of atomic weights might, therefore, lack a unique reference point. The discovery of the heavier isotopes of oxygen made it essential, therefore, to determine both the variability of the isotopic composition of oxygen from various sources and the exact abundance of the two isotopes in any given standard sources. For this reason, great efforts were devoted to the measurement of the natural abundances of $^{18}\text{O}$ and $^{17}\text{O}$ in the years immediately following their discovery.

* Based in part on an unpublished review on the isotopes of oxygen by D. Samuel and I. Dostrowsky.
Mecke and Childs (1931) determined the ratio of abundance of the isotopes of oxygen as $^{16}$O:$^{18}$O:$^{17}$O = 630:1:0.2, using the adsorption band spectra of the O$_2$ molecule in air. However, it was only when improved mass spectrometers were used to solve this problem that the measured abundances converged rapidly on the value accepted today. Thus, Aston (1932) obtained the values of $^{16}$O:$^{18}$O:$^{17}$O = 536:1:0.24 and Smythe (1934) the value of 503 ± 10 for the $^{16}$O:$^{18}$O ratio of oxygen prepared from lead dioxide. The currently accepted value for the relative abundance of isotopes in air oxygen is 99.759:0.0374:0.2039 (Nier, 1950), which is equivalent to an $^{18}$O/$^{16}$O ratio of 1:489.

As soon as the precision of the measurements of abundance reached a few per cent (in the late 1930s) it became clear that the isotopic composition of oxygen was not constant. Later work, particularly in the years following World War II, showed that variations of up to 10% occur in the natural abundance of $^{18}$O in oxygen derived from different natural sources. With the further increase in the precision of measurements, it became meaningless to speak of the abundance of the isotopes of oxygen unless the source of the sample analysed was carefully specified. In 1961 the International Union of Pure and Applied Chemistry abandoned oxygen as a standard for atomic weights and adopted a new "Table of Atomic Weights" based on a single isotope, i.e. carbon-12.

1.2. DISCOVERY OF DEUTERIUM

The discovery of deuterium by Urey in 1931 followed the theoretical prediction that there will be differences between the vapour pressure of isotopic species. Urey and co-workers (1932a) looked for deuterium in the residue of a low-temperature hydrogen distillation column where it was expected to be enriched and, indeed, succeeded in identifying the isotope by its atomic spectrum.

The natural concentration of deuterium was estimated to be D/$^1$H = 1/4000 by measuring the intensity of Balmer lines in the spectrum of natural hydrogen (Urey et al., 1932b). Bleackney and Gould (1933) determined a ratio of D/$^1$H = 1/5000 by means of mass spectrometry. On the basis of density differences between natural and depleted waters, Morita and Titani (1938) determined the deuterium content of Osaka tap water to be D/$^1$H = 1:6200. Almost pure D$_2$O as well as H$_2$O depleted in deuterium were prepared in 1934 by

---

1 Deuterium is the name given to the hydrogen isotope of mass 2, i.e. $^2$H ≡ D. The hydrogen isotope of mass 3 is named tritium and is symbolized by $^3$H ≡ T. This isotope is not stable but decays by beta decay.
electrolytic decomposition of water and thus the study of the physical properties of heavy water became possible. (The concentration of pure \(^{18}\)O was achieved much later in Switzerland through methods of thermal diffusion (Clusius et al., 1943); gram quantities of \(^{18}\)O and \(^{17}\)O enriched material are now made at Rehovot by a method of fractional water distillation (Dostrowsky and Raviv, 1958).)

1.3. EARLY MEASUREMENT TECHNIQUES

In the years up to World War II, the major analytical tool for measuring isotope abundance variations in water was based on the density difference between heavy and light water. As described by Kirschenbaum (1951), these measurements were brought to a state of great refinement so that differences in specific gravity of the order of 0.1 \(\gamma\) (1 part in ten million) were detected, which is equivalent to changes of 0.000093 mol\% of deuterium or of 0.000083 mol\% of \(^{18}\)O. Such variations are well within the range of natural variability.

The density of a given sample of water is a function of both its deuterium and its \(^{18}\)O content; since both may vary, great caution has to be exercised in interpreting density measurements. Some of the early workers in this field were aware of this problem and attempted to get around it by either normalizing water with respect to either the hydrogen or oxygen isotopes (for example, by decomposing water to hydrogen gas on iron fillings and then reoxidizing the hydrogen with oxygen of a standard isotopic composition) or using combined densimetric and refractometric methods of analysis (Teis and Florenski, 1940). These procedures, however, increased the error of analysis. Furthermore, various laboratories have used different standards of reference for their measurements, many of which are not readily comparable with one another today. As a result, much of the early work, while useful in indicating that appreciable variations in abundance do occur, is of limited use in quantitative comparisons with later data.

1.4. EARLY WORK ON ISOTOPE HYDROLOGY

Immediately following the discovery of the isotopic water molecules, laboratories throughout the world, primarily in the USA, USSR, Japan and Eastern Europe, investigated a wide spectrum of natural waters and geological materials. These early studies were reviewed by Rankama (1954). It is amazing that, with the limitations and uncertainties of the analytical methods employed, the major features of the isotope distribution pattern were already known at
FIG. 1. Histogram showing the number of papers on stable isotope hydrology published in the period 1930–1974.

the end of the 'thirties. Thus, the depletion of heavy isotopes in the meteoric water cycle compared with the oceans and the enrichment of the heavy isotopic species in surface waters exposed to evaporation emerged with considerable clarity.

The large differences between D$_2$O and normal water in properties such as vapour pressures, density, equilibrium constants and reaction rates added impetus to the study of the so-called 'isotope effects' on phase equilibria, reaction rates, and transport processes which involve the isotopic water species. These studies are the foundation for the quantitative understanding of natural abundance variations of isotopes of the light elements in nature.

A major breakthrough in the measurement of natural isotope abundances came with the Nier/McKinney mass spectrometer (Nier, 1947; McKinney et al., 1950). This machine was designed specifically for the measurement of small differences in isotope abundance through the use of a double inlet (for close comparison between sample and standard) and a double collector (so that direct
measurement of the ratio becomes possible). With its use, Urey and his pupils in Chicago started a detailed and refined survey of natural isotope abundances of all lighter elements, which lay the foundation for their present widespread use in hydrology, geochemistry, oceanography and other environmental sciences.

The growth and maturation of stable isotope hydrology can be seen in Fig.1, which summarizes the number of papers published on the use of stable isotope abundance in hydrological studies (Fidel, 1976). The upswing in the early 'sixties may, in part, be credited to the activities of the Agency's Section of Isotope Hydrology; 'local maxima' of 1963, 1970 and 1974 reflect the IAEA symposia on isotope hydrology held in those years.

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Chapter 2

PROPERTIES OF THE ISOTOPIC SPECIES OF WATER:
THE ‘ISOTOPE EFFECT’

2.1. THE ISOTOPES OF HYDROGEN AND OXYGEN:
NOMENCLATURE AND DEFINITIONS

The naturally occurring heavy isotopes of hydrogen of masses 2 and 3 have acquired the individual names of deuterium and tritium, respectively, in short, D and T. This nomenclature is often used instead of the more correct form of $^2\text{H}$ and $^3\text{H}$, and will also be used in this monograph, in deference to most of the isotopic hydrological and geochemical literature. The most abundant hydrogen isotope (of mass 1) is then simply designated as H, in lieu of $^1\text{H}$. The reader should be warned of a possible confusion which might arise because of the alternative usage of the symbol of an element without any mass assignment to designate the elements in their natural state, i.e. a mixture of their isotopes in their natural (standard) abundances. Tritium, which is unstable and decays by beta decay, is not considered further in this monograph.

No individual nomenclature exists for the isotopes of oxygen of masses 16, 17 and 18; these are simply designated $^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$, respectively.

The possible stable isotope water species are then:

$\text{H}_2^{16}\text{O}, \text{HD}^{16}\text{O}, \text{D}_2^{16}\text{O}, \text{H}_2^{17}\text{O}, \text{HD}^{17}\text{O}, \text{D}_2^{17}\text{O}, \text{H}_2^{18}\text{O}, \text{HD}^{18}\text{O}$ and $\text{D}_2^{18}\text{O}$.

All of these occur in natural waters but, considering the natural abundance of the isotopes, as outlined in Chapter 1, it is only the molecules of $\text{H}_2^{16}\text{O}$, $\text{H}_2^{18}\text{O}$, $\text{HD}^{18}\text{O}$ and $\text{H}_2^{17}\text{O}$ which are of any importance (or, for that matter, are amenable to accurate analytical assay). In terrestrial materials the $^{17}\text{O}$ geochemistry echoes that of the 5.5 times more abundant $^{18}\text{O}$, and this is also usually not considered separately. Hence, most of our discussions will involve just the abundance ratios of the isotopic pairs $^{18}\text{O}/^{16}\text{O}$ on the one hand and D/H on the other.

2.2. PHYSICAL AND TRANSPORT PROPERTIES

The substitution of isotopes of either oxygen or hydrogen in the water molecule affects first of all those properties controlled directly by the molecular mass, such as the specific gravity and the molecular diffusivities in the gas phase.
Here the molecular mass as a whole comes into play and hence the molecules H$_2^{18}$O, D$_2^{16}$O and HT$^{18}$O, which have almost the same mass, are to a first approximation similarly affected. The molecules HD$^{16}$O and H$_2^{17}$O have properties intermediary between those of 'light' and 'heavy' water.

The ratios of the densities of H$_2^{18}$O/H$_2$O and D$_2$O/H$_2$O, given by Szapiro (1965)$^2$ as $d_{20}^{18} = 1.112653$ and 1.108018, respectively, differ by only a few per mille from the respective mass ratios of 1.1110 and 1.1117. This is so because the interatomic distances are practically invariant under isotopic substitution, as exemplified by the close similarity of the molar volumes of the isotopic water species H$_2$O, H$_2^{18}$O and D$_2$O at 30°C, i.e. 18.0991, 18.0724 and 18.1589 (Szapiro, 1965).

Molecular diffusivities of gas A through gas B (e.g. of water vapour through air), whose molecular masses are $M_A$ and $M_B$ respectively, are given according to gas kinetic theory by the expression

$$D_{A,B} = \frac{C}{P \cdot \sigma_{A,B}^2 \cdot \Omega_{A,B}} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) T^3$$

(M = molecular mass, T = absolute temperature, P = total pressure, C = a constant, $\sigma_{A,B}$ = sum of atomic radii, $\Omega_{A,B}$ = an interactive correction term) (Chapman and Couling, 1951).

Simple gas kinetic calculations based only on mass differences (and neglecting interactive terms) give the ratio of diffusivities of isotopic water molecules in air as $D_{H_2^{18}O} / D_{H_2O} = 1.015$ and $D_{H_2^{18}O} / D_{H_2^{17}O} = 1.030$ (Ehnholt and Knott, 1965). For the molecules D$_2^{16}$O and H$_2^{18}$O, which are both of mass 20, the simple theory would predict similar diffusivities.

Recently, Merlivat (1978) has measured the ratio of diffusivities in air at 20°C and obtained the following values:

$$D_{H_2^{16}O} / D_{H_2^{18}O} = 1.0306 \pm 0.0007, \quad D_{H_2^{16}O} / D_{HDO} = 1.0250 \pm 0.0009$$

which differ from the value predicted by simple theory, especially in the case of the deuterated molecule. The effect of temperature on $D$ is relatively weak, being proportional to $T^{3/2}/P \approx \sqrt{T}$, and the ratio of diffusivities is practically temperature invariant.

In the liquid, the molecular self-diffusion coefficients of isotopic water species of equal mass are not equal. As measured by Wang et al. (1953) the diffusion coefficient of H$_2^{18}$O through water is larger by 14% than that of HTO; this may

$^2$ Szapiro uses H and O without a specific mass assignment for the elements with their natural standard abundance of isotopic species.
TABLE I. ISOTOPE EFFECT ON TRANSPORT PARAMETERS OF WATER

Molecular diffusivities of water molecules in air:

\[ D_{\text{HD}^{16}\text{O}}D_{\text{H}^{16}\text{O}} = 0.9755 \pm 0.0009^a \]
\[ D_{\text{H}^{18}\text{O}}D_{\text{H}^{16}\text{O}} = 0.9723 \pm 0.0007^a \]

Diffusion coefficient of isotopic water molecules through ordinary water (liquid).\(^b\)

<table>
<thead>
<tr>
<th>(\mathcal{D} \times 10^5 \text{ (cm}^2/\text{s)} \text{ at } 25^\circ\text{C} )</th>
<th>HD(^{16}\text{O})</th>
<th>HT(^{18}\text{O})</th>
<th>H(_3)(^{18}\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.34</td>
<td>2.44</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Viscosity of liquid water:

<table>
<thead>
<tr>
<th>(\eta \text{ (centipoise) at } 20^\circ\text{C} )</th>
<th>H(_2)(^{18}\text{O})</th>
<th>D(_2)(^{16}\text{O})</th>
<th>HD(^{16}\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0564(^c)</td>
<td>1.2471(^d)</td>
<td>1.1248</td>
</tr>
</tbody>
</table>

\(^a\) MERLIVAT, L., Molecular diffusivities of H\(_2\)\(^{18}\text{O}\), HD\(^{16}\text{O}\) and H\(_2\)\(^{18}\text{O}\) in gases, J. Chem. Phys. 69 (1978) 2864.

reflect the intermolecular binding forces which are activated by the diffusion process in the liquid state and for which the effect of the hydrogen isotopes is larger than that of the oxygen isotopes. Other transport properties in the liquid, such as viscosity and dipole relaxation, are similarly affected by intermolecular forces and especially by hydrogen bonding, and not just by mass difference.

Table I gives some measured values of the transport parameter.

2.3. EQUILIBRIUM ISOTOPE EFFECTS

The isotopic substitution affects the vibrational states of the covalently bound molecules and thus the value of the partition function of the isotopic
species\(^3\) (in the case of hydrogen isotopes, the rotational states of isotopic molecules also contribute to different degrees to the partition function at lower temperature). As a result, the equilibrium distribution of isotopes between water and other compounds, or between different phases of the water substance, is not uniform. These are quantum effects which become appreciable at low temperatures and disappear at the high-temperature limit when the partition function ratio of the molecular isotopic species converges towards the symmetry number ratio.

The electronic structure of the molecules, on the other hand, is nearly independent of the mass of the nuclei. This means that the potential energy surface and hence the interatomic distances as well as vibrational force constants can be treated, with considerable accuracy, as being invariant under isotopic substitution (Melander, 1960). A very slight isotope effect on the ionic radius (and bond length) was, however, recently utilized for the separation of ionic isotopic species (Heumann, 1975).

The so-called 'equilibrium isotope effects' can be expressed quantitatively as the constants of an appropriate exchange reaction, such as the following:

\[
AX + BX^* \rightleftharpoons AX^* + BX
\]

\[
K = \frac{[AX^*][BX]}{[AX][BX^*]}
\]

where \(X\) and \(X^*\) are the isotopic substituents. In a general case,

\[
\frac{1}{n} AX_n + X^* \rightleftharpoons \frac{1}{n} AX_n^* + X
\]

\[K^* = \left(\frac{AX_n^*/AX_n}{X^*/X}\right)^{1/n}\]

\(K^*\) is termed the reduced equilibrium constant of the exchange reactions of \(AX_n\). These constants are expressed as a ratio of partition functions of the isotopic molecules and can be quantum-mechanically calculated, based on spectroscopic data. A number of excellent reviews on this subject have been published by Bigeleisen and Mayer (1947), Urey (1947), Roginskij (1956), Boato (1961), Bigeleisen (1965), and Bigeleisen et al. (1973).

\(^3\) The partition function summarizes the way in which the energy of a system is partitioned among the molecular species. It is defined in terms of the a-priori probability \(p_i\) and the energy \(e_i\) of the molecules in each of the \(i\) quantum states as follows:

\[f = \sum_i p_i e^{-e_i/kT}\]

(where \(k\) is the Boltzmann factor and \(T\) is the absolute temperature). Based on the concept that stability corresponds to a state of minimum energy, it can be shown that the equilibrium distribution of isotopes among isotopic species is given by the partition function ratio of the appropriate isotopic molecules; this ratio can be calculated for reasonably simple molecules from the spectroscopic data.
An alternative formulation, which is of special relevance to isotope fractionation processes, is obtained by using an equilibrium fractionation factor $\alpha$, which is defined as the ratio of atom ratios of the isotopes in the exchange partners:

$$
\alpha = \frac{(X*/X)}{(X*/X)} \text{ in molecule A} \quad \frac{(X*/X)}{(X*/X)} \text{ in molecule B}
$$

The numerical value of $\alpha$ equals the value of the equilibrium constant $K$ in the simple monatomic exchange reactions. In a general case, $\alpha = K^*$, the reduced equilibrium constant, provided that the atomic sites are equivalent in the molecule and that the constants of the internal exchange reactions (scrambling reactions), such as $AX_n + AX_n^* \rightleftharpoons AX_{n-m}X_{m}^* + AX_mX_{n-m}^*$, have the statistical distribution value. The deviation of $\alpha$ from the value of 1 will be a measure of the 'equilibrium isotope effect'. Except for the case of exchange reactions involving hydrogen isotopes, where the $\alpha$-values may be as large as 3, the equilibrium isotope effects are of the order of a few per cent, at most, at room temperature. Some values of exchange reaction constants which are of relevance to the geochemistry of the water cycle are shown in Tables II, III.

Phase equilibria are a special case of equilibrium fractionation processes and the separation coefficient can be defined in an analogous fashion:

$$
\alpha = \frac{(X*/X)}{(X*/X)} \text{ phase 1} \quad \frac{(X*/X)}{(X*/X)} \text{ phase 2}
$$

In the water cycle the ice–liquid–vapour phase transitions are of prime interest; the crystal water solution system is also of some concern. The vapour/liquid fractionation factors

$$
\alpha_D = \frac{(D/H)_{\text{vap}}}{(D/H)_{\text{liq}}} \quad \alpha^{18}O = \frac{(^{18}O/^{16}O)_{\text{vap}}}{(^{18}O/^{16}O)_{\text{liq}}}
$$

have been measured in one of three ways:

(a) Through vapour pressure measurement of pure isotopic species (Szapiro and Steckel, 1967; Uvarov et al., 1962), assuming validity of the rule of geometric mean (Bigeleisen, 1962)

(b) By isotope analysis of water and vapour which are in equilibrium with each other (Bigeleisen, 1962; Majoube, 1971; Bottinga and Craig, 1969)

(c) By dynamic distillation methods (Borowitz, 1962).
TABLE II. EQUILIBRIUM CONSTANTS OF SOME ISOTOPIC EXCHANGE REACTIONS

<table>
<thead>
<tr>
<th>Exchange reaction</th>
<th>T (K)</th>
<th>$K^b$</th>
<th>Isotope exchanged</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + D_2 \leftrightarrow 2HD$</td>
<td>298</td>
<td>3.26(4)</td>
<td>H/D</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.90(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2 + T_2 \leftrightarrow 2HT$</td>
<td>298</td>
<td>2.56(4)</td>
<td>H/T</td>
<td>[2]</td>
</tr>
<tr>
<td>$H_2O(g) + HD \leftrightarrow HDO + H_2$</td>
<td>293</td>
<td>3.20(1)</td>
<td>H/D</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.28(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2O + D_2O \leftrightarrow 2HDO$</td>
<td>298</td>
<td>3.96(4)</td>
<td>H/D</td>
<td>[1]</td>
</tr>
<tr>
<td>$NH_3 + HD \leftrightarrow NH_2D + H_2$</td>
<td>570</td>
<td>2.41(5)</td>
<td>H/D</td>
<td>[3]</td>
</tr>
<tr>
<td>$NH_3 + HT \leftrightarrow NH_2T + H_2$</td>
<td>516</td>
<td>3.61(5)</td>
<td>H/T</td>
<td>[4]</td>
</tr>
<tr>
<td>$H_2S + HDO \leftrightarrow HDS + H_2O$</td>
<td>288</td>
<td>0.45(1)</td>
<td>H/D</td>
<td>[1]</td>
</tr>
<tr>
<td>$^{1}C^{16}O_2(g) + H_2^{16}O(\ell) \leftrightarrow ^{1}C^{18}O_2 + H_2^{16}O$</td>
<td>273</td>
<td>1.046</td>
<td>$^{18}O/^{16}O$</td>
<td>[5]</td>
</tr>
<tr>
<td>$H_2^{32}S + H_2^{34}SO_4 \leftrightarrow H_2^{34}S + H_2^{34}SO_4$</td>
<td>373</td>
<td>1.04</td>
<td>$^{38}S/^{34}S$</td>
<td>[6]</td>
</tr>
<tr>
<td>$^{12}CO_2(g) + ^{13}CO_2(aq) \leftrightarrow ^{13}CO_2(g) + ^{12}CO_2(aq)$</td>
<td>273</td>
<td>1.00117</td>
<td>$^{15}C/^{12}C$</td>
<td>[7]</td>
</tr>
<tr>
<td>$^{13}CO_2(g) + H^{12}CO_3(aq) \leftrightarrow ^{12}CO_2 + H^{13}CO_3$</td>
<td>298</td>
<td>1.0080</td>
<td>$^{12}C/^{13}C$</td>
<td>[8]</td>
</tr>
<tr>
<td>$^{13}CO_2(g) + ^{12}CO_3(aq) \leftrightarrow ^{12}CO_2 + ^{13}CO_3$</td>
<td>298</td>
<td>1.0093</td>
<td>$^{12}C/^{13}C$</td>
<td>[8]</td>
</tr>
<tr>
<td>$^{14}O_2(aq) + ^{18}O_2(g) \leftrightarrow ^{18}O_2(aq) + ^{14}O_2(g)$</td>
<td>298</td>
<td>1.0099</td>
<td>$^{16}O/^{18}O$</td>
<td>[7]</td>
</tr>
<tr>
<td>$^{15}NH_4(g) + ^{14}NO_3 \leftrightarrow ^{14}NH_4 + ^{15}NO_3$</td>
<td>298</td>
<td>1.041</td>
<td>$^{15}N/^{14}N$</td>
<td>[9]</td>
</tr>
<tr>
<td>$^{14}NH_3(g) + ^{15}NH_4(aq) \leftrightarrow ^{15}NH_3 + ^{14}NH_2$</td>
<td>298</td>
<td>1.031</td>
<td>$^{15}N/^{14}N$</td>
<td>[10]</td>
</tr>
</tbody>
</table>

---

a Further data are to be found in Chapter 11 of this monograph.
b The classical (statistical) value of $K$ is shown in parentheses, except where this is obviously equal to 1.

REFERENCES

### TABLE III. EQUILIBRIUM CONSTANTS OF OXYGEN ISOTOPE EXCHANGE REACTIONS BETWEEN WATER AND VARIOUS MINERALS

$\ln \alpha^s = 10^6 AT^{-2} + 10^3 BT^{-1} + C$ (or $10^6 AT^{-2} + C$)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Temperature range (°C)</th>
<th>$10^6 A$</th>
<th>$10^3 B$</th>
<th>C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>200 – 500</td>
<td>3.38</td>
<td></td>
<td>-3.40</td>
<td>[1]</td>
</tr>
<tr>
<td>Calcite</td>
<td>0 – 700</td>
<td>2.78</td>
<td></td>
<td>-3.39</td>
<td>[2]</td>
</tr>
<tr>
<td>Dolomite</td>
<td>300 – 500</td>
<td>3.20</td>
<td></td>
<td>-1.50</td>
<td>[3]</td>
</tr>
<tr>
<td>Clay (Smectite)</td>
<td>0 – 270</td>
<td>2.67</td>
<td></td>
<td>-4.82</td>
<td>[4]</td>
</tr>
<tr>
<td>Anhydrite</td>
<td></td>
<td>3.88</td>
<td></td>
<td>-3.40</td>
<td>[5]</td>
</tr>
<tr>
<td>Magnetite</td>
<td>500 – 800</td>
<td>-1.47</td>
<td></td>
<td>-3.70</td>
<td>[6]</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td></td>
<td>-0.021</td>
<td>17.99</td>
<td>-19.97</td>
<td>[7]</td>
</tr>
</tbody>
</table>

### REFERENCES


The most reliable data seem to be those of Majoube (1971) and of Szapiro and Steckel (1967). Like other isotope effects, the fractionation caused by the liquid – vapour phase transition is a function of temperature and can be shown to follow an equation of the type:

$$\ln \alpha = \frac{A}{T^2} + \frac{B}{T} + C$$

with B often of opposite sign relative to A, so that a change-over in isotopic preference occurs close to the high-temperature limit as $\alpha \to 1$. 
## TABLE IV. EQUILIBRIUM ISOTOPIC FRACTIONATION FACTORS DURING PHASE TRANSITIONS OF WATER

Expressed as $\alpha^* = R_{(\text{phase } 1)}/R_{(\text{phase } 2)}$, where $R$ is the ratio of either $^{18}\text{O}$ or D to the common isotope, $^{16}\text{O}$ or H, respectively.

<table>
<thead>
<tr>
<th>Phase Transition</th>
<th>$\alpha^*_{^{18}\text{O}}$</th>
<th>$\alpha^*_{\text{D}}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (ice) -- vapour at $0^\circ\text{C}$</td>
<td>1.0152</td>
<td>1.132</td>
<td>[1]</td>
</tr>
<tr>
<td>at $-10^\circ\text{C}$</td>
<td>1.0166</td>
<td>1.151</td>
<td>[1]</td>
</tr>
<tr>
<td>Liquid -- vapour at $20^\circ\text{C}$</td>
<td>1.0098</td>
<td>1.084</td>
<td>[2]</td>
</tr>
<tr>
<td>at $0^\circ\text{C}$</td>
<td>1.0117</td>
<td>1.111</td>
<td>[2]</td>
</tr>
<tr>
<td>Solid (ice) -- liquid at $0^\circ\text{C}$</td>
<td>1.0035</td>
<td>1.0208</td>
<td>[1][3]</td>
</tr>
<tr>
<td>Hydration water -- mother solution at $20^\circ\text{C}$, gypsum (CaSO$_4$·2H$_2$O)</td>
<td>1.0040</td>
<td>0.985</td>
<td>[4, 5][6]</td>
</tr>
<tr>
<td>Hydration water -- mother solution Epsomite (MgSO$_4$·7H$_2$O)</td>
<td>1.0084</td>
<td></td>
<td>[5]</td>
</tr>
</tbody>
</table>

* Compare with USGS professional paper No. 440-KK, Data of Geochemistry, Chapter KK, by I. Friedman and J. O’Neil (US Government Printing Office, Washington, DC, 1977), for graphical compilation of stable isotope fractionation factors. See also further data in Chapter 12 of this monograph.

### REFERENCES


Table IV and Fig. 2 give some equilibrium phase transition constants for isotopic water species. Some related properties of water molecules, such as the boiling point of isotopic water species, are given in Table V.

The separation coefficient $\alpha^*$, which has been defined in terms of the atomic concentration ratios, is a function of salinity as well as temperature. In other words, the ratio of activity coefficients, $\Gamma^*$, of the isotopic water species in saline
solutions may differ from the value of $\Gamma \sim 1$, as a result of the preferential binding of one or the other of the isotopic water molecules in the ionic hydration sphere. The salt effect has been measured by Feder and Taube (1952), Googin and Smith (1957), and others. The following formulae were given by Sofer and Gat (1972, 1975) for expressing the salt effect on the activity coefficient ratio, $\Gamma$, of the heavy-isotope species $H_2^{18}O$ and $HD^{18}O$ in mixed chloride solutions of sodium, potassium, calcium and magnesium at 25°C:

*for oxygen-18:*

$$\left( \frac{1}{\Gamma} - 1 \right) 10^3 = 1.11M_{\text{Mg}} + 0.47M_{\text{Ca}} - 0.16M_{\text{K}}$$

*for deuterium:*

$$\left( 1 - \frac{1}{\Gamma} \right) 10^3 = 6.1M_{\text{CaCl}_2} + 5.1M_{\text{MgCl}_2} + 2.4M_{\text{KCl}} + 0.4M_{\text{NaCl}}$$

where $M$ is the molality of the solution. Note the change in sign of the isotope effect for deuterium relative to that of $^{18}O$, in the case of alkaline earth ions.

To a good approximation, there is no salt effect on the $^{18}O$ fractionation factor in the case of $\text{NaCl}$ solutions and of sea-water (Craig and Gordon, 1965). The effect of anions on $\Gamma$ has been considered to be minor for the oxygen isotopes. However, Goetz and Heinzinger (1973) have reported an increase of
TABLE V. PROPERTIES OF ISOTOPIC WATER MOLECULES

<table>
<thead>
<tr>
<th>Property</th>
<th>$\text{H}_2\text{^{18}}\text{O}$</th>
<th>$\text{D}_2\text{O}$</th>
<th>HDO$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 20ºC (c poise)</td>
<td>1.0564$^a$</td>
<td>1.247$^a$</td>
<td>1.1248</td>
</tr>
<tr>
<td>Density (g/ml) (at 30ºC)$^{[3]}$</td>
<td>1.107845</td>
<td>1.10323$^{[3]}$</td>
<td>1.104945$^d$</td>
</tr>
<tr>
<td>Temperature of max. density$^{[3]}$ (ºC)</td>
<td>4.305</td>
<td>11.24</td>
<td></td>
</tr>
<tr>
<td>Molar volume (ml at 30ºC)</td>
<td>18.0724</td>
<td>18.1589</td>
<td>18.1290$^d$</td>
</tr>
<tr>
<td>Melting point$^{[3]}$</td>
<td>0.28</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>100.14$^d$</td>
<td>101.42$^d$</td>
<td>100.738$^i$</td>
</tr>
<tr>
<td>Ionic product (room temp.)</td>
<td></td>
<td>0.16 × 10$^{-14}$$^i$</td>
<td></td>
</tr>
<tr>
<td>Vapour pressure ratios</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 20ºC</td>
<td>1.0094$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 100ºC</td>
<td>1.0050$^a$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Compiled by F. Steckel.
$^b$ Deuterium at natural abundance.
$^c$ Oxygen at natural abundance.
$^d$ Calculated.

REFERENCES

45% in the correction factor for KCl to KI, with KBr solutions showing intermediate behaviour. The anion effect on the deuterium fractionation factor is important even in the case of sodium salts (Stewart and Friedman, 1975).

Unlike most other isotope effects which decrease with increasing temperature, it is claimed that the salt effect on the activity ratio of isotopic water species diminishes monotonically with increasing temperature only for solutions of MgCl₂ and LiCl; many other salt solutions show a complex behaviour due to the temperature-dependent formation of ion pairs (Truesdell, 1974).

2.4. KINETIC ISOTOPE EFFECTS

Rather large differences in reaction rates of isotopic molecules can occur when the breaking of covalent bonds or semi-covalent bonds is involved in the reaction. This so-called kinetic isotope effect can be quantitatively expressed in terms of the 'absolute reaction rate theory' of Glassstone et al. (1941) in which the speed of reaction is expressed as the dissociation rate of an activated semi-equilibrium complex through one of its vibrational modes. The rate constant (Cₜ) for the reaction A + B + . . . \rightarrow products, in which the transition state M* is formed according to the quasi-equilibrium A + B + . . . \rightarrow M* + N + . . ., is given by the absolute reaction rate theory (neglecting the tunnelling effect) by:

\[ Cₜ = \frac{\mathcal{J} kT}{h} K_+ \]

(h is Plank's constant, k the Boltzmann factor, T the absolute temperature; \(\mathcal{J}\) is the transmission coefficient or the fraction of transition states passing the energy barrier in the forward direction which will lead to completed reaction; \(K_+\) is the analogue of a thermodynamical equilibrium constant for the activation step.) It has been shown that the influence of isotopic substitution on the reaction rate will be exercised via its influence on \(K_+\) (Melander, 1960) or, in other words, through the difference in steady-state distribution of isotopes between reacting molecules and the activated reaction complex. The effect on the transmission coefficient \(\mathcal{J}\) is not too large (Hirschfelder and Wigner, 1939).

The kinetic effects are generally much larger than equilibrium isotope effects and diminish with increasing temperature. They are especially noteworthy in the case of hydrogen isotopes where, for example, there is a difference of one order of magnitude in the reaction rates of the hydrogen isotopes during the electrolytic decomposition of water on some electrodes (this effect is utilized in the commercial production of heavy water and the pre-enrichment of tritium for low-level counting). The kinetic effects depend on the mechanistic pathways of the reaction, and in particular on whether the bond connecting the isotope to
the molecule is severed in the rate-determining reaction step. So-called secondary kinetic isotope effects, i.e. the effects on the reaction rates of isotopic substituents which are not directly involved in the rate-determining reaction step, are smaller by orders of magnitude (Halevi, 1957) and can usually be neglected in our discussions.

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Chapter 3

ISOTOPIC FRACTIONATION

3.1. GENERAL

In an assembly of molecules containing N and N_i of each isotopic species, respectively, the isotopic abundance ratio R is defined as \( R = \frac{N_i}{N} \), where N_i represents the less abundant isotope. This is also the ratio of the mole fractions of these isotopic species: \( R = \frac{x_i}{x} \), where \( x = \frac{N}{N+N_i} \), \( x_i = \frac{N_i}{N+N_i} \). For the case of the natural oxygen and hydrogen compounds, \( N \gg N_i \). If, as a result of some process, molecules are removed from the assembly in such a manner that \( \frac{dN_i}{dN} \neq \frac{N_i}{N} \), then fractionation occurs between the isotopes and R changes as the process continues. \( \alpha = (\frac{dN_i}{dN})(\frac{N_i}{N}) \) is defined as the unit fractionation factor and the following equation holds:

\[
\frac{dR}{dN} = -\frac{1}{N} \left( \frac{dN_i}{dN} - \frac{N_i}{N} \right) = \frac{R}{N} (\alpha - 1)
\]  

(3.1)

or, in the more commonly written form:

\[
\frac{d\ln R}{d\ln N} = (\alpha - 1)
\]

(3.1a)

Equation (3.1) can be immediately integrated, provided \( \alpha \) does not change during the course of the process, to give

\[
R = R_0 \left( \frac{N}{N_0} \right)^{\alpha - 1}
\]

(3.2)

Since \( N \gg N_i \), N can be equated with the total amount of material in the phase, of which the fraction \( f = N/N_0 \) remains at the limit of integration; then

\[
R = R_0 f^{(\alpha - 1)}
\]

(3.2a)

This equation is termed the ‘Rayleigh equation’ as it was first derived by Lord Rayleigh for the case of fractional distillation of mixed liquids. Strictly

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4 In (x) is used to designate \( \log_a(x) \).

5 In \( \delta \)-nomenclature (to be discussed in Chapter 4) and using the approximate relationship of \( \lambda = \ln \left( \frac{R}{R_{std}} \right) = \ln (1 + \delta) \sim \delta \) and the definition of \( \varepsilon = (\alpha - 1) \), Eq. (3.2a) can be written as: \( \delta = \delta_0 + \varepsilon \ln f. \)
speaking, this term should be used only where $\alpha$ is an equilibrium fractionation factor. In other cases we will use the term ‘Rayleigh type’ equations.

Material balance considerations require that the isotope content of the total accumulated amount of the removed material approaches $R_0$ as $f \to 0$; it follows that, to avoid isotopic fractionation, any process should be carried out to completion (with 100% yield).

3.2. EQUILIBRIUM PROCESSES

When the isotopic species removed at every instant are in thermodynamic equilibrium with those remaining in the system we have the circumstances of the so-called ‘Rayleigh distillation’ and Eq. (3.1) applies. Under these conditions, the unit separation factor will be a thermodynamic equilibrium constant of the type described in Chapter 2, i.e. the vapour pressure ratio of the isotopic water molecules for the case of evaporation or condensation processes, or the equilibrium constant of an isotopic exchange reaction, as in the case of carbonate deposited from an aqueous solution.\(^6\)

The isotopic composition $R$ of the remaining material, as a function of $f$, when subject to ‘Rayleigh’ fractionation, is shown in Fig. 3. Obviously, the composition of the material which is removed at every instance is given by $\alpha^* R$ and describes a curve parallel to that of the remaining fraction. The integrated curve, giving the isotopic composition of the accumulated material thus removed, is also shown.

Other situations involving equilibrium isotope distribution can be envisaged. For example, material may be removed into a different phase which, however, remains (through some exchange mechanism) in equilibrium with the parent phase throughout. The progress of the isotopic composition of the remaining fraction of material is shown in Fig. 3 by the dashed curve. Compared with that of the Rayleigh plot, this distribution leads to markedly smaller changes in the isotopic composition. Incidentally, these two situations are the analogues of the so-called logarithmic and Nernst-Bertholet distributions of trace elements between mineral phases (Bonner and Kahn, 1951).

An in-between situation has been formulated by Epstein (private communication) as well as by Craig and Gordon (1965) to describe the isotopic separation accompanying the rain-out from a precipitating cloud system. The

---

\(^6\) Equilibrium separation factors have been marked by Craig and Gordon (1965) as $\alpha^*$ and $\alpha^* = 1/\alpha^*$, so that $\alpha^* > 1$, $\alpha^* < 1$. The choice of either $\alpha^*$ or its reciprocal value $\alpha^*$ is dictated only by convenience. Here we will use the value $\alpha^* = R_v/R_l$ when discussing atmospheric liquid–vapour equilibrium but, in accordance with general usage, the reciprocal value, $\alpha^*$, is used when discussing the evaporation process. Subscripts $l$, $v$ stand for the liquid and vapour phase respectively.
model is that of a two-phase system, with the two phases in isotopic equilibrium with one another; a part of one of the phases is removed without further fractionation, in this case by rain-out of the condensed phase. The basic equations governing this model are as follows:

\[ R_v = \frac{1}{\alpha^m} R_g \]  
\[ N = N_v + N_g \]  
\[ RN = R_v N_v + R_g N_g \]  
\[ L = \frac{N_g}{N_v} \]  
\[ d(NR) = R_g \, dN \]
where \( \nu \) and \( \xi \) refer to the vapour and liquid states, respectively. For constant liquid water content, \( L \), we have as an equivalent to Eq. (3.1a):

\[
\left( \frac{\partial \ln R_L}{\partial \ln \tau} \right)_L = \frac{\alpha^* - 1}{1 + \alpha^* L}
\]  

(3.4)

However, \( R_L \) can then change also without removal of material from the system, simply by internal transport between the two phases. In that case the change in \( R_L \), with \( N \) constant, is given by the following equations:

\[
\left( \frac{\partial R_L}{\partial L} \right)_L = \frac{\alpha^* dR_v}{(dN_v - LdN)/N_v} \quad (3.4a)
\]

\[
\left( \frac{\partial \ln R_L}{\partial L} \right)_L = \frac{\alpha^* - 1}{(1 + \alpha^* L)(1 + L)} \sim \frac{\alpha^* - 1}{(1 + L)^2} \quad (3.4b)
\]

The evolution of the isotopic composition for this model for the case of rain-out from the cloud is given in Chapter 6.

Since \( \alpha^* \) is a function of temperature, the unit separation factor is normally not a constant (for example in an ascending cloud in the atmosphere where temperatures decrease), even though thermodynamic equilibrium may prevail at any given time. The differential equations (3.1a) or (3.4) may still be integrated, provided the change of \( \alpha^* \) in the course of the process can be expressed. As an example, Dansgaard (1964) calculated the ‘Rayleigh distillation’ composition of precipitation formed in a cloud which is cooled adiabatically during its ascent. Details are given in Chapter 6.

In a system where more than one pair of isotopes is being fractionated and which is governed by Rayleigh equations, the relationship between the enrichment or depletion of the different isotopic species is fixed and depends only on the thermodynamic and ambient parameters. A case in point are the changes in the \(^{18}\text{O}\) and deuterium abundance ratios during the phase transition of water; according to Eq. (3.1a):

\[
\frac{d \ln R_D}{d \ln R_{18}} = \frac{d \lambda_D}{d \lambda_{18}} = \frac{\alpha_D - 1}{\alpha_{18} - 1}
\]  

(3.5)

where the subscripts D and 18 refer to deuterium and oxygen-18, respectively. This ratio is temperature-sensitive because \( \alpha_D \) and \( \alpha_{18} \) have different temperature coefficients. For example, within the temperature limits of relevance to the process of rain-out, the value of \((\alpha_D^* - 1)/(\alpha_{18}^* - 1)\) for the liquid–vapour phase transition of water varies from 8.22 at 30°C to 9.59 at 0°C. The equivalent ratio in Eq. (3.4):
\[
\frac{d\lambda_D}{d\lambda_{18}} = \frac{\alpha_D^* - 1}{\alpha_{18}^* - 1} \cdot \frac{1 + \alpha_D^* L}{1 + \alpha_{18}^* L}
\]

(3.5a)
yields values of 7.96 to 8.13 over the same temperature range (when \( L = 1 \)). It can be seen that this ratio (which incidentally measures the slope of the isotope curve in \( \delta D - \delta^{18}O \) space) also depends on the model and not just on the thermodynamic parameters.

The condensation process in the atmosphere is seemingly described by such equilibrium models, but this is not generally true of the reverse process, namely evaporation under natural conditions, as will be discussed below. However, when steam is boiled off a geothermal system, apparently isotopic equilibrium between the vapour and liquid phases is rapidly established (Giggenbach, 1971). At the high temperatures of these systems the slopes, in \( \delta D - \delta^{18}O \) space, are much smaller than at the lower temperatures and approach zero at a temperature of 220°C, which is the cross-over point for \( \alpha_D(T) \).

Other equilibrium processes are known in the water cycle. During the process of hydration of anhydrite to gypsum, isotopic equilibrium is apparently established between the crystal water and the residual brine; it has been found that a slope of \( d\delta D/d\delta^{18}O \) of \( \sim -5 \) describes the isotopic composition of the water in successive gypsum layers (Matsubaya and Sakai, 1973; Sofer, 1978). The negative slope \( (-5) \) reflects the fact that the deuterated species is discriminated relative to \( H_2^{18}O \) in the crystal water of gypsum, whereas \( H_2^{18}O \) is favoured relative to \( H_2^{16}O \) (Fontes and Gonfiantini, 1967).

### 3.3. NON-EQUILIBRIUM FRACTIONATION:
### EVAPORATION OF SURFACE WATERS

The flux of matter leaving a phase is not necessarily in thermodynamic equilibrium with the residual material. Examples are the diffusion-controlled evaporation into air as well as many biologically controlled processes which result in non-equilibrium fractionation between carbon or sulphur isotopes (so-called 'vital effects'). These usually increase the separation beyond that of the equilibrium processes. It may sound paradoxical that even non-fractionating processes, such as evaporation of water by means of droplet spray or sublimation of ice, result in non-equilibrium distribution of the isotopes between the phases concerned, since in this case

\[
\frac{dN_i/dN}{N_i/N} = 1 \neq \alpha^*
\]

As long as the value of \( \alpha \) remains fixed throughout a process, though its numerical value may differ from that of the appropriate equilibrium fractionation
factor, Eq. (3.1a) will describe the evolution of the isotopic composition. The difference between the actual and the thermodynamic separation factors, the excess separation de, is defined as: \( de = \alpha - \alpha^* \). A positive de value implies that the isotopic separation is larger than in the appropriate equilibrium process.\(^7\)

In the water cycle the most prominent example for a non-equilibrium process is the isotopic fractionation which accompanies the exposure of water surfaces to the atmosphere. In this case, since \( (dN_j/dN) < (N_j/N) \), it is convenient to use the unit separation factor in the reciprocal form, i.e. \( \alpha^* = 1/\alpha^* < 1 \).

In laboratory experiments by Dansgaard (1961), Craig et al. (1963) and Ehnhall and Knott (1965), it was found that, as water is evaporated into dry air, the isotopic enrichment is larger than that expected from the vapour pressure difference of the species concerned. Moreover, the ratio of deuterium/oxygen enrichments is relatively lower than in the distillation column which operates under equilibrium conditions. An excess separation factor operates, which is relatively larger for \(^{18}\)O than for deuterium. Moreover, with evaporation taking place into the atmosphere, which contains water vapour, Eq. (3.1a) does not apply anymore in a simple way and the heavy-isotope enrichment approaches a limiting value in the latter stages of desiccation (Craig et al., 1963). This value depends, among other factors, on the isotopic composition of the atmospheric moisture. The nature of the process involved is revealed at high ambient humidities (i.e. when the relative humidity approaches 100%) where isotopic equilibrium is established between the liquid and vapour phases by means of a mechanism of back and forth transport of the isotopic water species, i.e. a so-called exchange process. In other words, in the case of evaporation into non-saturated air an isotopic exchange reaction between the atmospheric moisture and the liquid is superimposed on the fractionation resulting from the evaporation process (and having a non-equilibrium component).

The evaporation process was modelled by Craig and Gordon (1965) as a consecutive series of steps in each of which the water flux is expressed as the quotient of a concentration difference and flow resistance. This model follows the classical approach of Rideal-Langmuir (Sverdrup, 1952). The model considers water evaporating from a virtually saturated sub-layer at the liquid surface (saturated at the surface temperature), through a region where molecular diffusion dominates the transport process, into a fully turbulent atmosphere where no further isotopic separations are expected.

The mathematical formulation of this model leads to the following expressions for the flux of the common water molecules, H\(_2\)\(^{16}\)O, and of the heavy-isotope species (be it HDO or H\(_2\)\(^{18}\)O), respectively:

\( e \), which is the deviation of the separation factor from unity, is by convention always chosen to be a positive number. So, when \( \alpha^* > 1 \), \( e^* = \alpha^* - 1 \); conversely, for the reciprocal separation factor, \( \alpha^* = 1/\alpha^* < 1 \); \( e^* = 1 - \alpha^* \). Note that \( e^* = e/\alpha^* \).
ISOTOPIC FRACTIONATION

\[ E = -\frac{dN}{dt} = (1 - h)/\rho \]  \hspace{1cm} (3.6)

\[ E_I = -\frac{dN_I}{dt} = (\alpha \cdot R_g - h R_q)/\rho_I \]  \hspace{1cm} (3.6a)

with \( \rho \) and \( \rho_I \) being the resistances of transport through the successive air layers. Subscript \( i \) stands for atmospheric moisture, subscript \( I \) for liquid; \( h \) is the relative air humidity with respect to saturated vapour at surface temperature.

The change in isotopic composition of the liquid is then given as:

\[ \frac{d \ln R_g}{d \ln N} = \frac{E_I/E}{R_g} - 1 \]  \hspace{1cm} (3.7)

with \( E \) and \( E_I \) given by Eqs (3.6) and (3.6a). In this case, \( \alpha \equiv (E_I/E)/R_g \) is a quantity which varies as evaporation proceeds and whose magnitude depends, among other factors, on ambient parameters (\( R_g, h \)). Equation (3.7) can be rearranged, using the relationship \( \Delta e \equiv (1 - h) (\rho_I/\rho - 1) \) introduced by Craig and Gordon (1965):

\[ \frac{d \ln R_g}{d \ln N} = \frac{h (R_g - R_q)/R_g - e^* - \Delta e}{(1 - h) + \Delta e} \]  \hspace{1cm} (3.8)

It can be seen that \( \Delta e \) is, in a sense, equivalent to an excess separation factor, \( de \), as defined at the beginning of this section.

The expected magnitude of the kinetic separation factor can be computed for different transport models and compared with values fitted to the experimental data. This procedure is particularly suitable for assessing the importance of molecular diffusion in the overall transport process. Preliminary experiments, in which the value of \( \Delta e_{18}/(1 - h) \) was estimated by means of Eq. (3.8) and shown to be proportional to \([ (D/D_0)^{1/2} - 1 ] \) (Craig and Gordon, 1965; Gat and Craig, 1966), were interpreted as consistent with a 'transient eddy' model of a randomly renewed surface layer (Brutsaert, 1965). A more elegant procedure was adopted by Merlivat and Coantig (1975) who measured the isotopic composition in the vapour profile over the evaporating surface and showed that there is indeed a region just above the air/water interface where mass transfer is dominated by molecular diffusion.

The saturated interface sublayer is obviously the site of the 'equilibrium isotopic fractionation'; the region through which the transport is 'diffusion controlled' adds the additional kinetic separation which affects the separation of \(^{18}O\) relatively more than that of the deuterated species.

Strictly speaking, Eqs (3.6) and (3.6a) relate to conditions (vapour pressure and isotopic concentration) at the liquid surface layer. These conditions correspond to the properties of the bulk liquid only when the liquid is extremely well mixed.
This mixing is not always realized in nature, especially not in those cases where a stable (vertical) density stratification exists. In this case there can be a build-up (enrichment) of the heavy isotopes in the surface layer as the evaporation proceeds, resulting finally in reduction of the overall enrichment of the process. From the viewpoint of the model this is equivalent to the introduction of a (negative) liquid resistance, $\rho_L$.

Craig and Gordon (1965) have formulated the flux of the isotopic species through such a liquid boundary layer of constant depth at steady state as follows:

$$E_i = ER_q - \frac{R_q - R_0}{\rho_q} \quad (3.6b)$$

This equation relates the isotopic composition at the surface ($R_q$) to that of the bulk liquid ($R_0$). Equation (3.6a), in which, strictly speaking, the first term should have been written as $\alpha^*R_q$, is then rewritten in terms of $R_q$ as follows:

$$E_i = [\alpha^*R_q(1 + E\rho_q) - h R_0]/(\rho_i + \alpha^*R_q) \quad (3.6c)$$

and the formula equivalent to Eq. (3.8) becomes:

$$\frac{d\ln R_q}{d\ln N} = \frac{h (R_q - R_0)/R_q - e^* - \Delta e}{(1 - h) + \Delta e + \alpha^*E\rho_q} \quad (3.9)$$

Depending on the transport mechanism, $\rho_q$ may or may not be a function of the isotopic species. Laboratory experiments by Siegenthaler (1975) have shown $\rho_q/\rho$ to vary between 0.0 and 0.2 when the conditions in the liquid surface layer range between those of good mixing and extreme stratification.

Neglect of the liquid resistance in evaluating the value of $\Delta e$, from the measured change of the liquid’s isotopic composition, results in an underestimation of this term. It can be shown by comparing Eqs (3.7) and (3.9) (Gat et al., 1975) that

$$\Delta e_{\text{app}} - \Delta e \sim \frac{\rho_q}{\rho} \left[ h \frac{(R_q - R_0)}{R_q} - e^* - \Delta e \right] \quad (3.10)$$

where $\Delta e_{\text{app}}$ is the apparent value of $\Delta e$ calculated by using Eq. (3.8) instead of Eq. (3.9). Obviously, the correction will usually be larger for deuterium than for $^1$H because $e^*_D \gg e^*_H$. Indeed, apparently negative $\Delta e_D$-values were computed in some cases of extreme surface layer stability (Gat, 1970) by use of Eq. (3.8), which show the importance of the stratification in the liquid surface layer.

The non-equilibrium evaporation process is characterized by a slope of less than $S = 8$ on the $\delta^{18}$O-$\delta^D$ diagram. (See Chapter 4 for a definition of the
FIG. 4. Isotopic composition of evaporating water, with different relative atmospheric humidities. The following values have been assumed: initial isotopic composition of water: $\delta^{18}O = -6_{\text{H2O}}, \delta D = -38_{\text{H2O}}$; isotopic composition of the atmospheric moisture: $\delta^{18}O = -12_{\text{H2O}}, \delta D = -86_{\text{H2O}}$ (Gonfiantini, 1980).
FIG. 5. Salinity effect on the isotopic composition of evaporating waters. Pure water evaporation lines at different ambient humidities are shown for comparison.

--- Change in isotopic composition of an evaporating NaCl solution, whose isotopic composition stabilizes at the saturation level where NaCl precipitates, so that water activity does not change further.

--- Evolution of isotopic composition of a brine (such as MgCl₂ solution), where evaporation and salinity build-up continue until its saturation vapour pressure matches the ambient humidity. However, isotopic exchange continues until equilibrium with the ambient vapour (δᵥ) is established. The δ-scale is arbitrary; δᵥ₀ signifies the isotopic composition of the sample before exposure to the atmosphere, δᵥ represents the ambient atmospheric vapour phase.

δ-scale.) The slope S of the ‘evaporation line’ is given to a good approximation by the following expression, which is based on Eq. (3.8) (Gat, 1971):

\[
S = \frac{\Delta \delta_v \cdot D}{\Delta \delta_v \cdot 18} = \frac{h(R_\delta/R_\delta - 1)D + \epsilon_D + \Delta \epsilon_D}{h(R_\delta/R_\delta - 1) + \epsilon_{18} + \Delta \epsilon_{18}}
\]

(3.11)

The parameters thus determining the slope of the evaporation line are: h, \(\epsilon\), \(\Delta \epsilon\), and the ratio of \(R_\delta/R_\delta\). Of these, \(\epsilon\) and h are temperature dependent for a given atmospheric moisture content. As we have seen, the parameter \(\Delta \epsilon\) depends on details of the evaporation process, especially on conditions at the liquid/air interface, such as its aerodynamic structure and thermal gradients (stability). A wide spread in values of S is thus possible; in most actual cases, however, the range of ambient conditions is not arbitrarily large, and the
**FIG. 5.** Calculated evaporation curves for NaCl and MgCl₂ solutions as a function of the residual water fraction at different humidities. Initial conditions and parameters for these calculations: salt concentration = 0.5 molal; $\delta^18_0 = 0.0\%$ for both $D$ and $^{18}O$; $\rho/\rho_{H_2O} = \rho/\rho_D = 0.982$; $(\rho_{L,L}/\rho)_D = (\rho_{L,L}/\rho)_{H_2O} = 0.19$; $\alpha_{T_0} = 0.9908; \alpha_{P} = 0.9269; the$ $dots$ $on$ $the$ $curves$ $indicate$ $a$ $decrement$ $of$ $0.05$ $in$ $the$ $fraction$ $of$ $residual$ $water$ (Sofer and Gat, 1975).

The observed slopes of the 'evaporation lines' lie within the range of $S = 3.5$ to about $S = 6$ (Fig. 4).

Equations (3.4) – (3.9) refer to evaporation from fresh-water surfaces, when the thermodynamic activity of water can be defined as unity at any given temperature. In the presence of high salt concentrations the activity of the water, a (defined as the ratio of saturation vapour pressure over the solution to that over pure water), is smaller than 1. The following equations are equivalent to Eq. (3.6) (Gonfiantini, 1965):
CHAPTER 3

Total evaporation rate:

\[ E = (a - h)/\rho = a(1 - h')/\rho \]  \hspace{1cm} (3.12)

Evaporation rate of the heavy isotope water molecules:

\[ E_a = (a_0^b R_S - h R_A)/\rho_i = a_0^b R_S - h' R_A)/\rho_i = a(\Gamma a^* R_S - h' R_A)/\rho_i \]  \hspace{1cm} (3.12a)

where \( h \) and \( h' \) are the relative air humidities based on saturated vapour over the pure water and over the saline solution, respectively, at the temperature of the surface layer;

\[ a_0^b = \frac{R_{\text{vapour at interface}}}{R_{\text{water at interface at equilibrium}}}, \text{ with the subscript } b \text{ standing for brine; } a^* \text{ is the equivalent value for pure water, and } \Gamma \text{ the ratio of the activity coefficients of the heavy and light isotopic species.} \]

Since salt concentration increases (except at saturation) as the evaporation proceeds, and since as a result of this the activity also changes, we find that the heavy-isotope concentration of the residue from an evaporating brine does not immediately reach a steady state. The process can be construed, qualitatively speaking, as an evaporation under conditions of increasing humidity; indeed, the effective humidity, \( h' = h/a \), increases as the salinity builds up and, as a result, the system tends towards a continuously changing steady-state concentration, corresponding to ever higher relative humidities. In the course of evaporation, the heavy-isotope content increases at first, but then this trend is reversed. Finally, a steady state can be reached at the saturation point of the salt ('a' then being a constant), or evaporation stops altogether at the point where the ambient humidity approaches the saturation vapour pressure of the brine; isotopic exchange will, however, continue and tend to bring the brine and atmospheric humidity into isotopic equilibrium, as illustrated in Fig.5.

In the presence of salts, such as magnesium and calcium salts, \( \Gamma \neq 1 \) and is a function of the salt concentration (Sofer and Gat, 1972). The process of isotopic fractionation in the presence of these salts has been treated by Sofer and Gat (1975) who found that an open loop is described on the \( \delta^{18}O - \delta^D \) plot by the isotopic content of the residual brine (Fig.6).

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Chapter 4

THE $\delta$-NOTATION AND THE MASS-SPECTROMETRIC MEASUREMENT TECHNIQUES

4.1. THE $\delta$-NOTATION FOR EXPRESSING STABLE ISOTOPE RATIO VARIATIONS

4.1.1. Definition of $\delta$

For reasons dictated by the measurement technique, as discussed later in this chapter, the absolute abundance ratio of isotopes is not usually measured in natural waters and in other natural compounds. Only the relative difference in the ratio of the heavy isotope to the more abundant light isotope of the sample with respect to a reference is determined. This difference is designated by the Greek letter $\delta$ and is defined as follows:

$$
\delta = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}}
$$

where the $R$'s are, in the case of water, the $^{18}$O/$^{16}$O or the D/H isotope concentration ratios. Obviously, positive values show the samples to be enriched in the heavy-isotope species with respect to the reference, negative values correspond to samples depleted in the heavy-isotope species. As the differences between samples and reference are usually quite small, it is convenient to express the $\delta$-values in per mille differences, i.e.

$$
\delta(\text{‰}) = \delta \times 1000
$$

In this chapter, all $\delta$-values are in per mille, even if the sign ‰ is omitted. Attention is drawn to the fact that in early papers on this subject, the $\delta D$-values were often reported in per cent instead of per mille. In the Russian geochemical literature, both $\delta^{18}$O and $\delta D$ are frequently expressed in per cent.

High accuracies, for example 0.1‰ for $\delta^{18}$O and 1.0‰ for $\delta D$, can be easily achieved in $\delta$-determinations, whereas they can be obtained only exceptionally in absolute isotope ratio measurements. The $\delta$-scale has been introduced because of this and because of the fact that a knowledge of the relative variations in heavy-isotope content among samples is sufficient for geochemical and hydrological investigations.

A convenient property of the $\delta$-values is that they are additive over a large range of values. In fact, if two water samples have $\delta_1$ and $\delta_2$-values in per mille
with respect to the same reference, the expression giving the δ-value of the first sample with respect to the second is:

\[ \delta_{1-2} = \delta_1 - \delta_2 \left( \frac{1000 + \delta_1}{1000 + \delta_2} \right) \]

which reduces simply to:

\[ \delta_{1-2} = \delta_1 - \delta_2 \]

when \( \delta_1 \) and \( \delta_2 \) are small in comparison with 1000 or, in other words, when the correction given by the term in brackets is small in comparison with the analytical error. This condition is much more often satisfied for \(^{18}\)O than for deuterium, since in the latter case the δ-values are about one order of magnitude larger.

Another convenient property of δ-notation is that the δ-value of a water sample resulting from the mixing of different waters is simply given by:

\[ \delta = \sum_{i=1}^{n} x_i \delta_i \]

\( x_i \) being the fraction of water having isotopic composition \( \delta_i \). A consequence of this is that the locus of mixtures of two waters on a (δ\(^{18}\)O, δD) plot is the straight line connecting the points corresponding to the mixing end-members.

The conversion of a δ-value (‰) of a sample S relative to a reference A into another δ-value relative to a reference B is given by:

\[ \delta_{S-B} = \delta_{S-A} + \delta_{A-B} + 10^{-3} \times \delta_{S-A} \times \delta_{A-B} \] (4.1)

where \( \delta_{A-B} \) is the value of reference A with respect to reference B.

4.1.2. The reference standard: SMOW and V-SMOW\(^8\)

One of the most serious problems in stable-isotope hydrology and geochemistry is the comparison of results obtained by different laboratories.

\(^8\) Since the establishment of the mass-spectrometric technique for measuring small stable-isotope variations, the samples with respect to which the values were measured on the mass spectrometer were most frequently called 'standards'. We believe, however, that the name 'reference' is in this case more appropriate, and we shall reserve the term 'reference standard' or even only 'standard' to those samples which are internationally accepted as common reference for reporting isotopic results.
These results are now usually reported in $\delta(\%e)$ with respect to a common international reference standard. Thus, a correct calibration of the reference samples used by different laboratories in routine measurements with respect to the international standard is necessary for intercomparison of results.

Until recently, the standard almost universally adopted as reference for oxygen and hydrogen stable-isotope variations in natural waters was the so-called SMOW (Standard Mean Ocean Water). It corresponds to a hypothetical water having both oxygen and hydrogen isotopic ratios equal to the mean isotopic ratios of ocean water, which have been evaluated by Craig (1961) from measurements made by himself, by Epstein and Mayeda (1953), and by Horibe and Kobayakawa (1960).

The choice of the 'mean' ocean water reference standard seems obvious for natural water samples, since the ocean contains 98% of the water present on the earth's surface and has a fairly uniform stable-isotope composition, thus constituting a logical departure point for describing processes of the water cycle in nature.

However, a serious disadvantage is that SMOW does not actually exist as a real water sample and therefore cannot be used to directly calibrate laboratory measurements. In fact, the isotopic ratios of SMOW were defined by Craig (1961) with respect to an existing water standard, the NBS-1, as follows:

$$(^{18}\text{O} / ^{16}\text{O})_{\text{SMOW}} = 1.008 (^{18}\text{O} / ^{16}\text{O})_{\text{NBS}-1}$$

$$(\text{D}/\text{H})_{\text{SMOW}} = 1.050 (\text{D}/\text{H})_{\text{NBS}-1}$$

Craig evaluated the isotopic ratios of SMOW as: $^{18}\text{O} / ^{16}\text{O} = (1993.4 \pm 2.5) \times 10^{-6}$ and $\text{D}/\text{H} = (158 \pm 2) \times 10^{-6}$.

The preparation of a large water sample having an isotopic composition as close as possible to that of the defined SMOW was entrusted in 1966 by the International Atomic Energy Agency (IAEA) to Professor H. Craig of the University of California. This water sample was obtained by mixing distilled ocean water (collected from the Pacific Ocean, lat. 0, long. 180°, in July 1967) with small amounts of other waters to adjust the isotopic ratios to the required values. Such a water sample, called VIENNA-SMOW (abbreviated as V-SMOW), is now available at the IAEA in Vienna, for purposes of intercalibration. According to Craig's measurements, the V-SMOW has the same $^{18}\text{O}$ content as the defined SMOW, but its D-content is 0.2% lower. (The errors quoted by Craig are 0.02% for $\delta^{18}\text{O}$ and 0.2% for $\delta\text{D}$.)

The absolute D/H ratio of V-SMOW was carefully determined by Hagemann et al. (1970) by mass spectrometry and found to be equal to $(155.76 \pm 0.05) \times 10^{-6}$. The same measurement was undertaken later by De Wit et al. (1980) who found a value of $(155.95 \pm 0.08) \times 10^{-6}$, and by Tse et al. (1980) who found a value
of $(155.6 \pm 0.12) \times 10^{-6}$ by nuclear magnetic resonance spectrometry. The $^{18}O/^{16}O$ ratio was determined by Baertschi (1976) who found a value of $(2055.20 \pm 0.45) \times 10^{-6}$, which is definitely different from that evaluated by Craig. No determinations have yet been made of the $^{17}O/^{16}O$ ratio. The tritium content of V-SMOW, determined at the IAEA Isotope Hydrology Laboratory by gas counting without enrichment, was found on 16 September 1976 to be $18.5 \pm 3.6$ TU (1 TU = one Tritium Unit corresponds to 1 atom of tritium per $10^{13}$ atoms of hydrogen). The maximum absolute density of V-SMOW is 999.975 kg/m$^2$ according to Girard and Menache (1972).

In this monograph it will be assumed that the defined SMOW and V-SMOW are isotopically identical for practical purposes, as was also recognized at a consultants' meeting organized by the IAEA (Gonfiantini, 1978). Therefore, no distinction will be made between data expressed versus either of the above reference standards; in addition, the abbreviation SMOW will be in general preferred to V-SMOW, unless there are specific reasons to use the latter. Unless otherwise stated, the $\delta$-values will generally be expressed with respect to SMOW, even if this notation is omitted.

4.1.3. Other water samples for intercalibration

Other water samples distributed by the IAEA (and by the United States National Bureau of Standards) for intercalibration purposes of stable-isotope measurements in natural waters are SLAP, NBS-1, NBS-1A and GISP.

SLAP — Standard Light Antarctic Precipitation — has been obtained by melting an amount of ice and firm collected in 1967 at Plateau Station, Antarctica. Its $^{18}O$ and D-contents are very low, almost at the lowest extreme of the range of variations of natural waters. The absolute D/H ratio of SLAP is $(89.02 \pm 0.05) \times 10^{-6}$ according to Hagemann et al. (1970), $(89.12 \pm 0.07) \times 10^{-6}$ according to De Wit et al. (1980), and $(88.88 \pm 0.18) \times 10^{-6}$ according to Tse et al. (1980). The tritium content was $374 \pm 9$ TU on 16 September 1976, as measured at IAEA.

NBS-1 and NBS-1A, formerly distributed by the United States National Bureau of Standards, have heavy-isotope contents intermediate between those of V-SMOW and SLAP. NBS-1, originating from distilled Potomac river water, is important because upon it were based the isotopic ratios of the defined SMOW. NBS-1A originates from snow from the Yellowstone Park (Mohler, 1960). The distribution of these samples has been discontinued since 1976, V-SMOW and SLAP being sufficient for intercalibration purposes.

GISP — Greenland Ice Sheet Precipitation — is a water sample with an $^{18}O$ and deuterium content intermediate between that of V-SMOW and SLAP. The $\delta$-values of GISP are now (1979) being determined independently by several laboratories (see preliminary results in Table VI).
<table>
<thead>
<tr>
<th>Name and origin</th>
<th>Isotopic composition versus SMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. V-SMOW, Vienna Standard Mean Ocean Water, prepared by H. Craig</td>
<td>$\delta^18O = 0$ by definition</td>
</tr>
<tr>
<td>2. SLAP, Standard Light Antarctic Precipitation, from melting of Antarctic ice</td>
<td>$\delta^18D = -428$ by convention (R. Gonfiantini, 1978)</td>
</tr>
<tr>
<td>and firm (E. Picciotto)</td>
<td></td>
</tr>
<tr>
<td>3. GISP, Greenland Ice Sheet Precipitation (W. Dansgaard)</td>
<td>$\delta^18O = -24.85$ (average of 11 labs)</td>
</tr>
<tr>
<td>4. NBS-1, distilled Potomac River Water (F.L. Mohler)</td>
<td>$\delta^18O = 0$ (H. Craig, 1961)</td>
</tr>
<tr>
<td>5. NBS-1A, snow from Yellowstone Park (F.L. Mohler)</td>
<td>$\delta^18O = -24.33$ (H. Craig, 1961)</td>
</tr>
<tr>
<td>6. NBS-30, biotite and hornblende separated from tonalite of the Southern</td>
<td>$\delta^18D = -47.60$</td>
</tr>
<tr>
<td>California batholith (I. Friedman, J.R. O’Neil, G. Cebula, L. Silver)</td>
<td>$\delta^18O = -7.94$</td>
</tr>
<tr>
<td>7. NBS-19, calcium carbonate from marble of unidentified origin, also called</td>
<td>$\delta^18O = -2.20$ versus PDB</td>
</tr>
<tr>
<td>TS (I. Friedman, J.R. O’Neil, G. Cebula)</td>
<td>$\delta^{13}C = +2.00$ (Friedman et al., 1981)</td>
</tr>
<tr>
<td>8. NBS-18, calcium carbonate from Kaisersuhl carbonatite (H. Friedrichsen, I.</td>
<td>$\delta^18O$ to be determined</td>
</tr>
<tr>
<td>Friedman)</td>
<td></td>
</tr>
<tr>
<td>9. OGS, barium sulphate precipitated from sea-water (Y. Horibe)</td>
<td>$\delta^18O$ to be determined</td>
</tr>
</tbody>
</table>

\* Provisional values.
### TABLE VII. STATISTICAL DISTRIBUTION OF ISOTOPIC SPECIES OF CO₂ DERIVED FROM PDB STANDARD (CaCO₃)\(^a\)

<table>
<thead>
<tr>
<th>Isotopic species</th>
<th>Molecular weight</th>
<th>Relative abundance(%) with respect to all isotopic species</th>
<th>all isotopic species with the same mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{C}^{16}\text{O}_2)</td>
<td>44</td>
<td>98.40</td>
<td>100</td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}_2)</td>
<td>45</td>
<td>1.106</td>
<td>93.67</td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}^{17}\text{O})</td>
<td>45</td>
<td>7.48 × 10(^{-2})</td>
<td>6.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.181</td>
<td></td>
</tr>
<tr>
<td>(^{12}\text{C}^{16}\text{O}^{18}\text{O})</td>
<td>46</td>
<td>4.092 × 10(^{-3})</td>
<td>99.79</td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}^{17}\text{O})</td>
<td>46</td>
<td>8.4 × 10(^{-4})</td>
<td>0.205</td>
</tr>
<tr>
<td>(^{13}\text{C}^{17}\text{O}_2)</td>
<td>46</td>
<td>1.4 × 10(^{-5})</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.410</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}^{18}\text{O})</td>
<td>47</td>
<td>4.6 × 10(^{-3})</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{17}\text{O}^{18}\text{O})</td>
<td>47</td>
<td>1.6 × 10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{17}\text{O}_2)</td>
<td>47</td>
<td>1.6 × 10(^{-7})</td>
<td></td>
</tr>
<tr>
<td>(^{12}\text{C}^{18}\text{O}_2)</td>
<td>48</td>
<td>4.3 × 10(^{-7})</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{17}\text{O}^{18}\text{O})</td>
<td>48</td>
<td>1.7 × 10(^{-6})</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{18}\text{O}_2)</td>
<td>49</td>
<td>4.8 × 10(^{-6})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2 × 10(^{-7})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Values calculated by using the isotopic ratios given by Craig (1957).

### 4.1.5. References and notations other than δ

In the early literature in isotopic geochemistry the δ-values are expressed sometimes versus the particular reference used in the measurements. The conversion of such data to the SMOW scale is often difficult, because it implies an evaluation of the δ-value of the reference used with respect to SMOW. This operation is possible only if at least one of the samples measured has an isotopic composition known versus SMOW. For example, in the case of the data reported by Friedman (1953) with respect to the reference 'Lake Michigan distilled water', one might assume the ocean samples collected at depths between 500 and 2000 m to be isotopically equal to SMOW. The mean δD-value of these
samples would then be zero on the SMOW scale, and all other values would be shifted accordingly.

In the past, some authors have reported results of isotopic composition of natural waters in terms of the absolute heavy-isotope content. Of these authors, Dansgaard (for oxygen isotopes) and the Saclay group in France (for hydrogen isotopes) may be mentioned.

Until 1961, Dansgaard (University of Copenhagen) reported his data as differences in $^{18}$O-content — expressed in ppm, i.e. in $^{18}$O atoms per million of oxygen atoms — of the CO$_2$ equilibrated with the water sample with respect to his working reference (tank CO$_2$, so-called DS — Danish Standard), divided by a factor 1.04, which accounts for the fractionation between water and CO$_2$. This difference is indicated by $\Delta a$, and its conversion to $\delta^{18}$O(\%) versus SMOW is given by Dansgaard (1961) as follows:

$$\delta^{18}\text{O}_{\text{SMOW}} = 0.482 \Delta a_{\text{DS}} - 18.1$$

Until 1963 the Saclay group has reported deuterium data in terms of D/H absolute ratios. As at that time they assigned the value of $161.7 \times 10^{-6}$ to the D/H ratio of SMOW (Roth, 1963), the conversion of their data to $\delta D(\%)$ versus SMOW is given by:

$$\delta D = \frac{(D/H)_{\text{sample}} - 161.7 \times 10^{-6}}{161.7 \times 10^{-6}} \times 1000$$

4.2. THE NIER MASS SPECTROMETER

After the second world war, decisive improvements and refinements in mass-spectrometry techniques (Thode et al., 1945; Nier, 1947; Nier et al., 1947; McKinney et al., 1950; Wanless and Thode, 1953; and others) enabled precise measurements of isotopic ratios in natural compounds; as a consequence, isotope geochemistry received a great impulse. The Nier mass spectrometer, the development of which (Nier, 1940 and 1947) has been decisive for the stable-isotope geochemistry of light elements such as hydrogen, oxygen, carbon, nitrogen and sulphur, will be briefly described. All modern mass spectrometers used in this field of research are derived to a large extent from the Nier mass spectrometer.

Essentially, a mass spectrometer consists of a tube in which high vacuum is maintained, with an ion source placed at one end of the tube and ion collectors at the other end. The middle part of the tube is curved and immersed in a magnetic field (Fig.7) normal to the curvature plane.
The vacuum in the mass spectrometer should be at least $10^{-4}$ torr, but usually it is better by one or two orders of magnitude. At $10^{-6}$ torr, the mean free path of the gas molecules is about 150 m, much more than the path that molecules and ions cover in the mass spectrometer. Therefore, the probability of collisions between molecules and ions is very low. In the ion source, where the analysing gas is admitted to the mass spectrometer, the gas pressure is much higher, of the order of $10^{-3} - 10^{-4}$ torr.

A good vacuum also reduces the background contribution to the ionic beams by reducing the amount of residual gases present in the mass spectrometer.

The gas pressure in the mass spectrometer is measured by means of ionization gauges. The vacuum is normally obtained with rotary pumps and oil or mercury diffusion pumps, equipped with a cold trap (liquid nitrogen or dry ice). Recently, new low-vapour-pressure oil diffusion pumps have been produced, by means of which a vacuum of $10^{-8} - 10^{-9}$ torr can be reached without a cold trap. Also, ion pumps may be used instead of diffusion pumps. Baking the whole analytical tube from time to time facilitates the attainment and maintenance of a good vacuum.
4.2.1. Ion source

The gas in which the isotopic ratio should be determined is admitted to the ion source of the mass spectrometer where it is partially transformed into positive ions by impact with electrons emitted by a tungsten or rhenium filament (Fig. 8). The electron beam, as a whole, is normal to the ion trajectory, but single electrons follow a spiral path, due to a weak magnetic field applied externally, in order to increase the probability of impact with the gas molecules. The electrons have an energy of the order of 100 eV, sufficient for ionizing the gas, and their flow across the ion source — of a few hundreds of microamperes — is kept constant by appropriate electronic circuits.

The ionization chamber in the ion source is kept at a positive high voltage, in most cases in the range of 1000—3000 V, depending on the characteristics of the mass spectrometer and on the masses of ions that should be detected. The positive ions are extracted from the ionization chamber by the drawing-out plate (having a lower voltage) and are then accelerated through the last collimating slit, which is grounded. The geometry of the ion beam is defined by the narrow collimating slits (which define the cross-sectional shape of the ion beam) and by the beam-centring plates which correct any misalignment of the ion beam.

Disregarding the small kinetic energy that the ions already had before being accelerated across the electric field, the positive ions will have acquired, at the exit from the ion source, a kinetic energy equal to:

\[ \frac{1}{2} mv^2 = neV \]  

(4.6)

where \( m \) is the mass of ions, \( v \) is their velocity, \( V \) is the accelerating voltage (i.e. the voltage of the ionization chamber), \( e \) is the electric charge of the...
electron, and \( n \) is the number of electrons lost by the gas molecules; therefore, \( ne \) is the total electric charge of the ions. In all the cases of interest to us, \( n = 1 \).

4.2.2. Magnetic field

The ions travel along the axis of the mass-spectrometric tube and then enter the magnetic field, the force lines of which are normal to their path. Here, they experience a force equal to \( Hne \), where \( H \) is the magnetic field strength. As a consequence, the ions follow a circular orbit, the radius \( r \) of which results from the balancing of the centrifugal force and of the deflecting force:

\[
Hne = \frac{mv^2}{r} \tag{4.7}
\]

By eliminating \( v \) from Eqs (4.6) and (4.7):

\[
r = \frac{1}{H} \left( \frac{2mV}{ne} \right)^{1/2} \tag{4.8}
\]

Thus, ions having different mass/charge ratios will emerge from the magnetic field following different trajectories and can be collected separately. For the same values of \( V \) and \( H \), ions having the same charge but higher mass will be deflected less than those having lower mass. By varying the acceleration voltage \( V \) and/or the magnetic field \( H \) in an appropriate way, ions of any mass/charge ratio can be made to fall on the ion collectors.

If \( H \) is expressed in gauss, \( V \) in volts, \( m \) in atomic mass units, and \( r \) in centimetres, Eq. (4.8) becomes:

\[
r = \frac{144}{H} \left( \frac{mV}{n} \right)^{1/2} \tag{4.9}
\]

In the Nier mass spectrometer, the angle formed between the pole faces of the magnetic sector is 60°; mass spectrometers with 90° or 180° magnetic sectors are also common. The magnetic field can be realized either with a permanent magnet (in this case, of course, only the acceleration voltage can be adjusted to collect ions of a given mass/charge ratio) or with an electromagnet.

4.2.3. Ion collectors

The mass spectrometers designed for highly precise isotopic ratio measurements are equipped with collectors (generally two), which collect simultaneously the isotopic ionic species the ratio of which is to be determined.
In the Nier mass spectrometer, the ions of the most abundant species (which is the lightest one in all the cases of interest to us) are collected over a plate (major collector); a slit present in this plate allows the ions of the less abundant isotopic species to reach a second collector (minor collector) consisting of a Faraday cage (Fig.9). The electron suppressors, having a negative potential of a few tens of volts, serve to return to the collectors secondary electrons emitted by the impact of the high-energy ions, the escape of which would alter the value of the current transported by each ionic species. The grounded guard rings prevent current leakage between the electron suppressors and the main collector.

High-value resistors are applied to each collector; typical values are $10^{11}$ ohms for the minor collector, and $10^9 - 10^{10}$ ohms for the major collector. Therefore, the currents transported by the isotopic ion beams (of the order of $10^{-11}$ A for the less abundant ion beam falling on the minor collector, and of $10^{-9}$ A for the more abundant ion beam, under working conditions) will produce, flowing across the resistors, voltages which are then amplified and compared with a potentiometric system as shown in Fig.9. The DC amplifiers used should be of high quality, i.e. high input impedance, low current noise and high stability. Vibrating capacitor type amplifiers are frequently used.

In the case of $^{18}$O/$^{16}$O determinations in CO$_2$, the isotopic species of masses 44 and 45 are generally collected together on the major collector, and a correction for this should be applied to the result, as will be seen later. Recently, mass spectrometers with three collectors have been constructed in order to collect separately the isotopic species of masses 44, 45 and 46. This arrangement allows the contemporaneous measurement of the $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O isotopic ratios.

The double collector shown in Fig.9 is not suitable for determining hydrogen isotopic ratios because the two ionic species to be measured, H$_2^+$ and HD$^+$, have too large a relative mass difference, and therefore the two ion beams will be too far from each other for the arrangement shown in Fig.9. In this case, two independent Faraday cages are used to collect ions of masses 2 and 3, one of which is placed in an additional tube arm in the Nier mass spectrometer (Friedman, 1953). The electronics remain unchanged.

4.2.4. Double inlet system

The relative variations of the isotopic composition of different samples can be measured with high accuracy with respect to a reference sample which is introduced into the mass spectrometer alternately with the sample under investigation by means of a double inlet system.

The commonly used double inlet system for gas samples consists of two gas reservoirs, one filled with the sample and the other with the reference.
FIG. 10. McKinney change-over valves for the mass spectrometer double inlet system. 
*a* - hemispherical ground joints;  
b* - iron core;  
c* - electromagnets. The gas from reservoir 1 is admitted to the ion source; the corresponding valve is closed towards the pump and open to the ion source. The gas from reservoir 2 is pumped off.

4.2.5. Measuring the difference between the isotopic ratios of reference and sample

The ion current $i_A$ flowing through the major collector (Fig. 9) gives rise to a potential drop $i_A \rho_A$ across the resistor $\rho_A$, corresponding to the voltage $V_A$:

$$V_A = -i_A \rho_A$$  \hspace{1cm} (4.10)

A fraction $C$ of $V_A$ is taken from the isotopic ratio potentiometer and applied to the minor collector:

$$CV_A = -Ci_A \rho_A = i_C \rho_C$$

The voltage resulting at the terminals of amplifier B will be as follows:

$$V_B = -(i_B + i_C) \rho_B = -i_B \rho_B + Ci_A \rho_A \rho_B / \rho_C$$  \hspace{1cm} (4.11)

where

$$C = \frac{\rho_C}{i_A \rho_A \rho_B} \left( V_B + i_B \rho_B \right)$$
The exact compensation between the voltage drops, due to the ion currents flowing through the two collectors, is reached when \( V_B = 0 \). If \( C^0 \) is the value of \( C \) corresponding to the exact compensation, we obtain from Eq. (4.11):

\[
C^0 = \frac{i_B \rho_C}{i_A \rho_A}
\]  
(4.12)

\( C^0 \) is proportional to the ratio of the intensities of the two ion beams produced by the different isotopic species.

Equation (4.11) shows that \( V_B > 0 \) when \( C > C^0 \) (overcompensation) and, vice versa, \( V_B < 0 \) when \( C < C^0 \) (undercompensation). With \( C = 0 \), \( V_B = -i_B \rho_B \) (in analogy with Eq. (4.10)), and the voltage read on the recorder is proportional to ion current flowing through the minor collector.

Recorder traces like those illustrated in Fig. 11 are obtained when reference and sample are alternately introduced into the mass spectrometer. Precise compensation values can be calculated for both the sample (subscript S) and the reference (subscript R) as follows:

\[
C^S = \frac{1}{P} \left( P_S + \frac{d_S}{D} \right)
\]

\[
C^R = \frac{1}{P} \left( P_R + \frac{d_R}{D} \right)
\]  
(4.13)

where \( P \) is the total resistance value of the isotopic ratio potentiometer, \( P_S \) and \( P_R \) are the gross compensation values read on the potentiometer, \( d = \Sigma d_i/n \) are the mean distances in millimetres of the traces from the zero line (\( n \) being the number of traces) for the sample and for the reference, and \( D = \Sigma D_i/n \Delta P_R \) is the displacement in millimetres of the trace for a unit change of the compensation potentiometer, evaluated from the calibration traces.

In modern mass spectrometers, the trace readings \( q_i \) are assessed by a digital integrator, which can feed a printer or a paper punch for computer calculations of \( \delta \)'s.

The values of \( C^S_0 \) and \( C^R_0 \) are directly proportional to the respective isotopic ratios \( R \) of the gases entering the ion source (disregarding some small correction factors which will be discussed in the following sections). In fact, because of the different pumping rate of isotopic molecules (see Section 4.2.4), it follows that

\[
R = \left( \frac{M_A}{M_B} \right)^{1/2} \frac{i_B}{i_A}
\]  
(4.14)
FIG. 12. Tail contribution of the mass-44 ion beam to mass-45 and mass-46 ion beams. For mass 45, the tail contribution is: \( t_{45} = \frac{(a + b)}{2} \); for mass 46: \( t_{46} = \frac{(b + c)}{2} \).

x being the fraction of the sample contributing to the reference and y the fraction of the reference contributing to the sample. For good valves, the overall mixing factor, \((x + y)\), should not exceed 1%. The last term in the denominator of Eq. (4.17) can therefore be usually neglected, and Eq. (4.17) reduces to:

\[
\delta_c = \delta / (1 - x - y) \tag{4.17'}
\]

The background contribution results from residual gases present in the mass spectrometer, having the same masses as the isotopic species measured, and from an incorrect zero-setting of the amplifiers.

The tail contribution results from the incomplete resolution of the different isotopic species, in such a way that the most abundant one may contribute slightly to the less abundant one (Fig. 12), the contribution of the less abundant isotopic species to the most abundant one being negligible. The reason for such an incomplete resolution is the slight spread of the kinetic energy of the ions and the imperfect geometry of the ion beam. Another possible reason suggested by Craig (1957) — the coulombic interaction among ions — has been proved to be of negligible importance (Mook and Grootes, 1973). It is
also important to remark that the tail contribution increases with the square of the gas pressure in the ion source.

If \( b \) and \( B \) are respectively the background contributions to the less abundant isotopic species \( m \) and to the more abundant species \( M \), and \( t \) is the tail contribution of \( M \) to \( m \), the value actually measured with the mass spectrometer is:

\[
\delta = \frac{m_S + b + t}{M_S + B} - \frac{m_R + b + t}{M_R + B} \times 1000
\]

The correct value is:

\[
\delta_c = \frac{m_S}{M_S} - \frac{m_R}{M_R} \times 1000
\]

Since the gas pressures in both the sample and reference reservoirs are adjusted to produce the same current through the major collector, \((M_S + B) = (M_R + B)\). Therefore, from a comparison of the previous equations, one obtains:

\[
\delta_c = \delta \left(1 + \frac{b + t}{m_R}\right)
\]

(4.18)

In good instruments and under good working conditions, the tail and background contributions together are less than 1% of the less abundant isotopic species \( m_R \), which therefore results in an equal correction to the \( \delta \)-values obtained. With a double-focusing mass spectrometer, the tail contribution can be reduced to a negligible value (Coplen, 1973).

When hydrogen is analysed, there is no tail contribution of the more abundant mass 2, \( H_2 \), to mass 3, HD*, because in this case the resolution is always complete, owing to the large relative mass difference.

4.2.7. Corrections specific to \( CO_2 \) isotopic analyses

When analysing \( CO_2 \) by mass spectrometry, different isotopic species with the same molecular weight interfere with each other and therefore further corrections should be applied to the \( \delta \)-value already corrected for valve mixing (Eq. (4.17)) and for tail and background (Eq. (4.18)).
As an example, the statistical distribution of the isotopic species of CO₂ derived from the PDB standard — which is a natural CaCO₃ — is given in Table VII. It can be seen that mass 45 is not only due to the isotopic species containing $^{13}$C but derives also to a significant amount (6.3%) from the species containing the $^{17}$O atom. Similarly, 0.2% of mass 46 derives from isotopic species containing $^{13}$C and/or $^{17}$O but not $^{18}$O. Masses higher than 46 have negligible abundances.

The $\delta$-values obtained so far can be indicated therefore as $\delta_{45}$ or $\delta_{46}$, representing the variation of the whole content of all isotopic species with mass 45 or 46, and need further elaboration in order to be transformed respectively into $\delta^{13}$C and $\delta^{18}$O.

For a double collector of the type shown in Fig.9 the relationships which should be applied are as follows (Craig, 1957):

\[
\delta^{13}C = \left(1 + \frac{2R_{17}}{R_{13}}\right) \delta_{45} - \frac{R_{17}}{R_{13}} \delta^{18}O
\]  
(4.19)

\[
\delta^{18}O = \frac{[R_{18}(1 + R_{13}) + 2R_{17} + R_{13}R_{17}]\delta_{46} + (R_{18} - R_{13})R_{13}\delta^{13}C}{R_{18}(1 + R_{13} + R_{17}) + R_{13}R_{17}/2}
\]  
(4.20)

where $R_{13} = ^{13}C/^{12}C$, $R_{17} = ^{17}O/^{16}O$ and $R_{18} = ^{18}O/^{16}O$ are the isotopic ratios of the reference.

For a mass spectrometer with a triple collector, the $\delta^{13}$C relationship is identical to Eq. (4.19), while for $\delta^{18}$O the following relationship is obtained:

\[
\delta^{18}O = \left(1 + \frac{R_{13}R_{17}}{2R_{18} + R_{13}R_{17}}\right) \delta_{46} - \frac{2R_{13}R_{17}}{2R_{18} + R_{13}R_{17}} \delta^{13}C
\]  
(4.21)

Finally, for a system with the major collector extending on both sides of the minor collector, and therefore collecting also ions with masses higher than those of ions falling on the minor collector, the $\delta^{18}$O equation is practically the same as Eq. (4.20), while for $\delta^{13}$C the following relationship is obtained:

\[
\delta^{13}C = \left(1 + \frac{2R_{17}}{R_{13}}\right) \delta_{45} - \frac{R_{17}}{2R_{13} \left(1 + 2R_{18}\right)} \left(\frac{R_{18} \left(R_{18} + 2R_{17}\right)}{R_{13} \left(1 + 2R_{18}\right)}\right) \delta^{18}O
\]  
(4.22)

All the above relationships are approximated and have been obtained by eliminating negligible terms and assuming that the $^{17}$O-variations, which are difficult to be directly measured because they are masked by the $^{13}$C-variations, correspond simply to the half of the $^{18}$O-variations ($\delta^{17}$O = $\delta^{18}$O/2). This last assumption is generally true for natural compounds of terrestrial origin, but might not be valid for extra-terrestrial material (Clayton et al., 1973).
As an example, let us calculate the values of the coefficients in Eqs (4.19–4.22), for a reference with the same isotopic ratios as those of CO$_2$ derived from the PDB standard, i.e. $R_{13} = 1123.72 \times 10^{-5}$, $R_{17} = 38.00 \times 10^{-5}$, $R_{18} = 207.90 \times 10^{-5}$ (Craig, 1957).

We obtain:

\[
\delta^{13}C = 1.0676 \delta_{45} - 0.0338 \delta^{18}O \quad (4.19')
\]

\[
\delta^{18}O = 1.0014 \delta_{46} + 0.0091 \delta^{13}C \quad (4.20')
\]

\[
\delta^{18}O = 1.0010 \delta_{46} - 0.0021 \delta^{13}C \quad (4.21')
\]

\[
\delta^{13}C = 1.0676 \delta_{45} - 0.0294 \delta^{18}O \quad (4.22')
\]

The mass spectrometer correction factors for CO$_2$ analyses have also been discussed by Dansgaard (1969), Deines (1970), Mook and Grootes (1973), and Halas (1977).

4.2.8. Corrections specific to H$_2$ isotopic analyses

When analysing hydrogen gas with a mass spectrometer, two isotopic ions are collected simultaneously on the two collectors: H$_2$ of mass 2, and HD$^+$ of mass 3. However, the ion H$_3^+$ of mass 3 is also collected together with HD$^+$, and a correction must be applied for the contribution of this parasitic ion to the mass-3 ion beam.

The ion H$_3^+$ is formed in the ion source by the reaction

\[H^+_2 + H_2 \rightarrow H_3^+ + H\]

The ionization of hydrogen is a first-order reaction; in other words, the concentrations of the hydrogen isotopic ions in the ion source are proportional to the partial pressure $p$ of the respective mother molecules:

\[[H_2^+] = A_pH_2\]

\[[HD^+] = A_pH_D\]

where $A$ and $A_1$ are the ionization rate constants, which can be slightly different if some discrimination in the ionization of H$_2$ and HD occurs.

The formation of H$_3^+$ ions is a second-order reaction; the H$_3^+$ concentration is proportional to the product of the concentration of H$_2^+$ and of H$_2$, and therefore to the square of $p_{H_2}$:

\[[H_3^+] = B_pH_2^2\]
FIG. 13. Mass-3/mass-2 ratio as a function of mass-2 ion beam current, to show the $H_2^+$ contribution. The value of $352.2 \times 10^{-6}$, obtained by extrapolation to zero mass-2 ion current, corresponds to the $[HD]/[H_2]$ ratio of the hydrogen gas in the ion source. For a mass-2 ion current of $5 \times 10^{-7} A$, the correction factor for $H_2^+$ contribution is (Eq. (4.26)): 

$$I + (367.8 - 352.2)/352.2 = 1.0443.$$

The compensation value $C$ obtained is then:

$$C = K \frac{[HD^+]}{[H_2^+]} = K \left( \frac{A_1}{A} R + \frac{B}{A} p_{H_2} \right).$$  \hspace{1cm} (4.23)

where $R = p_{HD}/p_{H_2}$ is the desired isotopic ratio, and $K$ is the constant already defined in Section 4.2.5.

From Eq. (4.23) it appears that $C$ is linearly correlated with the gas pressure in the ion source. Therefore, different values of $C$ are obtained for the same sample by operating at different pressures; i.e. at different $H_2^+$ current values, one obtains the correct compensation value $C^0$ by extrapolation to zero $H_2^+$ current, as shown in Fig. 13:

$$C^0 = \frac{KA_1}{A} R = C - \frac{KB}{A} p_{H_2}$$

In terms of $\delta$, we can write:

$$\delta D = \frac{R_S - R_R \times 1000}{R_R} = \frac{C^0_S - C^0_R}{C^0_R} \times 1000$$  \hspace{1cm} (4.24)
where \( C_S^0 - C_R^0 = C_S - C_R \) if both sample and reference are measured at the same \( H_2^+ \) current. Equation (4.24) can then be rewritten by using Eq. (4.13):

\[
\delta D = \frac{(P_S - P_R)D + d}{DP_R + d_R} \left( 1 + \frac{KBP_{H_2^+}}{AC_R^0} \right) \times 1000
\]  

which is the form normally used for \( \delta D \)-computations. \( C_R^0 \) is determined by extrapolation at zero \( H_2^+ \) current of the compensation readings for the reference, as is the factor \( KBP_{H_2^+}/A \), which is the compensation excess due to the \( H_2^+ \) contribution at the \( H_2^+ \) current selected for routine analyses.

Another method for a correct \( \delta D \)-computation is based on the analysis of a second laboratory reference sample (subscript SR), with \( \delta D_{SR} \) versus the first reference accurately measured once and for all by using the extrapolation technique. We then obtain:

\[
\delta D = \frac{\delta D'}{\delta D_{SR}} \delta D_{SR}
\]

where \( \delta D' \) and \( \delta D_{SR} \) are uncorrected \( \delta \)-values provided by the mass spectrometer.

With this method, the evaluation of \( C_R^0 \) by extrapolation to zero \( H_2^+ \) current is not necessary. Nevertheless, in order to obtain precise results, the isotopic composition of the second reference should be quite different from that of the first reference. The \( \delta D \)-values of samples should be within the interval 0 to \( \delta D_{SR} \).

Hydrogen isotope analysis thus appears to be sensitive to small differences in current of the main isotopic species between sample and reference, whereas CO\(_2\) isotope analysis is not. In fact, different \( H_2^+ \) currents imply different \( H_2^+ \) contributions which simulate differences in isotopic ratios. For instance, a difference in \( H_2^+ \) current of 2\% between sample and reference will produce a 2\% difference in the value \( C_S - C_R \) if the \( H_2^+ \) contribution is 10\%; 2\% is already twice the experimental error usually quoted by most laboratories. Therefore, the pressure in both the sample and reference reservoirs of the mass spectrometer inlet system should be adjusted very carefully to produce the same \( H_2^+ \) current.

Some modern mass spectrometers are equipped with an electronic unit to compensate automatically for the \( H_2^+ \) contribution; once this unit has been adjusted to the right value, the measurement becomes practically independent from differences in \( H_2^+ \) current between sample and reference.

The \( H_2^+ \) contribution can be reduced to a minimum value by proper design of the ion source and adjustment of its operating parameters. Of particular importance is the voltage drop between the ionization chamber and the drawing-out plates, by increasing which the residence time of ions in the ion source is reduced, thus reducing also the \( H_2^+ \) production rate.
Under good working conditions, the $\text{H}_2^+$ contribution should not exceed 5% of the HD$^+$ ion current, although contributions as high as 10% or even 15% can still permit good analyses. In fact, it is important that the $\text{H}_2^+$ contribution remains constant in time, without appreciable fluctuations during the analyses of a set of samples; otherwise, continuous time-consuming checks will be required.

4.3. DETERMINATION OF THE OXYGEN ISOTOPE COMPOSITION OF NATURAL WATERS

The most common method for determining the oxygen isotope composition of water is by equilibration with CO$_2$ and measurement of the isotopic ratio of CO$_2$. Other methods are in general more difficult and are applied only for special purposes or for very small samples of water.

4.3.1. The CO$_2$ equilibration method

This method, first proposed by Cohn and Urey (1938), was used later by Epstein and Mayeda (1953), who first reported accurate oxygen isotope analyses of natural waters.

4.3.1.1. Sample preparation

A sketch diagram of the sample preparation line is shown in Fig. 14. A given amount of water, in general a few millilitres, is introduced in a glass container, which is then coupled to a stopcock and connected to the line by means of ground joints. The water is frozen with a freezing mixture of acetone or carbon tetrachloride plus solid carbon dioxide (temperature about $-70^\circ$C), and the air in the container is evacuated. The water is then melted and warmed to room temperature in order to release the air dissolved and trapped in the ice during the freezing; this air is then evacuated after re-freezing the water.

Freezing is necessary in order to avoid water vapour losses during pumping for evacuation of air. These losses would alter the isotopic composition of the remaining water because of the isotopic fractionation occurring between vapour and liquid water.

Another method to remove air from a vessel containing a water sample was proposed by Roether (1970). It consists of pumping the air through a capillary tube, 50 mm long and 0.7 mm i.d., in which a stainless-steel wire is inserted to reduce the free cross-section to about 0.2 mm$^2$. The pumping rate is controlled by the capillary and the pressure drops to a few tens of torr within 5 minutes. It is not necessary to freeze the water samples; the water loss has been evaluated
as about 10 μl and this does not significantly affect the isotopic composition of samples of a volume of a few millilitres. Rother’s method is now applied in automated preparation lines available commercially.

After eliminating the air, commercial cylinder carbon dioxide of known isotopic composition is introduced in the sample container, at a pressure somewhat lower than atmospheric. If the tank CO₂ contains some air, it is previously purified by freezing in a trap with liquid nitrogen (temperature ca. −190°C), and by pumping out the air and other non-condensable gases.

With an appropriate preparation line, several water samples can be treated together. Some water samples of known isotopic composition (laboratory standards) are prepared at the same time and serve as a control of the whole preparation.

The containers with the water samples are then transferred into a thermostatic bath, at a temperature of 25.0 ± 0.1°C. Isotopic exchange takes place between CO₂ and water according to the reactions:

\[
\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+
\]

The isotopic exchange reaction is:

\[
\text{C}^{16}\text{O}_2 + \text{H}_2\text{O}^{18} \rightleftharpoons \text{C}^{16}\text{O}^{16}\text{O} + \text{H}_2\text{O}^{16}
\]

After a certain time this exchange reaction reaches equilibrium. The equilibration time may be reduced from one day or more to a few hours by shaking the samples (Fig.15). The equilibration process is described in detail by Roether (1970).

When isotopic equilibrium has been attained, the CO₂ is extracted from the container, separated from the water vapour by means of a dry ice trap, and used for mass-spectrometric analysis.
FIG. 15. $CO_2(gas) - H_2O\text{ (liquid)}$ equilibration rate at $25^\circ C$ with the IAEA system. The per cent fraction of non-equilibrated $CO_2$ at time $t$ is given by $(\delta t - \delta_{eq})/(\delta t - \delta_{eq})$. $\delta^{18}O_{eq}$ was determined after an equilibration period of 1 day with shaking and 3 days without shaking.

The equilibrated $CO_2$ has an $^{18}O/^{16}O$ ratio which is related to that of the water through a fractionation factor $\alpha$:

$$(^{18}O/^{16}O)_{CO_2} = \alpha (^{18}O/^{16}O)_{H_2O(\text{liq})}$$

which at $25^\circ C$ has a value of $1.0412 \pm 0.0001$ according to the most recent evaluation made by O'Neil et al. (1975), identical to that of Matsuhisa et al. (1971). Other values reported in the literature range from 1.0407 to 1.0424 (Staschewski, 1964; Majoube, 1966; O'Neil and Epstein, 1966; Bottinga and Craig, 1969; Blattner, 1973). At $25^\circ C$, the variation of $\alpha$ with temperature is $-0.00018$ per degree Celsius (O'Neil and Adami, 1969).

Apart from a small correction term (see next section), $\alpha$ cancels in the $\delta$-notation when expressing the isotopic composition of water samples with respect
to a water reference sample, as for instance the laboratory standard, prepared together. Therefore, a knowledge of the exact value of $\alpha$ is not strictly necessary, as long as one deals only with water samples. As a consequence, in principle the samples can be equilibrated with CO$_2$ at any temperature, provided that the laboratory standard is also equilibrated at the same temperature. However, when the oxygen isotope composition of a water sample is to be compared with that of a different compound, or with that of another water sample determined by a different technique, the fractionation factor between CO$_2$ and water must be taken into account in the calculation and therefore it should be known with high accuracy.

4.3.1.2. Correction for equilibration with CO$_2$

This correction results from the fact that the amount of oxygen introduced by CO$_2$ into the system water – CO$_2$ is not negligible. If $N$ are the gram-atoms of oxygen present in the water sample, and $n$ those in CO$_2$, we may write the balance equation:

$$N\delta_W^i + n\delta_G^i = N\delta_W + n\delta_G$$

(4.27)

where $\delta_W^i$ and $\delta_G^i$ represent the initial oxygen isotope composition of water and CO$_2$ before equilibration, and $\delta_W$ and $\delta_G$ those after equilibration. From Eq.(4.27) one obtains:

$$\delta_W = \delta_W^i + \frac{n}{N}(\delta_G^i - \delta_G)$$

(4.28)

which shows that the isotopic composition of water after equilibration is equal to the initial one (which is the desired one) only if $n$ is negligible with respect to $N$. On the other hand, $\delta_W$ and $\delta_G$ are related by the fractionation factor $\alpha$:

$$\frac{R_G}{R_W} = \frac{1000 + \delta_G}{1000 + \delta_W} = \alpha = 1.0412 \text{ (at } 25^\circ\text{C})$$

(4.29)

where $\delta_G$ is the value (measured by mass spectrometry) of CO$_2$ extracted from the system after equilibration. We should now determine the relationship between $\delta_G$ and the hypothetical value $\delta_G^0$ which CO$_2$ would have if equilibrated with an infinite amount of water ($n/N = 0$), in such a way that the water would not change its isotopic composition in the equilibration process. $\delta_G^0$ is defined by:

$$\frac{1000 + \delta_G^0}{1000 + \delta_W^i} = \alpha$$

(4.30)
By combining Eqs (4.28), (4.29) and (4.30), we obtain:

\[ \delta_G^o = \left(1 + \alpha \frac{n}{N} \right) \delta_G - \alpha \frac{n}{N} \delta_G^i \]  

(4.31)

This relationship was first derived by Craig (1957).

4.3.1.3. Correction for salts dissolved in water

CO₂ equilibrated with salt water may have an \(^{18}\text{O} / ^{16}\text{O}\) ratio different from that of CO₂ equilibrated with a water having the same isotopic composition but not containing any dissolved salts (Taubes, 1954). In fact, oxygen isotope fractionations occur between the water bound in the hydration sphere of cations and free water. The system may be represented as:

\[ \alpha \quad \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O} \text{(free)} \rightleftharpoons \text{H}_2\text{O} \text{(bound)} \]

\[ \alpha = 1.0412 \text{ being the equilibrium fractionation factor between CO}_2 \text{ and free water at } 25^\circ\text{C}, \text{ and } \alpha' \text{ the equilibrium fractionation factor between bound and free water, also at } 25^\circ\text{C}: \]

\[ \frac{1000 + \delta_G^S}{1000 + \delta_W^F} = \alpha \]  

(4.32)

\[ \frac{1000 + \delta_B^S}{1000 + \delta_W^F} = \alpha' \]  

(4.33)

where the indexes F and B stand for ‘free’ and ‘bound’. \( \delta_G^S \) is the value of the isotopic composition measured by mass spectrometry of CO₂ equilibrated with salt water, whereas the desired value is \( \delta_G \), i.e. the value which one would obtain if no salt were dissolved in the water:

\[ \frac{1000 + \delta_G}{1000 + \delta_W} = \alpha \]  

(4.34)

If \( x \) is the fraction of bound water, we may write the following isotopic balance equation:

\[ \delta_W = (1-x)\delta_W^F + x\delta_W^B \]  

(4.35)
By combining Eqs (4.32) to (4.35), one obtains:

$$\delta_G = \delta^8_G [1 + x(\alpha' - 1)] + 1000x(\alpha' - 1)$$  (4.36)

The fractionation factor \(\alpha'\), as well as the fraction of bound water \(x\), have different values for different cations; therefore, when \(n\) different cations are dissolved in the water, Eq.(4.36) becomes:

$$\delta_G = \delta^8_G \left[ 1 + \sum_{i=1}^{n} x_i(\alpha_i' - 1) \right] + 1000 \sum_{i=1}^{n} x_i(\alpha_i' - 1)$$  (4.37)

The fraction \(x_i\) of water bound by the cation \(i\) is equal to \(n_iM_i/55.56\), \(n_i\) being the hydration number of the \(i\)-cation and \(M_i\) its molality, and 55.56 the number of water moles per kilogram of water.

Sofer and Gat (1972) have studied the influence on isotopic analyses performed by means of the CO₂ equilibration method of the most common cations that may occur with high concentrations in natural waters. They report the following correction equation:

$$\frac{\delta^8_G - \delta^8_G}{1000 + \delta^8_G} = (1.11M_{Mg} + 0.47M_{Ca} - 0.16M_{K}) \times 10^{-3}$$  (4.38)

\(M\) being the molalities of the cations indicated as subscripts. The second term of Eq.(4.38) corresponds to the term \(\sum_{i=1}^{n} x_i(\alpha_i' - 1)\) of Eq.(4.37).

Sodium does not appear in Eq.(4.38); in fact, the fractionation factor \(\alpha'\) for sodium is equal to 1 at 25°C, and therefore the corresponding term is zero. In other words, oxygen isotope results obtained with the CO₂ equilibration method for waters containing only dissolved sodium salts do not need any correction (see also: Taube, 1954; Götz and Heinzinger, 1973).

From Eq.(4.38) one can also see that corrections larger than 0.1% (which is the normal analytical error) occur only when the molality of magnesium is higher than 0.09 (~2.2 g/l), or when that of calcium is higher than 0.21 (~8.4 g/l), or when that of potassium is higher than 0.62 (~24.2 g/l).

The results for the fractionation factor between ion hydration water and free water obtained by other authors show some discrepancies with respect to those reported by Sofer and Gat (1972).

Truesdell (1974) reported values identical or very similar to those of Sofer and Gat for sodium, calcium and magnesium, but he did not observe any fractionation for potassium at 25°C. He also studied the behaviour of the fractionation factors with temperature and showed that anions, in addition to
cations, also play an important role in determining the stable-isotope distribution among free and bound water.

Fontes (1975, personal communication) found no fractionation for calcium, 1% for MgSO₄ (per mole) and HCl, but only about 0.5% for MgCl₂, the values obtained for sodium and potassium being similar to those of Sofer and Gat. Fontes also showed that the equilibration rate is considerably slowed down by certain salts. For instance, the equilibration rate constant of a 4M solution of MgCl₂ is about seven times less than that of pure water, and that of a 4M solution of Ca(NO₃)₂ is three times less. Much less serious, or negligible, are the effects due to NaCl, KCl, KNO₃ and HCl. The decrease in equilibration rate should be compensated by a proportionally longer equilibration time when analysing samples of salt water.

Dissolved anions also have an effect, although small, on the isotopic composition of CO₂ equilibrated with water. Götz and Heinzinger (1973) reported, for instance, that the fractionation factor at 25°C between ion hydration water and free water passes from 0.9981 for KCl to 0.9972 for KBr and to 0.9967 for KI. This effect is, however, very small and can be neglected for natural waters.

Because of the present uncertainty of some correction factors associated with dissolved salts, one might think it preferable to distil saline water samples before CO₂ equilibration. However, distillation is a rather difficult operation to carry out without producing any isotopic fractionation. The distillation yield should be 100%, otherwise the distilled water would most probably be significantly different in isotopic composition from the mother water. If the salt concentration is high, a 100% distillation is more difficult because some precipitated salts may retain water, the release of which is often not easy, even at a high temperature. In conclusion, it is advisable not to distil saline water samples for ¹⁸O analysis unless the distillation procedure has been carefully tested. Generally, it is preferable to report the measured δ¹⁸O values, corrected by using Eq.(4.38), together with the concentration of the most abundant dissolved ions, to allow a future correction of the data to be made if the factors of Eq.(4.38) need some revision.

4.3.1.4. Example of δ¹⁸O calculation for a water sample

Let us assume that CO₂ equilibrated with a water sample is analysed with a mass spectrometer versus a given reference. We obtain the following results (from Fig.11; see Section 4.2.5 for notations):

\[
\begin{align*}
P_S &= 796 \, \Omega \\
P_R &= 800 \, \Omega \\
d &= -81.1 \, \text{mm} \\
d_R &= +31.6 \, \text{mm} \\
D &= 17.9 \, \text{mm}/\Omega
\end{align*}
\]
\[ P = 10000 \, \Omega \] being the total value of the compensation potentiometer. The values \( d_s, d_R \) and \( D \) can either be evaluated from the recorded traces by drawing lines through them and measuring the distances, or be provided by a trace integrator as digital values proportional to the distance of the trace from the recorder zero line.

Using Eq. (4.13) we obtain \( C_R = 0.080177 \). Compensation values of about 0.08 are normal for output resistors of \( 10^{11} \, \Omega \) for the minor collector and of \( 5 \times 10^9 \, \Omega \) for the major collector, the natural abundance of \(^{12}\text{C}^{16}\text{O}^{16}\text{O}\) being about 0.4%.

From Eq. (4.16') we then obtain:

\[ \delta = -10.64\% \]

Let us further assume that the change-over valves leak slightly (see Section 4.2.6). The sample contributes 0.5% to the standard, which in turn contributes 0.3% to the sample. The correction factor 1-x-y is then 0.992. From Eq. (4.17') we obtain the \( \delta \)-value corrected for valve mixing:

\[ \delta = -10.64/0.992 = -10.73\% \]

The background contribution to mass 46 is 3 mV, and the tail contribution is 5 mV. If mass 46 produces an output voltage of 1900 mV, the correction given by Eq. (4.18) is as follows:

\[ \delta = -10.73 \left(1 + \frac{8}{1900}\right) = -10.77\% \]

We correct now for interferences of other isotopic masses (see Section 4.2.7). Assuming that \( \delta^{13}\text{C} \) of CO\(_2\) used for equilibration is -7.7 with respect to the reference, we obtain:

\[ \delta = 1.0014(-10.77) + 0.0091(-7.7) = -10.86\% \]

This correction equation has been assumed to be equal to that for the PDB standard (Eq. (4.20')). It appears, however, that in principle it would be better to use as reference a CO\(_2\) having a \(^{13}\text{C}/^{12}\text{C}\) ratio equal or close to that of the CO\(_2\) equilibrated with the water sample; in such a case, the \( \delta^{13}\text{C} \) term of Eq. (4.20') would vanish or become very small. For this reason, many laboratories use as reference the same tank CO\(_2\) used in equilibration.

Let us now assume that in our equilibration we have used 10 ml of CO\(_2\) at 20°C and 760 torr, and 5 ml of water. Thus, \( n = 8.3 \times 10^{-4} \) g-atom O,
$N = 2.78 \times 10^{-1}$ g-atom O, $\alpha = 1.0412$, and, assuming that the initial $\delta^{18}$O of CO$_2$ before equilibration was $-20.0$, we obtain from Eq.(4.31):

$$\delta = 1.0031(-10.86) - 0.0031(-20.0) = -10.83\%$$

We now correct for dissolved salts (see Section 4.3.1.3). From a chemical analysis of our water sample we have obtained the following results:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration</th>
<th>$M_{\text{ion}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>6.1 g/l</td>
<td>0.25</td>
</tr>
<tr>
<td>Ca</td>
<td>2.0 g/l</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>12.1 g/l</td>
<td>0.31</td>
</tr>
</tbody>
</table>

As sodium does not affect the measurement, we may disregard its concentration. By introducing the above values in Eq.(4.38) we obtain:

$$\frac{\delta + 10.83}{1000-10.83} = (1.11 \times 0.25 + 0.47 \times 0.05 - 0.16 \times 0.31) \times 10^{-3}$$

$$\delta = -10.58\%$$

Let us now assume that the laboratory standards, prepared together with the sample and measured in the same way, give a mean $\delta$-value equal to $-5.32$. Let us assume also that $\delta^{18}$O of the laboratory standard, carefully calibrated, is $-12.50$ versus SMOW. We now have to transform the $\delta$ of the sample to $\delta^{18}$O versus SMOW, using the laboratory standard values. The value of the samples (subscript $S$) versus the laboratory standard (subscript L) is given by:

$$1000 + \delta_{S-L} = \frac{1000 + \delta_S}{1000 + \delta_L} \times 10^3$$

$$\delta_{S-L} = \left(\frac{1000-10.58}{1000-5.32} - 1\right) \times 10^3 = -5.29\%$$

Our final result, i.e. the value of the sample versus SMOW is given by:

$$\delta_{S-SMOW} = \delta_{S-L} + \delta_{L-SMOW} + \delta_{S-L} \times \delta_{L-SMOW} \times 10^{-3}$$

$$\delta_{S-SMOW} = -5.29 - 12.50 + 5.29 \times 12.50 \times 10^{-3} = -17.72\%$$
4.3.1.5. $\delta^{18}O$ calculation using two different laboratory standards

At an IAEA Panel in 1966, Dansgaard proposed the use of two different laboratory standards in order to avoid the daily determination of the correction factor due to valve mixing, tail and background. Also corrections due to mass interference and CO$_2$ equilibration are eliminated or reduced. In fact, it can be demonstrated (Dansgaard, 1969) that:

$$\delta_S^{\text{SMOW}} = \delta_1^{\text{SMOW}} + (\delta_2^{\text{SMOW}} - \delta_1^{\text{SMOW}}) \frac{\delta_S - \delta_1}{\delta_2 - \delta_1} \quad (4.41)$$

where the subscripts 1 and 2 refer to the laboratory standards 1 and 2, and $\delta_S$, $\delta_1$ and $\delta_2$ are expressed versus the reference CO$_2$.

Using the example given in the previous section, one obtains: $\delta_S = -10.64$ and $\delta_1 = -5.22$ (which would produce, after correction of the whole set, a value of $-5.32\%$, as assumed before). Let us assume also that the second laboratory standard would give an incorrect $\delta_S$-value of $-25.53\%$ and a correct value of $-25.97\%$. Its corresponding value versus SMOW would therefore be $-33.00\%$. Introducing all the above values into Eq.(4.41), one obtains:

$$\delta_S^{\text{SMOW}} = -17.97\%$$

This value should be further corrected for dissolved salt effect$^9$ by using Eq.(4.38). The final result is:

$$\delta_S^{\text{SMOW}} = -17.72\%$$

identical to the value obtained in the previous section.

In order to obtain reliable results, the two laboratory standards must have a rather different isotopic composition, otherwise the error associated with the second term of the right-hand side of Eq.(4.41) would be too high. It is also advisable to select the laboratory standards in such a way that $\delta_1 > \delta_S > \delta_2$; for this reason, the method is called the interpolation method.

4.3.2. Other methods of determining the oxygen isotope composition of natural waters

Other methods have been developed for determining the oxygen isotope composition of natural waters. These methods are not so widely used as the CO$_2$ equilibration method because they are more complex and, perhaps, less accurate.

$^9$ The correction for dissolved salt effect can be made either on the $\delta$-values versus the reference CO$_2$ or on those versus SMOW.
Nevertheless, they have the advantage of making the isotopic analysis of very small samples of water (microlitres) possible, whereas in the equilibration method some millilitres of water are required. Therefore they have found application for studies in which only small water samples were available. These methods are used also for the determination of fractionation factors between water and other compounds, because the $^{18}$O/$^{16}$O ratio measured is equal to that of water; in the equilibration method they are related through the CO$_2$–H$_2$O fractionation factor. The latter is rather large and not exactly known, and therefore might introduce an error when the isotopic composition of the water sample should be compared with that of a sample of a different nature.

4.3.2.1. Method of reduction of water over graphite

The water sample is vaporized and passed over a graphite rod at 1100–1200°C (Majoube, 1966). The following reaction occurs:

$$H_2O + C \rightarrow H_2 + CO$$

Also traces of CO$_2$ are formed. After eliminating the hydrogen by diffusion through a palladium membrane at 400°C, the carbon monoxide is transformed to carbon dioxide by decomposition over a nickel powder catalyst at 360°C:

$$2CO \rightarrow CO_2 + C$$

CO$_2$ is then used for mass spectrometry.

A memory effect occurs in sample preparation due to the nickel catalyst, which as usual can be removed by 'rinsing' the system once or twice with the sample before using the CO$_2$ for isotopic analysis.

Another method to transform a mixture of CO$_2$ + CO to CO$_2$ alone without isotopic fractionation, which could be applied here, consists of sparking the gas with a Tesla coil and trapping the CO$_2$ which is continuously formed in a liquid nitrogen trap (Longinelli and Craig, 1967).

4.3.2.2. Method of water fluorination

The water vapour is reduced with bromine pentafluoride at 150°C in a nickel reaction vessel according to the reaction (O'Neil and Epstein, 1966):

$$H_2O + BrF_5 \rightarrow BrF_3 + 2HF + \frac{1}{2} O_2$$

All the reaction products except oxygen are separated in a liquid nitrogen trap. The oxygen is converted to CO$_2$ by circulation with a Toepler pump over a carbon
rod heated at 550—600°C; at this temperature practically no CO is formed (Clayton and Mayeda, 1963). The CO$_2$ is trapped with liquid nitrogen, purified from non-condensable gases and then used for mass spectrometry. No detectable memory effects have been observed.

4.3.2.3. Direct mass-spectrometric analysis of water

The liquid water sample is directly injected into the mass-spectrometer inlet system consisting of two glass reservoirs (one for the sample and the other for the reference) heated at 100°C. The water vaporizes, and the vapour is directly admitted to the mass spectrometer ion source through two pyrex capillaries heated at 200°C to minimize adsorption and therefore memory effects. The isotopic ions with mass 18 (H$_2^{16}$O$^+$) and 20 (H$_2^{18}$O$^+$) are collected in two separate collectors and their ratio is compared with that of the reference (Majoube and Nief, 1968).

Memory effects are important and therefore the inlet system should be 'rinsed' with one or two preliminary sample injections.

Although this system seems attractive because it significantly reduces the work of the operator, it has not found wide application, probably because of the special type of mass spectrometer required and the difficulties deriving from memory effects in the ion source and from the parasite ions with mass 20, such as $^{17}$OH$_3^+$, $^{16}$OH$_2^+D^+$ and HF$^+$, the last being produced by impurities.

4.4. DETERMINATION OF THE HYDROGEN ISOTOPE COMPOSITION OF NATURAL WATERS

Hydrogen isotope analyses of water are carried out on the hydrogen gas obtained by quantitative reduction of water. Commonly, this reduction is performed in a special preparation line, but it is also possible to perform it directly in the inlet system of the mass spectrometer. These two different ways of sample preparation also imply two different methods of mass-spectrometric analysis.

The method of direct mass-spectrometric analysis of water has been proved impracticable for hydrogen isotope ratio determination, because of the presence of large amounts of parasite ions with mass 19, which fully mask the peak due to HD$^{16}$O$^+$ (Majoube and Nief, 1968).

4.4.1. Method of reduction of water in a separate line

This method was used by Friedman (1953), who first reported accurate hydrogen isotope analyses of natural waters, and it is at present the most commonly used.
4.4.1.1. Sample preparation

A sketch diagram of the sample preparation line is shown in Fig.16. The sample of about 10 microlitres of water is introduced into the line. This introduction can be made in different ways; the most common methods are described as follows:

(a) The water is introduced into a thin glass capillary tube of about 0.5 mm internal diameter, which is then sealed in a flame and placed in the line. After evacuation of air, the capillary is broken, the water vaporizes and is transferred to a liquid nitrogen trap where non-condensable gases are eliminated. Then the water is admitted to the oven for the reduction (Friedman, 1953).

(b) With a microsyringe or a capillary pipette a droplet of about 10 mg of water is deposited at the bottom of a small container, where it is frozen with liquid nitrogen and the air is evacuated. Then the water is admitted to the oven for the reduction (Horibe and Kobayakawa, 1960).

(c) With a microsyringe the water is directly injected into the evacuated system through a self-sealing rubber bung, as is currently done in gas chromatography.

In all the methods, heating up to about 200°C will help, not only in accelerating evaporation of the water from the inlet part of the line, but also, in the case of salt waters, in removing the water adsorbed by salts and in obtaining
complete distillation of the sample. If distillation is not complete, the isotopic results will be incorrect in most of the cases.

The reduction oven is filled with turnings of metallic uranium (Bigeleisen et al., 1952) or with granulated zinc (Friedman, 1953). The reactions which occur are:

\[ 2\text{H}_2\text{O} + \text{U} \rightarrow \text{UO}_2 + 2\text{H}_2 \]

\[ \text{H}_2\text{O} + \text{Zn} \rightarrow \text{ZnO} + \text{H}_2 \]

The oven temperature should be about 800°C for uranium (and in this case the oven should be made of quartz) and about 400°C for zinc.

The hydrogen evolved is collected in a container using an automatic Toepler pump; this can be followed by a Pirani gauge.

A liquid nitrogen trap at the exit of the oven traps the water which may not have reacted. When all the hydrogen formed has been removed, any non-reduced water is admitted again to the oven, by reversing the direction of flow, and the hydrogen formed in this second step is added to the container. With uranium, the water is in general quantitatively reduced during one pass.

Metallic uranium can be used to collect the hydrogen produced by the reduction of water (Friedman and Hardcastle, 1970). At a temperature of about 80°C the hydrogen reacts with uranium, producing \( \text{UH}_3 \). When the reaction is completed, the uranium is heated to about 650°C, and the uranium hydride is quantitatively decomposed to release hydrogen. This method eliminates the need of a Toepler pump.

Small memory effects might occur in some steps of the procedure; therefore, in order to reduce these to a minimum in preparing a set of successive samples, it is advisable, whenever possible, to start with the sample having the highest presumed deuterium content and to end with the sample having the lowest deuterium content, or vice versa. In many cases, the deuterium content of the samples can be roughly estimated from the oxygen-18 content, if this has already been measured, by making use of the parallelism in \( ^{18}\text{O} \) and D-variations in natural waters.

A modification of the zinc method has been proposed in order to eliminate the Toepler pump (Schiegl and Vogel, 1970). A larger amount of water (about 70 mg) is used and the hydrogen produced by reaction with zinc is circulated in the line by a small rotor pump magnetically operated. At the end of the reaction, a part of the hydrogen is collected in a container simply by expansion, while the remainder is pumped away. Nevertheless, this method produces isotopic fractionation due to the dissolution of hydrogen in the hot zinc. In order to apply a correction for it to the mass-spectrometric result, reference water samples should be prepared at regular intervals.
4.4.1.2. Example of δD-calculation

Let us assume that a hydrogen sample is analysed with a mass spectrometer versus a given laboratory reference. The results obtained are (see Section 4.2.5 for notations):

\[
\begin{align*}
P_S &= 360 \, \Omega \\
P_R &= 366 \, \Omega \\
d &= -39 \, \text{mm} \\
d_R &= +27 \, \text{mm} \\
D &= 15 \, \text{mm/Ω}
\end{align*}
\]

\[P = 10,000 \, \Omega \text{ is the total value of the compensation potentiometer. We then obtain:} \]

\[C_R^0 = 0.03678\]

Compensation values of about 0.03–0.04 are common for natural waters with output resistors of $10^{14} \, \Omega$ for the minor collector and $10^9 \, \Omega$ for the major collector, the mean natural abundance of deuterium being about 150 ppm. Nevertheless, large variations of the compensation values may be observed owing to the relatively large variations of the D/H ratio in natural waters and, more generally, in natural compounds, and to the setting of the mass spectrometer.

Under the chosen working conditions, the H\textsubscript{2} pressure is adjusted to produce a H\textsubscript{2} current of $5 \times 10^{-9} \, \text{A}$ across the major collector. By changing the pressure of the reference, we obtain the compensation values at different H\textsubscript{2} currents (Fig.13) which, extrapolated to zero current, give the value of 0.03522 for the term $C_R^0$ of Eq.(4.25). The difference between the extrapolated value and the value obtained in routine operation at $5 \times 10^{-9} \, \text{A}$ is 0.00156, corresponding to a H\textsubscript{2} contribution to the mass-3 current of 0.00156/0.03522 = 4.43%. This value also corresponds to that of the term $KBpH_2/AC_R^0$ of Eq.(4.25).

We may now compute δD for the sample analysed. From Eq.(4.25) we obtain:

\[\delta D = -23.4 \times 1.0443 = -24.4\%\]

−23.4\% being the uncorrected value of δD.

We now correct for change-over valve leakage and for background contribution (see Section 4.2.6). Assuming that the change-over valve correction factor is 0.992, as for $^{18}\text{O}$ computation (Section 4.3.1.4), we obtain:

\[\delta D = -24.6\%\]
If the background contribution is 2 mV and the total output voltage of mass 3 is 180 mV, \( \delta D \) becomes:

\[
\delta D = -24.6 \left( 1 + \frac{2}{180} \right) = -24.9\%
\]

Assuming now that the laboratory reference has a \( \delta D \)-value of \(-55.0\%\) versus SMOW, we finally obtain:

\[
\delta D_{\text{SMOW}} = -24.9 - 55.0 + (-24.9)(-55.0) 10^{-3} = -78.5\%
\]

If also a secondary reference is used, for which we know that its \( \delta D_{\text{SR}} \) versus the primary laboratory reference is \(-167.9\%\), we obtain under the same working conditions an uncorrected \( \delta D \)-value of \(-157.7\%\). From Eq.(4.26) we then obtain:

\[
\delta D = \frac{-23.4}{-157.7} (-167.9) = -24.9\%
\]

as with the other method. The product of all correction factors corresponds to the ratio between the corrected and the uncorrected \( \delta D \)-values of the secondary reference.

**4.4.2. Method of reduction of water in the mass-spectrometer inlet system**

In this method, developed by Nief and Botter (1959), the water sample (about 1 mg) is vaporized in a heated glass reservoir and a small portion is introduced into the mass-spectrometer system, at a constant rate, through a glass capillary and a quartz tube containing a thin uranium ribbon at 650°C, connected directly to the mass-spectrometer ion source. Thus, the sample is injected as water and passes the capillary leak as water vapour, but enters the mass-spectrometer tube as hydrogen. Reduction of the small amount of water involved is instantaneous and no separate hydrogen preparation step is required.

With this method the reference water and the sample cannot be analysed at the same time. In addition, it is not possible to adjust precisely the pressure of the gas to a predetermined value. Therefore, for each sample, readings of the compensation values of the ionic currents are made at several decreasing gas pressures (i.e. at different voltages of the mass-2 ions) obtained by pumping a part of the inlet system volume and successively allowing the residual-water vapour to expand into this evacuated volume. Afterwards, the exact compensation value for a specific mass-2 voltage is found by interpolation.
The reference water is introduced into the mass spectrometer at regular intervals. In this case, not only the interpolated compensation value at the predetermined pressure is obtained, which should be compared with those of samples, but also the compensation value at zero pressure is computed by extrapolation in order to correct for the \( \text{H}_2 \text{O} \) contribution.

To eliminate memory, which may reach values of 8–9%, each sample should be analysed three or more times, depending on the difference between its D/H ratio and that of the sample analysed immediately before. It is then advisable to run the samples in the order of increasing or decreasing presumable D/H ratios.

In spite of memory effects, the method has the advantage of not demanding a separate line and personnel for sample preparation, and in addition it can be fully automated. The precision obtained is comparable with that of other methods.

A modification of the method has been proposed by Thurston (1970) which also allows of a complete automatization of the isotopic analyses, including change of samples. Memory effects are eliminated by using a slowly increasing pressure system, with rapid measurement being done when a specific gas pressure (\( \text{H}_2 \text{O} \) voltage) is reached.

### 4.5. Reproducibility and Accuracy of Determinations of Stable Isotope Composition of Natural Waters

#### 4.5.1. Reproducibility

The reproducibility of a given determination is expressed by the variance \( \sigma^2 \) (or by its square root \( \sigma \), called standard deviation) of the results \( x_1, x_2, \ldots, x_n \) obtained in \( n \) independent measurements. If the results have a normal (Gaussian) distribution, the variance is given by:

\[
\sigma^2 = \frac{1}{n} \sum_{i=1}^{n} (x_i - x_m)^2 \]

where \( x_m \) is the mean value of all measurements. If \( n \) is small, then the value \( n - 1 \) is used instead of \( n \) at the denominator of the right-hand-side term. The variance of the mean value \( x_m \) is \( \sigma_m^2 = \sigma^2/n \).

If \( y = f(x_1, x_2, \ldots, x_n) \), the variance of \( y \) is related to the variance of \( x_1, x_2, \ldots, x_n \) by:

\[
\sigma_y^2 = \sum_{i=1}^{n} \left( \frac{\partial y}{\partial x_i} \right)^2 \sigma_i^2
\]  

(4.42)
Random errors determining the variability of the final results are associated with each step of the analytical procedure for determining the stable isotope composition of natural waters.

The reproducibility of measurements is, in general, better over a short period, for instance a day or a week, than over a long period. In fact, for a short period, it is more probable that the mass spectrometer and the sample preparation line maintain stable characteristics and that the operator repeats the whole analytical procedure almost exactly in the same way — errors included. Therefore, if small isotopic differences within a set of water samples should be detected, it is advisable to process the samples in the shortest possible period.

4.5.1.1. Reproducibility of the mass-spectrometric measurements

The standard deviation of the mean of individual readings of a mass-spectrometric measurement provides an indication of how stable the instrument is in the working conditions selected and gives an evaluation of the instrumental component with regard to the overall standard deviation of stable isotope analyses.

Let us take, as an example, the $^{18}$O measurement shown in Fig.11. The $\delta^{18}$O-value versus the reference CO$_2$ can be written as:

$$\delta = A\delta' + B$$

where $\delta'$ is the uncorrected value and $A$ and $B$ contain the instrumental correction terms:

$$\delta' = \frac{(P_S - P_R)D + d}{DP_R + d_R} \times 1000$$

$$A = \frac{1.0014}{1-x-y} \left(1 + \frac{b + t}{m_R}\right)$$

$$B = 0.0091 \delta^{13}$C$

The values of the parameters and their standard deviations are given below. The standard deviations of $D$, $d$ and $d_R$ have been computed from the readings of Fig.11; those of other parameters have been assumed according to a reasonable evaluation.
### CHAPTER 4

<table>
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<th>Value</th>
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<td>0</td>
</tr>
<tr>
<td>( P_R )</td>
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</tr>
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<td>( D )</td>
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</tr>
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<td>( x )</td>
<td>0.003</td>
<td>( 3 \times 10^{-4} ) (10%)</td>
</tr>
<tr>
<td>( y )</td>
<td>0.005</td>
<td>( 5 \times 10^{-4} ) (10%)</td>
</tr>
<tr>
<td>( b )</td>
<td>3 mV</td>
<td>0.3 (10%)</td>
</tr>
<tr>
<td>( t )</td>
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</tr>
<tr>
<td>( m_R )</td>
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<td>95 (5%)</td>
</tr>
<tr>
<td>( \delta^{13}C )</td>
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<td>0.2</td>
</tr>
</tbody>
</table>

According to Eq. (4.42), the variance of \( \delta^{18}O \) is the sum of several terms, the values of which are given below:

(a) \( \left( \frac{\partial \delta}{\partial D} \right)^2 \sigma_D^2 = 6.51 \times 10^{-4} \)

(b) \( \left( \frac{\partial \delta}{\partial d} \right)^2 \sigma_d^2 = 8.39 \times 10^{-4} \)

(c) \( \left( \frac{\partial \delta}{\partial d_R} \right)^2 \sigma_R^2 = 4.19 \times 10^{-5} \)

(d) \( \left( \frac{\partial \delta}{\partial x} \right)^2 \sigma_x^2 + \left( \frac{\partial \delta}{\partial y} \right)^2 \sigma_y^2 = 3.96 \times 10^{-5} \)

(e) \( \left( \frac{\partial \delta}{\partial b} \right)^2 \sigma_b^2 + \left( \frac{\partial \delta}{\partial t} \right)^2 \sigma_t^2 + \left( \frac{\partial \delta}{\partial m_R} \right)^2 \sigma_m^2 = 1.62 \times 10^{-5} \)

(f) \( \left( \frac{\partial \delta}{\partial \delta^{13}C} \right)^2 \sigma_C^2 = 3.32 \times 10^{-6} \)
The variance of $\delta$ is therefore $1.55 \times 10^{-3}$ and its standard deviation is 0.040. It appears that only terms (a) and (b) are important.

If the mass-spectrometric measurement is now repeated using $P_s = 792$, the value of $d$ would reduce to $-9.5$ mm. Assuming that $\sigma_d$ remains unchanged, term (a) would reduce to $9.50 \times 10^{-6}$, and, as a consequence, the standard deviation of $\delta$ would drop to 0.031. It is possible therefore to reduce the instrumental error by selecting the value of the compensation resistor for the sample, which minimizes the distance $d$ between the reference and the sample traces.

Values of standard deviation in the ranges $0.02-0.04$ for $\delta^{18}O$ and $0.1-0.3$ for $\delta D$ are normally obtained in routine measurements at the Isotope Hydrology Laboratory of the IAEA.

The long-term reproducibility of the mass-spectrometer measurements can be determined by periodical analyses of the same gas samples. For example, the same two laboratory hydrogen gas references routinely measured one against the other for a period of several months gave a mean $\delta D$-value of $-151.9\%$ and a standard deviation of 0.7.

4.5.1.2. Overall reproducibility of stable isotope measurements

The overall reproducibility of stable isotope measurements, giving an idea of the quality and reliability of the data obtained, is after all the most important parameter to determine. This can be evaluated only be repeated analyses of the same water samples.

As already mentioned, the short-term reproducibility is usually somewhat better than the long-term one. If samples of the same water are analysed, for instance, within the same day, the scatter of results is generally smaller and only slightly dependent on the $\delta$-value. For instance, in a calibration made at the IAEA Isotope Hydrology Laboratory, the $\delta D$-values obtained from eight independent samples of V-SMOW showed a standard deviation of only 0.4%o. On the same day, six samples of SLAP exhibited a standard deviation of 0.6%o, only slightly larger than that of V-SMOW, in spite of the much more negative $\delta D$-value of the SLAP samples with respect to the working reference ($\approx -431\%$).

The same observations were made with the $^{18}O$ determinations. For instance, measurements made on the same day gave a standard deviation of 0.03%o for samples of Vienna Tap Water ($\delta^{18}O \sim -6.5\%$ versus the working reference) and of 0.05%o for samples of SLAP ($\delta^{18}O \sim -49.5\%$).

The standard deviation values reported above for D/H and $^{18}O/^{16}O$ measurements are similar to or only slightly higher than those given by the mass spectrometer alone.

In the long term, the reproducibility of measurements is in general significantly worse, because of difficulties in keeping constant in time the
conditions of the whole analytical procedure. The long-term standard deviation is also dependent on the δ-value of samples, because of multiplicative correction factors which introduce an additional scattering of the results proportional to the δ-value.

For example, the long-term standard deviation of stable-isotope results at the IAEA Isotope Hydrology Laboratory is at present 0.08 for δ18O and 0.8 for δD, as computed from duplicate analyses of samples with δ-values ranging from +5 to −5‰ for oxygen-18, and from 0 to −100‰ for deuterium, with respect to the working references. Practically the great majority of natural water samples analysed in this laboratory have δ-values within the above ranges. For comparison, repeated measurements of SLAP samples, which are much more depleted in heavy isotopes, produce significantly larger long-term standard deviations: 0.22 for δ18O and 1.7 for δD.

The long-term standard deviations quoted above are sufficient for most hydrological applications, but might be insufficient for some particular studies or fields of investigation. For instance, in oceanographic studies a better reproducibility might be desirable, because the isotopic composition of sea-water varies within a narrow range.

A better reproducibility can be achieved with duplicate or triplicate analyses, and with repeated control measurements to correct for any small systematic error, which otherwise would be disregarded and included in the random error. For instance, Craig and Gordon (1965) quote standard deviations of 0.02 for δ18O and 0.2 for δD in their ocean-water routine isotopic determinations.

Duplicate isotopic analyses, normally performed in many laboratories for all or most of the water samples, also help in discovering serious mistakes, like interchange of samples or trace reading and calculation oversights which, although seldom, might occur when many samples are processed daily. These types of error, however, can often be discovered also from a comparison of the deuterium and oxygen-18 results — which are generally correlated in natural waters — or from the whole context of results in a hydrological investigation.

4.5.2. Accuracy of stable isotope results. The problem of intercomparison of results between different laboratories

To obtain good reproducibility of stable isotope analyses does not necessarily mean having accurate results. Accuracy depends in fact on how close the results obtained are to the true values which, however, are usually unknown. In principle, therefore, a given laboratory might produce highly reproducible data, although all are equally different from the true values because of systematic errors inadvertently introduced in the analytical procedure. Such systematic errors could be, for instance, a small but reproducible isotopic fractionation produced in a step of the sample preparation, or an inaccurate evaluation of some correction factors, or an incorrect calibration of the laboratory references.
Obtaining well-reproducible results is, however, a strong indication that the whole analytical procedure is basically correct. In addition, this means that the results are internally consistent and in general can be used for hydrological or geochemical investigations. However, difficulties might arise when comparing the results with those obtained in other laboratories if significant systematic errors occur in the measurements.

Two intercomparison exercises of stable-isotope measurements in natural waters have been organized by the IAEA in which many laboratories took part. The results showed that the agreement was reasonably good in most cases, but not always as good as desirable (Halevy and Payne, 1967; Gonfianti, 1978). At the international meeting organized in 1966 to discuss the first intercomparison results, it was felt that most of the shortcomings were due to the fact that the international reference standard, SMOW, was not physically existing and that the state of preservation of NBS-1, which was the basis for SMOW definition (Craig, 1961), was somewhat questionable. Professor H. Craig, of the University of California, La Jolla, was therefore asked to prepare a large sample of water with isotopic ratios as close as possible to those of the defined SMOW.

The water sample prepared by Craig, called Vienna-SMOW (V-SMOW), was distributed by the IAEA to a number of laboratories, together with NBS-1, NBS-1A and SLAP (see Section 4.1 for details on all these water isotopic standards). The new intercomparison showed that small but significant differences among laboratories were still occurring, but the agreement — especially in the deuterium results — improved significantly if pre-assigned δ-values were attributed to NBS-1A or to SLAP and the remaining results normalized accordingly. Therefore, at the meeting organized in 1976 to discuss the second intercomparison results, it was recommended to adopt for SLAP the δ-values of −55.5‰ for oxygen-18 and of −428‰ for deuterium versus Vienna-SMOW. These values were evaluated from all those submitted, by attributing slightly different weights according to the analytical method used. Although it is impossible to say how accurate these values are, it was the general consensus that this was the best evaluation possible at present.

With the adoption of the V-SMOW/SLAP scale for reporting δ-values, it is hoped that intercomparison of results will improve. This is, after all, the most important objective, irrespective of the accuracy of the recommended values of SLAP versus V-SMOW.

REFERENCES TO CHAPTER 4


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Chapter 5

REVIEW OF THE NATURAL ABUNDANCE OF HYDROGEN AND OXYGEN ISOTOPES

5.1. PRIMORDIAL ISOTOPIC COMPOSITION

Already the early surveys discussed in Chapter 1 established differences in the abundance of hydrogen and oxygen isotopes in various components of the earth's surface materials.

The observed variability in the oxygen and hydrogen isotope abundance of natural materials ranges about ±50‰ around the mean for 18O (see Fig. 17) and from ±300‰ to −500‰ for deuterium. The first question which arises is whether these variations are wholly the result of processes of isotope fractionation within a closed system or whether there are gains and losses of the isotopes in the terrestrial material. In other words, is the total mass of the isotopes conserved, so that the (amount weighted) mean elemental composition on the earth's surface equals that of the primordial composition, or is there a continuous evolution of the isotope abundance in the earth's surface?

Both hydrogen and oxygen isotopes are not, strictly speaking, conservative nuclides. They can be products and reactants in nuclear reactions initiated by natural radioactivity (e.g. the reaction 16O(α, n)23Ne) or by cosmic radiation. Moreover, hydrogen is accreted from the 'solar wind', with isotope abundances which are quite different from the terrestrial ones. This has recently been demonstrated in lunar surface rocks where it results in hydrogen extremely depleted in deuterium (Epstein and Taylor, 1972). It is believed, however, that all these processes play only a very minor role as far as the terrestrial isotope abundance is concerned.

In the case of hydrogen isotopes, the escape from the atmosphere following the photo-dissociation of water molecules in the upper atmosphere (Suess, 1953) seems of greater consequence. Upper atmosphere water vapour is very depleted in deuterium (Suess gave a value of δD = −100‰ to −160‰ for atmospheric hydrogen; Ehhalt (1974) reported values as low as −450‰ for water vapour in the upper troposphere; see also Chapter 6); further fractionation might result from the preferential escape of the lighter isotopic species. One would thus expect the primordial isotopic composition of hydrogen to be depleted relative to the mean isotopic composition of the present-day hydrosphere.

The composition of extra-terrestrial material is a poor guide to the primordial hydrogen isotopic composition because of this contamination by the 'solar wind'. We must, therefore, rely on the composition of deep-seated material which has surfaced to the earth, so-called juvenile material, as a measure of primordial
abundance, assuming that under these conditions there is no fractionation between material derived from the magma and that of the volatile phase. The δD-values for such materials are estimated to be between δD = −50‰ to −65‰; this estimate is based on the isotopic composition of water and hydrogen (gas) collected from the volcano of Surtsey, Iceland, by Arnason and Sigurgeirsson (1968) and on the water content of minerals believed to be of lower crustal or mantle origin (Sheppard and Epstein, 1970). Moore (1970) reports a similar value of δD = −60‰ for water inclusions in basalts erupted on the ocean floor, and further data are presented in the next section.

To the best of present knowledge, the amounts of oxygen isotopes on the earth’s surface are practically invariant. A value for the primordial oxygen isotopic composition may be obtained from the results of analyses of achondritic meteorites and whole ultramafic (igneous) rocks. Since these data are remarkably similar, it has been proposed that they be representative of the nucleo-genetic pool from which the celestial bodies are formed (Eberhardt and Geiss, 1961). The value suggested is between δ18O = +5‰ to +6‰, relative to SMOW. This composition would then, presumably, represent the composition of juvenile waters, i.e. water exhaled from the magma at such high temperatures that isotopes are equipartitioned between the different phases (Boato, 1961). However, recent concepts on the earth’s structure, to be discussed below, cast some doubt on
whether these materials are truly juvenile or contaminated to some extent by subducted and recycled surface material.

In any event, because of the conservative nature of the element, it is expected that the primordial isotopic composition of oxygen equals the weighted average oxygen isotopic composition in all crustal material, the relative depletion of $^{18}$O in the waters of the earth being balanced by its enrichment in the lithosphere and especially in carbonates and other sedimentary rocks.

5.2. DISTRIBUTION OF OXYGEN AND HYDROGEN ISOTOPES IN THE EARTH’S SURFACE MATERIALS

The primary cause for variations in the distribution of isotopes in materials of the earth’s crust is isotopic fractionation between the different minerals, and between minerals and water. Since the fractionation factors increase with decreasing temperature it is not surprising to find the largest deviations from the mean composition in materials produced at relatively low earth surface temperature.

The experimental data on the isotopic fractionation factors for mineral phases, as summarized by Taylor (1974), are not very good; they rely on laboratory studies on the distribution of isotopes in water and the different minerals in which true equilibrium apparently has not always been established. Possibly, the approach of Bottinga and Javoy (1975), which is based on the analysis of natural samples containing at least three coexisting minerals, gives more reliable data. It is found that, at any given temperature, the chemical composition determines the distribution of the isotopic species in the rock-forming minerals. Minerals in which Si–O–Si and C–O–C bonds predominate are richer in $^{18}$O than those containing Si–O–Mg and Si–O–Fe bonds, while minerals with Si–O–Al bonds are even poorer in $^{18}$O (Garlick and Epstein, 1967; O'Neil, 1977). Epstein and Taylor (1967) suggest the following order of minerals in terms of decreasing $\delta^{18}$O-values: quartz, dolomite, alkali feldspar, calcite, plagioclase, muscovite, pyroxene, amphibole, olivine, garnet, biotite, chlorite, ilmenite and magnetite (Fig.18). Since magmatic differentiation tends to enrich the magma in SiO$_2$, this process is accompanied also by an enrichment in $^{18}$O (Fig.18, insert).

The free waters on the earth’s surface are, in contrast to the rock-forming minerals, among the most depleted in $^{18}$O of the earth materials. To a large extent, this depletion is due to the preferred uptake of the heavy-isotope species in the sedimentary rock sequences, putting the latter in the isotopically most enriched part of the terrestrial scale. Within the hydrosphere itself the ocean waters, which of course constitute the major part of all waters on the earth’s surface, are still relatively high in both $^{18}$O and deuterium compared with the meteoric waters. The latter’s formation by low-temperature evaporation from the oceans results in further depletion in the heavy isotope species of both hydrogen and oxygen.
FIG. 18. Range of $^{18}$O-values in the lithosphere.
From general principles, one would expect the rocks formed under high-temperature conditions to show but little deviation from the mean composition of the magma, whereas lower-temperature phases, and in a most pronounced way the aquatic systems, will show relatively larger positive and negative deviation from the mean composition. This is indeed borne out in a general way (Fig. 18). This picture is, however, an oversimplification, with increased complexity introduced by the recycling of materials, especially in sea-water and fresh-water environments; this results in secondary changes in the crustal rocks, including a re-portioning of the isotopic species.

5.3. ISOTOPIC COMPOSITION OF MAGMA AND IGNEOUS ROCKS

Materials which are derived from deep-seated sources, e.g. xenoliths or megacrysts which accompany some types of magma and kimberlites, show a restricted range of $\delta^{18}O$-values. Garlick et al. (1971) observed values between +5 and +5.8‰ in eclogites and xenoliths, very similar to the mean observed value of ultramafic rocks in general (Taylor, 1968). This fact led Sheppard and Dawson (1975) to suggest the upper mantle to be relatively homogeneous as far as oxygen isotopes are concerned.

The regularities in the $\delta^{18}O$-distribution among different rock-forming minerals are reflected in systematic trends in $\delta^{18}O$-values of igneous rocks of different chemical composition.

Fresh unaltered basalts show $\delta^{18}O$-values of between 5.5‰ and 6.5‰ (Taylor, 1968; Muehlenbachs and Clayton, 1972). This range is true for basalts from submarine, oceanic islands as well as continental basalts. With increase of silica content, intermediate rocks (diorite and andesites) are more enriched and show values of up to $\delta^{18}O = +7.4‰$ (Taylor, 1968; Muehlenbachs and Clayton, 1971). Granitic rocks may be enriched up to a value of $\delta^{18}O = +13‰$ (Taylor, 1968, 1977; Taylor and Magaritz, 1978).

Two different processes may mask the simple systematics of isotopic composition of igneous rocks: 1. interaction with meteoric water or sea-water, and 2. assimilation of crustal material into the magma. The existence of low-$\delta^{18}O$ magmas had been shown in several studies (Taylor and Forester, 1971; Muehlenbachs et al., 1974; Friedman et al., 1974, and others). Rocks with values as low as $\delta^{18}O = -4‰$ are typically found in regions where extensive hydrothermal alterations have taken place, as discussed below. Since this isotopic effect cannot be explained simply through inflow of water into the magma chamber, one has to hypothesize that many of those magmas are produced by re-melting of the hydrothermally altered roof above the magma chamber.

Assimilation of crustal material is another factor which influences the $\delta^{18}O$-values of igneous rocks. This phenomenon of melting of the crust has been
suggested by Taylor and Turi (1976) in the Tuscan province, Italy, where rocks with $\delta^{18}O$-values as high as $\delta^{18}O = +13.4\%_o$ are found. The formation of magmas by melting or large-scale assimilation of high-$^{18}O$ argillaceous sedimentary rocks is indicated. Similar enrichment was reported by O’Neil and Chappel (1977) for the Berriedale batholith in NSW, Australia. A different environment in which sediments may be assimilated into a magma are the subduction zones. Magaritz et al. (1978) reported on high-$^{18}O$ rocks, up to $+15\%_o$ in $\delta^{18}O$, from the Banda arc, Indonesia: in this area there is no continental crust and the only source for high-$^{18}O$ material could be the subducted sediments from the Australian continent.

The more recent concepts related to plate tectonics are resulting in a re-evaluation of much of the isotope data for igneous rocks. For example, the hydrogen isotopic composition of hydrous phases from kimberlites, carbonatites and volcanic gases (H$_2$O), found to be between $\delta D = -50\%_o$ and $-80\%_o$ (Sheppard and Dawson, 1975), had been assumed to correspond to a 'juvenile pool'. However, this range is similar to that found in other magmatic rocks which are formed in the crust or mantle (Taylor, 1974; Magaritz and Taylor, 1976a). Isotopic measurements on high-pressure metamorphic rocks led Magaritz and Taylor (1976b) to suggest that this range of $\delta D$-values represents just the total dehydration of subducted material, subsequently cycled through the upper mantle.

What is then the composition of truly juvenile material? Samples from the ancient gneiss complexes (older than 3.3 billion years) in Swaziland and Rhodesia are relatively low in deuterium, i.e. $\delta D = -90\%_o$ to $-120\%_o$ (Taylor and Magaritz, 1975). One possibility suggested is that the water in this ancient gneiss was in fact derived from ‘juvenile’ waters. The composition of such water could be accounted for by the upper mantle not yet being heavily contaminated with hydroxylic minerals from the subducted oceanic lithosphere.

5.4. METAMORPHIC ROCKS AND ‘FOSSIL’ HYDROTHERMAL SYSTEMS

Metamorphism of sedimentary and igneous rocks involves the interaction between the constituent minerals of such rocks. These reactions take place without melting, but in the presence of a fluid phase composed of H$_2$O and CO$_2$. In the course of metamorphism the isotopic composition of oxygen and hydrogen of the minerals is changed. However, in many cases isotopic equilibrium between the phases is not achieved, especially at lower temperatures (Magaritz and Taylor, 1976b). The temperature at which the isotopic composition is ‘frozen in’ may actually be different for each mineral in the rock (Schwarcz et al., 1970).

Taylor et al. (1963) showed that during the metamorphic event the trend in an assemblage of rocks of igneous and sedimentary origin is for large-scale homogenization: igneous rocks become enriched in $^{18}O$, whereas sedimentary
rocks become depleted. Similar trends have been found during low-grade metamorphism by Magaritz and Taylor (1976b).

An extreme case was reported by Shieh and Schwarcz (1974) in the Greenville Province in Canada, where large areas of igneous and metamorphic rocks are found to be abnormally low in \(^{18}\text{O}\), indicating that very large quantities of \(\text{H}_2\text{O}\) or \(\text{CO}_2\) were involved in the metamorphism.

Evidence regarding hydrogen and oxygen isotopes indicates interaction of meteoric groundwater with certain epizonal plutons (those emplaced at relatively shallow depths in the crust) during their crystallization and cooling stages (Taylor, 1968; Taylor, 1971; Taylor and Forester, 1971). These isotopic criteria are powerful, particularly in regions where pluton emplacement occurs in highly fractured, relatively flat-lying, volcanic rocks and where large differences existed in isotopic composition between the different fluids at the time of pluton emplacement. The interaction between an intrusion and the groundwater creates a convective flow due to the heat emanating from the crystalline rocks.

The largest hydrothermal system so far reported was found to be related to batholithic intrusions of western North America (Magaritz and Taylor, 1976a). These systems are orders of magnitude larger than the near-surface intrusion; the depth of the hydrothermal system has to be greater than 6 km. Across central British Columbia, the width of the system is about 400 km, from the upper part of the Tertiary batholith in the west, across a broad zone, to the east. The rocks affected by the hot meteoric waters include not only volcanic rocks but also graywackes and shales. The largest oxygen exchanges were found in dike rocks, suggesting them to be pathways for the hydrothermal solutions.

5.5. ISOTOPE ABUNDANCE IN SEDIMENTARY ROCKS: RECENT OCEANIC SEDIMENTS

The minerals forming in the oceanic environment are, as a group, the most enriched in \(^{18}\text{O}\) among the earth's materials. Silica precipitated biochemically or chemically from ocean water is enriched up to 38‰ in \(^{18}\text{O}\) compared with the water, and carbonates are enriched up to 36‰. Biogenic silicates show an average \(\delta^{18}\text{O}\)-value of 38‰ (Mopper and Garlick, 1971). \(\delta^{18}\text{O}\)-values in silica, found in deep cores as opal-CT or microcrystalline quartz, range between 34 and 37‰ (Knouth and Epstein, 1975). These higher values obviously are related to the increase in isotopic fractionation factors at low temperatures.

Chemically precipitated aragonite and high-magnesium calcite, which is found in most of the oceanic sediments, are in isotopic equilibrium with sea-water; the large variations in isotopic composition (between 27‰ and 35‰) found in marine biogenic carbonates (Gross, 1964; Weber and Schmalz, 1968) are attributed to the fact that most of the biogenic minerals are deposited under non-equilibrium
conditions. Other variations in $\delta^{18}O$ found in species where isotopic equilibrium is established have been claimed to be related to changes in the isotopic composition of the oceans over the geological time-span and to ocean temperature changes (Emiliani, 1966; Hays et al., 1976).

During diagenesis and the rock-formation processes, carbonate minerals are dissolved and re-precipitated in the form of more stable phases. In most cases, the diagenesis took place in water, brackish or meteoric, which differs in its $\delta^{18}O$-values relative to the original marine solution. This fact may result in a lowering of $\delta^{18}O$-values in the carbonate minerals by up to 20‰, depending on the specific conditions. Gross (1964) has demonstrated in a study of the diagenetic history of Bermudan carbonates that the mineralogical and facies changes were accompanied by progressive enrichment in oxygen-16. Similarly, Gavish and Friedman (1969) and Magaritz et al. (1979) showed that, as cementation and recrystallization proceeds in the Holocene-Pleistocene sequence of the Israeli Coastal Plain, the $\delta^{18}O$-values in the carbonates are lowered from 32‰ to 26‰.

Savin and Epstein (1970) reported that the carbonate-free fraction of ocean sediments ranged from 11.5‰ to 28.5‰ in $\delta^{18}O$ and the $\deltaD$-values ranged from $-55‰$ to $-87‰$. These authors also noted that the clay minerals of detrital origin reflect the province and mode of origin of those minerals.

5.6. RECENT CONTINENTAL SEDIMENTS

Most of the surface of the continents is covered by one or other type of soil. Soil in general is a mixture of detrital material and authigenic phases. Oxygen and hydrogen isotopic compositions make it possible to determine the origin of these components.

Lawrence and Taylor (1971, 1972) made extensive studies of the D/H and $^{18}O/^{16}O$ ratios in soil minerals and showed that the isotopic variations in modern soils, which are formed on igneous parent rocks, show a marked parallelism to the variations of local meteoric waters (see Chapter 6). This parallelism indicates that the new in-situ clay minerals and hydroxides are formed more or less in isotopic equilibrium with the coexisting waters. However, quartz in Hawaiian soils is derived from atmospheric dust and its oxygen isotopic composition ($\delta^{18}O = +18‰$) is similar to the quartz in the pelagic sediments.

Salomons et al. (1975) also showed that the clay fraction in recent land sediments in Western Europe is of marine origin and that the $\delta^{18}O$-values range between +15.8 and +21.7‰. For older palaeosols, formed on granitic rocks of south-western England, Sheppard (1977) showed that the kaolinite had been altered by meteoric waters in a tropical climate during Cretaceous-Tertiary times.

The isotopic composition of carbonates in soils is even more difficult to interpret, since soil carbonates represent a mixture of several generations of
formation and of authigenic and detrital phases. Magaritz (1974) suggests that when the bed-rock is dolomite, the authigenic calcite in the soil can be separated chemically from the bed-rock material and by measuring its $\delta^{18}O$-value the 'in-situ' carbonate species can be characterized. Isotopic values thus found in soil calcites suggest the caliche carbonates to form by evaporation of soil water.

Speleothems, another carbonate type, are deposited in the unsaturated zone from meteoric waters. Variations of $\delta^{18}O$-values in these cave carbonates are quite large and are believed to be due mainly to changes in the composition of the meteoric waters which percolate through the rocks; in this connection, speleothems are of value in palaeoclimatic studies. However, some kinetic isotopic fractionation seems to occur during deposition; Hendy (1971) has suggested methods for recognizing equilibrium deposition in speleothems.

Variations of $\delta^{18}O$ of cave carbonates were reported by Hendy (1971) for New Zealand and by Duplessy et al. (1970) for the last interglacial epoch in Europe. In most of these cases there is no direct way to relate changes in carbonate composition to changes in the composition of the waters from which the carbonates were deposited because of possible temperature changes which would also affect the isotopic composition of the sediment. To overcome this problem, Schwarcz et al. (1976) suggested to measure the D/H ratios in the fluid inclusions of the stalagmites and then to estimate the $\delta^{18}O$-values on the basis of the known relationship between $^{18}O$ and D-values in meteoric waters (see Chapter 6).

Secondary calcite, formed near glacial areas, has rather singular $\delta^{18}O$ and $\delta^{13}O$-values and can be recognized through such data. Magaritz (1973) found high $^{13}O$-values and very low $^{18}O$-values in carbonates from the Alps and also from Mont Hermon. Similarly, Schmidt and Friedman (1974) identified 'glacial' carbonates in the Permian of Gondwanaland, using isotopic data.

Carbonates in lake sediments likewise contain some authigenic phases, which can be distinguished from detrital phases whose isotopic composition matches that of the country rock and soils of the drainage area. The authigenic carbonate can be a chemical precipitate or of biogenic origin. Fritz and Poplawski (1974) showed fresh-water mollusks to be in isotopic equilibrium with the lake-water in which they grow. Similarly, Covich and Stuiver (1974) showed that $\delta^{18}O$-values in a molluscan population of a tropical lake can be used as monitor for the degree of evaporation of the lake water. In Lake Kinneret, which is a warm-water lake, it was shown by Stiller (1976) that the authigenic carbonates, whose $\delta^{18}O$-values range from $+29\%$ to $+28\%$, are in equilibrium with the water in spring time, which is the period when these carbonates precipitate.

In extremely saline lakes of East Africa, where chert precipitated, O'Neil and Hay (1973) measured variations of $13\%$ in $\delta^{18}O$ (ranging from 31 to $+44\%$). These values correlate in general with lake salinities as inferred from geological evidence.
Some hypersaline lakes deposit dolomite; these dolomites in many cases have oxygen isotopic compositions which are similar to those of the coexisting calcites (Degens and Epstein, 1964). On the other hand, Aharon et al. (1977) found dolomite in the 'Solar Lake', Gulf of Elat, to be enriched in $^{18}$O, and the aragonite which coexists with it to be depleted of $^{18}$O by 3–4‰. They concluded that the dolomite replaced the aragonite under conditions similar to those prevailing at present, i.e. at temperatures of $\sim 50^\circ$C and with water whose composition was $\delta^{18}$O = +11‰.

Another common evaporitic mineral whose isotopic composition relates to the water cycle is gypsum, which carries some 'memory' of both hydrogen and oxygen isotopes in its hydration waters (the oxygen in sulphate ion is not readily exchanged by water, except under very acid conditions or when the sulphate undergoes a rapid cycle of reduction and oxidation — Fontes and Pierre, 1977). Sofer (1978) found gypsum, which is formed as a primary evaporite, with highly enriched $\delta^{18}$O and $\delta^D$-values, reflecting the enriched composition of the mother brines. However, massive gypsum deposits, which are formed through secondary hydration of anhydrite, show the depleted isotopic composition of the local meteoric waters, which are further slightly changed by the isotopic fractionation between the water and the crystal phase (see Chapter 2). As a result, very unique excessive deuterium isotopic compositions appear. Fontes et al. (1967) concluded from the isotopic composition of hydration water of gypsum in the Paris basin that these deposits were formed through evaporation of rain-water. It has been realized, though, that the hydration water in gypsum is easily exchanged with ambient waters. The primary composition is better preserved under arid conditions (Sofer, 1978).

5.7. ANCIENT SEDIMENTARY ROCKS

When a mineral is removed from its environment of formation, epigenetic isotopic exchanges can occur. These effects are minimal in the case of silicate minerals, but the exchanges are fairly rapid and extensive in carbonates.

Yeh and Savin (1976) showed that the $^{18}$O/$^{16}$O ratios of coarse clay fractions (>0.1 mm) show no alteration effect in sea-water during a period of several million years. Carbonate reached isotopic equilibrium with hydrothermal fluids at temperatures as low as 150°C (Clayton et al., 1968). By contrast, quartz is remarkably resistant to temperatures as high as 340°C. However, some change occurs, even at lower temperatures, over a long period of time. Degens and Epstein (1962) showed that the $\delta^{18}$O-values in both carbonates and cherts of the Cambrian were lower by more than 10‰ compared with modern sediments, because of post-depositional re-equilibration with surface or subsurface waters.
With regard to carbonates, two processes are noted: one of recrystallization and another of oxygen exchange. Whether these are two separate processes or not, is still being debated. Keith and Weber (1964) concluded that "post-depositional recrystallization and oxygen exchange in the presence of water different from those of the original environment" lowered the $\delta^{18}O$-value of the marine limestone to $\delta^{18}O = +20\permil$ (from the original values of +30 to +36\permil). The conclusions of Degens and Epstein (1964) and Fontes et al. (1970) were similar. Savin (1967), using diffusion coefficient data, estimates that diffusion may cause a change in the isotopic composition of fine-grained rocks during 1 to 10 million years. Magaritz (1975), who investigated the oxygen and carbon isotopic composition of Turonian limestone from Israel, concluded that the $\delta^{18}O$-values of rocks were depleted (+25\permil on average), regardless of evidence for recrystallization, and that they matched the composition of the fresh-water calcites (cave carbonates and veins, etc.) in this unit. These data suggested that $\delta^{18}O$ can change without recrystallization of the mineral.

The $\delta^{18}O$-values of palaeozoic dolomites range between +34\permil and +24\permil. In most of the cases, the dolomite is enriched in $\delta^{18}O$ compared with the coexisting calcite. Is this effect evidence for different conditions of formation of these minerals or is it related to different exchange rates? The answer is not known. Fritz and Jackson (1972) suggest the ocean to have been depleted by 5--7\permil in $\delta^{18}O$ during the Palaeozoic; evaporative palaeozoic dolomites have $\delta^{18}O$-values of between +30 and +25\permil, late diagenetic dolomites have $\delta^{18}O$-values of +17\permil.

Moving to older rocks, Perry and Tan (1972) found a range of $\delta^{18}O$-values of from 8 to 16\permil for old pre cambrian dolomites and from 11 to 19\permil for chert. These data indicate to Perry and Tan that ocean waters at that time were depleted by 15\permil relative to present values. On the other hand, Yeh and Epstein (1978), who also analysed the D/H ratio in similar cherts and who based their conclusions on a correlation between $\delta^{18}O$ and $\delta D$-values, suggested that the temperature of the ocean has decreased from 75 to 30°C, from the early Precambrian to the early Palaeozoic, and that no major shift in its isotopic composition had taken place.

We believe that there is so far insufficient evidence for postulating a change in ocean-water composition over the geological time-span, and that most data can be explained by the post-depositional exchange of oxygen isotopes with formation waters, hydrothermal sources or flushing by meteoric waters. The effect of such interaction on the isotopic composition of the formation water is well documented (Fleischer et al., 1977). Marine carbonates in contact with formation waters in deep wells at temperatures of between 40 and 70°C show appreciable oxygen shifts in both the water and rock, and at times reach isotopic equilibrium.
5.8. OCEAN WATER

The SMOW scale was based on the average composition of the present ocean water, since the ocean basins constitute the major water reservoir on the earth’s surface. The isotopic variations within the oceans are relatively minor and in most cases do not exceed ±2‰ in $\delta^{18}O$. Such variations as are encountered are the result of interaction with fresh water of meteoric origin, which by and large is much depleted relative to ocean water. In those surface ocean waters where evaporation exceeds both precipitation and run-off from adjoining continental areas the heavy isotope species are slightly enriched. A mean value for ocean surface waters was estimated by Craig (1965) to be $\delta^{18}O = +0.5‰$. The highest $\delta^{18}O$-values are encountered in semi-enclosed basins in arid zones, such as the Persian Gulf, the Red Sea and, to a somewhat slighter extent, the Mediterranean Sea. Values of $\delta^{18}O = +2‰$ for a salinity of $S = +42‰$ were reported (Craig, 1966). As the enrichment of the oxygen heavy isotope is the result of evaporation into slightly undersaturated air masses the commensurate enrichment of deuterium was found along an evaporation line of slope $S = \Delta D/\Delta^{18}O \sim 6$ (Craig, 1966).

In contrast, low $\delta$-values are characteristic of ocean masses close to the outflow points of major river systems, such as off the mouth of the Amazon River, the Black or Baltic Seas, and, in particular, along the ice shelves of the northern Atlantic (Epstein and Mayeda, 1953). In the northern Atlantic a very good linear correlation between isotopic and salinity data was established, and similar linear curves seem characteristic of other ocean areas (e.g. the Red Sea, Craig, 1966).

The usefulness of the isotopic data in the ocean environment results from the slightly different correlations between heavy isotope enrichment and salinity build-up, which are established in different areas of the ocean because of different evaporative (air and sea interaction) regimes. In particular, however, these are due to the fact that the circumpolar current, which plays a major role in deep-water formation of the major oceanic basins, is influenced by freezing and melting of sea-water. The latter process changes the salinity but has little effect on the isotopic composition, because $\alpha^*$ for ice--water transition is smaller by almost one order of magnitude than the fractionation in the liquid--vapour case (see Table IV, Chapter 2). These relationships are well brought out in Fig.19, adapted from Craig and Gordon (1965), which summarizes the composition of the major oceanic water masses.

The changes of the isotopic composition of the oceans during the glacial and interglacial stages of the Pleistocene and during the more distant past are of great interest, because of their bearing on the interpretation of isotopic data from ocean sediment and ice cores for palaeoclimatic purposes. It is assumed that the change in ocean-water composition during the Pleistocene is due mainly to the immobilization, or melting, of water on glaciers and on the ice caps. As glaciers are made up predominantly of rather depleted meteoric waters, one would expect
an increase in the $^{18}$O-content of sea-water during the glacial stages and a decrease during non-glacial epochs.

Craig (1965) has estimated a correction of $-0.5\%$ ($\delta^{18}$O) for ice, to be added to the mean ocean composition because of the melting of water nowadays immobilized on the Greenland and Antarctic ice caps. He further estimated a correction of approximately $+1\%$ in $^{18}$O to account for the period of a glacial maximum. The total glacial increment of ocean-water composition of $1.5\%$ would be equivalent to an apparent temperature effect of $6^\circ$C, based on the palaeo-temperature scale of Urey et al. (1951), if not corrected for.

The commensurate change in $\delta D$ is easily obtained by considering that the water abstracted from, or added to, the ocean has an isotopic composition which lies on the meteoric water line at about $\delta^{18}$O $= -30\%$ (Craig, 1965). The resultant slope of the 'glacial increment line' in the $\delta D - \delta^{18}$O space is thus found to be approximately

$$\frac{\Delta \delta D}{\Delta \delta^{18}\text{O}} = \frac{-230}{-30} \sim 7.6$$

The meagre evidence for changes of isotopic concentration over longer geological time-spans has been presented at the end of the previous section. We
believe that there is, to date, no clear-cut evidence about far-reaching changes in the mean isotopic composition of the ocean, except for those resulting from glaciation and ice melting.

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Chapter 6

ATMOSPHERIC WATERS

6.1. INTRODUCTION

The major changes in the isotopic composition of natural waters occur in the atmospheric part of the water cycle and in surface waters which are exposed to the atmosphere. Soil and subsurface waters 'inherit' the isotopic characteristics of the meteoric and surface water inputs and further change but little, except as a result of mixing with waters of a different composition.

Like many atmospheric properties, the isotopic composition of atmospheric water vapour and precipitation is quite varied. However, individual rainfall events leave little impression on most hydrological systems because of the latter's size and inertia. From the point of view of the hydrologist or limnologist, it is thus usually sufficient to have longer-term averaged data of the composition of precipitation\(^1\), in the form of both rain and snow, which can be taken to be the input into the hydrological and ocean systems. The global IAEA/WMO precipitation network was designed to provide such averaged 'climatic' characterization of precipitation, based on monthly composite precipitation samples. The international network data are supplemented by a number of local surveys, often carried out over a limited time-span, in conjunction with specific hydrological studies.

The early data of the IAEA network were discussed by Dansgaard (1964) who gave a salient phenomenological evaluation of these data. The degree of depletion of heavy isotopes was related to geographical parameters, such as latitude, altitude, distance from the coast, and intensity of precipitation (the so-called latitude, altitude and amount effects), all of which are a measure, in one form or another, of the degree of rain-out of moisture from any air mass. A detailed meteorological interpretation seemed to be beyond the capabilities of evaluation of the not sufficiently detailed data; this seems to be true even today. Individual meteorological elements, such as single rain-storms, were sampled occasionally; the results serve mainly to emphasize the underlying complexity of the averaged monthly data. However, in recent studies on hurricanes and hailstone growth, a more detailed insight into these meteorological phenomena is emerging.

\(^1\) Except for small run-off basins; in this case, Mook et al. (1974), Sklash et al. (1976), Blavoux (1978) and Levin et al. (1980) were able to take advantage of the variability in the isotopic composition of individual rainfall events for studying these systems.
FIG. 20. Stations co-operating in the IAEA-WHO network for the determination of the isotopic composition of precipitation.
Surface water-bodies respond to the isotopic composition of atmospheric waters by means of molecular exchange with the atmospheric moisture. Unfortunately, information on the isotopic composition of water vapour in the atmosphere is very scanty, because of the difficulty of continuous water vapour sampling in a way which avoids fractionation between isotopic species. This subject is reviewed towards the end of this chapter.

6.2. STABLE ISOTOPES IN PRECIPITATION: DATA FROM THE IAEA NETWORK

The IAEA, in co-operation with WMO, has been conducting a world-wide survey of hydrogen and oxygen isotopes in precipitation since 1961, in order to provide basic data for hydrological application of environmental isotopes. The global network selected for this purpose consisted of a total of 144 stations, of which 65 are still operative; their locations are shown in Fig.20. From these stations, monthly composite samples are collected\(^\text{11}\). These stations include island stations (including weather ships), stations situated near coasts and some inland continental stations.

The majority of the island stations are in the equatorial belt (20°N – 20°S) where the average monthly temperatures (for these stations) range between 23 and 28°C, and the average monthly rainfall is between 100 and 300 mm. The majority of the coastal stations are located between 40°N and 10°S, and the continental stations are rather uniformly distributed between 70°N and 30°S. Both coastal and continental stations in the network present a wide range of variation in average temperature and rainfall. Most of the stations are located between sea-level and 100 m a.s.l., and about 20% are located above 500 m.

The mean values of stable-isotope composition of precipitation, listed in Table VIII, represent the entire period of observation for each station, with a minimum of about 40 monthly data. The 'mean' values are the simple

\(^{11}\) The sampling instructions call for the use of the standard WMO rain gauge. The daily water yield is poured into a large, well-stoppered bottle, where a whole month's collection is accumulated. At the end of the month an aliquot is sent for isotopic analysis. Before 1973, most analyses were performed at the Geophysical Isotope Laboratory of the University of Copenhagen. At present, this is done mainly at the Isotope Hydrology Laboratory of the IAEA in Vienna, with a number of laboratories in France, India, Israel, New Zealand, South Africa, Sweden, USA and USSR co-operating. The \(^\text{18}O\), deuterium and tritium content as well as rainfall amounts, mean monthly temperatures and humidities for these stations are regularly published in the IAEA Technical Reports Series (TRS No.96, 1969; No.117, 1970; No.129, 1971; No.147, 1973; No.165, 1975; No.192, 1979).

Text continued on page 113.
## TABLE VIII. ISOTOPIC AND CLIMATIC DATA FOR STATIONS BELONGING TO THE IAEA/WMO NETWORK

<table>
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<tr>
<th>Stations</th>
<th>Mean values</th>
<th>Weighted mean values</th>
<th>Temperature</th>
<th>Average yearly precipitation (mm)</th>
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<td>$\delta$D (%)</td>
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<tr>
<td>Adelaide, Australia</td>
<td>-3.22</td>
<td>8.62</td>
<td>-17.0</td>
<td>331.90</td>
</tr>
<tr>
<td>Melbourne, Australia</td>
<td>-4.78</td>
<td>4.98</td>
<td>-25.8</td>
<td>329.78</td>
</tr>
<tr>
<td>Djakarta, Indonesia</td>
<td>-4.76</td>
<td>3.49</td>
<td>-27.1</td>
<td>209.85</td>
</tr>
<tr>
<td>Djajapura, Indonesia</td>
<td>-6.43</td>
<td>2.44</td>
<td>-42.3</td>
<td>155.81</td>
</tr>
<tr>
<td>Manila, Philippines</td>
<td>-5.10</td>
<td>7.22</td>
<td>-32.9</td>
<td>361.27</td>
</tr>
</tbody>
</table>
FIG. 21. Distribution of mean $^8$O of precipitation (based on stations having at least 2 years of record).
arithmetic mean of monthly $\delta^{18}$O-values. The 'weighted mean' value for each station is computed as follows:

$$\bar{\delta}_w = \frac{\sum_{i=1}^{n} P_i \delta_i}{\sum_{i=1}^{n} P_i}$$

where $P_i$ and $\delta_i$ denote the monthly precipitation and its $\delta$-value. The difference between the two means is not generally significant for stations with a rather uniform monthly distribution of rainfall, but the weighted mean values are more appropriate indexes for tracer-input considerations in hydrological applications. As can be seen from Table VIII, the range for the weighted mean values is $-1.2\%$ to $-25.17\%$o for $\delta^{18}$O, and $+1.0\%$o to $-185.9\%$o for $\delta$D.

The world-wide distribution of oxygen-18 in precipitation is shown in Fig.21. This map gives a general impression and should not be used for interpolation between data points, since local climatic and topographical features may cause local distortions of the regular isotope pattern.

The factors discussed by Dansgaard (1964) can be well recognized in these data. Stations located at higher latitudes, both in the northern and southern hemisphere, present more negative $\delta^{18}$O-values than those located near the equator. This is illustrated in Fig.22, where the mean isotopic composition of precipitation at each station is plotted against the latitude. For example, the latitude effect over the North American continent is about $-0.5\%$o per degree of latitude for $\delta^{18}$O.

Another factor is the location of the stations relative to the oceans. The mean $D$ and $^{18}$O concentrations of precipitation are generally lower in continental stations than in coastal and island stations located at comparable latitudes. The relationship between the stable-isotope composition of precipitation and the distance from the sea is illustrated in Fig.23, where the distribution of weighted mean values for island, coastal and continental stations is shown in the form of cumulative probability distributions. It is clearly apparent that the isotopic content of precipitation at continental stations has more negative $\delta^{18}$O-values than that of precipitation at island stations. The distribution curve for the coastal stations lies in between, as would be expected.

However, the gradient for continental stations varies considerably from area to area, and in the same area during the different seasons of the year. For example, in Western Europe the rate of depletion of heavy isotopes in precipitation as a function of distance from the coast is reduced in summer as compared with winter. This was interpreted by Eichler (1964) as being due to re-evaporation
FIG. 22. Mean δ¹⁸O of precipitation as a function of latitude.
of precipitation in summer. In the Amazon basin, the mean isotope gradient is extremely small, i.e. $-0.75 \times 10^{-3}\%{}^o\cdot \text{km}^{-1}$ (Salati et al., 1979), as compared with a four times higher value on the European continent (Sonntag et al., 1976).

Another aspect of spatial variations in the stable-isotope composition of precipitation, which is of practical significance for hydrological applications, is the altitude effect. In a given region, the $\delta$-values of precipitation at higher altitudes generally will be more negative. The magnitude of the effect depends on local climate and topography, with gradients in $\delta^{18}O$ of between 0.15 and 0.5%/100 m and gradients in $\delta D$ of between about 1.5 and 4%/100 m considered to be typical. An example of the altitude effect is given in a study by Payne and Yurtsever (1974), where the average rate of depletion is $-0.26\%{}^o (\delta^{18}O)/100 \text{ m}$.

In an attempt to derive a relationship between the mean isotopic composition of precipitation and basic geographical and climatological parameters, multiple linear regression analyses are performed. In these analyses, mean values of $\delta^{18}O$
### TABLE IX: RESULTS OF MULTIPLE LINEAR REGRESSION ANALYSES

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Independent variables used</th>
<th>Regression equation</th>
<th>Multiple correlation coefficient</th>
<th>Standard error of estimate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{18}O$ (‰)</td>
<td>T, P, L, A</td>
<td>$\delta^{18}O = -18.72 + 0.597 \delta^{18}T - 0.00593 \delta^{18}P + 0.00084 \delta^{18}L - 0.00077 \delta^{18}A$</td>
<td>0.833</td>
<td>$\pm 2.87$</td>
</tr>
<tr>
<td>$\delta^{18}O$ (‰)</td>
<td>T, P, L</td>
<td>$\delta^{18}O = -16.28 + 0.454 \delta^{18}T - 0.0067 \delta^{18}P + 0.00083 \delta^{18}L$</td>
<td>0.828</td>
<td>$\pm 2.90$</td>
</tr>
<tr>
<td>$\delta^{18}O$ (‰)</td>
<td>T, P</td>
<td>$\delta^{18}O = -11.78 + 0.418 \delta^{18}T - 0.0084 \delta^{18}P + 0.00084 \delta^{18}L$</td>
<td>0.821</td>
<td>$\pm 2.92$</td>
</tr>
<tr>
<td>$\delta^{18}O$ (‰)</td>
<td>T</td>
<td>$\delta^{18}O = -12.18 + 0.390 \delta^{18}T - 0.0091 \delta^{18}P + 0.0007 \delta^{18}L$</td>
<td>0.815</td>
<td>$\pm 2.96$</td>
</tr>
</tbody>
</table>

Mean $\delta^{18}O$:
- T, P, L, A: $-18.16 + 0.614 \delta^{18}T - 0.00513 \delta^{18}P + 0.00051 \delta^{18}L + 0.00071 \delta^{18}A$
- T, P, L: $-16.74 + 0.483 \delta^{18}T - 0.0067 \delta^{18}P + 0.00084 \delta^{18}L$
- T: $-11.88 + 0.390 \delta^{18}T - 0.0091 \delta^{18}P + 0.0007 \delta^{18}L$

Weighted mean $\delta^{18}O$:
- T, P, L, A: $-18.46 + 0.554 \delta^{18}T - 0.00593 \delta^{18}P + 0.00084 \delta^{18}L - 0.00077 \delta^{18}A$
- T, P, L: $-17.24 + 0.483 \delta^{18}T - 0.0067 \delta^{18}P + 0.00084 \delta^{18}L$
- T: $-11.99 + 0.385 \delta^{18}T - 0.00532 \delta^{18}P - 0.0022 \delta^{18}L$

*T = average monthly temperature (°C), P = average monthly precipitation (mm), L = latitude (degrees), A = altitude (metres, a.s.l.).*
FIG. 24. Relationship between mean $\delta^{18}O$ of precipitation and yearly average temperature for continental stations.

FIG. 25. Relationship between mean $\delta^{18}O$ of precipitation and yearly average temperature for coastal and island stations.
FIG. 26. Relationship between mean monthly $\delta^{18}O$ of precipitation and average monthly rainfall for island stations in the equatorial belt.
are taken as the dependent variable and are related to several selected independent variables with a linear equation of the type

$\overline{\delta^{18}O} = a_0 + a_1T + a_2P + a_3L + a_4A$

where $T$ is the average monthly temperature (°C), $P$ is the average monthly precipitation (mm), $L$ is latitude (degrees), $A$ is altitude (in metres a.s.l.), and $a_0, a_1, a_2, a_3, a_4$ are the regression coefficients. Using the data available from 91 network stations, as listed in Table VIII, the regression equations are computed, beginning with four independent variables and then eliminating them progressively. The results of these analyses are summarized in Table IX. It is evident that the spatial variations in the mean isotopic composition of precipitation of network stations are essentially correlated to the temperature variations. The correlation to the other parameters is not significant. The partial correlation coefficient of mean $\delta^{18}O$ for average monthly temperature is 0.815, for average monthly precipitation it is 0.303, for latitude it is $-0.722$, and for altitude it is 0.007. The use of latitude as an additional parameter besides temperature in regression analyses does not improve the correlation with mean $\delta^{18}O$ because these parameters are linearly correlated, with a correlation coefficient of $-0.938$. The apparently poor correlation observed between mean $\delta^{18}O$ and altitude appears to be an artifact, however, and is due mostly to the fact that a great majority of the stations are located at low altitudes. In any event, the spatial variations in the mean isotopic composition of precipitation observed at the network stations taken as a group are mainly due to the temperature effect. This is illustrated in Figs 24 and 25, where the mean $\delta^{18}O$ values are plotted versus mean temperature — in Fig. 24 for continental stations and in Fig. 25 for island and coastal stations.

The above general findings are true on a global scale, using data from all the network stations. However, on a regional scale, either the amount effect or the evaporation effect may be equally important factors in determining the spatial isotopic variations. For example, in Fig. 25, there are more negative mean $\delta^{18}O$-values in one group of stations which deviate from the general $\delta^{18}O$—temperature relation, apparently because these stations have significantly higher mean precipitation values. The amount effect is clearly illustrated in Fig. 26, where the mean $\delta^{18}O$-values are plotted against average monthly precipitation for all tropical island stations having comparable average temperatures. The least-squares fit to these data is:

$\overline{\delta^{18}O} = (-0.015 \pm 0.0024)P - (0.047 \pm 0.419)$

with a correlation coefficient of $r = 0.874$ and a standard error of estimate of $\pm 0.783\%$. Thus, the percentage of variation in mean $\delta^{18}O$-values at these
TABLE X. $\delta^{18}O-\delta D$ RELATIONSHIPS FOR ISLAND, COASTAL AND CONTINENTAL STATIONS USING LONG-TERM MEAN VALUES

<table>
<thead>
<tr>
<th></th>
<th>$n$</th>
<th>Equation</th>
<th>$r$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Island stations</td>
<td>25</td>
<td>$\overline{\delta D}<em>{w} = (8.47 \pm 0.25) \delta^{18}O</em>{w} + (11.11 \pm 1.24)$</td>
<td>0.990</td>
<td>$\pm 3.00%$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>$\overline{\delta D} = (8.51 \pm 0.24) \delta^{18}O + (10.21 \pm 1.04)$</td>
<td>0.991</td>
<td>$\pm 2.91%$</td>
</tr>
<tr>
<td>Coastal stations</td>
<td>29</td>
<td>$\overline{\delta D}<em>{w} = (8.07 \pm 0.12) \delta^{18}O</em>{w} + (10.44 \pm 1.07)$</td>
<td>0.997</td>
<td>$\pm 3.43%$</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>$\overline{\delta D} = (8.03 \pm 0.11) \delta^{18}O + (9.59 \pm 0.95)$</td>
<td>0.997</td>
<td>$\pm 3.30%$</td>
</tr>
<tr>
<td>Continental stations</td>
<td>15</td>
<td>$\overline{\delta D}<em>{w} = (8.14 \pm 0.15) \delta^{18}O</em>{w} + (9.17 \pm 1.64)$</td>
<td>0.998</td>
<td>$\pm 3.08%$</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>$\overline{\delta D} = (8.01 \pm 0.15) \delta^{18}O + (6.49 \pm 1.70)$</td>
<td>0.998</td>
<td>$\pm 3.69%$</td>
</tr>
</tbody>
</table>
island stations (76%, $r^2 = 0.76$) is due to the amount effect, which results in an average depletion rate of $-1.5\%$ per 100 mm of rainfall.

It should be mentioned that the parametric relations given in Table IX probably can be improved if similar regression analyses are performed on a regional basis by employing some additional climatological and/or geographical parameters. Nevertheless, the regression equations given in Table IX can be used to make preliminary estimates of the mean $\delta^{18}O$ of precipitation at sites where actual data do not exist.

The very good linear relationship which exists between weighted average $\delta^{18}O$ and $\delta D$-values of precipitation is shown in Fig. 27. The least-squares line fitted to these data is:

$$\overline{(\delta D)_{w}}(\%o) = (8.17 \pm 0.08) \times \overline{(\delta^{18}O)_{w}} + (10.56 \pm 0.64)$$

with a correlation coefficient of $r = 0.997$ and a standard error of estimate for
\( \delta D \) of +3.3‰. This line closely resembles the meteoric water line defined by Craig (1961) as the locus of isotopic composition of world-wide fresh-water sources:  
\[ \delta D \text{ (‰)} = 8 \delta^{18}O + 10. \]

The relationships for each group of stations considered, i.e. island, coastal and continental, do not deviate from the above equations. The least-squares-fit lines for each group, using both mean and weighted mean values of \( \delta^{18}O \) and \( \delta D \), are listed in Table X. If annual \( \delta^{18}O \) and \( \delta D \)-values (weighted and unweighted) from all of the network stations are used, rather than long-term mean values, the least-squares-fit linear relationship between \( \delta^{18}O \) and \( \delta D \) is as follows:

(a)  \textit{Unweighted:}

\[ \langle \delta D \rangle = (8.12 \pm 0.07) (\delta^{18}O) + (9.20 \pm 0.53) \]
\[ n = 159, \; r = 0.995, \; \sigma_{y,x} = \pm 4.1\% \]

(b)  \textit{Weighted:}

\[ \langle \delta D \rangle_w = (8.08 \pm 0.8) (\delta^{18}O)_w + (9.57 \pm 0.62) \]
\[ n = 153, \; r = 0.990, \; \sigma_{y,x} = \pm 4.3\% \]

The above derived equations for the global relationship between \( \delta^{18}O \) and \( \delta D \) are all similar and in essential agreement with the 'meteoric water' line.

However, the \( \delta^{18}O - \delta D \) relationship for precipitation in a given region often differs from the above global equations. Considering the continental stations in North America, for example, the \( \delta^{18}O - \delta D \) relationship for long-term weighted mean values is (least-squares fit):

\[ \langle \delta D \rangle_w = (7.95 \pm 0.22) (\delta^{18}O)_w + (6.03 \pm 3.08) \]
\[ n = 8 \text{ (Bethel, Waco, Flagstaff, Chicago, Goose Bay, Edmonton, Fortsmith and White Horse)}, \; r = 0.997, \; \sigma_{y,x} = 3.4\%. \text{ While the slope of the line for these stations is close to the value of } 8, \text{ the intercept deviates from the global value of } +10. \]

The data of stations in the Middle East, Australia and other regions show a definite deuterium excess compared with the meteoric water line. Whether the data for samples from the different regions follow a line parallel to the meteoric water line or whether they just cluster off this line is hard to say, since the number of data points is limited and the spread of \( \delta^{18}O \) relatively small.

In other geographical areas, the correlation lines have a different slope. This is true for arid zones, in which the stations cluster along evaporation lines (Gat and Dansgaard, 1972), but it is also true for tropical island stations.
Considering the long-term mean values of the island stations: Barbados, Canton, Johnston, Wake, Midway, Rarotonga, São Tome, Seychelles, Shop E, Bermuda, Diego Garcia, Guam, Azores, Apia, Ship V, the least-squares-fit linear relationship is:

\[
\bar{\delta D} = (6.17 \pm 0.51) \bar{\delta^{18}O} + (3.97 \pm 1.47)
\]

with \( n = 15, r = 0.959, \sigma_{Y,X} = \pm 1.79\% \). The slope of the line for these tropical island stations is significantly lower than 8. The long-term data available at present confirm the earlier findings for these stations by Dansgaard who used the limited data available for 1961-1962.

With the aim of providing readily available information on the \( \delta^{18}O - \delta D \) relationship for each station, we shall make use of the deuterium excess (d-excess) parameter, which was defined by Dansgaard (1964) as:

\[
d = \delta D - 8 \delta^{18}O,
\]

in order to relate the isotopic composition of any water sample to the meteoric water line. The mean and weighted mean deuterium excess values are listed in Table VIII. For most of the stations the mean deuterium excess values are close to the global average of +10\%, and there is no significant difference between the mean and weighted mean values. However, for some stations the deuterium excess values deviate considerably from +10\%. For example, of the stations listed, the extreme values observed for weighted mean of deuterium excess are \( \bar{d}_w = +15.9\% \) for Alexandria and \( \bar{d}_w = -0.3\% \) for Invercargill. Higher values of deuterium excess have been reported for other stations in the Mediterranean region, where the mean value is about \( d = +22\% \) (Gat and Carmi, 1970). The highest deuterium excess value observed at the network stations is from Karizimir, where \( d_w = 23.3\% \), as derived from 24 monthly data available at this station.

In the development of a linear relationship between \( \delta^{18}O \) and \( \delta D \) and in its use for hydrological interpretations, the common practice, so far, has been to designate \( \delta D \) as the dependent variable and \( \delta^{18}O \) as the independent one. In view of the fact that the analytical errors involved in \( \delta^{18}O \) and \( \delta D \)-data are usually comparable relative to the variations of the two isotopes, a linear regression based upon least-squared orthogonal deviations would be a better approach (reduced major axis line, Kermack and Haldane, 1950).

The linear relationship computed for these data, which are plotted in Fig.27, achieved by orthogonal regression and taking into account the scaling factor, is:

\[
\bar{(\delta D)}_w = 8.20 \bar{(\delta^{18}O)}_w + 10.80
\]

In this particular case, the two approaches yield almost identical results since the correlation between the mean values of \( \delta^{18}O \) and \( \delta D \) is very strong.
A warning is indicated against confusing the intercept (with the \( \delta D \)-axis) of the regression line of \( \delta D \) and \( \delta^{18}O \) data from any group of samples with the \( d \)-parameter of these data points. The latter would be the intercept with the \( \delta D \)-axis of a hypothetical line of slope 8, which is drawn through any of the points. In a way it is more instructive to consider the \( d \)-excess simply as a parameter which relates the position of a point in \((\delta D, \delta^{18}O)\) space to the meteoric water line: \( \delta D \,(\%) = 8 \delta^{18}O + 10 \). As shown in Section 6.4, the value of \( d \) may have geophysical significance in terms of the composition of the air mass from which the precipitation derives; no such simple interpretative significance can, however, be attributed to the intercept of the \( \delta D \) and \( \delta^{18}O \) regression lines if their slope differs appreciably from a value of 8.

The basic statistical parameters (mean and variance) for monthly \( \delta^{18}O \) and \( \delta D \)-data from all the network stations having a long record are listed in Table VIII. The monthly temperature data for each station are also given. In view of the fact that the relationship between \( \delta^{18}O \) and \( \delta D \) for meteoric waters is a linear one, the relationships derived between the \( \delta^{18}O \)-data and the climatological parameters would generally be valid also for \( \delta D \).

It can be seen that the continental stations generally exhibit relatively larger variations in stable-isotope composition of precipitation than the coastal and island stations. The magnitude of the variations is illustrated in Fig.28, where the standard deviation of the \( \delta^{18}O \)-data for each station is plotted against the

**FIG.28. Standard deviation of monthly \( \delta^{18}O \) plotted versus weighted mean \( \delta^{18}O \) values, showing that continental stations exhibit larger variations.**
mean $\delta^{18}O$-value. The larger variations at continental stations are well illustrated by the data for Fort Lamy, Bamako, Kano, Karachi, New Delhi, Teheran, Karizmir, Flagstaff and Chicago, which stations are distant from the coast. This observation is partly fortuitous, as most of the island stations are located in the equatorial belt, where the seasonal changes in temperature are relatively small.

A detailed study of the time variations in monthly $\delta^{18}O$ and temperature data from network stations was made by Yurtsever (1975). The time-series analysis performed for detecting the cyclic variations in the $\delta^{18}O$ time series includes variance—spectrum and auto-correlation analyses for 39 stations with a minimum of about 6 years of continuous monthly data. In the majority of the stations analysed, there is only a 12-monthly cycle in the $\delta^{18}O$ time series. Correlograms and variance—spectrum curves for the Vienna station are shown in Fig. 29 as a typical example. The annual cycle in the $\delta^{18}O$ time series and the mean monthly temperature series in Vienna are illustrated in Fig. 30; for both, a 12-month cycle exists. This is a common feature of the majority of the stations analysed, where the deterministic component of the $\delta^{18}O$ time series is composed of only a 12-month cyclic variation similar to the temperature variations. However, four stations have a 6-month cycle in addition to a 12-month cycle in the $\delta^{18}O$ time series, i.e. Bamako, Sao Tome, Kinshasa and Pretoria.

A third group of stations have no distinct cyclic variations in their $\delta^{18}O$ time series. Among these are Reykjavik, Tokyo, Salvador, Midway Island and Hilo-Hawaii. Apparently, the majority of the variations observed in the $\delta^{18}O$-values of precipitation at these stations are of random character and are related to local climatological conditions and possibly due to different effects being superimposed on each other. The cyclic variations in the $\delta^{18}O$ time series are generally more pronounced at continental stations, for most of which the explained variance by cyclic component is in the range of $50 \approx 64\%$ of the total variance. Exceptions are Teheran and Flagstaff, where the values are 22.7 and 36.1%, respectively. In coastal and island stations the variations resulting from cyclic components are smaller.

The month-to-month variation of the $^{18}O$ content seems to be well correlated (at any one station) with temperature changes. Figure 30 shows the monthly $\delta^{18}O$ and $\delta D$-content of precipitation in Vienna, together with the mean monthly temperature. The seasonal variations in $\delta^{18}O$ and $\delta D$ correspond closely to those in the mean monthly temperature values.

The least-squares fit defining the linear relationship between monthly $\delta^{18}O$-values and mean monthly temperatures, using 363 values (Fig. 31) of the stations Thule, Groenenedal, Nord and Vienna, is as follows:

$$\delta^{18}O = (0.521 \pm 0.014)T - (14.959 \pm 0.208)$$

(T is in degrees Celsius), with a correlation coefficient of $r = 0.893$ and a
FIG. 39. Time-series analysis of monthly $\delta^{18}O$ values of precipitation in Vienna.
FIG. 30. Seasonal variations of the isotopic composition of precipitation and of the temperature in Vienna.

FIG. 31. Relationship between monthly values of $\delta^{18}O$ in precipitation and of temperature for four stations in the northern hemisphere.
standard error of estimate of 3.94‰. Thus, for these four stations considered together, about 80% (r² = 0.80) of the variations in the stable-isotope composition of monthly precipitation can be explained by the temperature variations.

Figure 32 is a plot of variance of monthly $\delta^{18}O$ versus variance of monthly temperature, for all stations listed in Table VIII, showing increasing variance of $\delta^{18}O$-values with increasing variance of temperature. This is the generally expected result of the temperature effect, larger variations in temperature leading to larger variations in isotopic composition of precipitation. However, some of the stations, indicated as Group A and Group B in Fig.32, exhibit significantly larger variations in $\delta^{18}O$ as compared with the rest of the stations. At almost all stations of Group A, the precipitation amount is quite high. For station Yap (average monthly precipitation: 247 mm), a negative correlation exists between amount of precipitation and monthly mean $\delta^{18}O$-value, whereas the temperature curve is rather smooth, with very little variation. Similarly, at stations Apia and Madang, the months with higher amounts of rainfall tend to show more depleted values of $\delta^{18}O$. These are typical cases of the 'amount effect', as it was named by Dansgaard (1964). The least-squares
lines defining the relation between the amount of rainfall and the δ¹⁸O-values for these two stations are as follows:

(a) Apia

\[ δ^{18}O = (-0.010 \pm 0.003)P - (1.56 \pm 0.42) \]

n = 52, correlation coefficient = 0.670, standard error of estimate = ±1.45‰.

(b) Madang

\[ δ^{18}O = (-0.011 \pm 0.002)P - (3.95 \pm 0.69) \]

n = 48, correlation coefficient = 0.597, standard error of estimate = ±2.077‰.

The observed average depletion rate in δ¹⁸O as a function of precipitation amount is about −1% per 100 mm. The amount effect accounts for about 50% (r² = 0.50) of the variation in monthly δ¹⁸O-values in Apia and for about 36% (r² = 0.36) in Madang.

The second group of incongruent stations, shown as Group B in Fig.32, are stations which are rather deficient in rainfall. Here the relatively large variations in δ¹⁸O observed seem to be the result of isotopic fractionation accompanying partial evaporation from droplets. This is confirmed by the δ¹⁸O–δD correlation, as discussed below.

The average isotope data of fresh-waters and precipitation were shown to follow a linear relationship between the δ¹⁸O and δD-values, called the meteoric water line, δD(‰) = 8 δ¹⁸O + 10. However, the monthly rain data for individual stations show various patterns in this respect, as was noted by Dansgaard (1964) who studied a more limited set of data. Many stations, notably in humid and temperate climates, closely follow the meteoric water relationship; in others (for example Bahrain — see Fig.33), the data for months with low rainfall lie along low-slope lines, i.e. typical evaporation lines (see previous section), pointing to isotope fractionation accompanying evaporation as the main cause for variability in the isotopic composition. Rarer, though not less interesting, are data from stations where the slope of best-fit lines is higher than the average value of 8 (e.g. at Addis Ababa and Cuiaba). In still other stations the scatter of the monthly data is such that it is unreasonable to fit the data to any linear relationship.

Another way in which the relationship of the isotopic composition of precipitation for months with high and low rainfall can be illustrated is to compare monthly mean values and weighted mean values. This has been done by Dansgaard (1964) in order to classify the network stations and, in particular, to distinguish those cases where evaporation is a dominant feature.
FIG. 33. Relationship between $\delta D$ and $\delta^{18}O$-values in monthly precipitation at Bahrain. When monthly precipitation is less than 10 mm, the isotopic composition is frequently affected by evaporation occurring during the fall of the raindrops.

6.3. ATMOSPHERIC MOISTURE

Sampling of the atmosphere for stable-isotope analysis of its vapour content must be done without fractionating the isotopes; in practice, this requires the quantitative removal of water vapour from the air. Usually this is done by freezing out the water at very low temperatures (dry ice or liquid air) in carefully designed traps (Craig and Horibe, 1967). Some schemes of vapour removal by adsorption also seem to work successfully (Roether and Junghans, 1966). Since in most laboratories the sample size required for analysis is much smaller for hydrogen isotopes than for oxygen isotopes, the data at high altitudes (where vapour pressures are very low) are given mainly for deuterium.

A survey of water vapour over the major oceans has shown the atmospheric moisture to be depleted in $^{18}O$ relative to equilibrium vapour (Craig and Gordon, 1965). The deviation from equilibrium increases with saturation deficit in oceanic air. Over wide regions of the Pacific Ocean, values of between $-10.5$ and $-14\%o$ for a mean relative humidity of about 75% are obtained.
The evidence concerning overland moisture and its relationship to precipitation is conflicting. It appears that in continental areas the isotopic composition of vapour in surface air (on rainy days) is more or less in isotopic equilibrium with precipitation (Craig and Horibe, 1967). In coastal regions, on the other hand, there are at times large deviations from equilibrium with precipitation, surface air being closer in composition to vapour which is in equilibrium with ocean water (Craig and Horibe, 1967). Tzur (1971) measured the surface vapour composition at Rehovot for almost one year and found as wide a variation in the value of the δ-parameter as in that of the isotopic composition itself. On most rainy days, however, the isotopic composition of the vapour was situated on the local meteoric water line (i.e. on the slope-8 line drawn through the δ-values of local precipitation).

The effect of a local evaporation source on the atmospheric moisture in its surroundings has been investigated by Fontes and Gonfiantini (1970) at Lac Léman. Evaporated moisture could be detected in appreciable percentages up to a distance of a few hundred metres from the lake. As the composition of the lake’s water was more constant than that of the atmospheric water vapour, the lake actually had a stabilizing influence on the isotopic composition of the atmospheric moisture.

Upper-air data have been reported by Taylor (1966 and 1972) for continental Europe and by Ehnhalt (1974) for the continental USA. Upper air shows extreme depletion in heavy isotopes, with values as low as δD = -500‰ found in the upper troposphere. The universal meteoric water relationship between δ18O and δD seems to be generally preserved. However, according to Taylor’s data, the value of the d-parameter of upper-air moisture over Europe, d = 16 ± 7, is in excess of that of precipitation over that region.

6.4. MODELS AND INTERPRETATIONS: THE GLOBAL PICTURE

The prominent features of the world-wide isotope data of precipitation can be summarized as follows:

(a) Data from regions as diverse as the tropics, the arctic, the antarctic, and the European and American continental areas cluster along the so-called meteoric water line: δD(‰) = 8 δ18O + 10.

(b) Precipitation from oceanic island stations usually shows a deuterium deficit, while in some areas, like the Mediterranean Sea region, precipitation is characterized by a deuterium excess larger than that given in the equation for the meteoric water line.

(c) A good correlation between isotopic composition and temperature exists at various sites.
(d) Regional precipitation lines from semi-arid and arid regions have a slope of less than 8 on the $\delta D$ versus $\delta^{18}O$ diagram.

The depletion of the heavy-isotope species in precipitation relative to the oceanic water source is the result of the removal of moisture from the air. Since the removal of vapour from the air by condensation is affected by cooling, a close relationship with temperature was to be expected and actually found, as shown in the first part of this chapter.

The slope of the meteoric water line happens to be close to that which would be obtained in an equilibrium distillation column, i.e. a system in which the isotope fractionation is determined by the vapour pressure of the isotopic water molecules (see Chapter 2). This suggested to the early investigators that the condensation processes took place under equilibrium conditions. As a matter of historic interest, it should be noted that the atmospheric part of the water cycle has been described by Kirschenbaum (1951) as a two- to three-plate distillation column.

On the other hand, the 'meteoric water line' does not pass through the datum point of surface ocean water, as it should in a proper equilibrium column. Undoubtedly, evaporation from the ocean surface produces vapour which is not in equilibrium with its water. Numerous 'evaporation experiments' (Craig et al., 1963; Ehhalt and Knott, 1965; Gat and Craig, 1966; Gat, 1970; Merlivat and Coantic, 1975) have verified the non-equilibrium character of evaporation under natural conditions.

The model put forward at this stage was that of a marine vapour whose isotopic composition differs from vapour which is in equilibrium with ocean water (which is rarely found in nature). Precipitation, however, was supposed to be formed subsequently under conditions dominated by the equilibrium fractionation factors of water—vapour or ice—vapour transitions. According to this view, the value of the deuterium excess in the atmospheric moisture, and hence in the precipitation, is fixed by the vapour-producing processes. The latitude, altitude and amount effects are viewed simply as a measure of the degree of rain-out.

According to this model, precipitation over the major continental areas is being fed by the evaporation flux from the major source regions for atmospheric moisture. On the basis of material balance considerations it has been argued by Craig and Gordon (1965) that this flux should equal the world-wide mean precipitation, whose isotopic composition was estimated to be $\delta^{18}O = -4\%o$, $\delta D = -22\%o$. The actual vapour found over the ocean (its mean value is taken as $\delta^{18}O = -13\%o$, $\delta D = -94\%o$) was shown by Craig and Gordon not to be constituted simply of this flux but rather to represent the result of mixing of the evaporation flux with depleted residual vapour from the marine cloud layers, as shown in the schematic drawing.
Fig. 34. Evaporation/precipitation model and typical isotopic values of moisture masses in the atmosphere (from Craig and Gordon, 1965). The first value refers to the $^{18}O$ content, the second (in parentheses) to the deuterium content.

(Fig. 34). The isotopic composition of the evaporation flux, the marine vapour and the continental precipitation resulting therefrom lies on the meteoric water line.

Over the ocean one expects, and finds, local deviations from the mean vapour composition, which depend on the particular air/sea interaction pattern and mixing regime. Precipitation over island and coastal areas is quite variable in its isotopic composition and in particular the value of the d-parameter is at times quite different from the world-wide average value. In some cases, the precipitation at any one station follows lines with slopes of less than 8, to be interpreted probably as mixing lines between upper-air vapour, derived from fast evaporation, and moisture closer to the saturated vapour near the ocean surface. In extreme cases, precipitation results from an orographically induced condensation of moisture from close to the sea surface and is close to the composition of the sea-water itself.
Precipitation whose vapour source regions are warm, land-locked seas shows deuterium excesses of +20% or more; this is explained as being the result of evaporation into very dry air masses, favouring extreme non-equilibrium conditions. Such local vapour source regions are the Persian Gulf, the Red Sea, the Black Sea, and the Mediterranean Sea, in particular its eastern parts. Each of these areas produces its characteristic vapour composition; precipitation derived therefrom will then deviate from the world-wide meteoric water line.

The removal of precipitation from the vapour reservoirs was modelled in its crudest form as a simple Rayleigh process, whereby the condensed phase is formed in equilibrium with the vapour and then removed from the atmosphere as soon as it is formed. A continuous depletion of the heavy-isotope species in the residual vapour would be expected in accordance with Eq. (3.1) or (3.1a) of Chapter 3. The process is one of cooling, and so the unit separation factor will increase as the process continues. The Rayleigh equations can still be integrated (numerically), with α varying in a fashion prescribed by the change in temperature, for any given boundary conditions of initial temperature and moisture content. Dansgaard (1964) performed such integrations and found best agreement between his calculations and the observed temperature effect \( (d\delta^{18}O/dT = 0.7\%/{^\circ C}) \) for the case where cooling occurred adiabatically, with condensation starting at 20°C.

A modified Rayleigh model was formulated independently by Epstein (private communication) and by Craig and Gordon (1965), taking into account the liquid content of the cloud. Two phases are considered to be in isotopic equilibrium with one another (L, the liquid water content, measures the relative amounts of water in the form of liquid and vapour), with part of the condensed phase removed without further fractionation. The basic equations governing this two-phase Rayleigh model are given in Chapter 3.

Gat and Dansgaard (1972) have used a combination of such constant L and constant N steps to reproduce schematically the isotope content of rain under conditions where clouds build up and then dissipate as a result of topographic changes of the terrain (Fig.35). The two-phase model can indeed account (in principle) for the 'mountain shadow effect', which is the phenomenon of precipitation on the lee-side of mountains being more enriched in heavy isotopes than rain in regions lying upwind and closer to the vapour source (example given by Arnason, 1976). A simple Rayleigh model, which predicts a monotonous decrease of the isotope content downwind, obviously cannot account for such a phenomenon.

It should be stressed that both simple and two-phase Rayleigh models assume equilibrium fractionation factors, and hence account only for very minor changes in the value of the d-parameter.

Notwithstanding reservations concerning the simple Rayleigh models, they seem to be able to account for the observed inland and altitude effects,
FIG. 35. Change in the $\delta^{18}O$ content of precipitation ($\delta_R$) as a result of rain-out from an air mass with initial dew-point of $10^\circ C$, for the two-phase model assuming various values of $L$, the liquid water content of the cloud (adapted from Gat and Dansgaard, 1972).

through proper choice of the parameters of integration. In practice, one has to take into account in these formulations the possible effect of re-evaporation (recycling) of water, either in the form of evapotranspiration from the land or as a result of evaporation from lakes. Evapotranspiration returns the water to the atmosphere unfractionated (Zimmermann et al., 1967), thus restoring both the vapour content and the isotopic composition in the atmosphere as if rain had not fallen. This process then obviously decreases the gradient of the inland effect. This mechanism operates, for example, in the Amazon basin; there, the total integrated amount of precipitation exceeds the vapour influx rate many times (attesting to recycling), whereas inland the depletion of the isotope content is very small indeed.12

12 Incidentally, recycling is not the only mechanism responsible for small inland or altitude effects. As shown by Gat and Issar (1974) for arid zones, the non-continuous and patchy appearance of precipitation in deserts may result in the appearance of rain deep inland being similar in composition to precipitation which may occur, at other times, closer to the coast.
In contrast, the evaporation flux from open water surfaces is depleted in heavy isotopes, as is illustrated in the study on Lac Léman (Fontes and Gonfiantini, 1970) referred to above. The effect is, again, to restore to some extent the moisture content of the air, but here this moisture is depleted in heavy isotopes. The immediate effect would then be an apparent increase of the inland or altitude effects. This is, however, offset to some degree by isotope enrichment in the surface waters, where finally, in the hydrologically steady state, the isotopic composition of the re-evaporated moisture equals that of the local precipitation, just as it does in the case of the evapo-transpired waters.

A third important source of re-evaporated water are the falling raindrops themselves. The effect of evaporation on the isotopic composition of the rain is discussed below. The effect on the atmospheric water vapour is quite similar to that of re-evaporated lake water, in that it rearranges the water balance. Evaporation from both open water-bodies and raindrops is a non-equilibrium process, with the evaporated moisture flux favouring deuterium, ever so slightly, compared with heavy oxygen isotopes. Such a process is actually expected to somewhat increase the deuterium excess of the vapour phase. A slight increase in the deuterium excess of the precipitation in the inland parts of the Amazon basin has indeed been interpreted by Salati et al. (1979) as being the result of such a non-equilibrium process.

The apparent success of a simple Rayleigh model in describing the depletion of heavy isotopes in an air mass, as well as the excellent correlation found between stable-isotope composition ($\delta^{18}O$) of precipitation and ground temperature should be noted; one would rather have expected a relation with the in-cloud temperature.

There is a fast isotopic exchange between droplets, water vapour and falling raindrops in a cloud (Woodcock and Friedman, 1963), just as there is in the case of tritium (Booker, 1965); Bolin (1959) estimated that only heavy showers (rain-out rates of more than 10 mm/h) represent the isotopic composition in the cloud above 1 km from the cloud base. Because of the updraft currents in the cloud, raindrops fall counter-currentwise to the updrafting surface air, with isotopic equilibrium usually established at a small distance from the cloud base (Tzur, 1971; Ehhalt, 1967). The extreme depletion in heavy isotopes at the cloud top is 'forgotten' through this exchange and the precipitation is removed at isotopic equilibrium with the near-surface air, at a rate determined roughly by the average cooling rate of the whole air mass, as required by a Rayleigh model. Only snow or hail may 'keep the record' of the isotopic composition in the upper part of the cloud; hence, these have been extensively studied as probes of a cloud's internal structure (these studies have been reviewed by Gat, 1980).
Rain represents the cloud base composition only in humid climates and when it is abundant. When the air beneath the cloud base is unsaturated, the rain evaporates in part during its fall to the ground, with a modification of both the drops and their environment. This is again a non-equilibrium fractionation which results in the increase of the heavy-isotope content of the residual drops and a decrease of the value of the associated \('d\'-parameter. This was studied in the laboratory by Stewart (1975) who found the isotope enrichment of drops evaporating into a dry atmosphere to fit a Rayleigh-type equation with an exponent as predicted by theory for a gas-kinetically controlled diffusion process. In a sense, this is a mirror-image effect with regard to the fractionation in the primary evaporation process from the oceans which may offset the deuterium excess engendered thereby. This effect, which was first described by Ehnhalt et al. (1963), is of increasing importance in arid zones and has actually been suggested as an index of aridity by Gat and Dansgaard (1972).

Evaporation and exchange are probably the dominant factors responsible for the fact that the best-fit lines for local precipitation are often of the type 
\[ \delta D = a \delta^{18}O + b, \] 
with \( a < 8.\)\(^{13}\) This has been recognized by Dansgaard (1964) in his analysis of world-wide precipitation samples as a shift of the slope to less than 8 for the weighted and unweighted mean composition of precipitation. This process is, at least partially, responsible for the observed correlation between deuterium depletion and drop size (Woodcock and Friedman, 1963) and contributes to the altitude effect (in less humid conditions), appositely named pseudo-altitude effect by Moser and Stichler (1971).

From the point of view of the meteorological interpretation of isotope data, the exchange and fractionation effects have far-reaching significance. Since the isotopic composition of the surface air is continuously modified with increasing humidity by exchange processes and is brought closer to equilibrium with the following rain, it appears that the duration of a shower may enter as an additional parameter on which the isotopic composition of precipitation depends. This is probably a partial explanation of Dansgaard's amount effect. One would expect a discontinuity between the isotopic compositions of snow and rain, since snow is less susceptible to these exchange processes. Indeed, snow in Jerusalem, for example, was reported with a deuterium excess of 37%, which is higher than that of any of the rain samples collected in this area during that time (Gat andDansgaard, 1972). Another case in point is that the network station with the highest value of the 'd-excess' parameter, namely Karizimir in Afghanistan, is a station where most of the precipitation is in the form of snow.

\(^{13}\) An alternative process, applying to marine precipitation, is discussed above.
CHAPTER 6

These examples arouse the suspicion that the data of most rain samples are shifted to some extent relative to the composition at the cloud base, where rain is assumed to be in isotopic equilibrium with the atmospheric moisture. This might explain the difference between the value of the d-parameter in high-altitude vapour over Europe and that of precipitation in this region, as reported by Taylor (1972).

It appears from the foregoing discussion that most of the features of the isotopic data could be explained by the simplistic view that precipitation is formed through a continuous process of cooling of a marine air mass, with some local distortion due to the process of secondary evaporation or the addition of local vapour sources. In confirmation, the composition of the most depleted precipitation samples in Antarctica is quoted, whose measured content of $\delta^{18}O = -50\%$ (Epstein et al., 1965) is the value obtained by the simple Rayleigh equation: $\delta_c = \delta_0 (\alpha_c - 1) \ln f$, using a mean $\alpha_c$-value for the temperature range involved, $f$ being the water vapour pressure ratio between air cooled to $-50^\circ$C (which, according to Loewe (1967), is the mean temperature of the area) and air saturated at $20^\circ$C.

There are, however, a number of disturbing features which raise questions as to the validity of this approach. Among them are the following:

(a) The pattern of air movement is not consistent with a gradual poleward drift of surface air masses from low or middle latitudes, as implied by the simple Rayleigh model.

(b) Additional evaporation occurring from the ocean at middle and high latitudes could be expected to affect the results in proportion to the amount of secondary vapour thus added to the system.

(c) The simultaneous integration of the Rayleigh equation for both $^{18}O$ and deuterium under conditions of cooling, i.e. changing the $\alpha_c$-values, would result in a curved line on the $\lambda^{18}O$ versus $\lambda D$ plot because the ratio of $\lambda^{18}D - 1)/(\lambda^{18}O - 1)$ changes with temperature. This curve is straightened out to some extent on translation of $\lambda D$ to the $\delta D$-scale (Taylor, 1972). Recently, Merlivat and Jouzel (1980) claimed that non-equilibrium fractionation occurs during the formation of ice clouds, whose effect on the $\delta$-values just about balances the curvature imposed by the changing $\alpha^*$-values with temperature. However, it remains doubtful whether such effects suffice to account for the remarkably good linear dependence of $\delta D$ on $\delta^{18}O$ in the meteoric water line.

It has been suggested (Craig, private communication) that the world-wide meteoric water line could be considered a mixing line between surface moisture and moisture from the top of a large cloud system which is very depleted.
in heavy isotopes. (Mixing lines are indeed perfectly straight lines on a δD versus δ¹⁸O plot, as shown in Chapter 4.)

According to this view, the basic global fractionation step occurs vertically rather than horizontally across latitudes, with the clouds functioning as multi-stage fractionation columns. The world-wide isotope pattern is dictated by the mixing pattern of the upper tropospheric air with oceanic vapour, predominantly in areas of widespread air-mass subsidence. The slope of 8 of the meteoric water line, according to this view, does not represent a continuous fractionation process, but rather the relation between the mean isotopic composition of the upper air and that of surface air masses. Locally, one should be able to identify families of meteoric water lines, each of which extends over a limited range of isotopic compositions and is related to a limited system of precipitating air masses, mostly along a latitude band. The world-wide mixing and circulation patterns of tropospheric air and the build-up and dissipation of cloud fields thus assume a central role in determining the world-wide distribution pattern of stable isotopes in the atmosphere.

In this global model, the altitude or amount effect is still considered to be a manifestation of the moisture loss from an air mass by cooling; the latitude effect has a more complicated geophysical structure.

These models may have some merit, but it is evident that, for proposing a satisfactory global model of stable isotopes in atmospheric waters, sufficient data on atmospheric moisture are still lacking. However, the extensive precipitation surveys have established in reasonable detail the meteoric isotope input into hydrological systems, as a basis for ground or surface water studies.

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Chapter 7

ICE AND SNOW HYDROLOGY

7.1. INTRODUCTION

Shortly after deuterium and oxygen-18 measurements became sufficiently accurate and simple to use on a large scale, a number of investigators began to apply such measurements to the study of the nature and behaviour of snow and ice. A considerable amount of data has accumulated in this field, especially in connection with deep ice-core drillings, the technique of which has been developed during this period (Hansen and Langway, 1966; Ueda and Garfield, 1969; Arnason et al., 1974).

In this chapter the terms ‘polar’ and ‘temperate’ are used: ‘polar’ ice sheets are those whose temperature remains below the melting point throughout the entire ice mass; ‘temperate’ glaciers are those in which the temperature is at the pressure melting point.

Of the five zones into which glaciers have been divided schematically (Benson, 1962; Müller, 1962), three will be discussed. These are defined as follows:

(a) **Dry snow zone**: That part of the glacier where no melting occurs, not even in summer.
(b) **Percolation zone**: Some surface melting occurs. Water percolates some distance into the snow pack and re-freezes.
(c) **Soaked zone**: Meltwater percolates through the entire annual layer. The temperature of all snow deposited since the end of the previous summer has been raised to 0°C in the autumn.

Dansgaard et al. (1973) reviewed the studies on polar glaciers and discussed some of the future possibilities in this field. For temperate regions, stable isotope studies on snow and ice have also contributed to glaciological studies, although not as extensively as those for polar glaciers.

Of interest in these studies are the considerable variations in the isotopic composition of snow accumulating on the surface. One can distinguish between two groups of variations:

(a) **Time variations**

Variations due to individual showers or snow storms
Seasonal fluctuations
Long-term climatic variations.
(b) *Geographical (space) variations*

Altitude effects
Overland-travel variations.

Since glaciers are known to preserve the precipitation of the past in an unbroken sequence, it might seem that they are especially well suited for the study of the isotopic composition of precipitation and its variation with time. This is, however, not quite so simple. From the moment the snow has been deposited on the glacier surface, the isotopic composition of the snow pack begins to change owing to various processes. These processes not only affect the uppermost firn layers but may also affect the entire ice mass.

Isotope studies of firn and snow profiles have shown that, in every case, an appreciable isotopic modification is found to take place in glacier surface layers (accumulation) during firnification, i.e. when they undergo changes from snow to glacier ice. These modifying processes differ in nature, depending on whether the isotopic homogenization occurs in the dry snow zone, the percolation zone or the soaked zone. In the dry snow zone, the modifying processes occur as a result of snow drift and isotopic exchange in the ice—vapour system. In the soaked zone, isotopic exchange in the ice—water system is the dominating process.

Isotope studies of profiles in glacier ice below the surface layer have shown that further modification takes place throughout the glacier. In polar glaciers, where the temperature of the ice remains below the melting point throughout, this is caused by molecular diffusion in solid ice. In temperate glaciers, where the temperature of the ice remains at the pressure melting point throughout, the modifying processes have not yet been clarified. However, some observations indicate that isotopic exchange in ice—water systems plays an important role. In both cases, the isotopic content of the ice can be further modified by ice movements.

The next section discusses these post-depositional processes in more detail. Section 7.3 is devoted to the application of the isotope method to various processes of interest to glaciology, such as the measurement of accumulation rates, the study of the run-off process, ice flow patterns and the origin of drift ice, as well as the reconstruction of past climatic changes.

7.2. POST-DEPOSITIONAL CHANGES OF ISOTOPIC COMPOSITION

7.2.1. Snow drift

One parameter that can appreciably affect the isotopic composition of the snow after it has been deposited is snow drift.
The necessary conditions for snow drifting are: dry surface snow, which can be eroded, and wind to carry the snow particles. Consequently, snow drift can be expected throughout the year in the dry snow zones. In other zones, snow drift occurs mainly during the cold season. The extent of snow drift also depends on the windiness of the region.

Several studies from Antarctica show that, because of a very low accumulation rate (2–60 g·cm⁻²·a⁻¹) and the storminess of this region, the snow drift frequently plays an important role in disturbing the initial distribution of the deposited snow. Loewe (1954) estimated that about 25 × 10⁶ tonnes of snow per year and per kilometre of the coast drift out from the East Antarctic continent at Port Martin. Astapenko (1964) uses these data and suggests that 50% of the precipitation in Terre Adélie is removed by drift. On the other hand, 10–15% of the accumulation at Base Roi Baudouin could be drift snow from the continental slope (Kotliakov, 1964). The non-symmetrical variations in accumulation — between 2 and 60 g·cm⁻²·a⁻¹ — in the coastal area of Terre Adélie (Lorius, 1963) may also be ascribed to snow drift.

A redistribution of the isotopic composition of deposited snow has been observed by various authors, both in the dry snow and percolation zones at high latitudes and in the soaked zones of glaciers at lower latitudes. Normally, one would expect a decrease in δ-values from the margin of a glacier towards the higher central parts. In some cases, however, this picture seems to have been blurred because of drifting snow.

Since the snow drifts predominantly from higher to lower places and the drift is most effective in removing the isotopically light winter snow, it will affect the isotopic composition in such a way that the decrease in δ-values in the final snowpack towards the central glacier is less than expected from meteorological parameters.

Epstein et al. (1963) found considerably lower δ-values in blowing snow at Little America in Antarctica than in any layer in a pit. Similar trends can be seen from data reported by Gonfiantini et al. (1963). The data from Antarctica reported by Lorius et al. (1968 and 1969) show a more scattered relationship between the mean annual air temperature and the δ-values than data for Greenland obtained by Dansgaard et al. (1973). These authors point out that one of the reasons for the high scattering in the Antarctica values could be the lower accumulation rate and the greater storminess which makes the snow drift more effective in disturbing the isotope distribution pattern.

The data of Lorius et al. (1969) also suggest an inverse altitude effect at the Terre Adélie coast and at Marie Byrd Land. This can be explained only by the drift of isotopically light winter snow from higher to lower places.

On the Greenland ice sheet, where the average annual accumulation ranges from 10 to 90 g·cm⁻²·a⁻¹ (Benson, 1962), the snow drift is evidently not of such great importance as in Antarctica. No irregularities in the altitude effect of
the δ-values, such as those found in Antarctica, exist in Greenland. The relationship between the mean annual temperature and the δ-values is in accordance with what should be expected from theoretical considerations.

In temperate regions with heavy accumulation, snow drift is of limited importance. It should be mentioned, however, that in these regions it is essentially only the isotopically light winter snow that drifts. Also, the altitude effect on temperate glaciers is smaller compared with that on polar glaciers. In the Alps, Ambach et al. (1968) found a change of $-0.2\%$ per 100 m for $^{18}$O, compared with $-0.62\%$ per 100 m on the Greenland ice cap (Dansgaard, 1961). Therefore, if the δ-value of precipitation varies appreciably with season, the snow drift might be able to blur the expected isotopic picture to some extent. An example of this is reported by Ambach et al. (1968) whose data show an exceptionally high $^{18}$O content in a snow pack at the top of the Alpine glacier Kesselwandferner. The authors explain this as being due to the drifting of isotopically light winter snow from the top of the glacier.

7.2.2. Changes of isotopic composition in ice–vapour systems

Epstein and Sharp (1959a) first showed that, under favourable conditions, the seasonal δ-variations can survive the firnification processes and are preserved in glacier ice. Such favourable conditions, however, exist mainly in the dry snow zones and occasionally also in the percolation zones, provided the percolation of meltwater is very small. In the percolation zones and especially in the soaked zones the seasonal δ-variations are always more or less smoothed out. Even in the dry snow zone the seasonal δ-variations do not always survive the firnification process. The obliteration of the seasonal δ-variation during firnification in the dry snow zones seems to be inversely related to the accumulation rate, but probably it also depends upon other parameters such as the windiness of the region. The Antarctic continent with its low accumulation rate and storminess is an example of this. In cases where the seasonal δ-variations survive the snow drift process, they are frequently completely smoothed out in the firm within a few years (Epstein et al., 1963; Picciotto et al., 1968; Lorius et al., 1968). On the Greenland ice cap, which has a considerably higher accumulation rate than Antarctica, the seasonal δ-variations seem to have a better possibility of surviving the firnification processes and have been detected in the ice down to a depth of 1060 m, which corresponds to an age of 8300 years (Johnsen et al., 1972). In all cases, however, the seasonal amplitude is found to diminish considerably during firnification.

Figure 36 from Johnsen et al. (1972) shows how the seasonal δ-variations in an ice core from Camp Century, Greenland, diminish with increasing depth. The figure shows clearly that the seasonal amplitude is reduced by a factor of four (Fig.36, a–c). At the same time, variations of periods shorter than one
FIG. 36. $\delta^{18}O$ variations in firn and ice cores at various depths below surface, Camp Century, Greenland. $S$ and $W$ indicate data for summer and winter layers, respectively. As the ice sinks towards the bottom, the thickness ($h$) of the annual layers is reduced owing to plastic deformation. Within a few years, short-term $\delta^{18}O$ variations are obliterated by mass exchange in the porous firn (a, b). After some decades the seasonal $\delta^{18}O$ amplitude is reduced to about 2% (c, d). Further reduction takes place only by molecular diffusion in the solid ice and becomes effective only when, after thousands of years, the thinning of the layers has increased the $\delta^{18}O$ gradients considerably (d–i) (from Johnsen et al., 1972).
FIG. 37. $\delta^{18}O$ variations in firm and ice cores at various depths below surface, Byrd Station, Antarctica. Seasonal interpretation is difficult: (a) (note the depth scale) suggests mean accumulation rates of between 40 and 18 cm of ice, depending on the interpretation of summer peaks; (b–d) present similar difficulties, probably due to low accumulation and irregular distribution in the source area (from Johnsen et al., 1972).

year have practically disappeared. After being reduced in the firm zone, the amplitude then remains essentially unchanged for thousands of years, but finally disappears owing to molecular diffusion in solid ice.

Figure 37 from Johnsen et al. (1972) shows the $\delta^{18}O$-variations in an ice core from the Byrd Station in Antarctica. The seasonal $\delta$-variations in the uppermost Byrd Station core are much more difficult to interpret than those in the Camp Century core. They gradually disappear during firmification and are not detectable in the solid ice (Fig.37, a, b). Attempts to interpret successive summer and winter layers in the Byrd station core were unsuccessful, as they led to an
FIG. 38. Measured reduction of summer/winter difference $\delta^{18}O_{\text{snow}}$ in accumulated snow, as a function of time since deposition. Seasonal $\delta^{18}O$ variations, and thereby age and accumulation rates, can be determined as long as $\delta^{18}O_{\text{snow}}$ remains higher than 2%. If this is the case when firmification is completed, the stable isotopes can be used for age and accumulation measurements for thousands of years back in time (from Dansgaard et al., 1973).

An estimate of annual accumulation ranging from 8 to 70 cm of ice, which is too irregular to be acceptable (Johnsen et al., 1972).

In Figs 36 and 37, only two ice core profiles are shown, one from Greenland and one from Antarctica, but several profiles from both regions have been measured (Dansgaard et al., 1973; Giongantini, 1965; Merlivat et al., 1967; Paterson et al., 1977). These measurements show that the reduction of the seasonal amplitude varies widely from place to place.

Figure 38, from Dansgaard et al. (1973), shows the gradual reduction of the seasonal amplitude during firmification at four localities on the Greenland ice cap and at one locality in the Antarctic. The determination of the seasonal amplitude is possible as long as the difference $\delta^{18}O_{\text{winter}} - \delta^{18}O_{\text{summer}}$ remains higher than 2%. This is the case for the three Greenland stations, Dye 3, Crete and Camp Century, where the seasonal variations are known to survive the entire firmification process and are detectable over thousands of years. This is hardly true for station North Site. At Byrd Station the seasonal variations obviously have disappeared within approximately three years.

Since the seasonal amplitude in the dry snow zones is always strongly reduced during firmification, quite effective homogenization processes must be active in polar firm. Because of the lack of meltwater in the firm layers, isotopic modification due to percolation and subsequent re-freezing of meltwater or isotopic exchange...
between liquid and solid phases can be ruled out. Therefore, the isotopic modification necessarily must take place via the vapour phase or by molecular diffusion in solid ice. The latter process is very slow and will not appreciably affect the seasonal $\delta$-variations in the period during which the accumulated materials remain in the form of firm. Evidence for this is the preservation of the seasonal amplitude in the solid ice for a long time.

The firnification processes in dry snow zones have been studied in detail by Johnsen (1977) and are also referred to by Dansgaard et al. (1973). According to Johnsen, there are two processes by which isotopic homogenization in polar firm can occur; both are based on the isotopic exchange between vapour and solid ice: (a) vertical movement of vapour due to changes in barometric pressure, and (b) diffusion in the vapour phase. Both these processes can cause vertical exchange in the firm. Process (a) is particularly active in the uppermost part of the firm. Process (b) is most active in the layer down to the critical depth of the firm, i.e. the depth where the grains in firm become close-packed (Benson, 1962). Below the critical depth, the isotopic exchange through the vapour phase takes place at a much slower rate until pore close-off. From there on, the only active process left is slow molecular diffusion in solid ice and the isotopic variations remaining at that depth are preserved in the ice over thousands of years.

On the Greenland ice cap an accumulation of 24 g cm$^{-2}$ a$^{-1}$ is usually critical for the survival of the seasonal $\delta$-variation during the firnification process. In Antarctica, at least 34 g cm$^{-2}$ a$^{-1}$ seems to be necessary for the survival of the seasonal amplitude because of the storminess of this region (Dansgaard et al., 1973, Table 1). There may be some deviation from these values. For example, a slight melting on the surface during a warm season may produce ice layers in the firm and thus close off the lower layers from the uppermost ones and prevent mass exchange due to vertical air movement. Johnsen et al. (1972) mention this as a possible cause for the unusually high seasonal amplitude that appears in the Camp Century core at a depth of 776 m (Fig. 36e).

In general, the following can be concluded: The precipitation on polar glaciers shows strong $\delta$-variations with time. These can be long-term variations or seasonal variations or even variations of a still shorter period. Unless there has been heavy disturbance in the distribution of the annual accumulation due to snow drift or melting, the $\delta$-variations remain in the uppermost layers of the accumulated ice. During the firnification process, however, the variations can be strongly reduced. The reduction has been found to be due to mass exchange between strata via the vapour phase. Variations of periods shorter than one year usually disappear rapidly, but under favourable conditions the seasonal $\delta$-variations, although strongly reduced, survive the firnification process and can be detected in the ice core thousands of years back in time. The reduction of the seasonal amplitude changes inversely to the accumulation rate. Long-term variations are not affected by these processes.
7.2.3. Changes of isotopic composition in ice–water systems

Numerous studies on the isotope content of snowpack and ice profiles in the percolation and soaked zones have been carried out during the last fifteen years. In all cases, the investigators observed that the δ-variations of the precipitation which are still preserved in the snowpack at the end of the winter period usually are rapidly disturbed during the following melt season. In some cases, almost complete homogenization occurs. At the same time, the remaining firn becomes enriched in the heavier isotopes deuterium and ¹⁸O.

Since the summer precipitation on glaciers, such as those of the Alps and in North America, contains much more deuterium and ¹⁸O than precipitation deposited during the winter, authors who studied glaciers in these regions suggested that the isotopic homogenization and heavy-isotope enrichment of the remaining firn was due mainly to the freezing of rain and meltwater and the capture of snow in crevasses (Epstein and Sharp, 1959b; Sharp et al., 1960; Deutsch et al., 1966; Mackpherson and Krouse, 1967; West and Krouse, 1970). Sharp et al. (1960) also mentioned that part of the heavy-isotope enrichment may be ascribed to free-water content in the snow layers. Free water, which is thought to be about 10% by weight, is considered to be mainly from summer rain and is therefore considerably richer in the heavier isotopes than the winter snow. None of the above-mentioned authors considered isotopic exchange between ice and water to be important for the enrichment process.

Studies on Icelandic glaciers, however, have shown that such isotopic exchange may be one of the most important factors governing the homogenization processes and the enrichment of heavier isotopes during the firmification processes. Icelandic glaciers are especially well suited for such studies. Because of the mild oceanic climate, there is very little difference between the isotopic composition of winter and summer precipitation (Arnason and Sigurgeirsson, 1967; Arnason, 1969a, 1970, 1976). Therefore, summer rain and meltwater produced on the snow surface contain about the same amount of ¹⁸O and deuterium as the snowpack through which they percolate. Consequently, it is not possible to explain an isotopic enrichment in the solid phase during firmification in the way suggested by the previously mentioned authors. The only way to explain the isotopic enrichment observed in Icelandic glaciers is to assume that it is the result of isotopic exchange. The ice–water system tends to reach equilibrium, leaving the solid phase enriched and the liquid phase depleted in the heavier isotopes.

Figure 39 shows deuterium concentration versus depth for three pits and shallow boreholes on the Vatnajökull glacier in Iceland. In all cases, the sampling has been performed in spring, before any significant melting had begun. These profiles are typical examples for temperate glaciers, where the seasonal δ-variation is small and the mean isotopic content of the summer precipitation is similar to that of the winter precipitation. The profiles of V-1, V-10 and V-18 are located
FIG. 39. δD against depth from three pits and shallow drill holes on the Vatnajökull glacier, Iceland. The dotted vertical lines represent the weighted mean of a given layer. The profiles of V-1, V-10 and V-18, which are located at 1300, 1400 and 2000 m above sea-level respectively, are good examples of how the extent of the homogenization depends on the run-off ratio, i.e. the amount of water that percolated through the snowpack. At V-1, approximately 50% of the precipitation escapes as run-off during the summer thaw. At V-10, possibly 30% escapes as run-off and, at V-18, the amount of meltwater is so small that it does not markedly affect the initial δD variations of the snowpack.
at 1300, 1400 and 2000 m, respectively, and therefore are good examples of how
the extent of the homogenization depends on the run-off ratio, i.e. the amount
of water that percolates through the snowpack.

According to information from the Icelandic Meteorological Office
(A. Sigfúsdóttir, personal communication), the mean annual precipitation at
V-1 has been estimated at 300 g·cm$^{-2}$·a$^{-1}$. Density measurements of the firm
profile indicate that approximately 50% of the precipitation escapes as run-off
during the summer thaw. At V-10, possibly 30% escapes as run-off and, at V-18,
the amount of meltwater is so small that it does not markedly affect the initial
$\delta$-variations of the snowpack.

In V-1, the $\delta$-variations in the last winter layer are of the same magnitude
as those in the precipitation (Arnason and Sigurgeirsson, 1967). This is also the
case for V-10 and V-18. In the previous annual layer, below the summer layer
of 1967, extensive homogenization has apparently occurred in V-1. At the same
time, the remaining firm has apparently been enriched in such a way that it
became significantly richer in deuterium than even the summer precipitation.
Thus, the only way to explain the enrichment in the heavier isotopes of the firm
at V-1 is to assume that isotopic exchange occurs as the snowpack recrystallizes
and the ice–water system tends to reach equilibrium conditions. Ice in equilibrium
with water will contain approximately 20% more deuterium and 30% more $^{18}$O
than the water (Arnason, 1969b; O’Neil, 1968).

During ageing, the snow can change its isotopic ratio because of the
evaporation and condensation on the surface. Evidence for this was found by
Moser and Stichler (1970, 1974) who observed that the surface snow became
considerably enriched in deuterium and $^{18}$O owing to evaporation, even when the
air temperature was well below 0°C. Since this enrichment only occurs in layers
close to the surface, it will not markedly change the isotopic content of the
snowpack.

A comparison of the data for V-1 from below the summer layer of 1967
with those from below the summer layer of 1966 also suggests that the
homogenization at V-1 occurs mainly during the first summer.

At V-18, the amount of meltwater is so small that it does not markedly affect
the deuterium variations in the snowpack. In this case, the $\delta$-variations are
apparently preserved in the firm down to a depth of approximately 20 m, which
corresponds to six years of snow accumulation. At that depth, the $\delta$-variations
are rather rapidly smoothed out, although without noticeable changes in the mean
isotopic content of the firm.

In order to study the isotopic exchange during firmification on temperate
glaciers more quantitatively, a model experiment was carried out in the laboratory
(Arnason, 1969a). In the model experiment a fine-grained and isotopically
homogeneous snow column gradually melted from the top. The drain water was
collected at the bottom of the column and measured for its deuterium content.
FIG 40. Comparison of D and tritium values obtained for drain water by the theoretical model of Blaasen with direct measurements of D and tritium values of drain water from experiments at Weissfluhjoch, Switzerland. The broken lines connect the limits of double standard deviations. The solid lines indicate the hypothetical case of meltwater percolating the snowpack without any isotopic exchange (from Arnason et al., 1973).
An extensive isotopic exchange between the snow crystals and drain water was observed at the same time as the fine-grained snow changed to a coarser form. This laboratory model then led to the development of a theoretical model which should quantitatively describe the exchange processes in a melting snowpack (Büason, 1969). When water (rain and meltwater) percolates through a snowpack, isotopic equilibrium is only partially reached. In the theoretical model, a pair of linear first-order partial differential equations describes the exchange process at each stage in the melting snow column. The parameter \( r \) is a time constant, which is expressed as a fraction of the total melting time of the snow column. By choosing the proper time constant, the agreement between the laboratory experiment and the theoretical model was excellent (Büason, 1969). The theoretical model was then tested under natural conditions by comparison with isotopic data obtained from samples of snow cover, precipitation and snow--lysimeter drainage at the experimental site at Weissfluhjoch in Switzerland (Arnason et al., 1973).

Using this model, the isotopic composition of the drain water was computed. The computed data were then compared with results obtained by direct measurements (Fig. 40). Two experiments were carried out in 1970 and 1971. In the 1970 experiment, only deuterium was measured. In the 1971 experiment, both deuterium and tritium were measured. Figure 40 shows directly measured data and data obtained by least-squares adjustment, together with data computed by using different time constants and either 10% or 20% free-water content of the snowpack. The solid lines on the three right-hand diagrams indicate the hypothetical case of meltwater percolating the snowpack without any isotopic exchange (\( r = \infty \)). The agreement between the theoretical model and experimental results was good.

Numerous studies on isotope profiles in the percolation and soaked zones have established that the processes modifying the isotopic composition of the accumulation in these zones are quite different in origin from the modifying processes in the dry snow zones where post-depositional changes are mainly governed by isotopic exchange in ice—vapour systems. In some cases, snow drift also plays a role. In the percolation and soaked zones, the changes are mainly governed by isotopic exchange in ice—water systems.

In regions with great seasonal changes in isotopic composition, summer thaw and rain are initially much richer in the heavier isotopes than the winter snow into which they percolate. In such regions, the exchange process is often quite complicated and has therefore been overlooked. This is the case, for example, in numerous glaciers in North America and in the Alps. In the glaciers of the Alps, where the difference between summer and winter precipitation is of the order of \( \Delta \delta^{18}O = 14\% \) (Deutsch et al., 1966), the deuterium and \( ^{18}O \) content in the run-off is sometimes higher than that in the remaining firn, although the reverse might be expected from isotopic exchange. Similar results
were found in studies carried out at the Weissfluhjoch sampling point, where drainage samples collected from the snowpack sometimes showed higher δD-values than the mean δD-value of the remaining snowpack. However, the results obtained at Weissfluhjoch fitted satisfactorily into Büason’s theoretical exchange model (Arnason et al., 1973).

In regions with low seasonal differences between the mean isotope content of summer and winter precipitation, the exchange effect appears more pronounced. This is the case, for example, on Icelandic glaciers, which seem especially well suited for studying these phenomena, not only because of the low seasonal amplitude but also because the extent of such exchange can be studied continuously from zones where the run-off ratio approaches unity to zones where the run-off ratio is so small that it has practically no effect on the δ-variations of the accumulation.

When not affected significantly by meltwater, the δ-variations of the snowpack are preserved in the firn for several years or down to the depth where the firn changes to clear ice (Fig.39). The transformation of firn to clear ice at between 20 and 30 m is obviously followed by very extensive isotope homogenization, although without any apparent enrichment of deuterium in the ice. The process governing this homogenization is not clearly understood, but some recent studies indicate that the ice–water system is involved in the transformation of firn to ice. Temperature measurements in a 415 m deep drill hole located not far from V-18 (Fig.39) showed that, at approximately 15 m depth, the temperature approaches zero and then remains at the pressure melting point through the entire depth of the hole. At a depth of 34 m, which is the depth where the firn has completely changed to clear ice, the drill went through a water table in the glacier (Arnason et al., 1974).

Since the isotopic variations of the accumulation on temperate glaciers usually become heavily disturbed during the first summer thaw, such glaciers are unsuitable for studies of parameters related to atmospheric changes of precipitation. For such studies, only the dry snow zones are suitable. Exceptions might be such places as the highest part of the Vatnajökull glacier in Iceland where summer melting is small and the glacier can be classified as in the percolation zone.

The study of the post-depositional changes in the isotope content of snowpacks of the percolation and soaked zones during the firnification is of great importance since these changes reflect the recrystallization processes occurring when fine-grained snow is transformed to coarse-grained firm and then finally to clear ice. Therefore, such studies may be an important contribution to the understanding of the development and nature of temperate glaciers.

7.2.4. Changes of isotopic composition in solid ice

7.2.4.1. Diffusion in polar glaciers

The processes modifying the isotope variations in glacier ice may differ, depending on whether the ice is at a temperature below its melting point
throughout the glacier or at a pressure melting temperature. The first is the case for polar glaciers, the latter for glaciers in temperate regions.

In polar glaciers, the only way in which the seasonal $\delta$-variations still preserved in the ice can be affected is by molecular diffusion in solid ice. The vertical diffusion is described by the equation:

$$\frac{\partial \delta}{\partial t} = D \frac{\partial^2 \delta}{\partial x^2}$$

where $D$ is the diffusion coefficient and $x$ the depth. If the seasonal fluctuations about the mean concentration are approximated by a sine wave of length $\lambda$ and an initial amplitude $\Theta_0$, this amplitude will decrease exponentially with time because of diffusion. The diffusion equation for the time constant $\tau$ gives the following relation:

$$\tau = \left(\frac{\lambda}{2\pi}\right)^2 \cdot \frac{1}{D}$$

Using $D = 2.6 \times 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$ for $-24^\circ\text{C}$ (Ramsay, 1967) for an oscillation of the wavelength of 38 cm, which is the seasonal wavelength in the uppermost part of the Camp Century ice core (Fig.36), and assuming no thinning of the annual layers, $\tau$ would be 450 000 years. The molecular diffusion in solid ice is seen to be a very slow process.

As the annual layers in the ice gradually get thinner with increasing depth and pressure, diffusion will become more effective in smoothing out the seasonal $\delta$-variations and at a sufficiently great depth in the ice they are completely obliterated. For example, at a depth of 1000 m in the Camp Century ice core, where the annual thickness of the layers has diminished to approximately 5 cm and the temperature is $-20^\circ\text{C}$, $\tau$ would be 5000 years. Qualitatively, this is in agreement with the experimental results of Johnsen et al. (1972) which indicate that the seasonal $\delta$-variations in the Camp Century ice core are detectable down to a depth of approximately 1100 m (corresponding to 9000 years), at which depth the annual layer has decreased from 38 cm to 4 cm.

Johnsen (1977) accounts also for the temperature dependent on molecular diffusion and gradual thinning of the ice layers with depth and obtains a solution which can be used in most cases to calculate the reduction of the isotopic amplitude in polar ice sheets (see also Dansgaard et al., 1973).

For the Camp Century ice core, Johnsen et al. (1972) found by computation that after firmification a further reduction of the seasonal amplitude by 10%, 50% and 90% takes 5000, 8000 and 10 000 years, respectively. This is in fair agreement with the experimental data (Fig.36).
The long-term \( \delta \)-variation in polar ice will be detectable much longer. Dansgaard et al. (1973, Table 2) give a good example of this. It appears from Johnsen's method that \( \delta \)-variations over periods of 10, 100 and 1000 years can be detected in the Camp Century ice core 19,000, 43,000 and 100,000 years back in time, respectively.

7.2.4.2. Changes in temperate glaciers

In temperate regions, molecular diffusion in solid ice probably does not play an important role in the obliteration of the \( \delta \)-variations. The annual accumulation in temperate regions is usually much higher than in polar regions, giving much thicker ice layers for each year. The ice at the bottom of temperate glaciers is also much younger than in polar ice sheets, at most only a few thousand years old. However, there may be other processes in temperate glaciers which considerably affect the \( \delta \)-variations.

In a 415 m deep drill hole on the Vatnajökull glacier, the ice has been found to be at the pressure melting point from 20 m below the surface down to the bottom of the hole (Arnason et al., 1974). The deeper layers of the glacier could therefore contain some water. When ice near the surface submerges to a depth of 500 m, some water will be produced in the glacier because of an increase in pressure and a lowering of the melting point. Additional water can also be produced at certain places within the glacier because of shear strain, especially on slip planes. This water can possibly move through the ice mass and thus result in appreciable mass transport, followed by changes in isotope content within the glacier.

Recently performed studies of the ice crystal size and the chloride content of the 415 m long ice core of the Vatnajökull glacier in Iceland indicate that percolation and isotopic exchange processes, similar to those occurring in the uppermost firm of the percolation and soaked zones, continue through the entire ice mass. A gradual increase of crystal size going downward in the ice core shows that recrystallization occurs through the entire core (Björnsson, personal communication).

Measurements of the chloride content of the ice core show that at the same time as the chloride variations are gradually smoothed out, the chloride content of the ice gradually decreases from 1.0 \( \mu \)g per gram ice at the surface to 0.1 \( \mu \)g per gram ice at a 415 m depth. The chloride must have been dissolved in water layers between the ice crystals and escaped out of the ice with this water. How this happens is not clear and more studies are needed until the mechanism of the process can be explained satisfactorily. It is clear, however, that such a process might reduce the \( \delta \)-variations that survive firnification, even in regions where the percolation of meltwater is so small that practically the whole precipitation is preserved in the ice.
Therefore, stable isotope studies on such glaciers as the Vatnajökull ice cap in Iceland might not be so well suited to study past climatic changes as was hoped. Deuterium measurements have already been found to reflect climatic changes in the Vatnajökull ice core for the last 100 years (Arnason, 1970). Whether this is also the case for deeper strata of the core will be clear when detailed studies from that part of the core have been performed. On the other hand, stable isotope studies of ice profiles of temperate glaciers, especially in connection with tritium measurements, are of great interest since they may contribute greatly to the study of the nature and development of the interior of such glaciers.

7.3. APPLICATION OF ISOTOPE DATA TO GLACIOLOGY

7.3.1. Accumulation rates

One of the most important parameters for the study of the mass balance of the glaciers is the determination of the accumulation rates. Several methods have been applied, such as snow stake measurements, classical stratigraphic methods (Schytt, 1958), measurements of beta-activity profiles to identify reference horizons (Picciotto and Wilgain, 1963; Wilgain et al., 1965; Crozaz et al., 1966; Ambach et al., 1967, 1969a, 1971b; Ambach and Eisner, 1970), and measurements of tritium profile (Ambach et al., 1969b; Ambach and Dansgaard, 1970; Merlivat et al., 1973; Theodorsen, 1972, 1977). In regions where the seasonal δ-oscillations survive in the firn and ice they offer an excellent opportunity to measure the accumulation rate. Several authors have applied the stable-isotope method to determining the accumulation rates in the polar regions and have compared these results with results obtained by other methods (Epstein et al., 1965; Johansen et al., 1972; Gonfiantini et al., 1963; Lorius et al., 1968; Picciotto et al., 1966, 1968; Reeh et al., 1978).

The recent accumulation rate can be determined by stable isotopes on most of the Greenland ice sheet. In Antarctica, the stable isotope method is found to give satisfactory results only in relatively restricted coastal areas.

On temperate glaciers where the seasonal δ-variations are strongly modified by percolation of meltwater and where there is intensive homogenization, the stable isotope method does not work (Deutsch et al., 1966) unless the conditions are favourable.

The determination of the accumulation rate by the stable isotope method is relatively simple, as far as the firn and the uppermost part of the glacier are concerned. One need only count the summer maxima down the ice profile and determine the density of the ice. At greater depths, the thickness of the annual layers must be corrected for vertical strain since the time of deposition. Since the strain also depends upon the temperature history and the thickness and slope
Therefore, it seems that, on temperate glaciers, other methods have to be used. In some special cases, however, measurements of stable isotopes can be useful to estimate the age of the ice in such glaciers. For example, Koerner et al. (1973) were able to state that, because of its high $^{18}$O content, the Meighen ice cap in the Canadian Arctic is post-Wisconsin.

7.3.4. Run-off

A knowledge of the characteristics of run-off systems from temperate glaciers is one of the most important topics in the study of the water budget of a glacier.

Glacier streams are fed by different water components: (a) melted glacier ice, (b) melted surface snow and rain, and (c) subglacial groundwater.

The subglacial water may contain all the previously mentioned components or only one of them. How these components move on from places on or under the glacier and to what extent they contribute to the glacial river is not fully understood. The systematic measurement of stable isotopes, preferably together with tritium measurements, can give us better insight into these phenomena.

Several authors have studied the isotope content of run-off from snowpacks and glaciers (Dincer et al., 1970; Ambach et al., 1970, 1971b; Behrens et al., 1971; Moser et al., 1972). Probably the most extensive studies are those carried out on run-off from the glaciers of the Alps.

Because of isotopic exchange between ice and water in the soaked zones, one would expect the glacier ice to be relatively enriched and the meltwater which escapes from the remaining firn to be relatively depleted in deuterium and $^{18}$O. Glacial rivers can therefore change their isotopic content from time to time, depending upon how much each of these components contributes to the river water. A great quantity of melted ice results in a high content of the heavier isotopes and a small quantity of melted ice results in a low content of the heavier isotopes.

Ambach et al. (1970, 1971a) regularly studied the time fluctuations of deuterium and tritium in glacial streams from the glaciers of the Alps for a period of several years. Tritium is an important parameter in such studies because ice deposited before the nuclear weapons tests contains practically no tritium, but snow and rain deposited since then contain considerable amounts of it. Tritium thus makes it possible to distinguish between melted glacier ice deposited before 1950 and melted surface snow.

Ambach et al. (1971b) found that daily and annual variations of both tritium and deuterium occurred in glacial streams; however, these variations were in opposite phases. The daily variations showed high tritium and low deuterium in the early morning but low tritium and high deuterium in the afternoon. The annual variations showed minimum tritium and maximum deuterium in late summer. The investigators assumed that these variations reflected the relative
amounts of the different components, glacier ice, snow melt and subglacial water, in the glacial stream. High tritium and low deuterium found in the cold season when practically no melting takes place on the glacier surface indicated a high proportion of subglacial water in the river. Increases in deuterium and decreases in tritium during the summer, with maximum deuterium and minimum tritium towards the autumn, indicated an increasing contribution of melted ice and firn to the river as the warm season progresses. Daily fluctuations could be explained in a similar way.

It is interesting to note the high tritium content of the subglacial water together with the low deuterium content. The high tritium content indicates that the source of meltwater percolating through the snowpack during the summer is mainly summer rain and snow deposited in late winter. The tritium content of the precipitation increases in late winter and reaches its maximum in early summer. Since the deuterium concentration is higher in summer precipitation than in winter, the low deuterium content of the subglacial water indicates that, as the meltwater percolates through the snowpack, an appreciable exchange takes place. These results are in good agreement with a study of deuterium and tritium on snowpack and drainage samples from snow-lysimeters at the Weissfluhjoch sampling point in Switzerland (Arnason et al., 1973). Furthermore, the high tritium content of the subglacial water shows that the meltwater which percolates through the firn layers in the accumulation areas probably never flows downslope for a long distance but rather finds some channels through the ice sheet down to the bottom of the glacier. There it mixes with a relatively small reservoir of subglacial water from which it escapes into the stream.

Using balance equations, Ambach et al. (1971b) found that the discharge of melted ice amounted to a maximum of 60% of the total discharge of the Kesselwandferner glacier. In more detailed studies in Alpine glaciers, Behrens et al. (1971) were able to use balance equations for tritium, deuterium and, in a few cases, oxygen-18 for estimating quantitatively the daily variations of the run-off portions of the components subglacial water, melted ice and snow in the discharge from the glacier.

7.3.5. Ice flow pattern

Modern theories consider ice to be a plastic material. Therefore, when forces such as gravity and shear stresses act on an ice sheet, the ice will flow downslope.

Reid (1896) first proposed a flow pattern for a normal glacier (Fig. 41). According to Reid's model, snow deposited in the accumulation areas submerges and flows down the glacier where it appears as surface ice in the ablation area. Snow accumulated in the uppermost part of the glacier will appear as ice in the lowest part of the ablation area near the terminus.
FIG. 41. Flow pattern for a normal glacier: (a) longitudinal section, (b) view from above. Snow deposited in the accumulation areas submerges and flows down the glacier where it appears as surface ice in the ablation area. Snow accumulated in the uppermost part of the glacier will appear as ice in the lowest part near the terminus (from Reid, 1896).

The isotopic composition of the precipitation depends upon elevation. Normally we would expect the heavier isotope content of the accumulation to decrease towards the upper and inner parts of the glacier. Isotopic homogenization in the firm does not change this trend; it enriches the firm in heavier isotopes relative to the initially deposited snow. However, the extent of homogenization and enrichment depends on the meltwater percolating through the snowpack and it is to be expected that at lower elevations, where more of the total precipitation melts and escapes, the firm would be more enriched in the heavier isotopes than at higher elevations. The homogenization process, therefore, tends to increase the δ-gradient in the accumulation area. Below the firm limit, the δ-profile should be reversed, i.e. the lowest δ-values have to be found near to the terminus, because of the ice flow. A transverse profile would show increasing δ-values from the crest towards the margin. Also, a hole drilled through the ice should give decreasing δ-values with depth, in accordance with the origin of the ice.

From the above consideration, it might seem obvious to use stable isotope measurements not only to test the validity of the classical idealized Reid’s model but also to study the real flow pattern in a glacier. Since the flow pattern will strongly depend on the geometry of the glacier sheet and the topography of the bottom underneath it, in a real glacier it will differ considerably from the simple flow pattern shown in Fig.41. Flow patterns also differ from one glacier to another.

The situation is not very simple. Climatic variations might have changed the isotopic composition of the accumulation at a given place and thus may blur the picture. As an example, if the ice collected in the ablation area has been
deposited during periods when the climate was colder than at present, isotope measurements would indicate that the ice originates from a place on the glacier higher up or further inland than it really does. Therefore, any prediction about the flow pattern of a glacier obtained by isotope studies should be taken with great caution. This is particularly the case for the polar ice sheets where the ice can be several hundred thousand years old and has therefore deposited during times when the climate was possibly quite different from that of today. On temperate glaciers, which are unlikely to contain ice more than one to two thousand years old and therefore contain no ice deposited when the climate was dramatically different from that of today, the method might be useful to some extent.

Several authors have applied this concept to interpret the flow pattern in a glacier. Dansgaard (1961) used this method to trace the region of formation of 11 West Greenland icebergs. According to their $^{18}$O content, the icebergs were found to have come from the ice cap anywhere from 60 to 460 km inland. Data of $\delta$-values have been reported from the Malaspina and Saskatchewan Glaciers (Epstein and Sharp, 1959b), the Blue Glacier (Sharp et al., 1960), the Hubbard and Kaskawulsh Glaciers (Macpherson and Krouse, 1967), the Fox Glacier (Krouse, 1971), and the Rusty Glacier (West and Krouse, 1972). All these authors found some trend in longitudinal profile where the $^{18}$O decreased from the firm line towards the terminus. In some cases also the $^{18}$O content of a transverse profile seemed to decrease from the central glacier stream towards the margin. In all cases, however, the trends were small and irregular and it seems questionable whether the method is applicable on such small glaciers as those mentioned above. In cases where samples have been collected in the accumulation areas, the altitude effect is rather small. In fact, for the Rusty Glacier, West and Krouse (1972) found similar $\delta$-values at all places where samples were collected in the accumulation area, independent of altitude.

In those cases where the accumulation area has a small altitude gradient, it is unlikely that the method will give any results, because even slight long-term climatic changes could dominate the altitude effect.

When Dansgaard and Johnsen (1969a, 1969b) reported data on ice cores from Camp Century, they had to use a flow model that related depth to time. In this model, the ice layers become progressively thinner with depth, because of the weight of the overlying ice and the general outward movement. For example, the model showed that the ice at a depth of 550 and 1360 m was respectively about 2000 and 100 000 years old. The model was found to be better than other proposed models (Nye, 1963) because its calculated temperature profile corresponded satisfactorily to the profile measured by Hansen and Langway (1966) and also because the stable isotope data for the core samples varied in accordance with all known climatic changes within the last 70 000 years.

Although stable isotope measurements have partially failed in monitoring the flow pattern of small temperate glaciers, they are expected to be of use on
FIG. 42. $\delta^{18}O$-record for the Greenland ice sheet at Camp Century (down to 17 m above the bottom), plotted on a time scale (in units of $10^3$ years before present) that is based on the assumption of persistent $\delta^{18}O$ oscillations for a period of 2400 years. The curve is provided with tentative interpretations in European and American terminology. A correction for the influence of changing surface altitudes is suggested by the dashed curve, which is assumed to roughly reveal the $\delta^{18}O$ trends in case of constant climatic conditions (from Dansgaard et al., 1973).
larger ice sheets, such as, for example, the temperate ice sheet at Vatnajökull in Iceland. Samples taken from Vatnajökull give $\delta D = -65\%$ at the firn limit of the southern slope. The deuterium content then decreases gradually to

$\delta D = -100\%$ on the central glacier. Such a gradient should, in principle, be easily detectable in a reverse profile in the ablation areas.

Finally, it should be pointed out that samples from the accumulation areas should be collected with caution. Since homogenization is found to give $\delta$-values in the submerging firn which are different from those initially found in the snowpack, one must be sure to collect samples from a depth where the homogenization is completed. Available data show that, at least in some cases, the $\delta$-values of the accumulation do not change appreciably after the first summer season has passed. Therefore, samples collected from firm below the uppermost annual snowpack might give reliable values for the submerging ice. This should, however, be checked in each case and sometimes it might be necessary to obtain samples from a depth where the firm has changed to clear ice.

7.3.6. Paaleoclimates

One of the dominating parameters determining the stable isotope ratio of a given precipitation is the temperature of its formation. This is reflected in the seasonal variation of the isotope content. In a similar way, it is to be expected that long-term climatic variations are reflected in the isotope content of the precipitation of the past and should be detectable in ice profiles.

Dansgaard (1954) first proposed that the $^{18}O$ content in glacier ice might reflect climatic conditions of the past. Since then, extensive work has been carried out in this field, on both of the large polar ice sheets.

Compared with the seasonal variations which, even if they survive the firnification process, gradually disappear in polar ice within some thousands of years, the long-term variations are much less affected by molecular diffusion and can be preserved in the ice much longer, up to hundreds of thousands of years, depending on the length of the period. Moreover, the firnification process, which under unfavourable conditions is found to obliterate the seasonal variations, will not affect long-term variations appreciably. Consequently, the old ice sheets obviously contain climatic information spanning a very long time.

The most successful work that has been done in this field is undoubtedly the establishment of the $^{18}O$ profile for the Camp Century ice core which is 1390 m deep (Dansgaard et al., 1969), (Fig.42). The time scale was evaluated by choosing a certain ice flow model, which was corrected to make the time scale independent of ice parameters (Dansgaard and Johnsen, 1969a; Dansgaard et al., 1971). The record is given tentative interpretation in European and American terminology and obviously reflects all of the climatic events known from other independent studies of the last 80,000 years. The authors stressed that although the record evidently reflects changes in climate, every caution should be taken in translating
the record into a temperature scale. There are many reasons for this, the most important being changes in the thickness of the ice. Thus, not only do the extremely low values during Wisconsin correspond to a lower temperature in general but this lower temperature has also increased the thickness of the ice sheet, which again results in a still lower temperature at the respective place due to higher altitude. Corrections for the influence of changes in altitude are shown by the dashed curve in Fig. 42.

Another deep ice core, approximately 2000 m long, has been obtained by drilling through the Antarctic ice sheet at Byrd Station (Ueda and Garfield, 1969) and its $^{18}$O content measured through its entire length (Johnsen et al., 1972). Although the physical conditions of the Byrd Station core are considerably better than those for Greenland (no core pieces were lost or broken), the Byrd Station core is much more difficult to interpret, mainly for the following reasons: Since the accumulation rate is low, seasonal isotope variations are absent, which makes it impossible to date the Byrd Station core by counting the annual layers. The glaciological regime at Byrd Station is much more complicated than at Camp Century. Thus the time scale, based on flow model calculations, contains large uncertainties. Consequently, it is not possible to compare the two records in detail. The general trend in climatic changes, however, is apparently the same in the Southern and Northern hemispheres.

Such long climatic records as those obtained on the two polar ice sheets have two main applications: the study of climatic changes as far back in the earth's history as possible and the use of this information for predicting possible climatic changes of the future.

The Camp Century ice core suggests climatic changes with periods of 78, 180, 400 and 2400 years. Since they are anti-correlated with the variation of $^{14}$C in tree rings, all these oscillations appear to be caused by various kinds of solar activity (Dansgaard et al., 1971). Johnsen et al. (1970) used the oscillations of 78 and 180 years for climatic prognosis for the next 30--50 years. They concluded that if man's influence such as pollution is not considered, a 'cooler' climate is generally to be expected for the next one or two decades, followed by an increase to maximum 'temperature' towards A.D. 2010--2020.

With regard to climatic records for a longer period than covered up to now, it is believed that at certain places in Greenland one might find ice cores which span one million years back in time and in the Antarctic ice cores spanning even up to several million years (Dansgaard et al., 1973). Reasonable dating of the lowest part of such an ice core still remains a problem. Dansgaard et al. (1973) point out that this problem might be solved by dating methods based on $^{81}$Kr and $^{53}$Mn. Such an ice core would be of unique value since it could be used to record glacial sequences spanning most of the Pleistocene and would thus give independent supplement to Emiliani's glacial chronology (1972), which is based on $^{18}$O profiles obtained from drilling cores from the sea floor.
The use of stable isotope profiles of glacier ice to record past climatic changes is mainly of interest in relation to polar glaciers. Temperate glaciers are of less interest for this field, mainly for two reasons. First, the ice at the bottom of the temperate glaciers is very young compared with that of the polar glaciers; such a record therefore only spans a very short time period — under favourable conditions possibly 2000 years. Second, the percolating water is found to obliterate the seasonal variations and in some cases strongly to change the original isotopic content of the accumulation.

Under favourable conditions, however, temperate glaciers might be useful to give ‘short-time’ climatic records. Studies carried out on a 415 m long ice core obtained from one of the highest places on the Icelandic glacier Vatnajökull suggest such possibilities (Arnason et al., 1974; Arnason, 1976). Detailed deuterium measurements on the uppermost part of the core show that the δ-variations of the accumulation are only slightly affected by percolation of meltwater. At a depth of 20 m, corresponding to the year 1963, the δ-variati ons within each year are mostly smoothed out, but apparently without any appreciable change in the mean δ-value of the ice (Arnason, 1970). Only recently a detailed δ-record back to the year 1900 has been obtained. When compared with meteorological data from Iceland, this record shows lower δ-values in the core for the years 1948–1952 and several years before 1920 when the mean annual temperature was relatively low.

Whether the ice core from Vatnajökull can be used to interpret past climatic changes is still a matter for debate. This can be seen only when a detailed record has been obtained from the entire core. Such a record is of interest, although spanning a relatively short time, because it offers the possibility of obtaining a climatic record for the North Atlantic which is more representative than the record from North Greenland.

Because of the lack of the seasonal amplitude in temperate glaciers, dating of the ice by the stable isotope method is not possible. Ice cores from such glaciers therefore must be dated by other methods. Iceland offers a special opportunity for dating this ice, since volcanic ash layers from recorded eruptions are found to be preserved in it, allowing very accurate dating. In the 415 m long ice core, more than 30 tephra layers were found and many of them have been identified (Steinthórsson, 1977).

7.3.7. Drifting sea ice

Studies of the stable isotope content of sea ice might possibly contribute to the solution of certain oceanographic problems, such as the formation and drifting of sea ice.

As previously mentioned, ice formed at sea under equilibrium conditions will contain about 20‰ more deuterium and 3‰ more $^{18}$O than the mother liquid.
In nature, these conditions are not likely to be exactly realized because of the inclusion of brine in the ice. However, measurements reported by Friedman et al. (1964) have shown that the above values are not far from the actual ones. Ice samples collected at Woods Hole and Hopedale Bay, Labrador, contained approximately 20% more deuterium than the sea-water when corrections were made for entrapped brine on the basis of the salt content of the ice. In principle, therefore, it should be possible to distinguish between ice masses frozen out from waters with different isotope content.

As discussed in a previous chapter, the ocean is rather uniform in its isotopic composition. In some cases, however, differences exist between different ocean masses. As an example, the surface water in the Canadian basin of the Arctic ocean contains appreciably less deuterium ($\delta D = -19\%$ to $-30\%$) than that of the North Atlantic ocean ($\delta D = +1\%$ to $+5\%$) (Redfield and Friedman, 1969). This offers the possibility of estimating the origin of sea ice drifting along the East Greenland coast into the Atlantic.

In May 1969, several profiles were collected from ice that had drifted into the Húnaflói Bay in Northern Iceland and these were measured for their deuterium content. The thickness of the ice ranged from one to three metres. Except for the uppermost 30–50 cm, which have a deuterium content of $\delta D = -80\%$ similar to that of the winter precipitation north of Iceland, the deuterium content of the ice was almost uniform throughout, $\delta D = -7.5\%$. Since ice frozen out in the sea between Iceland and Spitzbergen would be expected to have $\delta D = +20\%$, it is likely that the ice which drifted into Húnaflói in the spring of 1969 was formed somewhere in the Arctic Ocean.

Redfield and Friedman (1969) measured the deuterium content of an approximately 3 m long core of sea ice collected near Ice Island, T3 (80°15'N, 113°W). The uppermost 15 cm of the core was snow with $\delta D = -260\%$, but the average deuterium content of the core was $\delta D = -44\%$. According to these authors, this $\delta$-value should result when the ice as a whole was derived from 86 parts of frozen sea, with $\delta D = -23\%$, and 14 parts snow. The deuterium profile of the core was complex, but three or four minima found in the core might represent annual periods.

The studies mentioned above indicate that isotope measurements on drift ice could give information about its origin and even its age. Such studies have, however, been given rather little attention until now and much more detailed measurements are necessary to prove whether this method is valid or not.

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Chapter 8

RIVER WATERS

8.1. INTRODUCTION

Water flow in most river systems has two principal components: surface run-off of precipitation and groundwater. Their respective contributions differ in each system and depend on the physical setting of the drainage basin as well as on climatic parameters. These will determine how much water can infiltrate, how much will be temporarily stored at the surface in the form of ice and snow or in lakes, and what portion becomes direct run-off. Groundwater discharges are also controlled by the characteristics of the basin, although theoretical analyses by Freeze (1972, 1974) show that precipitation input is often the principal controlling parameter for the release of groundwater during flood discharges which follow major precipitation events.

Water in a river may thus originate from many sources and because of this its isotopic composition can vary: seasonal variations will be observed in rivers and creeks in which surface run-off dominates the discharge, whereas small variations will be observed in rivers with only a single groundwater source. In most rivers, however, contributions from different surface and subsurface sources, each with their characteristic isotope contents, will determine the isotopic composition of the water. Where it is possible to describe the isotopic composition of these sources, isotope analyses of river waters can yield direct information about the origin and quantity of the various contributions. If used in conjunction with more classic hydrologic tools and other chemical techniques, descriptions of parameters and processes controlling river flow can be obtained. Applications could range from input into water management programmes to model verifications.

This chapter attempts to summarize isotope data available from river systems and their use in applied studies. It commences with a discussion of variations in isotopic composition observed in small watersheds, followed by a brief discussion of evaporation from river systems. Attention will then focus on larger rivers and their isotopic variations. It is shown that local precipitation characterizes the isotope content of the river in the head waters of large basins. In the lower reaches the sum of the head waters controls the isotopic composition and local additions appear to be of minor importance. It is then demonstrated how the short-term variations of smaller rivers and creeks provide a unique tool for the separation of run-off hydrographs and the quantification of run-off components. Rather detailed information about the hydrogeological characteristics of a drainage basin can be obtained from such analyses. The last
<table>
<thead>
<tr>
<th>River</th>
<th>n</th>
<th>Sampling period</th>
<th>$\delta^{18}$O (%) versus SMOW</th>
<th>Flow (m$^3$·s$^{-1}$)</th>
<th>Size of basin (km$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piave (Nervesa)</td>
<td>43</td>
<td>2/70 - 12/74</td>
<td>Maximum: 7.6 (09-70), Minimum: -11.0 (04-72), $\delta$: -9.78, $\sigma$: 0.70</td>
<td>Maximum: 808 (06-72), Minimum: 78.5 (08-73)</td>
<td>2100</td>
</tr>
<tr>
<td>Adige (S. Michele)</td>
<td>11</td>
<td>1/71 - 12/74</td>
<td>Maximum: 11.4 (02-72), Minimum: -13.0 (09-72), $\delta$: -12.21, $\sigma$: 0.61</td>
<td></td>
<td>1700</td>
</tr>
<tr>
<td>Adige (estuary)</td>
<td>38</td>
<td>1/71 - 6/75</td>
<td>Maximum: 10.3 (11-71), Minimum: -12.9 (06-72), $\delta$: -11.96, $\sigma$: 0.59</td>
<td></td>
<td>11956</td>
</tr>
<tr>
<td>Bacchiglione (Padova)</td>
<td>17</td>
<td>8/71 - 12/72</td>
<td>Maximum: 5.6 (11-71), Minimum: -8.9 (02-72), $\delta$: -7.83, $\sigma$: 1.06</td>
<td>Maximum: 194 (06-72), Minimum: 6.9 (11-71)</td>
<td>1384</td>
</tr>
<tr>
<td>Brenta (Padova)</td>
<td>40</td>
<td>2/70 - 9/75</td>
<td>Maximum: 6.8 (07-70), Minimum: -11.6 (05-72), $\delta$: -10.03, $\sigma$: 0.73</td>
<td>Maximum: 470 (06-72), Minimum: 11.0 (01-73)</td>
<td>1862</td>
</tr>
<tr>
<td>Po (Ponte lagoscuro)</td>
<td>43</td>
<td>10/71 - 10/75</td>
<td>Maximum: 9.2 (04-73), Minimum: -10.9 (05-74), $\delta$: -9.98, $\sigma$: 0.32</td>
<td></td>
<td>30000</td>
</tr>
<tr>
<td>Sile (Treviso)</td>
<td>41</td>
<td>4/70 - 6/74</td>
<td>Maximum: 7.4 (11-70), Minimum: -10.2 (01-72), $\delta$: -9.33, $\sigma$: 0.69</td>
<td></td>
<td>1500</td>
</tr>
</tbody>
</table>
section deals with river/groundwater interactions and the usefulness of environmental isotope techniques in projects related to river-water infiltration.

8.2. ISOTOPIC VARIATIONS OF SMALL RIVERS

Most groundwater bodies are isotopically constant and closely reflect the average annual isotopic composition of local precipitation. This is also true in basins where the seasonal variations of $^{18}$O and D in precipitation are very large. However, in many small drainage basins the groundwater storage reservoir is very limited and therefore discharge from the basin is strongly dependent on precipitation events and the more or less direct run-off.

This is especially true in alpine environments where one would expect that the magnitude of the seasonal variations in the isotopic composition of the creeks is inversely proportional to the size of the basin, i.e. the size of the subsurface reservoir which can respond to precipitation events. Unfortunately there are virtually no data to document this, although the data listed in Table XI, collected by Bortolami et al. (1973, 1980), could lend support to this assumption. It can be noted that Bacchiglione creek, which drains the smallest basin, shows the largest standard deviation in its isotopic composition.

The seasonality of $^{18}$O and D contents in precipitation has been described in previous chapters. Thus, in direct run-off-dominated systems one would expect higher heavy isotope concentrations during the summer months and lower ones during the winter. This is the case in moderate climates and was documented, for example, by Gonfiantini et al. (1973) for the Arno and Era rivers of the Tuscany region in central Italy (Fig.43).

In alpine and nordic environments, however, this is not necessarily the case because there the temporary storage of winter precipitation on ice and snow covers and their melting during summer can reverse or at least shift the isotopic cycles. This explains why the largest of the rivers listed in Table XI, the Adige, shows its less negative $\delta^{18}$O value in the only sample collected in winter: $\delta^{18}$O = $-11.4\%{\text{oo}}$, compared with the average value of $-12.21\%{\text{oo}}$ for five summer samples.

The Brenta, deriving from the Pre-Alps and therefore not affected by seasonal snow melt, has a remarkably constant isotopic composition: isotopically light samples collected monthly from July 1970 to March 1971 give a mean $\delta^{18}$O value of $-10.0\%{\text{oo}}$, the extreme values being $-9.7\%{\text{oo}}$ and $-10.2\%{\text{oo}}$. In this case the seasonal variations of precipitation appear to be completely smoothed out, as if only groundwater were discharged.

Seasonal $^{18}$O variations, probably resulting from both snow-melt and variation of isotopic composition of precipitation, have also been observed in the Areuse River in Switzerland (Burger et al., 1971). This river drains a karstic
(1) Oxygen isotopic composition of water relative to SMOW.
(2) Mean volume flow in m³/s during the ten days preceding each sampling for the Arno river, and average depth of water in cm above river-bed level during the ten days preceding each sampling for the Era river.
(3) Monthly amount of precipitation on the watershed.
(Gonfiantini et al., 1963.)
system and shows an amplitude of about 3‰ for $^{18}$O around a mean value of approximately $-10\%$. It is interesting to note that in the nearby Serrière River, the seasonal variations are much smaller, although the discharge variations are much larger (by about a factor of six) in the Areuse River than in the Serrière River. The average $^{18}$O value of the Serrière River is also slightly lower and indicates that not only a more complete mixing takes place but also the average altitude of the recharge area is slightly higher (approximately 200 m) than the one of the Areuse River.

No clear seasonal variations have been observed in the Aare River in Switzerland, only a slight tendency towards more negative $^{18}$O values during summer. There the total variation does not exceed 0.5‰ and might reflect some snow-melt contributions (Siegenthaler et al., 1970). The different behaviour of these rivers reflects the hydrological regimes which control the river supplies. A river dependent on discharges from a karstic system with short transit times will show more pronounced seasonal variations than one fed by groundwater discharging from aquifers in more 'normal' porous media where the average residence time in the subsurface can be much longer.

The most comprehensive study of alpine river systems was carried out in the Lainbach valley of the Bavarian Alps and preliminary results were presented by Hermann et al. (1978); run-off data are graphically shown in Fig. 44. The δD-curve contains a basic sinusoidal wave, which reflects the base-flow input, and superimposed peaks resulting from rapid responses to isotopically heavy summer rains, light winter precipitation and/or snow-melt. The variations in base-flow values reflect, with an attenuated amplitude, the isotopic variations of precipitation: The annual range of monthly average values of deuterium in precipitation in the project area is close to 60‰ and is attenuated by 9/10 in the run-off.
A careful analysis of all data available also led to the recognition of a phase shift of a few months of the base-flow curve from the precipitation curve. It was shown that this is a function of groundwater reservoir characteristics which are related to the physiography of the area.

From these data, mean residence times of groundwater \( (\tau_0) \) in the drainage basin can be calculated using the relationship

\[
\tau_0 = \frac{(1/t^2 - 1)^{1/2}}{2\pi}
\]

where \( f \) describes the attenuation of the amplitude of the precipitation curve with respect to the output curve. Mean residence times of approximately 2 years were determined for groundwaters in the Lainbach drainage basin. This in turn permits a direct estimate of the size of the groundwater reservoir because the discharge volume from the basin is known (Stichler, personal communication, 1979).

Run-off from an alpine basin depends strongly on snow-melt, which in such environments can occur very rapidly and can induce very sharp changes in the amount and isotopic composition of discharge. This is shown in Fig.45 where data from two major melt events in the Lainbach basin are reported. The observed changes in isotopic composition reflect the variable contributions from isotopically different sources, which can be evaluated if isotopic characterization of the various sources is possible. In mountain terrains this can be rather difficult because the existence of subsurface and surface 'reservoirs' (and the
FIG. 46. Deuterium content of tributaries of the alpine river Isar with drainage basin at different altitudes. The lengths of the horizontal bars correspond to the elevation of the tributary between spring and confluence (Moser et al., 1971).

TABLE XII. δD AND δ¹⁸O-VALUES FOR THE RIVER CHIMBO IN THE ANDES, ECUADOR

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>δ¹⁸O</th>
<th>δD</th>
<th>Date</th>
<th>Elevation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(‰)</td>
<td>(‰)</td>
<td></td>
<td>(m)</td>
</tr>
<tr>
<td>Guaranda</td>
<td>-11.72</td>
<td>-83.0</td>
<td>10/11/76</td>
<td>2600</td>
</tr>
<tr>
<td>Guaranda</td>
<td>-11.37</td>
<td>-80.8</td>
<td>15/12/76</td>
<td>2600</td>
</tr>
<tr>
<td>At confluence with</td>
<td>-9.33</td>
<td>-63.2</td>
<td>11/11/76</td>
<td>746</td>
</tr>
<tr>
<td>Coco River</td>
<td>-8.99</td>
<td>-60.4</td>
<td>16/12/76</td>
<td>746</td>
</tr>
<tr>
<td>Bucay</td>
<td>-7.40</td>
<td>-46.8</td>
<td>11/11/76</td>
<td>317</td>
</tr>
<tr>
<td>Bucay</td>
<td>-6.33</td>
<td>-40.1</td>
<td>16/12/76</td>
<td>317</td>
</tr>
</tbody>
</table>

climatically induced rapid release from both), and the variations in altitude might produce isotopic changes which over-impose on the seasonal variations of precipitation. In particular, the altitude effect would be reflected in both surface run-off and subsurface aquifers. The importance of such altitude effects was documented by Moser et al. (1971) in a survey of tributaries of the river Isar which originates in the Alps and passes through the town of Munich to discharge into the Danube river. Figure 46 shows the δD-values in tributaries with drainage basins at different altitudes. The altitude effect is close to -3.5‰ per 100 m rise, a value typical for such environments in mid-latitudes. Another example
where altitude effects control the oxygen isotopic composition of a mountain river was presented by Payne and Schroeter (1979), following investigations of groundwater supplies in Ecuador. The results are listed in Table XII; an altitude effect of a reduction of 2.3‰ in $^{18}$O and a reduction of 18‰ in D per 1000 m rise in altitude is recognized.

8.3. EVAPORATION FROM RIVERS

The isotopic labelling imparted to a river by the different contributions from surface and subsurface systems can be profoundly modified if evaporation occurs. In moderate climates this process is usually not important unless lakes or large dam systems affect the flow in the river considerably. For example, no evaporation effects are known for the Rhine despite its passage through Lake of Constance. Even in the Amazonas river, surface evaporation does not have any recognizable effects (Matsui et al., 1976), but evapotranspiration and recirculation of river and groundwater to the atmosphere appear to be essential for the hydrologic cycle in the Amazonas basin (Salati et al., 1979).

The situation is different in arid zones because there seasonal variations, with high D and $^{18}$O contents in river-waters during the summer months, are normally not caused by the changing isotopic compositions of precipitation in the head waters but by evaporation from the rivers in the lower-lying parts of the drainage basins where rainfall is less abundant. This is of economic importance if the lack of base-flow in the lower reaches of such rivers and dwindling supplies in the head waters, combined with water loss by evaporation and possibly infiltration into the subsurface, result in no flows during the dry season.

It is extremely difficult to quantify water loss through evaporation, although to have knowledge of it is crucial for many hydrological studies in arid zones. No studies have been published in which water loss through direct evaporation from a river has been evaluated. This should be possible, however, and would be of practical importance in water resource management studies for situations where it is important to know how much of a river disappears as subsurface run-off within or outside the river bed and is thus potentially available and how much is irretrievably lost to the atmosphere.

The use of environmental isotope analyses for the quantification of evaporative water loss from running surface waters was documented by Fontes and Gonfiantini (1967) who investigated the hydrogeology of sebkhas in Algeria. Such sebkhas are often fed by surface run-off following precipitation events, with the run-off partially evaporating before arriving at the sebkha. By evaluating the evaporation pattern (i.e. isotopic enrichment versus residual volume) and curve-fitting of the observed data it was shown that 46% of the run-off was lost before the water reached the sebkha. A similar approach was taken by
Stolf et al. (1979) in estimating water loss from a dam in N.E. Brazil. There the result obtained from isotope data could be confirmed by the salt budget because the investigation dealt with a closed system.

Isotopic enrichment caused by evaporation from an open surface is recognizable when the $\delta^{18}\text{O}$ and $\delta\text{D}$-values are compared (see Chapter 3). This comparison provides a unique labelling of the river-water and is of importance in attempts to trace the possible infiltration from rivers into groundwater reservoirs. This method was applied in an unpublished study of the Kano River in Nigeria (R.N. Farvolden, personal communication) where it was possible to show through comparison of groundwaters in the immediate vicinity of the river with actual river-water that river-water infiltration occurred only during major run-off events. Isotopically enriched water was found only within the bank, but never at any distance from it, despite favourable hydraulic gradients.

Analyses on samples from rivers feeding Lake Chad in North-Central Africa provide another example for river systems in which evaporation is responsible for most of the seasonal variations observed (Fontes et al., 1970). Figure 47, which indicates discharge and $^{18}\text{O}$ variations, shows that these rivers carry evaporated water throughout most of the year but respond strongly to the Monsoon rains, from July to September. At that time the river-waters closely approach the isotopic composition of the precipitation, which could suggest that most of the flow is direct run-off of seasonal precipitation. However, it is also noted that at the time of maximum discharge the $^{18}\text{O}$ values have passed their
minimum and show a slight increase. This is thought to be due to the development of shallow ponds from which significant amounts of water are lost by evaporation already during the rain season.

In a study conducted in the Jordan River System, Gat and Dansgaard (1972) describe the difference in behaviour with seasons in the upper part of the basin. During the winter rain season, the isotopic composition of the Jordan River is in good agreement with that calculated by assuming a simple mixing of the tributaries and precipitation. In summer, the isotopic picture is more complex because of considerable losses of water through evaporation, accompanied by a significant enrichment in heavy isotopes. The data can be explained by a model which takes into account the water removed from and then returned into the main stream via branch streams and water pumped from the system. However, evaporation occurs not so much in these branch streams or in the Jordan River but mostly in ponds and dams constructed for irrigation systems.

Similar is the experience on the Colorado River System, which has been studied by Payne et al. (1979) for a project dealing with groundwater origin and salinity in the Mexicali Valley in N. Mexico. The Colorado River supplies much of the local groundwaters, and through groundwater and river-water analyses it was possible to distinguish ‘old’ Colorado River water ($\delta^{18}O = -14.6\%$, $\deltaD = -112.1\%$) from ‘recent’ water ($\delta^{18}O = -12.1\%$, $\deltaD = -99\%$). The difference is due to evaporation from the reservoirs behind dams which have been constructed on the Colorado River since 1930. With these two indices it was possible to ‘trace’ water movements to the subsurface and to show that the salinity increases in the basin are not due to a mixing with sea-water but are due to infiltration of saline surface waters and the dissolution of evaporitic salts.

8.4. ISOTOPIC VARIATIONS OF LARGER RIVERS

8.4.1. Seasonal variations

In small basins the presence and amplitude of seasonal variations in river waters depend very much on the ratio between the discharge and the storage capacity of the basin or, better, the fraction of stored water which can be mobilized seasonally by precipitation and/or temperature changes. This is also true in large river systems, even if a certain smoothing-out of short-term fluctuations can occur. Despite this, seasonal variations of precipitation may still have an influence, as shown for the Dutch rivers Meuse, Vecht and Meppelerdiep (Mook, 1970). There, precipitation is almost uniformly distributed throughout the year and the $^{18}O$-concentration in the three rivers is about $1\%$ higher in summer than in winter, whereas the seasonal $^{18}O$-variation in averaged monthly precipitation is about $5\%$. The amplitude of these variations is the same in all
three rivers, in spite of the fact that the Meuse River has a much larger catchment area than the other two rivers. On the other hand, the prevailing climatic conditions are very much the same over the three catchment areas and therefore the Meuse River can be considered, at least to a first approximation, as the resultant of summing up several identical smaller sub-units, each one having a behaviour similar to that of the Vecht and Meppelerdiep Rivers.

Spring and summer snow-melt are thought to be responsible for the stable isotope variations observed in the Rhine (Mook, 1970), whose $^{18}$O-content drops from $-8.8\%$ in winter to $-10.5\%$ in summer. If one assumes that the Rhine water is derived from the mixing of two components, one of Alpine origin and the other from the lower part of the basin extending from Basel to the Netherlands, the fraction of each component can be estimated. If the lower-basin component has an average $\delta^{18}$O-value of $-7.7\%$ as found for the Meuse, and if the Alpine component has a mean $\delta^{18}$O-value of $-13.5\%$ (Mook, 1970), then a simple balance equation shows that the Alpine component is about 50% of the river discharge in summer, dropping to 20% in winter.

An example for a river with very large seasonal variation is the Red River which has its head waters in the Dakotas of the North-Central USA and flows through Manitoba (Canada) to discharge into Lake Winnipeg, which in turn drains into the Hudson Bay. This river has been sampled in Winnipeg (Manitoba) more or less regularly since 1972 and first results were presented by Fritz et al.
(1974). Figure 48 shows seasonal variations for 1974 and 1975. The total variation in $^{18}O$ exceeds 10% and is lowest during spring run-off when the river discharge may exceed 100 m$^3$/s. During base-flow, the $\delta^{18}O$-values are close to $-7\%_0$ and discharges may become as low as 10 m$^3$/s. The $^{18}O$ and D-contents of the base-flow during summer are much higher than those of the young groundwaters and the average precipitation in Manitoba, both of which have $\delta^{18}O$-values between $-13$ and $15\%_0$. Therefore, it was originally thought that evaporation from irrigation and flood control dams in the Dakotas and Manitoba might be responsible for the discrepancy. However, a comparison of the $\delta^{18}O$-values with the $\delta D$-values demonstrates that the high $^{18}O$-content is not due to evaporation from open water but reflects isotopically heavy precipitation as occurring in the Dakotas.

The drainage basin receives thus precipitation from two distinct air masses—cold Arctic air and warm and moist air from the Gulf of Mexico. Southern Manitoba is a point of convergence. The seasonal variations in the Red River are thus related not only to seasonal variations in the isotopic composition of precipitation but also to regionally and seasonally different contributions. The results show that the summer base-flow originates primarily in the Dakotas and that little water is added in Manitoba. During the snow-melt, however, surface run-off becomes important throughout the entire basin and isotopically light melt-water dominates the discharge during the flood stages. Unfortunately, nothing is known about groundwater contributions from aquifers in Manitoba; however, some contributions might be expected.

The Rhine and Red River studies are of a similar kind; no investigation has been made of the importance of the seasonally varying groundwater inflow into major rivers. This has been recognized to be a dominant component during flood run-off for small basins (see below) and, on a more regional scale, it may be so also for larger rivers. However, little is known about the discharge of major, deep, regional flow systems from sedimentary basins such as, for example, the discharge from the Tertiary Basin in Southern Germany into rivers such as the Danube. Piezometric maps indicate that such inflow must occur, but for quantifying it the tools of classical hydrology are of little assistance although, in combination with chemical and isotope techniques, at least semi-quantitative estimates might be possible.

8.4.2. Continental drainage systems

The head waters of most rivers and streams will reflect the isotopic composition of local precipitation, but in the down-stream areas the quantitative importance of all water sources will control the isotope contents. Thus a large river can give little detailed information on local hydrogeological characteristics or minor meteorological events but will reflect regional hydrogeology and major
events. This has been documented in a number of studies done in North and South America.

Friedman et al. (1964) reported deuterium measurements of surface waters in the Missouri-Mississippi Drainage Basin during the period 1948–1959. Although the data distribution reflects spot samples taken at different seasons over a long period (Fig. 49), the main features are quite clear. At its source, in the mountains of Wyoming and Montana, the Missouri River has a δD-value of about −150‰; by the time it reaches the confluence with the Mississippi at St. Louis, the inflow of waters with less negative δD-values has changed the deuterium content of the Missouri River to about −95‰. After St. Louis the Mississippi is about 30‰ less negative in δD. From this confluence point up to the sea, the positive trend in δD continues, but apparently the main stream at its mouth still exhibits values about 20‰ more negative than those of nearby small rivers. In this case, the main stream retains its isotopic contrast to local waters throughout its entire altitude and latitude range.

Both altitude and climatic (latitude) features can be recognized if the isotope values of smaller rivers are compared on a continental scale. This was done by Brown et al. (1971) for Canadian Surface waters during 1967–1969. As shown in Fig. 50, the δD-values in coastal basins on the eastern and western sea-board decrease very rapidly from about −50 to −150‰ as the Rocky Mountains are crossed. The iso-delta lines shown, based on river data, broadly reflect the average annual composition of rainfalls in the different regions of Canada.

The Mackenzie River Basin of Northwestern Canada was subsequently studied in considerably more detail by Hitchon and Krouse (1972). They document the strong dependence of the isotope contents in sub-basin surface waters on climatic parameters, which control both the isotopic composition of precipitation and apparent loss by evaporation from large open water surfaces. Unfortunately, these investigators did not present any deuterium data and, therefore, the importance of the latter was only inferred but not proven. However, it is noteworthy that the average isotopic composition of the Mackenzie River is constant within ±1‰ (δ18O) over more than 1500 km.

It has been indicated that within the Amazon system significant differences in isotope content occur; the Rio Solimões contains 2–2.5‰ less 18O (δ18O between −5.0 and −8‰) than the Rio Negro. Matsui et al. (1976) propose that differences in origin and thus an ‘altitude effect’ may account for this and note that “the Negro receives most of its water from basins in the northern hemisphere, and the Solimões is fed by rivers coming from southern and northern hemispheres and is influenced also by waters from melting of Andean snow”.

The preservation of the isotopic composition of the head waters is here especially surprising since the Rio Solimões traverses more than 1000 km of jungle where enormous amounts of water are recirculated through the atmosphere and a loss of these head-water characteristics would have been expected.
FIG. 49. Map of the Missouri-Mississippi river system, with δD-values (‰) given at collection points. Data on additional rivers in the southern section are also included for comparison (Friedman et al., 1964).

FIG. 50. Deuterium contents in Canadian surface waters. The deuterium concentrations are given as ppm values and can be converted to δD(‰)SMOW by the relationship: 

δD(‰)SMOW = [(D/ppm)/156.7 − 1] × 1000. 156.7 is the deuterium content in ppm of SMOW as determined by Atomic Energy of Canada Ltd, Chalk River (Brown et al., 1971).
8.4.3. Mixing of large rivers

A problem specific to large river systems is the distance over which complete mixing of two rivers after their confluence will have taken place. Krouse and McKay (1971) determined the oxygen isotopic composition in ten cross-sectional profiles of the Liard–Mackenzie River system at various intervals over 480 km downstream from their confluence. At their confluence, the Liard and Mackenzie Rivers had average $\delta^{18}O$-values of $-21.3\%_o$ and $-17.4\%_o$, respectively. This isotopic difference was large enough for a detailed monitoring which showed that a distance of about 300 km was required for a thorough lateral mixing of the waters of these rivers.
Similar observations were made on the Rhine which was monitored with dyes and deuterium analyses after the inflow of the Main River at Mainz. Despite its rather turbulent flow in the following section, the mixing was complete only below the town of Bingen, at a distance of more than 50 km from the confluence (Fig. 51) (Behrens and Stichler, 1979).

A third case documented is that of the confluence of Rio Solimões and Rio Negro forming the Amazon. As already pointed out, their isotopic contents and chemical compositions are quite different. In 23 pairs of samples collected between September 1971 and December 1973 from the Rio Solimões and the Rio Negro, just above their confluence at Manaus, the $\delta^{18}O$-values of Rio Solimões are consistently more negative than those of Rio Negro. As expected, the water of the Amazon River has an isotopic composition intermediate between those of the two main tributaries. Mixing between the two is slow; Matsui et al. (1976) observe on the basis of the isotopic differences that the waters of Rio Solimões and Rio Negro were still incompletely mixed about 120 km below Manaus. Taking seasonal variations and mixing into account, it is possible to determine from this information the relative contributions of the two river systems to the Amazon. It was thus found that the relative contribution from Rio Negro to the total run-off was smallest in January (20 ± 5%) and greatest in July (68 ± 7%). Similar determinations were made earlier with conventional methods. For Rio Solimões, Oltman et al. (1964) observed for July 1963 a contribution of 62%, and Matsui et al. (1976) report for July 1972 a contribution of 57 ± 9% to the Amazon discharge. It thus appears that it is possible to obtain with the isotope method rather reliable results with little effort and expense, compared with those required by conventional techniques.

8.5. SHORT-TERM ISOTOPIC VARIATIONS.

ISOTOPIC HYDROGRAPH SEPARATION

The quantification of the components contributing to flood discharges has occupied hydraulic engineers for a long time. A number of different techniques were presented in the literature and all were based on empirical analyses. Only through chemical and isotopic analyses was it possible to substantiate or negate these concepts and also to verify mathematical model calculations performed during recent years.

Variations of the isotopic composition of river waters immediately following periods of intense precipitation were first documented for two rivers of Central Italy, the Arno (with a drainage basin of about 8000 km²), and its tributary, the Era (Gonfiantini et al., 1963). In both cases, the $\delta^{18}O$-values showed a remarkable correlation with the mean discharge during the ten days preceding sampling. The correlation was particularly striking for the small Era River (Fig. 43) which
has largely impermeable clay outcrops in its catchment area. For both the Arno and Era, the major changes in $\delta^{18}O$ and in discharge were related to the December rains. Precipitation falling from September to November, although very abundant, did not cause comparable discharge increases or $\delta^{18}O$-variations. In fact, in September and October, evapotranspiration is still important and, in addition, the rains are mainly used to recharge the groundwater reservoirs depleted during the dry summer. However, a large proportion of the December rains, falling on a saturated watershed, is conveyed directly to the river. This is demonstrated by the simultaneous increase of discharge and change of $^{18}O$-content during this season. This finding is further confirmed by the April rains which cause a smaller but similar effect. It is also interesting to note that for both Arno and Era a better correlation between discharge and isotopic composition was obtained if mean values for a ten-day discharge were used instead of the values obtained at the time of sampling.

These results suggested that it should be possible, under certain conditions, to evaluate from the changing isotope contents of the river water the relative proportions of groundwater versus surface run-off or, in other words, to arrive at a hydrograph separation. The conditions required are: a strong input (in general precipitation) occurring during a short period (ideally this input should be almost equally distributed over the entire basin), and an isotopic composition of the input which is homogeneous over the entire basin and significantly different from that of the base-flow, i.e. the groundwater component. These conditions are more frequently realized and more easily studied in small basins.

Actual hydrograph separations based on environmental isotopes were first performed in snow-covered or glacial basins, with the aim of quantifying the melt-water run-off. The Modry Dul watershed, a small mountain basin (2.65 km$^2$) in Northern Czechoslovakia was selected for studying snow-melt/run-off relationships (Dinger et al., 1970). The flow at the stream-gauging station varied from 20 – 30 l/s to a maximum of 3 m$^3$/s during the snow-melt season.

The evaluation of the melt-water component was made using the simple relationship:

$$Q_G = \frac{C_T - C_M}{C_G - C_M} Q_T$$  \hspace{1cm} (1)

where $Q_G$ is the run-off component derived from groundwater having an isotope concentration $C_G$ (or $\delta_G$ if expressed in units), $Q_T$ is the total run-off having an isotope content $C_T$ (or $\delta_T$), and $C_M$ (or $\delta_M$) is the isotope content of the melt-water component. In the Modry Dul study, the values for both tritium and oxygen-18 indicated that, during high flow, on average about two-thirds of water derived from groundwater and only one-third directly from snow-melt. In other words, only a minor fraction of the snow-melt discharged directly into the
stream. The major fraction infiltrated, accumulated, and finally displaced the existing subsurface storage. Consequently, the main discharge is storage water recharged in previous years.

In the Modry Dul study, it was also found that the logarithm of $Q_G$, calculated from Eq.(1), and that of $Q_T$ are linearly correlated, according to the equation:

$$Q_G = 1.55 Q_T^{0.86}$$

(both $Q_G$ and $Q_T$ are expressed in l/s). The fraction of the groundwater component decreases from 100% at $Q_T = 20$ l/s, to 81% at $Q_T = 100$ l/s, to 59% at $Q_T = 1000$ l/s.

The Modry Dul study was paralleled by investigations of discharges from small glaciated alpine basins where the flow varied between 2 and 25 m$^3$/s (Behrens et al., 1972, 1979). There it was found that no increase in groundwater discharge occurred during melting processes in glaciated areas. The reason for this is that the melt-water from a glacier feeds mainly the direct run-off via a discharge system within the glacier.

Extremely detailed studies on snow-melt and rainstorm run-off events were made in the Lainbach valley of the Bavarian Alps. The snow-melt components were sampled in specially placed lysimeters and thus they were isotopically well known. Also known are the groundwater values, so that run-off hydrograph separations could be made. The results were surprising.

During snow-melt run-off, as shown in Fig.52(a), only 10 – 20% of the discharge into the Lainbach creek was direct snow-melt run-off; on other occasions, 15 – 30% was measured. The indirect run-off via a subsurface reservoir ($Q_G$) was thus always more than 70%. Noteworthy is also the cyclic nature of this run-off which is caused by daily temperature fluctuations and the associated increase or decrease of melting snow.

Slightly different is the situation if rainstorm run-off is considered in this basin, because then the direct rain run-off component ($Q_R$) can be as high as 50% of the total discharge (Fig.52(b)). The results of the Lainbach valley investigation support observations made in earlier studies.

Run-off hydrograph separation following rainstorm events in the small catchment basin (6.5 km$^2$) of the Hupsel Brook in the Netherlands (Mook et al., 1974) show that the fraction of precipitation infiltrating to recharge groundwater is 87%, the remaining 13% being drained by the brook.

Similar investigations have been made in four different basins in Canada by Fritz et al. (1976) and Sklash et al. (1976), using a combination of stable isotopes and chemical analyses. In the Wilson Creek watershed (22 km$^2$, Central Manitoba) the study was made after a rainstorm of 40 mm with an $^{18}$O-content which was 5.5$\%$ lower than that of the base-flow. The isotopic hydrograph
FIG. 52. (a) Total discharge of the Lainbach creek ($Q_T$), during the periodically regular snow-melt, with deuterium content, $\delta D$, and calculated run-off components. $(Q_m/Q_T) \times 100$ is the percentage of direct run-off of melt-water.

(b) Total discharge of the Lainbach creek ($Q_T$) during snow-melt and rainstorms, with deuterium content, $\delta D$, and calculated run-off components. $(Q_R/Q_T) \times 100$ is the percentage of direct precipitation run-off of the total discharge.
separation showed that the storm contribution was limited to the rain fallen
directly on the stream channels and that the rest of the flood derived completely
from groundwater stored in the basin.

Three other watersheds, Kenora on the Canadian Shield (1.8 km²), Big Creek
(135 km²) and Big Otter Creek (700 km²) in Ontario, yielded similar results
which confirmed that at least 50% of the total run-off following major rainstorm
events was groundwater which discharged into creeks in response to 'hydraulic
stress' generated during the storms.

Similar observations have been made in many other areas, notably the
Paris Basin, for which Blavoux (1978) describes a number of case studies. In all
cases the principal run-off component was groundwater, with the rain-water
components depending on the physiographic setting and groundwater tables
in the area.

The conclusion must be that stable isotopes provide an information on the
origin of river-water during floods which is quantitatively more accurate than that
provided by other methods. The conventional method of hydrograph separation is
very often subjective and its empirical basis does not permit of distinguishing
between the water derived directly from precipitation and that derived from
storage being mobilized by precipitation. Hydrograph separation based on water
chemistry may be affected by large errors due to salt dissolution during surface
run-off. In fact, the chemical composition is not a conservative property of
water, whereas the isotopic composition is. The main difficulty of the isotopic
method is that it necessitates the collection of precipitation samples in order to
obtain a precise evaluation of the isotopic composition of the input. If the
basin is large, such a collection should be organized at several stations and can
become a major problem. Another limitation of the isotopic method is that it
can be applied only if the isotopic composition of precipitation input is quite
different (by some per mille for ¹⁸O and some tens of per mille for deuterium)
from that of the groundwater, in order to achieve a reasonable accuracy in the
results. However, as documented by Herrmann et al. (1978), an accuracy of
±5% can be obtained without unreasonable effort if these conditions are met.

8.6. RIVER-WATER INFILTRATION

In all examples discussed, groundwater contributions and/or loss from
rivers to subsurface reservoirs were of some importance: rivers simply cannot
be discussed without taking all contributors into account. Therefore, to a large
degree, this short section can be viewed as an appendix to preceding sections
because it considers the variation of isotopic composition in river-water as a tool
not only for understanding run-off but also for monitoring river-water in
subsurface aquifers. Here, we thus reflect briefly on some aspects of river-
water/groundwater interaction and specifically on cases where water loss occurs from the rivers to the subsurface. Such infiltration will take place wherever hydraulic gradients slope away from a river and where the hydraulic conductivities are such that significant flow is possible. This can be a natural or induced process and can lead to temporary or permanent loss of water from the river discharge.

Temporary storage of flood waters in river banks can markedly influence the isotopic composition of rivers whose flow is directly dependent on precipitation. For example, Fontes et al. (1970) argued that in the rivers feeding Lake Chad, such temporary water storage in river banks, shallow 'ponds', etc. was responsible not only for the discharge pattern towards the end of the rain season but also for the changes in isotopic composition. Maximum discharge and lowest heavy-isotope contents did not coincide as one would expect if a direct run-off situation would prevail because highest rainfalls are normally associated with lowest $\delta^{18}O$ or $\delta D$-values.

Where groundwater recharge occurs from river beds the seasonal variations of the isotopic composition of the river-water and/or isotopic differences between river-water and groundwater formed by infiltration of precipitation through an unsaturated zone can be used as natural tracer to describe the amount and movement of river-water in the subsurface system. Moser and Stichler (1977) document such a case for river-connected aquifers along the Iller valley in South Germany where natural hydraulic gradients are responsible for the infiltration.

More important from a practical point of view is induced infiltration because it almost always occurs in response to withdrawal of water from a groundwater reservoir adjacent to a river. Environmental protection, danger of groundwater pollution or indirect water supplies from rivers might be reasons for trying to understand how much and where river-water infiltrates. For this, environmental isotope analyses are the most reliable tool if isotopic differences exist between the different components under consideration. As an example, one might refer to a study by Carlin et al. (1975) in which they consider the inflow of Reno river-water (northern Italy) into groundwater systems in response to pumping of a number of wells located at between 200 and 800 m from the river banks. Although there the difference between groundwater and river-water amounted to only about 5‰ for D and to less than 1‰ for $^{18}O$, the relationship between isotopic composition and distance from the river clearly shows that river-water had infiltrated. This is also confirmed by tritium measurements.

The Mexicali valley project (Payne et al., 1979) has already been introduced. It is an interesting example through which it is possible to show on the basis of environmental isotope analyses that the infiltration of Colorado River water into groundwater reservoirs occurs on a relatively large scale. In addition, it was possible to distinguish old and young Colorado River water not only on the basis of tritium concentrations but also because the construction of dams along the Colorado River resulted in enhanced evaporation and enrichment in heavy isotopes.
by about 2.3% for $^{18}\text{O}$ and 13% for $D$. The different river-waters were recognized in the subsurface and a comparison with chemical data permitted a detailed discussion of the reason for the increased salinization which has been observed during recent years over wide areas in the Mexicali valley.

8.7. SUMMARY

Isotope variations as occurring in the discharge from small drainage basins were first discussed in this chapter. The complexity of input/output interactions was introduced, although few detailed studies using long-term records of isotope data have been presented. Where attempts in this direction had been made it was possible to gain very detailed insight into the surface and subsurface hydrology of basins. The results permitted conclusions to be made on the size of groundwater reservoirs, mean residence times in these, and hydrograph separations in which direct run-off and subsurface run-off were compared.

In arid zones the evaporation from rivers and dams becomes very important and a unique labelling of the surface waters occurs as a result of evaporative isotope enrichment. This is of special importance in projects where river-connected aquifers are studied because then it is possible to recognize such evaporated waters even in the subsurface.

Unfortunately, no detailed studies of large river systems have yet been undertaken. The few surveys which were done show, however, that also very large rivers can exhibit seasonal isotope variations in response to the available discharge from subdrainage basins. It was thus possible to estimate from $^{18}\text{O}$-data the seasonally variable contribution of alpine water to the Rhine. Relationships for mixing of waters from different tributaries of a river system are discussed and it is shown that environmental isotope techniques are ideally suited to document the extent needed for thorough mixing of the waters in large rivers after the confluence of major tributaries. It is astounding to note that it can take up to several hundreds of kilometres before complete lateral mixing is achieved.

Singularly successful were environmental isotope techniques in the analyses of snow-melt and rainstorm run-off hydrographs. These hydrograph separations are based on the different isotopic composition of groundwater discharges and of direct precipitation or snow-melt run-off. The results document that in most run-off events the groundwater discharge into the river increases significantly during maximum flow and does not decrease as suggested in many earlier publications. This is also true for snow-melt where, in the cases studied, only a maximum of 30% of the spring run-off was from snow-melt, the remainder being water which had stayed up to several years in the subsurface.

Environmental isotope analyses are thus an extremely powerful tool in studies designed to understand stream generation and discharge mechanisms.
However, the most successful studies are those where it was possible to employ a combination of isotope, chemical and physical techniques. Where possible, this should be borne in mind, already during the planning stage of a project, despite the fact that many projects carried out to date were based on isotopes alone. This resulted in a similar neglect of isotope techniques by those not familiar with them. Furthermore, the number of published case histories of river studies is very limited and nothing like a global river survey has yet been attempted. Because of this combination of circumstances, these techniques are not as widely applied as their potential would demand.

REFERENCES TO CHAPTER 8


CHAPTER 8


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Chapter 9

LAKES

9.1. INTRODUCTION

Lakes and other surface water bodies which lose water by evaporation are characterized by an enrichment of the heavy isotopic species. Deuterium and $^{18}$O are enriched (along so-called evaporation lines) in such a way that the water composition is diverted from the meteoric water line; lake waters thus acquire a distinguishable isotopic composition which is of use in the investigation of a number of lake properties.

The ‘lake isotopic composition’ is first of all utilized in tracing the contribution of such waters to groundwater recharge. This important practical application of the isotopic properties of surface waters is taken up in more detail in Chapter 13.

In combination with other geochemical parameters, such as temperature, salinity and trace elements, a stable isotope survey of a lake’s waters informs about the homogeneity or mixing state of the lake, the occurrence of stagnant water pockets, and cases of ‘throughflow’ of a river without mixing with the lake. It can also be used to identify the location of inflow points; in any case, a survey of the homogeneity of isotopic composition will often be conducted as a pre-requisite for more quantitative applications in water balance studies.

As the theory of isotope enrichment accompanying the evaporation process is now fairly well advanced (Chapter 3), there have been a number of attempts to quantify the water balance of lakes, based on the degree of enrichment of stable isotopic species in them. In particular, it has been tried to assess the relative importance of evaporative water loss compared with surface or subsurface outflow (leakage). These efforts have been only moderately successful, for reasons to be discussed below in more detail, yet they remain the only practical method to be used in many (saline) systems in which salt balancing cannot be carried out.

Finally, the $^{18}$O record of a lake can be preserved in those sediments (carbonates in particular) which are deposited in equilibrium with the lake waters (see Section 5.6). The isotopic analysis of carbonates in a lake’s sedimentary column thus provides a tool for palaeolimnology, which under favourable circumstances can yield palaeoclimatic evidence. Examples of such uses are given in publications of Stuiver (1970), Katz et al. (1977) and Stiller and Hutchinson (1980).

9.2. ISOTOPIC COMPOSITION OF HOMOGENEOUS (SHALLOW) LAKES:
THEORETICAL CONSIDERATIONS

In a lake which can be considered uniform with respect to its isotopic composition, i.e. where internal mixing is fast relative to the residence time of
water in the lake, the following material balance equations apply:

\[
\frac{\Delta V_k}{\Delta t} = \sum_i \left( F_{in, i} - F_{out} \right) - E + P
\]

(9.1)

\[
\frac{\Delta (\delta V_k)}{\Delta t} = \sum_i \left( \delta_{in} F_{in, i} \right) - \delta_{out} F_{out} - \delta_E E + \delta_P P
\]

(9.2)

where \( V_k \) is the lake volume, \( F \) the flux of (inflowing or outflowing) water streams, \( P \) the direct precipitation onto the lake (which is often merged into the inflow term \( \sum_i F_{in, i} \)) and \( E \) the evaporation. \( \delta \)-values have to be averaged over the period of observation (\( \Delta t \)) and over the lake’s entire area.

In order to assess the factors involved in the evolution of the isotopic composition of a lake, it is instructive to consider first some simple systems, namely: (a) water bodies drying up without inflow; (b) lakes without outflow – so-called terminal lakes; and (c) lakes at constant volume (e.g. lakes whose water level is controlled by overflow over a dam).

9.2.1. Desiccating water bodies

The case of a surface water body which dries up when there is no further inflow (a closed system, except with respect to evaporation) has been treated by Craig and Gordon (1965); Eq. (3.8) applies to this case. At relatively high ambient humidities a limiting isotopic enrichment is approached in the residual waters of the shrinking water body. In \( \delta \)-notation, this limiting value is approximately given by:

\[
\delta^* \approx \delta_a + \epsilon/h
\]

(9.3)

It is to be noted that this value is independent of the initial isotopic composition of the pond and is fixed solely by the ambient parameters \( h \) and \( \delta_a \), as well as the isotopic separation factor which depends on both temperature (through the effect on \( \epsilon^* \)) and humidity, and the conditions at the interface (through \( \Delta \epsilon \)).

There is thus no direct hydrological information content in the value of \( \delta^* \), but it is precisely this fact which led to the suggestion of using such a system (e.g. a large

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14 Similar equations were first given in the Guidebook on Nuclear Techniques in Hydrology (Gat, J.R., et al.), Technical Reports Series No. 91, IAEA, Vienna (1968), and repeated in various forms by a large number of authors using different symbols for the flux terms, such as \( I' \), \( I' \), \( O \), \( Z \), \( A \).
evaporation pan) as an indirect measure of these ambient parameters (namely humidity and the isotopic composition of atmospheric vapour); as will be shown, the poor knowledge of properly weighted values of \( \delta_a \), \( h \) and \( e \) usually limits the quantitative application of isotopic data to the study of the water balance of lakes.

The limiting isotopic composition may not be reached in many natural situations, especially at low relative humidities (see Fig. 5). In such cases, rather than rely on imprecise extrapolation of data, one can use the rate of change of the isotopic composition in a lake which is drying up for the purpose of determining the ambient parameters. As an example, Fontes and Gnosiantini (1967), who studied the desiccation of two Sahara basins, approximated Eq. (3.8) in the form

\[
(\delta_E - \delta_E^0) = A \left(1 - \epsilon B\right)
\]

\[
A = \frac{h (\delta_a - \delta_E^0)}{h - e}
\]

\[
B = \frac{h - e}{1 - h} \approx \frac{h}{1 - h}
\]

and then computed the values of \( A \) and \( B \) by fitting experimental \( \delta_E \)-points to the value of \( \epsilon \) as measured by the build-up of a supposedly conservative chemical element, namely Mg**. A value of \( h = 24\% \) was derived from the computed \( B \).

Welhan and Fritz (1977) suggested the use of measurements of isotopic composition in evaporation pans for estimates of mean values of ambient parameters and in particular \( \delta_E \), which, as will be shown, is a problematic parameter to estimate either theoretically or experimentally. They manipulated Eq. (3.8) into the form

\[
\frac{\delta - \delta^*}{\delta^0 - \delta^*} = f^m
\]

(9.5a)

with

\[
m = \frac{h - e}{1 - h + \Delta e} \approx \frac{h}{1 - h}
\]

and also

\[
m = \frac{\delta_E - \delta_E^0}{\delta_E - \delta^*}
\]

(9.5b)

\( m \) was first obtained from fitting of \( \delta_E \)-values to \( f \) using Eq. (9.5a) and then \( \delta_E \) was calculated through Eq. (9.5b). However, Allison et al. (1979) cast doubt on the possibility of obtaining useful integrated (averaged) data from pans, in view of the variations of the meteorological conditions to which the pan waters do not respond adequately.
Friedman et al. (1976) use a much simpler approach, by fitting data from a desiccating brine lake to an empirical Rayleigh equation:

\[ \frac{R}{R_0} = f(\alpha^{-1}) \]

and using the \( \alpha \) thus determined empirically for other lakes in the same climate zone. The authors used the build-up of \( \text{Li}^+ \) in the desiccating lake as a measure of \( f \). They could show that for the case of deuterium enrichment the empirical \( \alpha \)-values agree quite well with \( \alpha^* \), as computed from vapour pressure data. However, this approach can be justified only when evaporation occurs into very dry air and as long as the enrichment of the heavy isotopes in the lake is still small and does not approach its limiting value.

The case of a leaking pond, i.e. a system in which water loss occurs simultaneously by leakage (or outflow) (\( F_{\text{out}} \)) and evaporation (\( E \)), was discussed by Gat and Tzur (1967). The equation analogous to Eq. (3.8) then becomes:

\[ \frac{d\lambda}{d \ln f} = \frac{h (R_0 - R_f) / (1 - h + \Delta \epsilon)(1 + F_{\text{out}} / E)}{1} \]  
(9.6)

Such a leaky system never reaches a steady isotopic value before drying up. The average composition of the leaking waters (the infiltrate to the subsurface systems) can be obtained by integrating Eq. (9.6) between the limits of \( f = (1, 0) \). Gat and Tzur (1967) assumed a constant ratio of \( F/E \) and also \( \delta_a = \delta_0 - \epsilon^* \), to obtain\(^{15}\):

\[ (\delta - \delta_0)_{\text{leak}} = \frac{\epsilon^* h - \epsilon}{(1 - h) F/E + 1} \]  
(9.7)

Numerical integration can be performed for more realistic cases of varying ratios of \( F/E \).

The \( \delta \)-value of the infiltrate is of course of relevance when assessing the contribution of transient surface water accumulations (in mud or puddles) to groundwater recharge. For the climatic conditions of the Mediterranean region, Gat and Tzur (1967) estimated a range of enrichments, up to a maximum of \( 6\%e \) (in \( ^{18}\text{O} \)), for a wide range of evaporation and infiltration rates.

Obviously, the procedure described could be reversed, so that by comparing the initial evolution of \( \delta_a \) in a leaky system with that of a 'closed-system' pond, one could estimate the outflow rate (\( F_{\text{out}} \)), or more precisely the ratio of \( F/E \).

\(^{15}\) In the paper of Gat and Tzur (1967), Eq. (4) is in error and should have read:

\[ (\delta - \delta_0) = \int_1^0 (\delta - \delta_0)_b \, df = \int_1^0 \frac{h \epsilon^* - \epsilon}{h (1 - f)} \, df \approx \frac{h \epsilon^* - \epsilon}{1 + (1 - h) F/E} \]
By comparing Eqs (9.6) and (3.8) one obtains:

\[ \frac{F}{E} = \frac{S_1}{S_2} - 1 \]

where

\[ S_1 = \left( \frac{d \lambda^0}{d \ln f} \right)_{\text{closed system}} \]

\[ S_2 = \left( \frac{d \lambda^0}{d \ln f} \right)_{\text{open system}} \]

The superscript 0 signifies that the comparison of the slopes has to be made by extrapolation to conditions of equal values of \( \delta \) in the two systems.

9.2.2. Terminal lakes

In a terminal lake, \( F_{\text{out}} = 0 \), and, unless the inflow rate is exactly balanced by evaporation, the lake will undergo fluctuation in its volume \( (V_t) \) in response to changes in inflow rate and intensity of evaporation. In lakes (except for lakes with extremely steep banks, such as some artificial impoundments or crater lakes) usually \( (dA/dV) > 0 \), where \( A \) is the surface area. Thus, any change in the lake level (volume) due to a hydrological imbalance is compensated for by an increase or decrease of its surface area and hence of its evaporation rate. The lake can then find a balanced position for any given inflow rate and intensity of evaporation (i.e. evaporation rate per unit surface area). Lake levels fluctuate around such balance points.

The isotopic composition of a terminal lake in such a balanced state of \( F_{\text{in}} \approx E \) will approach a steady-state value, so that

\[ \overline{\delta_E} = \overline{\delta_{\text{in}}} \]  \( (9.8) \)

(for simplicity’s sake, precipitation is merged in a weighted fashion into the inflow flux).

To relate the steady-state situation to the isotopic composition of the lake water, an explicit expression for \( \delta_E \) must be substituted. This can be done, for example, by using the formulations of Craig and Gordon as outlined in Chapter 3. These authors (Craig and Gordon, 1965) find

\[ \delta_E = \frac{\alpha^* \delta_{\text{in}} (1 + E \rho_E) - h \delta_a - \epsilon}{(1 - h) + \Delta \epsilon + \alpha^* E \rho_E} \]  \( (9.9) \)
LAKES

FIG. 5.3. Isotopic composition of a coastal lagoon and brine ponds situated on the Mediterranean coast of the Sinai peninsula.

X–X– Data from Sabkha 51, a closed pond (no inflow) which approaches steady-state isotopic composition ($\delta^*$) as it dries up in spring:

○ ○ Sabkha Y, a sabkha with water inflow from adjacent dunes, which is assumed to approach a steady-state value, $-\delta_{\text{sd}}(Y)$;

--- Main Bardawil lagoon, which is in partial communication with the Mediterranean sea and whose isotopic composition undergoes a yearly cycle with changing ambient conditions.

Assuming similar ambient conditions (humidity and atmospheric vapour composition) and using Sabkha 51 as an index lake (Eq. (9.3)) we calculate inflow water composition in early May for the main lagoon and for Sabkha Y, using a mean humidity of 60%, according to Eq. (9.11). This calculation is shown graphically. The values of $\delta_{\text{in}} (L) \sim +1\%$ and $\delta_{\text{in}} (Y) \sim -1.7\%$ are reasonable values for the situation.
which can be approximated, through neglect of the liquid resistance term and for values of \( h \) for which \( \Delta e \) can be neglected relative to \((1 - h)\), by the expression

\[
\delta_E = \frac{\delta e - h\delta_a - e}{1 - h} \quad (9.10)
\]

From Eqs (9.8) and (9.10) the steady-state isotopic composition of a terminal lake is found to be:

\[
\delta_{in} \simeq (\delta_E^0 - h\delta_a - e)/(1 - h) \quad (9.11)
\]

\[
\delta_E^0 \simeq h\delta_a + (1 - h)\delta_{in} + e \quad (9.11a)
\]

or, in a more useful form,

\[
(\delta_E^0 - \delta_{in}) \simeq h(\delta_a - \delta_{in}) + e \quad (9.11b)
\]

\( \delta_E^0 \) tends towards the value of \((\delta_a + e^*)\) at high humidities (in which case the exchange with the atmospheric moisture becomes dominant); at low humidity, \( \delta_E^0 \) approaches the value of \((\delta_{in} + e)\), i.e. the isotopic composition of the influx becomes dominant. When \( h \to 1 \), the steady-state isotopic composition of a terminal lake imparts no further information, except possibly as a monitor of the atmospheric parameters, i.e. by serving as an 'index lake', as suggested by Dincer (1968)\(^{16}\).

However, under arid conditions, when the steady-state value strongly reflects the composition of the inflowing water, a choice could be made concerning the origin of the inflow, if this were in doubt. For example, Fig. 53 shows the case of a coastal (saline) pond for which a distinction should be made between marine and meteoric water inputs.

The approach to a steady-state isotopic composition of a lake which is at a steady state hydrologically but not isotopically has been discussed by Zimmermann (1979) for the more general case of a lake with both in- and outflow. We give here a simplified version of this derivation, for the case of a terminal lake at constant volume and, for the sake of simplicity and instructiveness, neglect liquid resistances, second-order terms in \( \delta \), etc., realizing that a more exact formulation should be used when dealing with hydrogen isotopes. We have for water balance

\(^{16}\) Highly saline terminal lakes cannot be used as 'index lakes' because of the effect of salinity on isotopic composition, as can be seen in Section 9.5.
\[
\frac{dV_k}{dt} = \sum_i F_{in} - E = 0
\]

and for isotopic balance

\[
\frac{d(V_k \delta_k)}{dt} = \sum_i (\delta_{in} F_{in} h_i - \delta_E E)
\]

From these two expressions we get:

\[
\frac{d\delta_k}{dt} = \frac{E}{V_k} \left( \delta_{in} - \delta_E \right)
\] (9.12)

substituting Eq. (9.10) and rearranging terms to obtain a differential equation of \(\delta\) in the form

\[
\frac{d\delta}{dt} + p\delta - q = 0
\] (9.13)

We then have

\[
p = \frac{E}{V_k} \cdot \frac{1}{1 - h}
\] (9.13a)

\[
q = \frac{E}{V_k} \cdot \frac{\delta_{in}(1-h) + h\delta_a + \epsilon}{1 - h}
\]

The solution of this differential equation, which describes its approach to the steady-state value \(\delta_k^*\), can be shown to be

\[
(\delta_k^* - \delta_k) = (\delta_k^* - \delta_k^0) \exp(t/\tau) = (\delta_k^* - \delta_{in}) \exp(t/\tau)
\] (9.14)

with \(1/\tau = p\).

As shown by Zimmermann (1979) for some recently excavated groundwater lakes (Fig. 54), a straight line results when \(\ln(\delta_k^* - \delta_k)\) is plotted versus time; the reciprocal of the slope of this line, \(\tau\), represents the turnover time of the lake (V/E or
$V \Sigma F_{in}$ multiplied by $(1 - h)$. In the case of a very dry atmosphere with $h \to 0$, this procedure then exactly yields a measure of hydrological turnover rate unencumbered by any ambient parameters such as $h$ and $\delta_a$, or of mechanistic ones, such as $e$. This method thus yields a measure of the inflow or evaporation rate, free from the uncertainties usually associated with the isotope method, namely the lack of knowledge of atmospheric parameters. On the other hand, it is restricted to a rather infrequently encountered situation of having a system in hydrological but not in isotopic steady state.

9.2.3. Lakes with inflow and outflow

In the general case of a lake open to both inflow and outflow, the enrichment of heavy isotopes in the lake is reduced in proportion to the weight of the non-fractionating outflow rate relative to evaporation. Again for the sake of clarity of presentation we discuss a lake with constant volume (which actually is not too unrealistic an assumption for most lakes with river outflow). From Eqs (9.1) and (9.2) it is easy to derive the steady-state composition of the lake:

$$\delta^w = \delta_{in} \frac{F_{in}}{F_{out}} - \delta_E \frac{E}{F_{out}}$$  \hspace{1cm} (9.15)

$\delta^w \to \delta_{in}$ when $E \ll F_{out}$, and conversely $\delta_E \to \delta_{in}$ when $E \gg F_{out}$, as in a terminal lake. Introducing the value of $\delta_E$ from Eq. (9.10) we obtain:

$$\delta^w = \left[ \left( \frac{e}{h} + \delta_a \right) + \frac{F}{E} \cdot \frac{1 - h}{h} \cdot \delta_{in} \right] / \left[ 1 + \frac{F}{E} \cdot \frac{1 - h}{h} \right]$$  \hspace{1cm} (9.16)
This equation, which was first derived by Gat and Levy (1978), has the interesting property that the parameters $\delta_a$ and $e$ appear in the form $(e/h) + \delta_a$, which corresponds exactly to the limiting isotopic composition, $\delta^*$, of Eq. (9.3), for a closed pan or pond. This property of the equation enabled Gat and Levy (1978) to determine $F/E$ in a number of sakhias without having to resort to sampling of atmospheric moisture, using only the isotope data of a pond with no outflow, exposed to the atmosphere under comparable ambient conditions. Obviously, the values obtained from an evaporation pan could also have been used for the same purpose.

From Eq. (9.15) we then have:

$$\frac{F}{E} = \frac{h}{1 - h} \cdot \frac{\delta^* - \delta_{ls}}{\delta_{ls} - \delta_{ln}}$$

(9.17)

Humidity values are needed only to complement the measurements of $\delta$-values in the lakes.

As has been shown, the ratio of $E/V$ can also be estimated from the kinetics of approach to the steady state (Zimmermann, 1979).

9.3. DESCRIPTIVE ISOTOPE HYDROLOGY OF LAKES

9.3.1. Mixing of water layers

Large lakes with a complicated physiography, especially shallow lakes, are poorly mixed horizontally and quite large differences in the surface distribution of many parameters, including the stable isotope composition, may appear. The most marked differences appear in arid-zone lakes where the strong evaporation results in the successive enrichment of isotopes, in parallel with salinity build-up with increasing distance from inflow points. For example, in Lake Chad the heavy isotope content increases away from the mouth of the river Chari (Fontes et al., 1970), reaching an enrichment of up to 20\% in $\delta^{18}O$ and of 110\% in $\delta D$ in the far northern reaches of the lake, at a distance of some 200 km from the river mouth. In extreme cases, horizontal mixing can almost be neglected and the lake can be viewed as a stream which evaporates as it flows inland. Different areas in a swamp in the Okavango marshes of Botswana, where horizontal mixing is further hindered by dense vegetation, were described by Dincer et al. (1979); each area had to be treated essentially as an isolated entity when making material balance calculations.

Horizontal inhomogeneities are, however, not confined to arid zones, as evidenced by data from the shallow Neusiedlersee, Austria (Rank and Schroll, 1979).

Another situation with marked isotopic inhomogeneities is the case of the 'short-cut' flow of a river from inlet to outlet point, without mixing with stagnant
pockets of water in the lake. This can occur when warm river-water floats on top of a lake, as described by Sauerwein (1967), or when a river just runs through a lake without mixing (Gilat and Stuhl, 1971). Zimmermann et al. (1976), in a study of Lake Kainji, Nigeria, attempted to quantify the degree of mixing from inflow/outflow relationships by comparing the difference between the isotope contents of the lake's input and output to that expected under ideal mixing conditions. They thus define an effective mixing volume, which for the special case of Lake Kainji is claimed to change from 60% of the lake volume at low water stand to close to 100% under flooding conditions. In the case of Lake Kainji, with its very short residence time of water, the method depends essentially on the seasonal changes in composition of the inflowing floods and the interpretation of data may be ambiguous. In a lake whose waters are highly enriched in the heavy isotopic species through evaporation, such an approach would appear much more promising.

Lakes with less extreme dimensions are more homogeneous laterally because of the strong action of winds; important inhomogeneities occur rather in the vertical dimension, as a result of seasonal or more permanent stratification (meromixis). Indeed, most temperate-zone freshwater lakes develop a warm epilimnion during the summer season, thus isolating the deeper water masses (the hypolimnion) from the surface waters, except for an insignificant exchange of water by means of a diffusion mechanism. The isotopic composition of the hypolimnion remains fixed throughout the period of stratification, with its δ-value being that of the overturned lake at the time stratification begins (Gat, 1970). The isotopic balance equations describing the evolution of the composition of the epilimnion must take into account the possible deepening of the pycnocline (thermocline in this case) by considering a volume change and including a term for the incorporation of hypolimnic waters.

In some very deep lakes, such as the African Rift Valley lakes of Malawi (Gonfiantini et al., 1979) and Tanganyika (Craig, 1975), the overturn is not an annual event and the deeper water mass is colder than the overlying one. Rather surprisingly, the hypolimnion of both Lake Malawi and Lake Tanganyika was found to be more enriched in heavy isotopes, by about 0.5‰ in 18O and by 2–4‰ in D, than the mixed layers on top. This was interpreted by Craig (1975) as being due to a period of cooler but also drier climate, possibly early in this century.

Meromixis is, of course, the rule among deep saline water bodies, as is discussed below.17

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17 It might be useful to recall the definitions of some limnological terms used in this chapter. In a lake which is not well mixed vertically because of differences in density due to temperature and/or salt concentration changes, the upper, less dense region is called 'epilimnion'; this is generally fairly turbulent and warmer with respect to the deep, more dense and relatively undisturbed region, called 'hypolimnion'. The intermediate region of relatively rapid change
9.3.2. **Seasonal and secular changes in the isotopic composition of lakes**

The most notable variations in isotopic composition are the seasonal changes which are superimposed on long-term drifts in isotopic composition; these changes occur in response to meteorological fluctuations and hydrological imbalances. Obviously, fluctuations are largest in small lakes with short water residence times and are dampened in larger systems. The analysis of the isotopic variations is complex; changes in water residence time, in the importance of evaporation relative to other water losses, in isotopic composition of inflow (in response to changes in the hydrographical structure — discussed in the first part of this chapter) and in atmospheric moisture composition, all affect the composition of the lake waters. Obviously, the isotopic composition of a lake should not be represented by a single point on the δ-diagram but rather by a wider field of compositions.

The problem of correctly averaging the parameters under non-steady flow conditions in a mixed lake has been discussed by Nir (1973).

9.4. **APPLICATION OF THE ISOTOPE METHOD TO THE DETERMINATION OF THE WATER BALANCE OF LAKES**

As outlined by Gat et al. (1968), often a number of terms in the water balance equation of a lake (Eq. (9.1)) are unknown and additional relationships are necessary for calculating the value of these unknown terms or verifying their estimates. Terms such as the evaporation flux and the in- and outflow rates of flooding or subsurface leakage are particularly difficult to estimate by standard hydrological methods. Conservative salts (i.e. chemicals which do not interact with material in the lake bottom or sediments) and isotopic tracers can be used for this. A great number of lake studies on this subject were initiated over the last decade (Dincer, 1968; Zimmermann and Ehhalt, 1970; Gat, 1970; Merlivat, 1970; Friedman et al., 1956; Friedman and Redfield, 1971).

Salts, which do not partake to a large degree in the water-to-atmosphere transition, are very useful tracers for establishing additional balance equations, of density, of very small dimensions, is called 'metalimnion'. The plane of maximum density gradient with depth is the 'pycnocline', generally called 'thermocline' if temperature is responsible for the vertical density variation. A thermocline is established in most lakes during summer. Lakes which do not undergo the annual mixing cycle and therefore are more permanently stratified are called 'meromictic', and 'meromixis' is the related phenomenon. The deeper, stable region of these lakes is called 'monimolimnion', while 'mixolimnion' is the upper region, open to free circulation of water. (Hutchinson, G. E., A Treatise on Limnology, Vol. 1, Chapter 7, Wiley, New York, 1957.)
and especially the Cl⁻, magnesium (Fontes and Gonfiantini, 1967; Gat and Levy, 1978) and lithium content (Friedman et al., 1976) were found reasonably conservative under a variety of situations. However, the method fails when saline seepage contributes unknown amounts of salt, as in Lake Kinneret (Gat, 1970).

Measurements of the changes in the isotopic composition of a lake provide, in principle, another useful balance equation. The prerequisite for the use of the isotopic method is for the lake to be well mixed with regard to this tracer; this can be tested simply by proper routine sampling. (In a stratified lake the balance equation, as outlined above, should be restricted to the epilimnic volume.)

The inherently conservative behaviour of isotopic tracers (except as regards the evaporation process) makes the isotope method so promising. It has another distinct advantage over the water balance and chemical tracer methods, in the evaluation of the terms $\sum F_{in,i}$ of the inflow fluxes. Their direct measurement often poses insurmountable problems in the case of rain-storm run-off and subsurface leakage; also, their salinity may be varied and unknown. The value of $\delta_{in,i}$, however, can usually be estimated quite accurately from the known hydro-meteorological structure of the area and in favourable cases the isotopic composition of all inflowing streams can be represented by the composition of the local precipitation, so that the terms $\sum (\delta_{in} F_{in,i})$ can be lumped into a single term $\delta_{in} F_{in}$.

It is the evaporative flux term $\delta_E E$ which poses a big problem in the isotope method because, in a sense, a number of new unknowns are introduced through it, namely the atmospheric variables ($h, \delta_a$) as well as the mechanistic parameter $\epsilon$. As discussed above, $\delta_E$ can be expressed either theoretically, based on Eq. (9.8) — but still requiring data or estimates of $h$ and $\delta_a$, or semi-empirically through the measurement of the isotopic enrichment in 'model evaporation systems', such as a terminal 'index lake' (Dincer, 1968), a drying-up pond (Gat and Levy, 1978) or evaporation pans (Gat, 1970; Welhan and Fritz, 1977). In the final analysis the main problem posed is the proper averaging of the atmospheric and mechanistic variables over the time of observation and over the entire surface of the lake. A simple, continuous vapour sampling, for instance, will not yield properly weighted average data on atmospheric humidity because the intensity of exchange (and evaporation) changes drastically with changes in wind strength and aerodynamic structure at the water/air interface. To overcome this problem, Tzur (1971) suggested a sampling procedure where the air pump is activated at a rate dictated by an anemometer; Welhan and Fritz (1977) used evaporation pans as instruments for properly weighting the exchange flux. However, Allison et al. (1979) doubt that a proper weighting is thus obtained.

The averaging over the lake's surface, which especially in large lakes may introduce major errors due to modification of humidity and aerodynamic properties in the atmosphere by the water/air interaction, has so far not been treated and its effect on balance estimates is not known.
Zimmermann (1979) and Lewis (1979) estimated the accuracy with which
the evaporation flux could be calculated by both the water balance and isotope
balance equations, taking into account the uncertainties in the values of different
parameters; with a critical and rather pessimistic approach they estimated an
error of ± 50% for the case of Lake Neusiedl and of ± 30% – 15% (the latter under
optimal conditions) for Lake Kinneret. While these estimates may be overly
conservative, the present author feels that sometimes too much trust is put in the
power of the isotope balance method; this is the case, for example, in the study
of Lake Titicaca by Fontes et al. (1979a) who suggested a 7% leakage rate on the
basis of this method.

Zimmermann and Ehnhalt (1970) as well as Friedman et al. (1976) advocated
the use of deuterium data rather than $^{18}$O data because of the smaller influence
of the (poorly known) kinetic separation factor on the overall isotope enrichment
factor $\varepsilon$ in the case of deuterium. On the other hand, Gat (1970) showed that the
kinetic term is better understood in the case of $^{18}$O than in the case of deuterium
and thus preferred the use of $^{18}$O data.

9.5. APPLICATION OF THE ISOTOPE METHOD TO SALINE LAKES

In the case of highly saline systems, the stable isotope method requires minor
modifications in measurement techniques as well as in some theoretical considera-
tions: the salt effect on the fractionation factors and on the vapour pressure of
water has to be taken into account (this was reviewed by Gat, 1979). On the
other hand, stable isotopes have been of particular usefulness in the study of saline
systems for a number of reasons: salt balances are difficult to make under
conditions where salts precipitate and dissolve readily; also, salt lakes have not
been studied much by conventional limnological techniques and the origin of their
salt and water is often in dispute.

One important group of saline water bodies is made up of the marine lagoons
and coastal ponds and sabkhas with connection to the sea. Lloyd (1966) showed
that as a result of the evaporation of sea-water (causing first the deposition of
gypsum and later that of halite) the heavy isotope enrichment reaches a limiting
value. Other authors (Gonfiantini, 1965; Sofer and Gat, 1975) showed that,
as the solutions evaporate and become more saline, $\delta_q$ reaches a maximum value
and then decreases. This is so because the relative humidity, normalized to the
condition at the liquid surface, continuously increases as the salt concentration
increases, since the latter is accompanied by a parallel decrease of the water activity
coefficient and of the corresponding saturated vapour pressure. As a result, $\delta_q$
do not tend monotonously towards a limiting value, but after a certain enrichment
stage it reverses its trend and the water becomes less and less enriched in the heavy
isotopic species. Such systems are then characteristically not very enriched in
heavy isotopes, as for example in the case of Lake Asal, Djibouti (Fontes et al., 1979b).

Except in extremely dry climates, evaporation will finally cease at the point where the ambient humidity approaches the saturation vapour pressure of the brine; isotopic exchange will, however, continue and will tend to bring atmospheric moisture and brine into isotopic equilibrium (Fig. 6).

In many coastal lagoons the increasing density of the evaporated brines favours the establishment of a two-layered flow regime which then results in enriched brine being spilled back into the ocean. The data from the Bardawil Lagoon reported by Gat (1979) are an example for this. Such a flow regime then limits the build-up of both salinity and heavy isotopes. A similar density-stratified in- and outflow pattern can be established even when the salt pool is separated from the sea by a sand-bar, as was described in the case of the Solar Pool near Eilat (Aharon et al., 1977).

A permanently stratified structure is a common occurrence in many salt lakes. When the density difference between monimolimnion and mixolimnion is large enough, the stratification may survive even a heating-up of the bottom waters to near boiling temperatures (the solar pool effect). Natural examples are those of the Solar Pool at Eilat mentioned above and the Antarctic Lake Vanda (Ragotzkie and Friedman, 1965). The stable isotope content of the (fossil?) deep water masses of such permanently stratified lakes then identifies the origin of their waters. In the case of the Solar Pool, marine origin could be established (Mazor, unpublished results, and Aharon et al., 1977). For Lake Vanda and Lake Bonney in the Antarctic the deep water was found to originate from glacial meltwaters (Matsubaya et al., 1979). Matsubaya et al. were able to distinguish deep waters which had once been lake waters exposed to surface evaporation from other deep waters which corresponded to unchanged melt-waters. In the Dead Sea, Jordan Rift Valley, the isotopic composition of the monimolimnion waters, $\delta^{18}O = +4.14 \pm 0.02\%\text{o}$, $\delta D \sim 0.0\%\text{o}$ (Craig, unpublished data), is consistent with their formation by evaporation as a terminal lake in the Jordan River system. This composition then does not differ significantly from the mean composition of the mixolimnion (Gat and Dansgaard, 1972).

Perennially ice-covered lakes form a special category. Such lakes are maintained by virtue of continuing seepage of melt-water, which makes up for the loss of matter by sublimation. The steady-state condition of $\delta I = \delta E$ is established when the lake waters (the unfrozen part) are somewhat depleted in heavy isotopes relative to the inflow, by virtue of the fractionation accompanying the freezing process. The freezing process is also responsible for the increase in salinity in these lakes.
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Chapter 10

GROUNDWATER

10.1. INTRODUCTION

The study of the characteristics and origin of groundwaters has been among the most successful areas of application of natural stable isotope abundance variations. To a large extent this is due to the conservative nature of the stable isotope composition of water in an aquifer, as a result of which it is possible to characterize the origin of the waters unambiguously: groundwaters 'remember' the isotopic composition of their origin over rather long periods, of the order of ten thousand years, provided they are not exposed to temperatures above 60–80°C. Some specific case studies where the stable isotope composition of groundwaters is used for the solution of specific hydrological problems are presented in Chapter 13.

Subsurface waters can be grouped into a number of categories, based on their origin:

Meteoric waters are derived directly from precipitation or from fresh surface waters, usually by recharge through an unsaturated soil zone. An active circulation of water through the subsurface is implied and the rock layers function as an aquifer in the proper sense of the word. The isotopic composition of the meteoric groundwaters generally matches that of local precipitation, at least in the humid climate zones. As discussed below, in the more arid regions an enrichment of the heavy isotopes in groundwaters relative to precipitation often occurs, but the opposite is also known.

Palaeowaters are meteoric waters which originated in the more distant past, especially in periods during which different climatic conditions prevailed. The distinction between these two groups of water is somewhat arbitrary. By common usage, Pleistocene waters (as dated for example by \(^{14}\)C measurements) belong to the palaeowaters and in many instances the isotopic composition of waters of that age indeed differs from that of present precipitation. Younger waters, which originate in a period of different climate, might also be classified as palaeowaters, although other waters of a similar age (in whose isotopic composition no change is indicated) are still considered simply as meteoric waters. Chapter 12 is devoted to a fuller discussion of palaeowaters.

When aquifer temperatures reach values of 80°C or more, a rather rapid change of the stable isotope composition of waters occurs so that this composition no longer corresponds to the original one. This situation is typical for geothermal conditions, as is discussed in Chapter 11, which is devoted to geothermal waters.
Finally, at greater depths in the sedimentary column there are saline groundwaters, which are either remnants of the original marine interstitial waters or which have replaced these waters by post-depositional water movements. Since such waters are almost stagnant, interactions with rocks dominate their geochemical nature. These brines are being studied extensively because of their frequent association with oil and gas deposits. The term formation waters is preferred, since it has no connotation as to the origin of these waters. The isotopic composition can be used to study their origin and evolution, as is shown in Section 10.5.

10.2. GROUNDWATER OF METEORIC ORIGIN

In many cases, the isotopic composition of meteoric groundwater is found to match the mean composition of precipitation over the recharge area to a fair approximation. Because of this property, shallow and locally derived groundwater is often used to characterize the isotopic content of meteoric waters in any given locality instead of resorting to precipitation sampling (which is a drawn-out process).

The match between the isotopic composition of precipitation and that of the groundwater derived from it is, however, by no means perfect. Cases are known where groundwater is either more enriched or more depleted in heavy isotopes. The distortion becomes larger under more arid conditions, usually in the direction of (evaporative) enrichment of heavy isotopes in the groundwater; the opposite has, however, been reported in the case of groundwater of some arid regions in South Africa (Vogel and Van Urk, 1975) and other desert areas (Levin et al., 1980).

The changes in isotopic composition are mainly the result of the recharge process. To a lesser extent, they come about as a result of the non-conservative behaviour of water in the aquifers, through interaction with rock components or mixing with fossil pocket of interstitial waters. Mixing of groundwaters from different points of origin has also to be considered.

As we have seen, there is a scatter in the isotopic composition of rainfall at any one place, and seasonal variations and longer-term trends are superimposed on it. Not all of the precipitation reaches the groundwater body, some of it being diverted as surface run-off and more re-evaporated from the soil, especially through the action of plants (transpiration). As long as this loss of water is random and not correlated with variations in isotopic composition, it should not distort the average values. However, when the lost water is characterized by a distinct isotopic composition as, for example, during the preferential re-evaporation of summer rains (which are more enriched in $^{18}O$ than is average precipitation), the isotopic composition of recharged water may differ to some extent from that of the amount-weighted mean precipitation. This process has been named selection.
by Gat and Tzur (1967) to distinguish it from systematic fractionation, such as would accompany evaporative water loss from open water surfaces.

Measurements on lysimeter percolates in temperate climates by Halevy (1970), Eichler (1965) and Siwertz (1973) show that the composition fluctuations of individual rainfalls are smoothed out by transition of the water through the unsaturated soil zone, to an extent that the seasonal fluctuations seem to have disappeared completely. In these experiments, the percolated waters were found to be slightly depleted in heavy isotopes with respect to the precipitation. This effect was attributed to a preferred selection of winter rains, i.e. to a seasonal effect (Saizyay, 1974). Somewhat similar results are obtained in South Africa (Vogel and Van Urk, 1975) when groundwater and rainwater data are compared: a selection in favour of the more depleted waters occurs in the recharge process. In this case the selection seems to be based on the amount of rainfall, with recharge occurring preferably from more intense rains.

Under more arid conditions, on the other hand, an enrichment of the heavy-isotope species in groundwater is observed, in parallel with a decrease in the value of the deuterium excess parameter (along typical evaporation lines). This suggests that the change comes about as a result of evaporation processes. The degree of isotope enrichment in the coastal plain of Israel, for example, was found to be up to about 1%o in $\delta^{18}O$ (Gat, 1974). No simple correlation with any clear geographical factor could be seen, except in some areas of very heavy soils where larger enrichments were observed. Possible causes for such an enrichment could be the following: (1) A delay of water near the surface before infiltration, in the form of mud or puddles, following the occurrence of intense showers, in excess of the infiltrating capacity of the soil (Gat and Tzur, 1967); these surface waters are then partially evaporated. (2) Infiltration of recycled irrigation waters, which are exposed to additional evaporation. (3) Evaporation of soil water from the uppermost soil layers (it has indeed been observed that the drying up of the top layer of sandy soil is accompanied by isotope enrichment in the soil profile (Zimmermann et al., 1967; Dincer et al., 1974)). Later rains may then flush down these enriched soil waters to the water table, resulting in a systematic enrichment of the recharged waters relative to the precipitation. In plant-covered areas, however, the water loss is primarily by transpiration, which is non-fractionating with respect to the water isotopes. One is thus faced with the paradoxical situation that the small evaporation loss from a bare surface results in larger changes in isotopic composition than are associated with the much larger evaporotranspiration losses from vegetation-covered areas.

The perturbations introduced through the recharge processes are schematized in Fig.55. These perturbations in isotopic composition are relatively minor and, all in all, recharge waters represent the mean precipitation with reasonable fidelity. The variability in isotopic composition from one area to the next is first and foremost a reflection of the geographic variability of the isotope content of the
precipitation; the altitude effect on the isotopic composition of precipitation is the most commonly encountered factor, as discussed in Chapter 6.

The magnitude of the altitude effect depends on the local climate and topography; gradients of 0.15—0.5%o/100 m (for δ18O) or of about 1—4%o/100 m (for δD) have been encountered. Taking into account the good reproducibility of the measurements, with σ (δ18O) = ± 0.10%, a resolution of about 25 m in the elevation of recharge sites can be achieved in an ideal case.

Another geographic factor which can be utilized for hydrological investigation comes into play in border zones between different climatic regions, where the air masses from each region produce precipitation with distinguishable properties.
A notable example is found in the Konya Plain of Central Turkey, as described by Sentürk et al. (1970). Mediterranean-type precipitation, with its characteristic deuterium excess, falls on the Taurus Mountains south of the plain and marks the southern drainage into the plain quite distinctly, distinguishing it from the continental type waters which flow into the area from the north (Fig.56). Another such transition zone is the Pacific Sea Coast of Central and South America, where recharge due to precipitation on the Andes, originating in the eastern part of the continent, can be distinguished from the local ‘Pacific’ precipitation.

In the examples discussed so far, changes in isotopic composition of precipitation as a function of the geographic location came into play. Further possibilities for tracing the origin of groundwaters depend on the distinctive composition of surface waters (primarily lakes and reservoirs) which are enriched in the heavy-isotope species as a result of evaporation. The fact that the enrichment proceeds along ‘evaporation lines’, which usually have a lower slope than the meteoric water lines, makes it possible to distinguish between ‘evaporated’ waters and waters directly recharged from precipitation. (Unfortunately, the pseudo-altitude effect discussed in Chapter 6 is also an evaporation effect, so that the distinction between these two cases hinges only on the degree of enrichment and on other possible tracers of the surface waters, such as salinity.) A number of practical applications are discussed in Chapter 13.

For any quantitative application of the stable isotope labelling of waters as a geo-hydrological tool, it is necessary to establish how well the isotopic composition of a groundwater source is defined in a supposedly homogeneous geographic setting. We have to consider both time and space variations.

The isotopic composition of water samples from wells of large sandstone or limestone aquifers was found to remain constant, within analytical reproducibility, over a number of years (Fritz et al., 1974; Gat, 1974). These observations must be treated with some reserve, however, since the time span of observation was possibly too short for detecting meaningful changes, taking into account the slow rate of water movement in these aquifers. Discharges from springs and water in small-capacity aquifers in fractured media, such as basalts or granites, are more changeable with time.

Spatial scatter within an aquifer is found in most cases to be more significant than variations in time; in one example, with no striking geographic variability, it was found to be about 0.5% over distances of single kilometres. One must realize that no area is really uniform from a topographical, morphological and ecological point of view, and somewhat different recharge relations may apply at each point. This larger variability in space than in time is interpreted as showing the soil column to act as an efficient homogenizer of recharge waters at any one spot; but the mixing in the aquifer proper is a slow process so that the groundwater systems can be viewed as an assemblage of discrete water parcels which move along defined flow paths. For the case of the coastal plain of Israel, Gat (1974)
FIG. 56. Water sources of the Konya Plain, Turkey, showing the confluence of two isotopically different meteoric water types. The inset in Fig. 56(a) shows the water types, based on isotopic criteria. The prevalence of these water types in the area is indicated in Fig. 56(b) where the different water types are distinguished by different shading as in the inset. (Adapted from Sentürk et al., 1970.)
estimated that it would be necessary to pool about four years of input waters in order to smooth out the variations in isotopic composition of the annual precipitation samples to the observed level of constancy in time (the analytical reproducibility). While this can certainly be achieved on passage through a deep soil layer, it may not be the case where the water table is very shallow or when recharge occurs through fractured or open-pore media.

The isotopic composition within aquifers varies not only from place to place but also as a function of depth, in particular under unconfined conditions (Moser and Stichler, 1972). Evidently, groundwaters mix slowly and occupy a position somewhere between the fully mixed systems, such as streams or shallow lakes, and non-mixed systems, such as tree-rings, lake varves and snow layers (Simpson et al., 1972). Probably most of the mixing actually occurs at the discharge point or by pumping.

Temporal variations in the composition of recharge waters, be they seasonal or long-term changes, are expressed under steady flow conditions as time variations at any observation point along the underground flow path. However, if the travel time from recharge to observation point differs from place to place these temporal changes will have to be translated into space variations even without the occurrence of mixing. In fact, the non-steady nature of recharge and exploitation results in mixing of waters from different flow paths and in mingling of time and space variability, making it impossible to distinguish between them. Extreme conditions are caused by human activities, such as artificial recharge operations, large-scale irrigation or simple over-exploitation of aquifers. The latter practice results in large-scale distortion of the flow pattern, leading to the admixture of extraneous water sources, such as sea-water.

Some of the very large variations in isotopic composition found within certain aquifers are believed to be due to a large time span represented in the system, so that large climatic changes (related, for example, to the interglacial stages of the Pleistocene) manifest themselves (Moser and Stichler, 1972). The palaeo-effect is discussed in detail in Chapter 11. Other causes may also contribute to the scatter of isotope data within an aquifer unit, such as mixing with fossil (possibly marine) water bodies, and interactions and isotopic exchange with the rock matrix, the latter especially in deep aquifers which are at more elevated temperatures. Effects such as these become increasingly important when water movement is slow so that there are long sojourn times in the aquifers. Thus it is not surprising that an increased variation in the isotopic composition of aquifers is an attribute of the more arid areas. Many causes for variability are found there, namely a greater variety in the input isotopic composition due to the smaller number of rain events, increased distortion of the isotopic composition of precipitation by evaporation processes before recharge, and finally the more sluggish water movement due to the limited amount of recharge, giving more chances for interaction with the rock systems and with stagnant water pockets.
10.3. GROUNDWATER OF ARID ZONES

We have seen that in temperate and humid climates the stable isotope composition of groundwaters closely matches that of the precipitation of the recharge areas, except where lakes or other surface water bodies, which have undergone evaporation losses, contribute to the recharge. The distortion of the isotopic composition as a result of the recharge process is minor and the isotopic composition of both precipitation and groundwater obeys a 'meteoric water' relationship. The high recharge rates result in continuous flushing of aquifers of 'non-meteoric' waters.

In semi-arid zones the water loss by evaporation assumes importance, often with the result that the heavy-isotope species in the groundwater are enriched relative to those in precipitation, shifting the isotopic composition of groundwater away from the meteoric water line along 'evaporation lines'. This tendency is enhanced through re-use and recycling of waters in dry areas mainly for irrigation purposes, which further builds up both salinity and isotope enrichment.

Desert regions are areas of little precipitation, insufficient to maintain a permanent vegetation cover. Rain occurs irregularly and usually in patches, often in the form of local cloudbursts of rather high intensity. The absence of a proper soil cover favours the occurrence of floods, except in sand-dune areas. Since there is so little flushing, there is an increased chance for survival of groundwaters unrelated to present-day local precipitation. These include waters originating in far-away mountainous fringe areas (Slayter and Mabbut, 1964), sometimes of great antiquity and belonging to the group of palaeowaters, i.e. waters recharged in the past during periods of cooler climate (Munnich and Vogel, 1962). Fossil brines also play a role, often causing a deterioration of the quality of fresher-water sources.

Under arid conditions, because of the lack of continuity in aquifers and intermittent flow regimes, the classical hydrological research methods are fraught with difficulties. However, through dating methods, in particular tritium measurements, it was established — contrary to previously expressed opinions — that direct rain infiltration is widespread, even in regions of deficient rainfall. Verhagen et al. (1974) came to such conclusions in the Kalahari Desert, and Gat and Issar (1974) established the young age of springs in the crystalline province of the Sinai Desert, an area with only 50 mm annual precipitation. Levin et al. (1980) showed that groundwaters in limestone aquifers were recharged without notable isotope enrichment. The efficient infiltration of even very small rain amounts in sand-dune areas is also well established and was demonstrated by Dincer et al. (1974) in studies in Saudi Arabia. On the other hand, water loss by evaporation can occur through the relatively open structures of sand dunes down to depths of a few metres and it will thus depend on local conditions whether the hydrological balance of such dunes is positive or negative in the long run (Fontes, private communication).
The contribution of floods to the recharge of aquifer pockets under the stream beds or to regional aquifers is also under investigation. Many investigators believe this to be the major recharge route in arid zones. The isotopic evidence, however, is somewhat ambiguous; in some cases the contribution of flood waters to wells close to the river beds can be demonstrated. A case in point is the study by the IAEA in Northern Hodna, Algeria (Gonfiantini et al., 1974), where the flood waters, which have a higher tritium content, can be traced into the wells adjacent to the river. A similar situation is encountered in Wadi-el-Arish in northern Sinai (Gat, 1975). However, the extent to which these contributions are important on a regional scale is debatable. Gat and Issar (1974) concluded in the case of the wells of the big oasis of Feiran, which is situated within a dry river (wadi) frequently traversed by floods, that the abundant flood waters are not recharged from the wadi but rather from a system of cracks in the crystalline massif. The oasis is located at the junction of a major fault system with the dry river bed and the role of the river is simply that of exposing the regional water table.

Shallow water sources in the alluvial deposit of wadis in the Negev Desert were found by Levin et al. (1980) to be enriched in heavy isotopes relative to both the average rainfall and the flood waters, more so than groundwaters derived by direct rain infiltration. This seems to indicate that recharge from floods is not a fast process but occurs, in this case, through the intermediacy of stagnant water pools which are left on the wadi floor after the passage of the flood.

An inherent difficulty in isotope hydrology of desert water sources is the small number of rain events; various localities cannot be rigorously characterized in terms of isotopic composition and a year-to-year variation is to be expected. The variability of the well waters, both with respect to salinity and isotopic composition, as it was encountered in Brazil by Salati et al. (1980), must be considered as a typical attribute of locally recharged arid-zone water sources. This will be true in particular in crystalline or basaltic terrain, where aquifer porosity is low and water transport occurs essentially through a system of cracks.

The variability in the isotopic composition of desert storms is truly surprising; values as low as $\delta^{18}O = -12\%_o$ (the long-term average of precipitation is $\sim -6\%_o$) were recently measured by Levin et al. (1980) in the Negev Highlands. Similar low values in single storms have been reported from Saudi-Arabia by Tongiorgi (personal communication). The depleted waters belong to high-intensity rains and were shown to be preferentially represented in run-off and flood flows. This mechanism may contribute to the ‘negative shift’ in the isotopic composition of desert highland waters relative to the mean annual precipitation, in contrast to the ‘positive shift’ of lowland waters in which evaporation effects dominate. The occasional appearance of such depleted desert rains can obscure the difference between meteoric waters and palaeowaters (from cooler climatic periods), except in regions such as the Middle East, where palaeowaters differ from modern meteoric waters also in their ‘deuterium excess’ and not simply in the degree of depletion of either $^{18}O$ or deuterium.
The limited data available from desert areas seem to show that desert lowland waters are enriched in heavy isotope species along evaporation lines, whereas highland waters follow the local meteoric water line and appear quite 'normal' by comparison with less arid regions, except for a larger scatter in composition in time and space. The 'normality' is explained as being due to the fact that precipitation occurs in winter time (often in the form of snow) when low temperatures minimize the evaporation effects (see Chapter 6). On the other hand, it was observed that in the highlands there is no significant altitude effect, presumably because rainfall is patchy and discontinuous, so that a relatively small percentage of the air moisture is condensed and removed by rainout. As a result of these characteristics, one can distinguish clearly between lowland and highland water sources, but there is little resolution in each of these two groups that would make it possible to specify in detail the altitude levels from which the water originated.

10.4. STUDIES ON THE SOURCES OF SALINITY IN GROUNDWATER

The salinity of groundwater and its origin and prevention are important components of the groundwater problem, especially in the context of the deterioration of water quality resulting from pollution or exploitation of groundwater resources.

Many of the sources of salinity, such as sea-water or surface brines, are associated with waters of a characteristic isotopic composition which is distinct from that of the meteoric waters. The isotope technique is based on identifying the admixture of water accompanying the salinity in the groundwater. The isotopic marking is often much better conserved in the aquifer environment than the salinity components, which may undergo processes of ion exchange, precipitation, etc. This approach is particularly useful in near-coastal areas where all the salinity ultimately originated from the marine environment, so that little chemical distinction exists between salinity originating for example from sea-spray or from direct sea-water encroachment, from surface lagoons or from interstitial waters.

The most common pathways of introduction of salinity into the fresh-water systems (Yaalon, 1967; White et al., 1963) are wash-out and flushing of airborne salts directly by precipitation or by dissolution of evaporitic minerals from the surface, the soil or aquiferic formations; and encroachment of sea-water or admixture of connate brine pockets. Lately, anthropogenic sources such as fertilizers or industrial sources also have to be considered.

Obviously, dissolution and flushing of dry salts by precipitation or by other meteoric waters will not result in any change in the water's isotopic composition (we note, however, the analytical problems posed by the presence of high
concentrations of salt — see Chapter 4). On a diagram of δ versus salinity such a process shows a horizontal displacement of the datum points, whereas no change is recorded in δ\(^{18}\)O – δD space (Figs 57, 58). Any accompanying dissolution or change in the rock matrix itself might, on the other hand, be accompanied by isotopic exchange and interaction with newly exposed rock surfaces, resulting in some shift in the isotopic composition of the water, as indicated in the figures. Generally, however, diagenetic reactions and exchange are of relevance only in geothermal systems and over longer periods.

The isotopic composition of sea-water is rather well defined, with surface waters usually slightly enriched with respect to SMOW, δ\(^{18}\)O = +1‰, δD = +6‰ being representative values. The isotopic composition of a coastal lagoon or evaporation basin in which salinity increases through evaporation has been described by Lloyd (1966), Gat and Levy (1978) and others (e.g. Nadler and Magaritz, 1979). Figure 58 shows a typical curve for the evolution of δ-values in an evaporate at moderate salinity and relatively high humidity. At later stages of the desiccation process the salt effect results in the trend of isotope enrichment being reversed (see Chapter 3).

Evaporitic minerals containing crystal waters, such as gypsum, are associated with a wide range of rather weird isotopic compositions (Sofer, 1978; Matsubaya and Sakai, 1973; see also Chapter 5). The amount of water involved is, however, rather small (a few moles of water per mole of salt) so that the addition of the crystal water to the brine as a result of the dissolution of such minerals is detectable only when these minerals are a major component of the brine.

Finally, fossil brines, formation waters and magmatic or geothermal fluids display a variety of compositions, as discussed in other sections. Most of these
FIG. 58. Change in isotopic composition of water, associated with different salinization processes: plot of $\delta D$ versus $\delta^{18}O$.

also show distinctive chemical and trace-element composition, to that their admixture to the groundwater can be identified readily through combined chemical and isotopic analyses (Fig. 59).

The isotopic composition of mixtures of fresh and saline waters describes a straight mixing line on the $\delta^{18}O$ versus $\delta D$ diagram, each datum point being situated according to the percentage of the saline source in the mixture. A case study is that of Arad et al. (1975). In this and other cases, the isotope method is suitable for identifying the saline component only in rather brackish waters, since with less saline waters the change in isotopic composition of the medium as a result of brine addition may be below the sensitivity of the isotopic analysis in dilute solutions; for example, the minimum detectable addition of sea-water to groundwater (when the $\delta^{18}O$-value of the groundwater is $-5\%$) is of the order of 2–3%, which is equivalent to an added salinity of almost 500 mg chloride per litre.

The proportionality between salinity and change in isotopic composition is realized only when the salinity is not perturbed by chemical interactions. Therefore, conservative elements are to be preferred, such as chlorine at low
salinities or lithium concentrations and values for total dissolved solids (TDS) at higher ones. Alkaline earth ions are usually not suitable, as they are subject to ion-exchange interactions and replacement of carbonates.

It should be noted that the mixing lines on a plot of δ versus salinity are curved when the salinity is expressed in concentration units of grams per litre, reflecting the decreasing percentage of the solvent in the more concentrated solution. This can be eliminated by using a molality scale (Craig, 1966).

Figure 58 schematizes the isotopic relationships of the different salinization pathways. Obviously, a clear-cut distinction between different mechanisms depends on a singularity in the change of the isotopic composition for each such pathway. The method works best when the isotopic composition of meteoric waters is well defined. Under certain circumstances (range of δ18O in water of between −2‰ and −5‰) the evaporation line and the sea-water/fresh-water mixing line almost coincide, and processes of evaporative enrichment and of sea-water additions cannot be distinguished easily. However, for more depleted waters such a distinction can be made without ambiguity.
Quite a large number of studies on the sources of salinity have appeared in the literature, dealing with sea-water encroachment (Arad et al., 1975; Stahl et al., 1974), fossil marine brines (Gat et al., 1969) or inland evaporation systems (Gat and Naor, 1979). A case where dissolution of salt deposits occurs has been described in a study of saline waters in Iran (Zak and Gat, 1975). Mazor (1976) has used a combined geochemical and isotopic approach to identify the sources of salinity in a number of water sources in the Jordan Rift Valley.

10.5. FORMATION WATERS

Formation waters is the general 'non-generic' term for water found during drilling operations in association with various geological formations below the cycling aquifer systems. Slowly moving or completely stagnant, these waters range in salinity from sea-water concentrations to dense brines which are saturated with respect to NaCl (occasionally brackish waters are encountered, remnants of some flushing phase). In chemical composition they range from slightly modified sea-water to chloridic brines dominated by magnesium and calcium ions. As a rule, chloride is the dominant anion, mainly because the build-up of sulphate or carbonate is limited by the low solubility of their calcium salts.

Undoubtedly, many of the formation waters have been in contact with their host formation for extended periods of time, mostly at elevated temperatures. As a result, both salinity and isotopic composition are modified by this association, approaching equilibrium with the mineral phase. However, in many other cases the formation waters are considerably younger than the original interstitial water which they replace as a result of fluid movements induced by tectonics riftting or sea-level changes.

Unlike younger groundwaters, the origin of formation waters is masked to some extent by these secondary processes of isotopic exchange and interaction with rocks which shift the isotopic composition of the water. These interactions affect the $^{18}O$-content first and foremost, because of exchange with carbonates and silicates. Usually these interactions result in an increase of the $^{18}O$-content of the waters, to an extent which depends on the relative volume of the fluid and the rock mass with which they are in contact (Hitchen and Friedman, 1969), on the temperature controlling the interaction rate and also on the degree of partitioning of the isotopes between the phases.

It has been claimed (White et al., 1963) that deuterium exchange can occur in the presence of clays, resulting in a slight decrease of the $\delta D$-values. Interactions with organic matter, with $H_2S$ (Hitchen and Friedman, 1969) or with hydrocarbons (Blaga, 1968) would have a similar effect, although this is usually not very pronounced owing to the small amounts of these materials.
A further change in isotopic composition occurs as a result of hydration or dehydration of mineral phases; especially the gypsum-to-anhydrite transition may be a major cause of isotopic change.

Finally, the effect of ultra-filtration on the isotopic composition of water must be considered. This process is favoured by some authors (Graf et al., 1965; Hitchon and Friedman, 1969; Fleischer et al., 1977) as an explanation for the occurrence of a meteoric water component in formation waters which retain their salinity, although chemically altered. Coplen and Hanshaw (1973) simulated the process in the laboratory by pressure filtration of dilute NaCl solution through clay membranes. According to these experiments, a slight enrichment of $^{18}$O and D results in the residual brine. The single-stage isotope fractionation factor in dilute NaCl solutions as a result of this process is 0.9993 for $^{18}$O and 0.998 for deuterium; the effect is thus smaller by an order of magnitude than that of the evaporation process. The relationship between the increase of salinity and that of the $^{18}$O content by ultra-filtration, under conditions of Rayleigh fractionation, is given by Fleischer et al. (1977) as

$$S = S_0 \exp (\Delta \delta^{18}O/0.7)$$

where $S$ is the NaCl salinity. Assuming that, initially, sea-water is being pushed through a clay filter until the salts are concentrated four-fold, to a value of about 150 g/l (which is a typical value for many formation waters), this relation would predict an enrichment of 1‰ in the $^{18}$O-content of the brine; an increase in the Ca/Na ratio would also occur (White, 1965). If additional fresh water then flows through the system, a further increase in the Ca/Na ratio may result (forming a CaCl$_2$-type water), accompanied, however, by a slight decrease of the total dissolved salt content. The $^{18}$O-content of the residual brine then approaches a steady-state value which is enriched by about 0.7‰ relative to the composition of the inflow water (this being the single-stage fractionation factor for this process). The ultra-filtration process is mass accepted, however, by some authors (e.g. Starinsky, 1974) as the primary mechanism operating in the deep formations. These authors claim that the geochemical changes encountered in the formation waters can be explained also by other geochemical processes.

In studies on formation waters in the American great basin (Clayton et al., 1966) and the Canadian shield (Hitchon and Friedman, 1969) it was established that the aqueous phase in the formation waters is related to the meteoric water cycle. In deep drillings in southern Israel, Fleischer et al. (1977) also identified a meteoric water component in the formation waters of the mountain region. However, the brines associated with oil occurrences in the coastal area were characterized as slightly modified sea-water. Brines originating from evaporated inland lakes are found as deep formation waters in locations close to the Rift Valley, where their penetration into the deep layers is activated by the tectonic movement in that area (Fleischer et al., 1977; Starinsky, 1974).
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Chapter 11

GEOTHERMAL WATERS

11.1. INTRODUCTION

Potentially, the interior of the earth is an almost infinite reservoir of thermal energy which, however, is generally buried too deep for exploitation with the available technology. There are places, however, where the heat approaches or even reaches the earth’s surface: volcanic eruptions, hot springs, geysers and fumaroles are surface evidence of the earth’s internal heat. In some cases, the conditions are such that an exploitation of this heat becomes possible; we then speak of geothermal energy resources.

The way and degree of exploitation of the geothermal resources depend mainly on the physical and chemical characteristics of the medium transporting the heat to the surface. In general, high-enthalpy aqueous fluids are mainly exploited for electrical power production, while low-enthalpy fluids are widely used in space heating (including greenhouses for agriculture). In addition, chemical compounds carried by the geothermal fluids can sometimes be economically recovered for industrial uses.

Electricity production can be undertaken directly with geothermal fluids when the following conditions are met:

(a) High temperature (> 150°C) and high enthalpy (> 150 cal/g) of the fluid
(b) Depth of the geothermal reservoir not greater than about 3 km
(c) Adequate volume of the reservoir (> 5 km³)
(d) Sufficient reservoir permeability to ensure adequate fluid production by each well
(e) Impermeable cover of the reservoir to avoid diffuse losses of fluid at the surface
(f) Sufficient rate of renewal of the fluid in the reservoir in order to ensure a continuous transfer of energy to the surface and to the power plant.

Practically, some of these conditions can be fulfilled only if water is the major fluid component (hydrothermal systems).

The above characteristics are encountered in nature only rarely all together and therefore techniques are currently being developed or refined for extending the exploitation of the geothermal energy to less favourable cases. In particular, studies have been undertaken to use low-enthalpy fluids for power production and to extract heat from hot and dry rocks which, like molten lava, have not yet found exploitation.
FIG. 60. Major geothermal systems in the world.
### TABLE XIII. THE GEOTHERMAL DEVELOPMENT (Garnish, 1978)

<table>
<thead>
<tr>
<th>Country</th>
<th>Electrical generating capacity (MW(e))</th>
<th>Non-electrical uses in 1976 (MW(th))</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>522</td>
<td>6000</td>
</tr>
<tr>
<td>Italy</td>
<td>421</td>
<td>800</td>
</tr>
<tr>
<td>New Zealand</td>
<td>202</td>
<td>400</td>
</tr>
<tr>
<td>Mexico</td>
<td>78.5</td>
<td>400–1400</td>
</tr>
<tr>
<td>Japan</td>
<td>70</td>
<td>2000</td>
</tr>
<tr>
<td>Philippines</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>El Salvador</td>
<td>60</td>
<td>180</td>
</tr>
<tr>
<td>Nicaragua</td>
<td>-</td>
<td>150–200</td>
</tr>
<tr>
<td>Iceland</td>
<td>2.5</td>
<td>150</td>
</tr>
<tr>
<td>Costa Rica</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Guatemala</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Honduras</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Panama</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>Taiwan</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>Portugal (Azores)</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Kenya</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Guadeloupe</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Spain</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>USSR</td>
<td>5.7</td>
<td>20</td>
</tr>
<tr>
<td>Turkey</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Canada</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Hungary</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>France</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 60 shows the location of the major geothermal systems, and Table XIII summarizes the position of the major users of geothermal energy.

It should be noted that most of the systems known are located in regions with geothermal gradients much higher than the world average (25–30°/km). This is not surprising; in fact, a higher geothermal gradient implies higher temperature at a relatively shallow depth and higher probability for the geothermal fluid to manifest itself at the surface as a hot spring or a geyser. This facilitates the identification, exploration and exploitation of geothermal fields.

World-wide experience derived from geothermal exploration indicates that most of the heat is transferred within a system by convective circulation of hot water or steam rather than by thermal conduction through the rocks. In the majority of the cases, water in liquid phase is the dominant pressure-controlling fluid in the reservoir rocks, and there the systems produce at the surface a mixture of hot water with 10–30% of steam. Only in a few cases—which are also the most favourable for electrical power production—the dominant fluid consists of water vapour which is delivered at the surface as saturated or often superheated steam with a high heat content (more than 600 cal/g). These two types of hydrothermal convection systems, which differ in the dominant pressure-controlling phase, are commonly referred to as ‘hot-water’ and ‘vapour-dominated’ systems, according to the definitions proposed by Truesdell and White (1973). Classical examples are Wairakei (New Zealand) and Cerro Prieto (Mexico) among the hot-water-dominated fields, and the Geysers (California, USA) and Larderello (Italy) among the vapour-dominated systems.

In the major geothermal systems the heat source is given by a recent igneous intrusion, but there are also systems in which the water is heated simply by circulating at great depth under normal or slightly above-normal geothermal gradients.

Geochemistry, including isotope geochemistry, has greatly contributed to the present understanding of the geothermal systems. The chemical and isotopic composition of geothermal fluid components provides information on their origin, their recharge area and flow patterns, and may allow an evaluation of the subsurface temperatures. In addition, cooling processes of the fluid during ascent to the surface, due to heat conduction, admixtures with cold waters or steam losses, can be studied by means of the changes introduced in the chemical and isotopic composition. Therefore, isotope techniques are a valuable tool in geothermal prospecting as well as in studying the evolution of geothermal fields as a consequence of exploitation. Among the various isotopes, the variations of stable isotopes of oxygen, hydrogen and carbon in some of the major fluid components, i.e. water or steam, carbon dioxide, methane, hydrogen and dissolved sulphate, are those which have provided the most useful results and will be discussed in this chapter.
11.2. ORIGIN OF GEOTHERMAL WATERS AND PROCESSES AFFECTING THEIR STABLE ISOTOPE COMPOSITION

11.2.1. Water/rock interaction

Before the advent of isotopic methods, no geochemical tools were available to identify the origin of water in high-temperature hydrothermal systems. For a long time, the favoured theory was that they are of magmatic and/or juvenile origin. Only in 1953, Goguel, on the basis of a thermodynamic study, first reached the conclusion that the superheated steam of the geothermal field of Larderello, Italy, is of meteoric origin, possibly with a minor fraction (not exceeding 10%) of juvenile or magmatic water. Ten years later, the meteoric origin of geothermal waters was definitely proven by systematic measurements of the hydrogen and oxygen isotopic composition of water and steam from well-known geothermal fields (Craig, 1963).

Figure 61 shows the isotopic composition of water and steam from most of the geothermal fields so far investigated, with the values for juvenile and magmatic water reported for comparison. The D/H ratio is in all cases identical to that of the local groundwater, proving their common origin from meteoric water infiltration, while the $^{18}$O/$^{16}$O ratio is significantly higher, as a consequence of isotopic exchange with the rocks constituting the geothermal reservoir. In fact, water and rocks are generally in isotopic disequilibrium and therefore tend to exchange their isotopes in order to approach the equilibrium corresponding to the temperature of the geothermal reservoir. This process is, however, effective only for oxygen, the hydrogen content of rocks generally being too low to significantly affect the isotopic composition of geothermal waters. For oxygen isotopes, the extent of exchange depends on the relative proportions of oxygen in the water and in the rocks, on the initial $^{18}$O contents, on the specific water-mineral fractionation factors (which are temperature dependent), and on the time and surface of contact. The exchange process, which is usually negligible at normal temperatures owing to its very slow rate, is greatly accelerated by the high temperature occurring in geothermal fields, with the result that the $^{18}$O content of water increases while that of rock decreases (the latter fact has also been observed by Panichi et al., 1974, and by Clayton and Steiner, 1975).

On the other hand, if geothermal waters would result from the mixing of water of meteoric origin with juvenile water, the mixing lines representing each geothermal system in a ($^{18}$O, $^{8}$D) plot would tend to converge at a single point — representing the isotopic composition of juvenile water — instead of being parallel, as in Fig. 61. Also, in the case of mixing with magmatic water, the D/H ratio would not remain constant in all cases, but would move towards that of the magmatic water present in each geothermal system. However, it should be pointed out that, as far as magmatic water is concerned, "the distinction between an exchange
between meteoric water and rock, and the presence of magmatic water, breaks down as the water gets closer and closer to the magma, so that some of the effects observed might well be due to a slight addition of 'recycled' meteoric water which could actually have gotten into the magma and emerged again with unchanged hydrogen isotopic composition” (Craig, 1963).

The positive shift in the $^{18}$O content alone seems to occur in all high-thermality areas -- although in some cases it is as small as 0.5–1.0‰, for instance in New Zealand, India and Colombia. The small oxygen shift in the geothermal waters at Wairakei has been explained by Clayton and Steiner (1975). They found that the $^{18}$O content of the hydrothermally altered rocks, ranging between $+2.6$ and $+5.2$‰, was depleted by 3–6‰ with respect to that of unaltered mother rocks (andesite, rhyolite, tuff) and was close to that corresponding to isotopic equilibrium with the geothermal water ($^{18}$O = $-4.9$‰); for comparison, the fractionation factor for alkali feldspar–water is in fact 7.2‰ at 250°C (O’Neil and Taylor, 1967), which is approximately the temperature of the geothermal reservoir. Also,
carbonates, present as alteration products, are already in isotopic equilibrium with water. Therefore, it may be concluded that the small $^{18}$O shift is due to the fact that the system is already close to the steady state, in which the rock will finally adjust its $^{18}$O content to be in equilibrium with that of the recharging water, and even intense exchange will not produce any further variation in the isotopic composition of the system components.

11.2.2. Evaporation effects on geothermal waters

Acid waters from hot springs frequently exhibit a positive correlation between deuterium and oxygen-18 contents, as shown in Fig. 62. This parallel enrichment in the two heavy isotopes has been attributed by Craig (1963) to evaporation taking place at shallow depth and/or on the surface, at a temperature ranging from 70 to 90°C. The ultimate origin of these waters is meteoric, since the lines extend from the local meteoric water isotopic composition; and, once again, there is no evidence of convergence towards a single point (mixing with juvenile or magmatic water).

The two situations to be considered, i.e., subsurface evaporation and evaporation on the surface, are discussed below.
11.2.2.1. Subsurface evaporation

Subsurface evaporation has been discussed by Giggenbach (1971) and by Truesdell et al. (1977). In natural systems, steam is produced by ascending hot water as pressure decreases. Adiabatic steam production is accompanied by a temperature decrease. Two extreme cases can be distinguished: (i) the steam coexists with the liquid phases during the fluid ascent and separates only at the surface ('single-stage steam separation'); (ii) the steam is continuously removed as soon as it is produced ('continuous steam separation').

In the single-stage separation the fraction \( f \) of residual liquid can be obtained from the enthalpy balance:

\[
f = \frac{(H_S - H_{LO})}{(H_S - H_L)}
\]

where \( H_{LO} \) is the enthalpy of the liquid water at the initial stage (before evaporation), and \( H_L \) and \( H_S \) are the enthalpies of the liquid and of the steam at the separation stage. It can be shown that the slope \( S \) of the \((\delta^{18}O, \delta D)\) plot is approximately:
GEOTHERMAL WATERS

\[ S \approx \frac{eD (\delta_0 D + 1000)}{e^{18}O (\delta_0^{18}O + 1000)} \]

where \( \delta_0 \) represents the initial isotopic compositions and \( e \) stands for the equilibrium enrichment factors at evaporation:

\[ \alpha = 1 + e = R \text{ (liquid)}/R \text{ (vapour)} \]

with \( R = D/H \) or \( ^{18}O/^{16}O \) as usual. It is interesting to note that at temperatures above 220°C and independently from the mechanism by which evaporation occurs, the slope \( S \) becomes negative, i.e. the oxygen-18 content increases while the deuterium content decreases. This is because \( \alpha D < 1 \) and \( eD < 0 \) above 220°C. On the contrary, \( \alpha^{18}O \) is always greater than 1 up to 374°C, the critical temperature of water. Figure 63 shows the values of the fractionation factors at temperatures above 135°C.

If the deep (initial) temperature of the geothermal fluid is known or can be estimated, also \( f \) can be computed and from this the initial isotopic composition of the water.

More complex is the case of the continuous steam separation. This process can be considered in principle a non-isothermal Rayleigh distillation. The isotopic enrichment of residual liquid water with respect to initial water can be evaluated from the expression (Truesdell et al., 1977):

\[ \ln \frac{1000 + \delta_L}{1000 + \delta_{LO}} = \int_{H_{LO}}^{H_L} \frac{1}{H_S - H_L} \text{d}H_L \quad (11.1) \]

with \( \alpha = \alpha (T) \). The integral on the right-hand side can be integrated numerically.

The two models, single-stage and continuous steam separation, produce significantly different results only if the difference between initial and final temperature is above, say, 150°C.

The changes induced by subsurface evaporation in the isotopic composition of the Yellowstone thermal waters (Norris Geyser Basin, Lower Geyser Basin, Shoshone Geyser Basin), together with the chloride content variations, were investigated by Truesdell et al. (1977) on the basis of the models discussed above and of mixing with low-chloride groundwater. Hydrogen isotopes were preferred because they are not affected by exchange with rocks. Similar investigations were made by Giggenbach (1978) for the El Tatio (Chile) geothermal waters.
11.2.2.2. Evaporation on the surface

Evaporation on the surface has been discussed by Giggenbach (1978) for the
geothermal pools at El Tatio (Chile). Isotopic exchange with atmospheric vapour
is considered negligible because of the very low relative humidity in the arid area
of El Tatio and, even more important, the high temperature of the hot springs.
The latter consideration applies to most geothermal areas, and therefore Giggenbach’s
models can be regarded as very good approximations to all cases of importance.

Two processes can be considered: (i) steady-state evaporation, and (ii) Rayleigh
batch distillation.

In the steady-state evaporation model the pool consists of water, originally
cold and probably deriving from shallow groundwater, which is heated by geo-
thermal steam flowing through it. As a consequence, isotopic exchange between
steam and water takes place, and the initial isotopic composition $\delta_{SO}$ of the steam
can be evaluated as follows:

$$\delta_{SO} = \delta_{WO} + (\delta_{W} - \delta_{WO})y - 1000(\beta - 1)$$

where $\delta_{WO}$ and $\delta_{W}$ are the isotopic compositions of the cold water feeding the
pool and of the water leaving the pool (after exchange with the steam),
respectively, and $y$ is the fraction of vapour entering the system (equal to that
leaving the system, the quantity of steam needed to heat the pool being considered
negligible). $\beta$ is the overall fractionation factor, taken as:

$$\beta = \alpha (D/D_i)^n$$

where $\alpha$ is the equilibrium fractionation factor between liquid water and steam,
and $D/D_i$ the ratio between the diffusion coefficients in air of $H_2O$ and $HDO$ or
$H_2^{18}O$. The exponent $n$ is derived empirically and may range from 0 (equilibrium)
to 0.58 (observed in falling drops by Stewart, 1975).

In Rayleigh batch distillation the equation for obtaining $\delta_{SO}$ becomes:

$$\delta_{SO} = \delta_{WO} + \left[ (\delta_{W} + 1000)(1 - y)^{1-1/\beta} - (\delta_{WO} + 1000) \right]/y$$

However, this process, which closely approximates the steam losses accompanied
by adiabatic cooling in flow channels (Section 4.2.2.1), does not fit the El Tatio
data. In fact, it produces values of $\delta_{SO}$ ranging from +100 to +150‰ for both
oxygen-18 and deuterium, which obviously are unacceptable. It appears that
Rayleigh batch distillation is significant only in water flowing out of pools, but
does not produce any important enrichment in $^{18}O$ and deuterium (Giggenbach,
personal communication).
TABLE XIV. COMPARISON BETWEEN THE CONCENTRATIONS REACHED BY THE THERMOGRAVITATIONAL EFFECT AFTER 25000 AND 75000 YEARS AND THOSE OBSERVED IN BRINES
Thermal gradient: 0.25°C/m; porosity: 10%; thickness of rock layer: 300 m (Costeseque et al., 1977)

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration (ppm)</th>
<th>Concentration after 25000 years (ppm)</th>
<th>Concentration after 75000 years (ppm)</th>
<th>Concentration observed in brines (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>6</td>
<td>370</td>
<td>560</td>
<td>400</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.01</td>
<td>1.0</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Ba⁴⁺</td>
<td>0.05</td>
<td>400</td>
<td>610</td>
<td>250</td>
</tr>
<tr>
<td>Ca⁴⁺</td>
<td>100</td>
<td>34000</td>
<td>53000</td>
<td>28800</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.001</td>
<td>1260</td>
<td>2000</td>
<td>5</td>
</tr>
<tr>
<td>K⁺</td>
<td>500</td>
<td>14000</td>
<td>22000</td>
<td>17500</td>
</tr>
<tr>
<td>Na⁺</td>
<td>500</td>
<td>38000</td>
<td>60000</td>
<td>53000</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1500</td>
<td>96000</td>
<td>160000</td>
<td>155000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Initial δ-SMOW (‰)</th>
<th>δ-SMOW after 25000 years (‰)</th>
<th>δ-SMOW after 75000 years (‰)</th>
<th>δ-SMOW observed in brines (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>-90</td>
<td>-76</td>
<td>-71</td>
<td>-75</td>
</tr>
<tr>
<td>¹⁸O</td>
<td>-11</td>
<td>-1.7</td>
<td>+3</td>
<td>+2.3</td>
</tr>
</tbody>
</table>

11.2.3. Effects due to thermal diffusion

The geothermal wells of Salton Sea, California, and Cesano, Italy, deliver highly concentrated hot brines. The total salinities can be as much as 180 g/l at Salton Sea (Craig, 1966) and more than 300 g/l at Cesano (Calamai et al., 1976), with an underground temperature of 330 and 260°C, respectively. In particular, the Salton Sea brines exhibit a large oxygen shift (Fig. 61), which is attributed to isotopic exchange with the rock matrix. This process, accompanied by a continuous leaching of the rock, results in a logarithmic relationship between chloride content and oxygen-18 shift, as reported by Craig.
Recently, another explanation for this process has been proposed by Costeseque et al. (1977). They were able to demonstrate, on the basis of a model combining thermal diffusion and thermal convection, that isotope enrichment and salt concentration vary in a similar way as observed in the Salton Sea brines. The calculations were based on equations describing the thermogravitational effect in porous media, on the Soret coefficient for hydrogen and oxygen isotopes and for several ions, and on a knowledge of the geometry and the thermal characteristics of the hydrothermal system. The results are reported in Table XIV and show that salt concentrations of the same order of magnitude as those observed in brines can be reached by means of the thermogravitational effect within relatively short geological times. Also the parallel changes in deuterium and oxygen-18 content compare well with those reported for the Salton Sea geothermal field.

11.3. SPACE AND TIME VARIATIONS OF THE ISOTOPIC COMPOSITION OF GEOTHERMAL WATERS

Variations of the deuterium and $^{18}$O contents in water or steam within any given geothermal area generally occur. Three hypotheses for the causes of these variations are possible:

(a) The isotopic variations result from mixing in varying proportions of waters with different $^{18}$O/$^{16}$O ratios; this is the case, for instance, when waters of different origin feed the same hydrothermal system, or when deep geothermal water enriched in $^{18}$O by isotopic exchange mixes with shallow, relatively cold groundwater which has preserved its original isotopic composition;

(b) The isotopic variations are due to different degrees of isotopic exchange with rocks in various places; for instance, it might be expected that, along the underground flow in a geothermal field, the $^{18}$O content increases in the water as a consequence of a progressive isotopic exchange;

(c) The isotopic variations are due to steam losses during ascent of the fluid; these losses are generally more significant for springs.

Generally, the processes described above produce also variations of the chemical composition, but most frequently the correlation between chemical and isotopic data is not simple and straightforward.

11.3.1. Isotopic variations of geothermal waters depending on the altitude of the recharge area

In cases where underground temperature is not high enough to enable significant isotopic exchange between water and rocks, and where the total salinity of the waters is exceptionally high, coupled chemical and isotopic analyses can be adopted
usefully to distinguish source regions and path-lines of thermal fluids emerging in the same area. This is actually observed at Abano, Italy, where a number of thermal springs in a relatively small area have temperatures ranging from 30 to 90°C and \( \delta^{18}O \) values ranging from -7.5 to -12.0‰ (Panichi et al., 1976; Norton and Panichi, 1978).

The first \( \delta^{18}O \) value corresponds to that of groundwater recharged by local precipitation, the second to that of precipitation in the Alps, which might be a source of groundwater recharged through infiltration from rivers descending to the Po valley (Bortolami et al., 1973). A plot of the chloride content versus \( \delta^{18}O \) is shown in Fig. 64. The colder and less salty waters (SO4-type) derive from the limestone aquifer overlying the crystalline basement. The upper part of the basement, in turn, constitutes the main reservoir for the hot, more salty waters (Cl-type). On the basis of their chemistry, the Cl-type waters seem to form two different systems and mix with waters in the upper aquifers before reaching the surface.

When the original isotopic composition is not preserved in the geothermal water, it can be evaluated from plots similar to those of Figs 61, 62, i.e. from the intercept of the geothermal lines with the meteoric water line. Hydrogen isotopic compositions of water are less affected by processes occurring in geothermal fields, so that their use for the purpose of identifying the origin of waters should be preferred to the use of oxygen. Using \( \delta D \) values, Arnason (1977b) was able to identify the recharge areas of several geothermal systems in Iceland and to reconstruct in some detail the main geothermal water flow paths.
FIG. 65. $\delta^{18}O - \delta D$ relationship in geothermal waters from Campi Flegrei, Italy, and Arima, Japan, indicating mixing of deep brines with recent fresh groundwaters of meteoric origin. The tritium and chloride contents of selected samples are also indicated.

11.3.2. Mixing of geothermal waters with cold water

Frequently, deep hot waters or steam may undergo mixing with other waters, generally colder and fresher, during their ascent to the surface or on their way to geothermal wells. If the cold and hot waters have different isotopic compositions the mixing process will result in a parallel variation of the $\delta D$ and $\delta^{18}O$-values according to a linear relationship.

Figure 65 shows the cases of Campi Flegrei, Italy, and of Arima, Japan. The stable isotopes, tritium and salt contents clearly indicate a mixing of deep old brines with young fresh waters of meteoric origin.

Some problems remain, however, concerning the origin of brine water. In the case of Campi Flegrei, the deuterium and oxygen-18 contents of the sample with the highest salinity correspond quite well to those of Mediterranean sea-water, which is slightly enriched in heavy isotopes with respect to SMOW (the Mediterranean Sea is a partially enclosed sea where evaporation exceeds the freshwater inflow). This suggests that the brine water is sea-water which, however, evidently has lost some chloride (about 21 g/l for the case of Mediterranean water) in a geochemical process (filtration?) which did not affect the isotopic composition (Baldi et al., 1976).
The parent water of the Arima brine could be of magmatic origin, as suggested by Sakai and Matsubaya (1974, 1977) because the $\delta D$ and $\delta^{18}O$-values of the most enriched samples are well within the inferred range of magmatic waters. Alternatively, these authors suggest also a meteoric origin, followed by a complex and not well known combination of several geochemical processes (exchange, ultrafiltration, etc.) which would have determined the final chemical and isotopic composition of the brine.

The chemical data do not appear to be related in a simple manner with isotopic data of geothermal fields delivering superheated steam. In this case, only gaseous compounds (mainly CO$_2$, but also NH$_3$, CH$_4$, H$_2$, N$_2$, H$_2$S and rare gases) and compounds easily volatile in hot steam (like boric acid) accompany the steam. However, the isotopic data might provide useful information on the main flow-paths of the geothermal fluid and on the recharge mechanisms.

An example of this type of application of the isotope technique has been reported by Celati et al. (1973) and by Panichi et al. (1974) who studied the $^{18}O$ and tritium distribution at Larderello (Figs 66, 67). The groundwater, recharged in the limestone outcrops in the south, moves into the geothermal field, following two different paths in the more permeable formations (anhydrites, limestones, and the upper part of the basement which is rather fractured) and in the deeper, less permeable zones of the basement.

The deeper circulation waters, which experience higher temperatures and longer residence times, appear to be responsible for the higher $^{18}O$ content observed in steam emerging in the inner zones of the field. On the other hand, the negative $\delta$-values of the southern zones of the field appear to be the result of mixing with water of relatively shallow circulation, with lower temperature and shorter residence time.

The mixing is particularly evident in the Castelnovo area, where an inflow of recent water (tritium concentration up to 49 T.U.) occurs through permeable or semi-permeable formations. This infiltration area, located on the same anticline as the steam field, is connected with the latter through the main fracture system along the anticlinal axis. Therefore, the water infiltrated at Castelnovo can affect a significant zone of the geothermal field.

Similar conclusions were drawn by Truesdell et al. (1978) from the distribution of the $\delta^{18}O$-values of geothermal fluids delivered in the Cerro Prieto field. The pattern of oxygen-18 values reported in Fig. 68 is believed to be the result of draw-down of fluids into the production aquifer from an overlying lower-temperature aquifer.

11.3.3. Changes of the isotopic composition of geothermal waters as a consequence of their exploitation

Geochemistry, including environmental isotopes, appears to be particularly useful in monitoring the evolution in time of a geothermal field as a consequence
FIG. 66. $^{18}$O-content distribution in Larderello, Italy.
FIG. 67. Tritium-content distribution in Larderello, Italy.
of its exploitation. Ellis (1977) suggests that the detection of even small changes in the chemical composition of a geothermal fluid enables a precise assessment of the long-term stability of the field. For instance, in steam-dominated systems, the gas fraction should remain constant in the fluid if this is obtained from storage in a reservoir. On the contrary, a decrease of the gas fraction should be expected if the steam is at least partially produced by boiling from a deep water table (White, 1970).

A decreasing gas content, as found at Larderello, could be related to an increasing proportion of steam deriving from evaporation of shallow, modern groundwater, as described in the previous section. This hypothesis is strongly supported by the variations observed with time of the $^{18}O$ content of the steam. Figure 69 shows these variations schematically. It appears that in the inner zones the wells have generally shown no variations, indicating that by now they are fed by one single source of steam which is probably that produced by deeper evaporation in the central zone.

In the immediately adjacent area characterized by $\delta^{18}O$-values ranging from $-1$ to $-4\%$, there is a clear tendency towards more positive values with time. This is evidently due to the widening of the zone in which the contribution of the deeper steam is prevalent, as a consequence of exploitation.

On the contrary, in the most peripheral areas, where the isotopic composition ranges from $-3$ to $-5\%$, there is a clear tendency towards the production of steam with more negative $\delta^{18}O$-values. This indicates that the relative contribution of the water coming from the permeable outcrops is increasing.
FIG. 69. Variation of $^{18}O$ content of Larderello geothermal waters with time.
Similar trends are observed at the Wairakei geothermal field, for which Clayton and Steiner (1975) reported that the $^{18}$O-values measured in six well-waters are from 0.6 to 2.6$\%$ lower than those measured thirteen years ago (Craig, 1963), given $\delta$-values of $-4.9\%$. Even though no systematic measurements are available, these variations with time of the oxygen isotope characteristics of geothermal waters can certainly be interpreted in terms of exploitation effects.

11.4. ISOTOPIC GEOTHERMOMETERS

If the variation with temperature of the equilibrium fractionation factor of a given isotopic exchange reaction is known, it is in principle possible to evaluate the reaction temperature by measuring the difference in isotopic composition between the two reactants. In other words, any pair of natural compounds containing the same element with more than one isotope — such as hydrogen, oxygen, carbon and sulphur — may constitute in principle an isotopic geothermometer, provided that the compounds co-exist (or have been produced) in isotopic equilibrium in the same geochemical system. In addition to this basic prerequisite, the following other requirements should be fulfilled:

(a) In the temperature range of interest, the isotopic fractionation factor must show a regular gradient with temperature which is large enough to be readily measured

(b) Mixing with chemically identical compounds of different origin — and therefore having probably different isotopic composition — should be excluded or at least evaluated for correcting the results

(c) For geothermal studies, the isotopic ratios at the surface — where the samples are collected — should be identical to those in the geothermal reservoir

(d) The isotopic ratios should not be affected by the sampling technique and should remain unaltered until the analysis is performed.

$\text{H}_2\text{O}$ (steam), $\text{CO}_2$, $\text{CH}_4$ and $\text{H}_2$ are normally present in high-temperature geothermal fluids and represent, together with $\text{H}_2\text{S}$ and $\text{N}_2$, the main components of the gas phase. The following isotopic exchange reactions may occur:

$$^{12}\text{CO}_2 + ^{13}\text{CH}_4 = ^{13}\text{CO}_2 + ^{12}\text{CH}_4$$

$$\text{CH}_3\text{D} + \text{H}_2\text{O} = \text{CH}_4 + \text{HDO}$$

$$\text{HD} + \text{CH}_4 = \text{H}_2 + \text{CH}_3\text{D}$$

$$\text{HD} + \text{H}_2\text{O} = \text{H}_2 + \text{HDO}$$

$$\text{C}^{16}\text{O}_2 + \text{H}_2\text{O}^18\text{O} = \text{C}^{16}\text{O}^18\text{O} + \text{H}_2\text{O}^{16}\text{O}$$
FIG. 70. Variation with temperature of the isotopic equilibrium constants of some reactions commonly used as geothermometers. Curve A' refers to the experimental data obtained by Craig (1975). Curves A, B, C have been obtained by fitting the theoretical values calculated by Richet et al. (1977).

In water-dominated systems the sulphate–water exchange reaction is used for geothermometry:

$$S^{16}O_4^- + H_2^{18}O = S^{16}O_3^{18}O^- + H_2^{16}O$$

The dependence of the fractionation factors on temperature of some of the above reactions is shown in Fig. 70.\(^{18}\)

If the temperature of the fluid remains constant for a period which is sufficiently long to allow all the exchange reactions to reach isotopic equilibria, we would expect all of them to give the same isotopic temperature. If, however, the temperature of the fluid does not remain constant as it proceeds towards the point of discharge, the different rates at which each exchange reaction adjusts to

\(^{18}\) Plots of fractionation factors and temperature, and equations of many reactions have been compiled by Friedman and O’Neil (1977).
TABLE XV. ESTIMATED REACTION TIME FOR SOME ISOTOPIC EXCHANGE REACTIONS (Hulston, 1977)

<table>
<thead>
<tr>
<th>Isotopic exchange reaction</th>
<th>T_{\sim 0.9} (years)*</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$CH$_4 - ^{13}$CO$_2$</td>
<td>&gt; 5</td>
<td>Hulston (1973)</td>
</tr>
<tr>
<td>$^{18}$O$_4 - ^{16}$H$_2$</td>
<td>&lt; 1 at 300$^\circ$C</td>
<td>Lloyd (1968)</td>
</tr>
<tr>
<td></td>
<td>~ 5 at 200$^\circ$C</td>
<td></td>
</tr>
<tr>
<td>HS$^{18}$O$_4 - ^{16}$H$_2$</td>
<td>~ 1</td>
<td>Hulston (1973)</td>
</tr>
<tr>
<td>HDO - H$_2$</td>
<td>&lt; 1</td>
<td>Hulston (1973)</td>
</tr>
</tbody>
</table>

* T$_{0.9}$ = 3 × T$_{1/2}$ (half-time of the reaction).

the new equilibrium conditions will produce for each of them a different isotopic temperature.

Considering gas-phase reactions only, Lyon (1974) suggests that the reaction rates decrease in the following order: H$_2$ - H$_2$O, H$_2$ - CH$_4$, CO$_2$ - CH$_4$. This sequence could actually begin with the reaction CO$_2$ - H$_2$O, the kinetics of which is fast, as shown by the data obtained by Panichi et al. (1977) for the Larderello geothermal field. Laboratory experimental data and field observations suggest the rough estimates of the reaction rates reported in Table XV (Hulston, 1977).

Currently available data indicate that the isotopic composition of the pair CO$_2$ - CH$_4$ always gives temperatures which are higher by 50–150$^\circ$C than the measured ones, while the pairs H$_2$O - H$_2$, CH$_4$ - H$_2$ and CO$_2$ - H$_2$O generally produce temperature values much closer to those observed.

When different pairs are considered in the evaluation of the base temperature of a certain geothermal field, the discrepancies between them are explained in terms of differences in the reaction rates, assuming that isotopic equilibrium is achieved between the gas pairs after their formation, independent of the chemical reactions governing their actual concentrations. It should, however, be recognized that the activation complexes through which the isotopic exchange reactions can proceed are indeed very little understood and quite difficult to define. In this respect, the Fischer-Tropsch reaction, 4H$_2$ + CO$_2$ = CH$_4$ + 2H$_2$O, probably does not provide the main exchange mechanism for the pairs CO$_2$ - CH$_4$, CH$_4$ - H$_2$, and H$_2$O - H$_2$. Panichi et al. (1979) suggest that CO$_2$ and CH$_4$ are formed independently from amorphous carbon and graphite, while CO$_2$ might also be formed by hydrolysis of carbonates. Gunter (1978) also concluded that the reaction of carbon dioxide and hydrogen was not the primary source of methane of the Yellowstone Park geothermal gases. Recently, Sackett and Chung (1979)
showed that no isotopic exchange occurs between \( \text{CO}_2 \) and \( \text{CH}_4 \) at high temperature (200–500°C) in the presence of water and calcium montmorillonite, which might act as a catalyst. However, the duration of their experiments – 32 days at 200°C and 10.5 days at 500°C – was perhaps short with respect to the residence time of fluids in geothermal systems.

Let us now examine more closely some particular isotopic geothermometers. The thermometer based on the system \( \text{CO}_2 - \text{CH}_4 \) is excluded because carbon isotopes are not discussed in this monograph. Furthermore, it is questionable whether the temperature values provided by the \( \text{CO}_2 - \text{CH}_4 \) pair are meaningful because of the very slow exchange rate. Also, the geothermometer \( \text{H}_2\text{O} - \text{CH}_4 \) is not discussed because the hydrogen isotope fractionation factor shows only a slight variation in the temperature range of interest in geothermal studies.

### 11.4.1. The \( \text{CH}_4 - \text{H}_2 \) and \( \text{H}_2\text{O} - \text{H}_2 \) geothermometers

The hydrogen isotope fractionations in the methane–hydrogen and water–hydrogen systems have been calculated by Bottinga (1969) and, more recently, by Richet et al. (1977). Experimental data now available for the system methane–hydrogen (Craig, 1975) are in reasonable agreement with the computation of Richet et al., as shown in Fig. 70, and fit the equation:

\[
1000 \ln \alpha = -90.9 + 181.27 \times 10^6/T^2 - 8.95 \times 10^{12}/T^4
\]  \((11.2)\)

where \( \alpha = (\text{D}/\text{H})_\text{CH}_4/(\text{D}/\text{H})_\text{H}_2 \) and \( T \) is expressed in kelvin. This equation is valid at temperatures higher than 200°C. The equation fitting the theoretical data by Richet et al. (1977) in the temperature range 100–400°C is:

\[
1000 \ln \alpha = -238.3 + 289.0 \times 10^3/T + 31.86 \times 10^6/T^2
\]  \((11.2')\)

Least-squares fitting of theoretical data (Richet et al., 1977) for \( \text{H}_2\text{O} \) (vapour) and \( \text{H}_2 \) in the temperature range 100–400°C produces the equation:

\[
1000 \ln \alpha = -217.3 + 396.8 \times 10^3/T + 11.76 \times 10^6/T^2
\]  \((11.3)\)

where \( \alpha = (\text{D}/\text{H})_\text{H}_2\text{O}/(\text{D}/\text{H})_\text{H}_2 \).

Table XVI summarizes the limited data available on geothermometry obtained from hydrogen isotopes. It appears that the isotopic temperatures match reasonably well the temperatures directly measured in each geothermal field, with the exception of Reykjanes in Iceland where the isotopic temperature is about 80°C higher; Arnason (1977a) suggests that this discrepancy is due to mixing between ocean water and inland meteoric water, the latter being equilibrated with hydrogen at a temperature of 400°C or more before mixing with the first.
TABLE XVI. COMPARISON BETWEEN OBSERVED TEMPERATURE AND ISOTOPIC TEMPERATURE BY THE CH₄ − H₂ AND H₂O − H₂ SYSTEMS

<table>
<thead>
<tr>
<th>Area</th>
<th>System type</th>
<th>Water phase</th>
<th>Observed temperature (°C)</th>
<th>Isotopic temperature (°C)</th>
<th>Temperature (°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larderello, Italy</td>
<td>VD</td>
<td>steam</td>
<td>216 ± 25</td>
<td>314 ± 30</td>
<td>254 ± 25</td>
<td>Panichi et al. (1979)</td>
</tr>
<tr>
<td>Krisuvik, Iceland</td>
<td>WD</td>
<td>w. water</td>
<td>223</td>
<td>223</td>
<td>196 − 201</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Krisuvik, Iceland</td>
<td>WD</td>
<td>s. water</td>
<td>223</td>
<td>217</td>
<td>217</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Nesjavellir, Iceland</td>
<td>WD</td>
<td>w. water</td>
<td>220</td>
<td>240</td>
<td>244</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Namaskard, Iceland</td>
<td>WD</td>
<td>w. water</td>
<td>240</td>
<td>244</td>
<td>283</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Namaskard, Iceland</td>
<td>WD</td>
<td>w. water</td>
<td>268</td>
<td>283</td>
<td>283</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Reykjanes, Iceland</td>
<td>WD</td>
<td>w. water</td>
<td>292 (1800)b</td>
<td>362 − 380</td>
<td>362 − 380</td>
<td>Arnason (1977a)</td>
</tr>
<tr>
<td>Broadlands, N.Z.</td>
<td>WD</td>
<td>w. water</td>
<td>245</td>
<td>265c</td>
<td>265</td>
<td>Lyon (1974)</td>
</tr>
<tr>
<td>Imperial Valley, CA, USA</td>
<td>WD</td>
<td>brine</td>
<td>211 (surf.)</td>
<td>255</td>
<td>220</td>
<td>Craig (1975)</td>
</tr>
<tr>
<td>Yellowstone Park, WY, USA</td>
<td>VD</td>
<td>steam</td>
<td>82</td>
<td>105c</td>
<td>105c</td>
<td>Gunter and Musgrave (1971)</td>
</tr>
</tbody>
</table>

a VD: vapour-dominated system; WD: water-dominated system; w. water: well-water; s. water: spring-water.
b Highest temperature in a drill hole in the area.
c Recalculated using Eq. (11.3).
11.4.2. The CO$_2$ – H$_2$O geothermometer

The oxygen isotope distribution in the carbon dioxide–water vapour system has been calculated theoretically by Richet et al. (1977); in the temperature range 100–400°C it fits the equation:

$$1000 \ln \alpha = -8.87 + 7.85 \times 10^3/T + 2.94 \times 10^6/T^2$$  \hspace{1cm} (11.4)

where $\alpha = (^{18}\text{O}/^{16}\text{O})$ CO$_2$/(^{18}\text{O}/^{16}\text{O})$ H$_2$O, and $T$ is expressed in kelvin.

Panichi et al. (1977) used a slightly different equation, based on data published by Bottinga (1969), which produces practically identical results.

This isotopic geothermometer has been used only in the geothermal field of Larderello by Panichi et al. (1977, 1979). With the exception of a few cases, the isotopic temperature of the geothermal wells is equal to or higher than the temperature measured at the well-head. This is a clear indication that the isotopic temperature corresponds to the actual temperature of the geothermal reservoir tapped, where carbon dioxide and water vapour are in isotopic equilibrium. The difference between the isotopic temperature and the temperature at the well-head is a measure of the cooling undergone by the geothermal fluid on its way up to the surface, the duration of which is too short to bring about any significant isotopic re-equilibration.
TABLE XVII. COMPARISON BETWEEN OBSERVED TEMPERATURE AND ISOTOPIC TEMPERATURE BY THE SO₄ – H₂O SYSTEM

<table>
<thead>
<tr>
<th>Area</th>
<th>Maximum observed temperature (°C) (depth, m)</th>
<th>Isotopic temperature (°C)ᵃ</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onhuma, Japan</td>
<td>220</td>
<td>260–290 (100–220)ᵇ</td>
<td>Sakai (1977)</td>
</tr>
<tr>
<td>Ohtake, Japan</td>
<td>234</td>
<td>180–280 (150–220)ᵇ</td>
<td>Sakai (1977)</td>
</tr>
<tr>
<td>Larderello, Italy</td>
<td>310 (1500)</td>
<td>152–329</td>
<td>Cortecci (1974)</td>
</tr>
<tr>
<td>Campi Flegrei, Italy</td>
<td>300 (1800)</td>
<td>215</td>
<td>Cortecci et al. (1978)</td>
</tr>
<tr>
<td>Ilan Tuchung, Taiwan</td>
<td>173 (240)</td>
<td>187</td>
<td>in Truesdell (1976)</td>
</tr>
<tr>
<td>Steamboat Spring, NV, USA</td>
<td>186 (222)</td>
<td>220</td>
<td>in Truesdell (1976)</td>
</tr>
<tr>
<td>Yellowstone Park, WY, USA</td>
<td>95</td>
<td>360ᶜ</td>
<td>McKenzie and Truesdell (1977)</td>
</tr>
<tr>
<td>Long Valley, CA, USA</td>
<td>177</td>
<td>240ᶜ</td>
<td>McKenzie and Truesdell (1977)</td>
</tr>
<tr>
<td>Raft River, ID, USA</td>
<td>130</td>
<td>142ᶜ</td>
<td>McKenzie and Truesdell (1977)</td>
</tr>
<tr>
<td>Zakopane, Poland</td>
<td>41 (1020)</td>
<td>37–47</td>
<td>Cortecci and Dowgiallo (1975)</td>
</tr>
</tbody>
</table>

ᵃ Calculated by HSO₄ – H₂O scale of Mizutani and Rafter (1969).
ᵇ Values in brackets have been calculated with the BaSO₄ – H₂O scale of Kusakabe and Robinson (1975).
ᶜ Evaluated after corrections of ¹⁸O contents due to boiling and dilution effects on the hot spring waters.
The above conclusion is also supported by Fig. 71, showing the distribution of the difference between the temperature at the well-head and the isotopic temperature. Such a distribution is not normal. The modal value corresponds to the isotopic equilibrium between carbon dioxide and vapour ($T_m - T_i = 0$), but 69 wells out of 115, i.e. 60%, definitely exhibit a cooling ($T_m - T_i < 0$) which in extreme cases can be more than $50^\circ$C. Only 20 wells (17%) had a well-head temperature higher than that given by the carbon dioxide–water isotopic equilibrium; although there is no definite explanation, some hypotheses explaining these values are reported by Panichi et al. (1979). Anyhow, it is interesting to note that all wells showing an isotopic temperature lower than that measured are located in the central, most exploited area of the geothermal field.

11.4.3. The $\text{SO}_4^{2-} - \text{H}_2\text{O}$ geothermometer

The oxygen isotope distribution in the pair sulphate–water provides a geothermometer which is probably the most useful for water-dominated geothermal fields. The fractionation factor between sulphate and water has been experimentally determined by Lloyd (1968) and by Mizutani and Rafter (1969) who found respectively:

$$1000 \ln \alpha = 3.251 \times 10^6/T^2 - 5.6$$
$$1000 \ln \alpha = 2.88 \times 10^6/T^2 - 4.1$$

where $\alpha = (\text{^{18}O/^{16}O})\text{SO}_4/(\text{^{18}O/^{16}O})\text{H}_2\text{O}$ and $T$ is in kelvin. The above two equations almost coincide at $200^\circ$C, and are in reasonable agreement ($\pm 10^\circ$C) in the temperature range $0$–$300^\circ$C. The results obtained so far with this isotopic thermometer are reported in Table XVII.

Lloyd (1968) showed that the isotopic exchange rate between sulphate and water is slow in alkaline and neutral solutions and increases as the pH decreases. Assuming a pH of 7 – a value which is close to reality for deep geothermal waters – and a first-order reaction for the isotopic exchange, the time required to reach 99.9% equilibrium is 2 years at $300^\circ$C and 18 years at $200^\circ$C, but it goes up to as much as 500 years at $100^\circ$C. However, the residence time of waters in most high-temperature reservoirs is probably sufficient to ensure isotopic equilibrium. For instance, at Steamboat Springs (about $200^\circ$C) the age of the water has been estimated to be about 50 years (White et al., 1963). Geothermal waters are mostly tritium-free, which indicates that they entered the system before 1953 when large quantities of tritium started to be introduced in the hydrosphere through thermonuclear explosions (see, for a brief account of tritium history, Suess, 1969, and Bradley et al., 1972).

The main problem in the application of the sulphate–water isotopic geothermometer concerns the conservation of the isotopic composition of the two compounds.
In fact, water and the dissolved sulphate from a hot spring collected at the surface might not have the same isotopic composition as at depth. Changes in the water isotopic composition can be introduced by evaporation or by mixing with shallow groundwater. McKenzie and Truesdell (1977) showed that corrections are possible under certain circumstances and they proposed models to evaluate the evaporation effect and the mixing effect. Results corrected by these effects are reported in Table XVII.

Mixing with sulphate-bearing shallow groundwater also affects the isotopic composition of the dissolved sulphate, which will no longer reflect that of the deep geothermal sulphate. However, the sulphates dissolved in these shallow groundwaters often also show changed $^{34}$S/$^{32}$S values as a consequence of their origin from oxidation of volcanic sulphur and hydrogen sulphide in fumarolic areas or because they were affected by reducing bacteria activity in marine sediments and soil (Sakai, 1977; Cortecchi et al., 1978). Therefore, a determination of the $^{34}$S/$^{32}$S ratio in sulphate might help in detecting and discarding those $^{18}$O-data unsuitable for geothermometry.

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Chapter 12

PALAEOWATERS

12.1. INTRODUCTION

Palaeowaters are those groundwaters, formation waters, interstitial waters of sediments or waters of mineral crystallization originating from water cycles under environmental conditions which are different from the present ones.

The stable isotope content of waters of meteoric origin depends upon climatic factors, such as origin of air moisture, temperature of condensation, and humidity and temperature profiles of the atmosphere. Furthermore, in groundwaters the $^{18}$O and deuterium contents also depend upon the mechanism and time of recharge and, chiefly, upon the local distribution of rainfall with respect to evapotranspiration. On the pluri-annual scale, groundwaters are thus expected to reflect the average local climatic conditions, resulting in a rather constant stable isotope content. This was observed in the temperate climate of Central Europe (Eichler, 1965) and also in the climatic conditions of the eastern Mediterranean (Gat, 1974). However, any significant climatic variation over a period of time which is long compared with local aquifer turnover will be marked by a change of the stable isotope content. Compared with recent waters, this palaeoclimatic labelling may consist of differences in $\delta^{18}$O (and $\delta$D) or in deuterium excess, or both.

The identification of palaeowaters which are related to old evaporitic episodes (brines) or marine transgressions is generally easy on the basis of their salt content. However, because deuterium, and oxygen-18 at low temperatures, are, with some reservations, conservative parameters in groundwater systems, they allow the recognition of primary brines whose high content of heavy isotopes will still reflect the evaporitic enrichment; secondary brines obtained from leaching of salts by meteoric water will have a low content of heavy isotopes. In a $\delta$D–$\delta^{18}$O diagram, primary brines will exhibit enrichment by evaporation and secondary brines will lie on, or close to, the local meteoric water line. The dilution stages of a primary brine by meteoric water will describe a straight mixing line whose slope is similar to that of an evaporation line. Furthermore, chemico-physical reactions with the aquifer matrix or with existing fluids can occur even at low temperatures and can modify the stable isotope content of waters. In circulating systems (residence time of some tens of thousands of years) these effects are insignificant because of very low reaction rates and also because permeable strata are generally poor in reactive minerals (e.g. clays) or fluids. In stagnant waters (formation waters or interstitial waters of sediments), however, reactions can become important and must be investigated.
FIG. 72. Schematic representation of compiled palaeoclimatic data from the Mediterranean regions, the Sahara and intertropical Africa. Ordinate: arbitrary scale of 'humidity' (precipitation or precipitation/evaporation ratio), abscissa: $^14$C ages in years BP. (Rognon, 1976, modified.)

FIG. 73. Eustatic fluctuations during the last glaciation. Although the amplitude of sea-level variation is still under discussion (and may have been different from place to place), it appears that a significant increase of the hydraulic gradient (and of the drainage rate) has affected the coastal aquifers between about 25 000 and 10 000 years BP. (Mörner, 1971, modified.)
12.2. PALAEOWATERS IN AQUIFERS

12.2.1. Palaeoclimatological framework

In circulating groundwater systems the influence of climatic changes on recharge and discharge processes has to be taken into account. It was generally considered that glacial periods at high latitudes and altitudes were correlated with low evaporation and/or high rainfall periods at mid latitudes. It is now established that this popular concept is over-simplified. For the late Quaternary of both hemispheres, for latitudes of up to about 25°, the following general palaeoclimatic picture was recently proposed (Fig.72) (Rognon, 1976; Rognon and Williams, 1977):

40 000 — 20 000 BP: heavy rainfall and high lake levels
17 000 — 12 000 BP: intertropical aridity, dune building and lake desiccation
11 000 — 5 000 BP: high precipitation and very high lake levels.

Precipitation at low latitudes of the northern hemisphere is largely controlled by pressure systems of the atmosphere of the southern hemisphere. This control is of great importance for palaeoclimatological reconstructions, because of the high-pressure zone which was probably associated with the development of the large Antarctic ice cap during glaciation. During the late Quaternary the major glacial episode started at about 25 000 BP and produced a major eustatic decrease, with a minimum oceanic level of about −90 m to −120 m (Fig.73) at 18 000 BP (Mörner, 1971). Then the climatic set-back produced the melting of ice caps and the rise in sea-level, which was practically terminated at 7000 BP. Thus, taking into account the fluctuations in precipitation and the hydraulic gradients of the aquifers, one would expect that intertropical basins with external drainage were actively drained during low-sea-level and low-rainfall periods, i.e. between 20 000 and 10 000 BP, and recharged when opposite conditions prevailed, i.e. between 10 000 and 5000 BP.

For periods older than 20 000 BP any palaeohydrological reconstruction is very risky because the radiochronology of precipitation events is uncertain and, above all, because important changes in the aquifer regimes occurred during the interval 20 000 — 5000 BP.

12.2.2. The ¹⁴C determination of groundwater ages

These palaeoclimatological considerations suggest that aquifers have been largely renewed in a time interval which is theoretically accessible to ¹⁴C dating. Therefore it becomes of primary importance to attempt the dating of the total dissolved inorganic carbon (DIC) in order to identify palaeowaters and to discuss their mechanism of recharge. This requires that the hydrochemistry of major
ions and the $^{13}$C-content of DIC be available for age correction. Basic principles for the correction of $^{14}$C activities of DIC have been discussed recently (Mook, 1976; Fontes and Garnier, 1979). Several specific limitations were applied to groundwater dating. Because of dilution of the active carbon from soil zones into the inactive carbon of the aquifer matrix during carbon mineralization, the $^{14}$C content of DIC is, in most cases, lower than in a wood sample of the same age. Furthermore, because DIC is not a closed reservoir, contributions of recent carbon are possible and would introduce relatively major errors for old ages. Therefore, $^{14}$C age estimations of DIC are generally limited to about 20,000 to 25,000 years. As stated before, this time interval covers the range of major hydrological events in groundwater systems with external drainage. For these and other hydrological reasons and also for geochemical reasons, apparent ages greater than, say, 25,000 BP would not be considered as true ages. Furthermore, a solution of carbon can be in equilibrium with the solid phase for each chemical species and also for stable isotope content, but not for $^{14}$C, which tends to diffuse towards the solid. Since, for the time being, we have no method available to investigate this process on a long time range, one can only suspect that DIC with corrected ages of 30,000 or 35,000 years can actually be much younger.

12.2.3. Stable isotope and $^{14}$C evidence for palaeowaters in confined aquifers

Because of the low flow velocities predicted from Darcy’s law, one can expect to find very old waters even after a flow confinement of some kilometres or some tens of kilometres. Palaeowater occurrences were thus first investigated in confined aquifers. The pioneering work of Münich and Vogel (1962) and of Degens (1962) dealt with an aquifer of the Nubian sandstones (lower Cretaceous) in Western Egypt. They found stable isotope contents ($\delta D \approx -85\%_o$, $\delta^{18}O \approx -11\%_o$) much lower than those of present-day precipitation in this area. The calculated ages, assuming an initial $^{14}$C activity of 72.5% after carbon mineralization, were in the range of 18,000 to 40,000 (Fig. 74). The interpretation was that these artesian palaeowaters were recharged in pluvial times after an episode of eustatic drainage. Because of the low dissolved salt contents (150 to 300 ppm) a local recharge through outcrops of Nubian sandstones during a cold episode was preferably assumed, rather than a hypothetical recharge in the Tibesti mountains followed by a long underground transit.

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19 Carbon-14 activities (contents) are conventionally expressed in ppm (per cent of modern carbon), namely as percentage of the $^{14}$C activity (content) of plants before 1890, i.e. before injection into the atmosphere of large quantities of $^{14}$C-free CO$_2$ derived from fossil fuel combustion. The half-life of $^{14}$C is 5730 years.
The aquifer of Nubian sandstones was also investigated in the Sinai and Negev deserts (Gat, 1971; Issar et al., 1972; Gat and Issar, 1974). The dissolved inorganic carbon was dated from 13,000 years to more than 31,000 years, after correction of the dilution according to the $^{13}$C content. The oxygen-18 and deuterium contents are substantially higher ($\delta^{18}O \approx -6.0$ to $-7.5\%$, $\delta D \approx -30$ to $-65\%$) than in the Egyptian part of this aquifer (Ketsch et al., 1962). However, waters from Sinai were attributed to palaeoclimatic recharge on the basis of $^{14}$C ages and also because the deuterium excess ($\delta D = +10\%$) was lower than that of the present-day meteoric waters in the area ($+22\%$, Gat et al., 1969; Gat and Carmi, 1970).

In the region of Chott-el-Hodna, at the border between the Atlas plateau and the Sahara in Algeria, Gonfiantini et al. (1974b) investigated deep and shallow groundwaters around the Chott. On the northern and eastern sides of the Chott, artesian groundwaters show a correlation between $^{14}$C and stable isotope contents.
FIG. 75. Variations in stable isotope content of groundwater from north and east of Chott-el-Hodna (Algeria). Triangles: shallow and recent waters. Circles: deep and confined (or semi-confined) waters. Filled circles: the DIC of these waters contain practically no $^{14}$C, suggesting an old period of recharge. Open circles: the significant amount of $^{14}$C is attributed to a mixing with shallow waters. The difference in stable isotope content between shallow and deep waters can be due either to a palaeoclimatic effect (cooler climate when deep water was recharged) or to different altitudes of recharge. (Gonfiantini et al., 1974b.)

FIG. 76. Stable-isotope content of confined aquifers of 'Continental intercalaire' (equivalent to Nubian Sandstone) and of 'Complexe terminal' in the area of the Gulf of Gabès (S. Tunisia). Circle A: average value and standard deviation for waters of 'Continental intercalaire' in north-eastern Sahara. Square B: average value for 'Complexe terminal' waters in south-east Tunisia. Both aquifers are confined and mix through a draining fault network. All the waters are old, as indicated by the very low $^{14}$C activities of DIC. The slope of the mixing line close to 8 suggests that waters are not evaporated and that the deuterium excess is low for these Saharian palaeowaters. (Gonfiantini et al., 1974a.)
(\(14^\text{C} = 10.9\) to 0 pmc; \(\delta^{18}\text{O} = -7.5\) to \(-9.4\%\); \(\delta\text{D} = -49\) to \(-62\%\)). In a \(\delta\text{D} - \delta^{18}\text{O}\) diagram, all these waters lie on a rough correlation line with a slope close to 8, indicating that they were recharged without evaporation (Fig. 75). The range of stable isotope contents is interpreted as a result of mixing between deep water, depleted in heavy isotopes and \(14^\text{C}\), with more recent waters having a heavy isotope content similar to that of local recharge. The authors explained the difference in stable isotopes between artesian deep water and local recharge by a palaeoclimatic effect, i.e. a change in the isotopic composition of the recharge waters. However, in this case, the flow patterns are complicated because the aquifer is made of continental deposits of Tertiary and Quaternary age. These deposits are not continuous and the deep aquifer is therefore semi-confined. Thus, if mixing occurred between waters precipitated at different altitudes, this could also account for the observed difference in stable isotopes.

East of the Gulf of Gabès (southern Tunisia) the aquifer of the 'Continental intercalaire' (mainly continental sandstones equivalent to Nubian sandstones) leaks through a fault network into the aquifer of the 'Complexe terminal' (limestones and dolostones of Upper Cretaceous and Tertiary). Both aquifers are artesian. Waters from the 'Continental intercalaire' have a very homogeneous heavy isotope content (\(\delta^{18}\text{O} = -8.4 \pm 0.4\%\); \(\delta\text{D} = -61 \pm 3\%\)) and DIC is \(14^\text{C}\)-free (Gonfiantini et al., 1974a). In the area of the Gulf of Gabès, the waters from the 'Complexe terminal' are also very uniform (\(\delta^{18}\text{O} = -6.1 \pm 0.15\%\); \(\delta\text{D} = -44 \pm 2.5\%\)) and \(14^\text{C}\) is low (4 pmc). In the area of the draining faults, all the points fall on the line joining the two points representative of the two aquifers, indicating the occurrence of mixing (Fig. 76). This line is parallel to, but lower than, the so-called meteoric water line (\(\delta\text{D} = 8 \delta^{18}\text{O} + 10\)), suggesting that the end-members have an isotopic composition probably characteristic of a palaeo-recharge with a lesser deuterium excess (+6%) than present precipitation. The \(\delta\)-excess of recent precipitation in 1969 was +9%, but this is probably more an average, since the major part of the rains in Gabès comes from Mediterranean vapour which produces a higher deuterium excess. It should be noted that low values of deuterium excess were also encountered in the Jordan Rift Valley (Gat et al., 1969) but, as no \(14^\text{C}\) data are available on the age of these waters, one cannot say whether they belong to the same group of waters whose deuterium excess was the result of the formation of oceanic vapour in conditions closer to equilibrium than nowadays, as suggested by Sonntag et al. (1979a).

For temperate regions, a number of data are available. The confined aquifer of the Albian sands of the Paris basin shows \(14^\text{C}\) contents decreasing from about 95% in the recharge area to a few per cent in the discharge zones of Paris and Rouen, over distances of 200 km (Evin and Vuillaume, 1970). The \(18^\text{O}\) content is slightly lower (\(-7.0\) to \(-9.0\%\)) than that of present-day precipitation (\(-6.50\%\)) (Laboratoire de géologie dynamique, Paris, unpublished data) and suggests a palaeoclimatic recharge under a cooler climate than at present. Frequent anomalies
in $^{14}$C and $^{18}$O evolution along flow lines reveal that leakage from above is likely in this aquifer.

The chalk of the London Basin (Smith et al., 1976) and the Lincolnshire limestone (Downing et al., 1977) in eastern England exhibited the same tendency. Between the discharge areas and the outcrops the $^{18}$O content decreased by about 0.7‰ (Fig. 77). Ages of DIC were estimated using the mixing model presented by Ingersoll and Pearson (1964). They ranged between recent and more than 25,000 years in both the aquifers. Since this time-range covers the last glacial epoch, the waters were expected to be much more depleted in heavy isotopes. (For instance, Dansgaard et al. (1969) claim that in Greenland the end of the ice age (≈ 10,000 BP) is marked by an increase of about 13‰ in the $^{18}$O content of precipitation.) It was thus proposed that recharge took place only during warm interstadials, because the catchment areas were iced and supposed to be impervious during glacial stages.

A similar small change in $^{18}$O between recent and old waters was observed by Fontes and Garnier (1977, 1979) in the aquifer of the ‘Calcaires carbonifères’ in the north of France (Fig. 78). The age of the older water collected in this system was adjusted to about 15,000 years using an exchange-mixing model, but no satisfactory explanation was proposed to account for the depletion in heavy isotopes being small; one would have expected the depletion to be greater because the climate should have been much colder at the end of the glacial period. However,
it was pointed out that the isotopic content of precipitation depends on several factors (isotopic content of vapour sources, precipitation distribution, humidity and temperature profiles of the lower atmosphere). Thus no simple correlation should be expected between the respective variations in stable isotope content of precipitation and average temperatures for past periods with climatic patterns different from those of today.

In an investigation of the calcareous aquifer of South Dobrogea in Rumania, Tenu et al. (1975) calculated ages ranging from 1500 to 25 000 years, using the correction proposed by Vogel (1970). Low contents of $^{18}$O ($-11.0$ to $-12.8\%$o) and D ($-64.6$ to $-78.2\%$o) are attributed to palaeoclimatic recharge. The deuterium excess $d$ is high, showing the participation of vapour evaporated under conditions of low relative humidity. The observed range for $d$ is $+17.2$ to $+26.6\%$o.
As the value of d increases with the deficit in air moisture, which is positively correlated with temperature, it is pointed out that d should be positively correlated with air temperature. Plotting the apparent ages versus the deuterium excess of groundwaters, a curve results which resembles that of Milankovitch's air temperature curve. Evaluations of temperature differences between present times and the time of recharge were thus proposed. This approach is undoubtedly interesting, but it should be noted that more efforts are needed to ascertain some critical points: (i) radiometric ages are generally undercorrected by Vogel's approach; (ii) Milankovitch's curves still need experimental support; and (iii) there is a large inherent uncertainty in the calculation of the deuterium excess because of the summation of analytical errors for both deuterium and oxygen-18.

Deep confined waters from the Patigua Basin in north-east Brazil with practically no $^{14}$C show stable isotope contents ($\delta^{18}O \equiv = -4.5\%$, $\deltaD \equiv = -26\%$) lower than recent recharge in the area ($\delta^{18}O \equiv = -3\%$, $\deltaD \equiv = -18\%$). Salati et al. (1974) interpret these differences in terms of palaeoclimatic effects (cooler climate between 20 000 and 100 000 years ago). However, no significant variation was observed in the deuterium excess.

In the Tulum Valley in central western Argentina, Vogel et al. (1972) found variable $^{18}O$ contents for confined groundwaters ($-5.8$ to $-12.0\%$). The apparent ages of DIC evaluated using Vogel's correction range between 2000 and 13 200 BP. The $^{18}O$ content of shallow and recent (bomb-carbon-bearing) groundwater is very low, owing to their recharge by Andean rivers coming from high altitudes. In this preliminary work, no explanation could be proposed for the higher stable isotope content of palaeowaters as compared with recent waters. This is interesting since generally palaeowaters are supposed to be depleted in $^{18}O$ with respect to recent waters, if precipitated under more humid and cooler periods.

Continuing with investigations in the southern hemisphere, Vogel and Van Urk (1975) point out that confined and old (regarding the $^{14}C$ content) groundwaters from Kalahari (Africa) do not show any significant decrease in $^{18}O$ as compared with recently recharged waters. If this were confirmed by further investigations in mid and tropical latitudes of the southern hemisphere, such a positive difference or a similarity in heavy isotope content between old waters and present-day recharge would imply the need for reassessment of the origin of air moisture masses and condensation mechanisms in these regions during pluvial periods.

Bortolами et al. (1973) do not observe a palaeoclimatic effect on the stable isotope content of artesian waters in the plain of Venice. The dissolved inorganic carbon of these waters has a $^{14}C$ content of about 72 pmc in the recharge areas and a value close to zero in the centre of the plain. However, the average $\delta^{18}O$-values of deep groundwaters are similar to those of the respective present-day surface waters recharging the aquifer.
12.2.4. Palaeoclimatological significance of stable isotope content of water in confined aquifers

A rather complex picture emerges from a review of the data available on deep aquifers. The deuterium excess could provide a good index of changes in the global atmospheric circulation, but it is difficult to estimate it accurately from experimental data. It may vary from rain to rain or on a seasonal basis, and may show interannual variations. Furthermore, it should be kept in mind that a small evaporation during rainfall, or before infiltration, results in a decrease of the deuterium excess. It appears therefore that deuterium excess of groundwaters cannot be transferred simply to the precipitation from which it originates.

With reference to a plot of δD versus δ18O values from confined aquifers of different geological formations in northern Africa, Egypt, Israel, Algeria, Brazil and Rumania (Fig. 79), for which the occurrence of a palaeoclimatic effect has been established, the following should be pointed out:

(a) The slope of the linear correlation is close to 8 (except for the data from Rumania), with an intercept rather close to +10‰. It seems that these waters are mainly due to oceanic precipitation and have not undergone any significant evaporation. The slightly higher deuterium excess observed for the Rumanian aquifer could mean that the origin of atmospheric vapour (and thus
of rains) was different from that of the other waters. It is difficult to say whether this would be due to global variations in origins and atmospheric circulations of air masses during the period of recharge or to 'instantaneous' situations corresponding to exceptional events of precipitation (and recharge).

(b) The difference in heavy isotope content between these waters could be discussed in terms of temperature variations. According to Dansgaard (1964) a difference of about 7°C between the mean annual temperatures should be calculated for the recharge areas of Egyptian Nubian sandstones and the 'Complexe terminal' in Southern Tunisia (Djerba Island). The two areas are at approximately 2000 km of longitudinal distance, but only at 500 km of latitudinal distance; the difference in temperature appears irrelevant. This treatment assumes that: (i) recharge takes place during the entire year, and (ii) Dansgaard's relationship between temperature and heavy isotope content of recent precipitation can be extrapolated to the past. The second assumption may be reasonably accepted since the slope of the correlation between temperature and heavy isotope content in precipitation accounts for an equilibrium and thus a reproducible process (slope of 8 in Fig. 79). The first assumption is certainly wrong, since recharge does not occur on an annual basis, even in temperate regions. Thus the treatment should be modified, assuming that the $^{18}$O temperature gradient is still valid during the respective recharge periods. This is highly questionable. Until numerous supplementary data are available, one will thus have to remain cautious in interpreting the heavy isotope content of deep groundwaters in terms of palaeotemperature variations.

A palaeotemperature effect cannot account for the observed differences between recent and old waters; this is substantiated by examples of groundwaters which are clearly of different ages and where no palaeotemperature effects or only small ones could be observed (England, France, Italy). This strongly suggests that the palaeotemperature effect on the heavy isotope content of groundwaters is very reduced ($<1\%$ in $^{18}$O and $<10\%$ in D). In this case, the larger variations observed in Rumania and Egypt should have another explanation. In each case, and as a general rule, the heavy isotope content decreases with increasing depth within the aquifer or with increasing piezometric head. In our opinion this reflects differences in altitude of the recharge. This altitude effect would thus account for stratification in isotopic content and flow patterns. In Rumania and Egypt the systems are correlated with the basins of major rivers (Danube and Nile) and an altitude effect is conceivable. For the other systems (Hodna, Israel, Sahara and even Brazil), variations in altitude do exist in the catchment area which could explain the lower isotope content. However, an interpretation of the stable isotope content of groundwaters in arid and semi-arid regions must also take into account the influence of major precipitation events. In these regions heavy rains are given
by polar front occlusions which precipitate water with low heavy isotope content. For instance, in a two-year collection of individual rains in Béni Abbès (northwestern Sahara) the following results were obtained (Conrad and Fontes, 1970):

<table>
<thead>
<tr>
<th>Collection period</th>
<th>Number of rains</th>
<th>Total amount</th>
<th>$\delta^{18}O$ (weighted mean)</th>
<th>Number of heavy rains ($&gt;10$ mm/day)</th>
<th>Heavy rains, cumulative rainfall</th>
<th>$\delta^{18}O$ of heavy rains (weighted mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/1966 to 08/1968</td>
<td>18</td>
<td>97.3 mm</td>
<td>$-5.5%$</td>
<td>3</td>
<td>55.5 mm</td>
<td>$-8.7%$</td>
</tr>
</tbody>
</table>

Heavy rains ($>10$ mm/day) are the only ones which can contribute to groundwater recharge. If they infiltrate in fractured base rocks without significant evaporation they give a groundwater with low isotopic content which will be taken as a palaeoclimatic index if no tritium or $^{14}C$ measurements are available. Tritium generally is of poor help in confined aquifers because the transit times are much beyond 30 or 40 years, this being the limit of tritium determination.

Thus the major problem of the validity of $^{14}C$ ages arises. From several studies (Fontes and Garnier, 1976, 1977, 1979; Reardon and Fritz, 1978; Wigley et al., 1978; Plummer, 1977) it appears that the $^{14}C$ ages obtained by the earlier correction methods of Vogel (1970), Tamers (1967) and Ingerson and Pearson (1964) are in many cases too old. Except for basins with internal drainage, we insist on the fact that, due to palaeoclimatic and eustatic control of recharge/discharge processes (see Section 12.2.1), most of the confined aquifers were recharged between about 10 000 and 5000 years BP. During that period the main climatic features of the present-day climate and of recent atmospheric circulations were probably established. For instance, the Rumanian samples from Jurassic limestone aquifers show deuterium excesses that are very similar to present ones in the eastern Mediterranean, and a reassessment of $^{14}C$ ages will possibly give younger values.

Thus, it might be suggested that no significant palaeoclimatic information (palaeotemperature) could be expected from stable isotope studies of deep groundwaters. They are either Holocene in age and will not show any variations in heavy isotope content or too old to be $^{14}C$-dated. Furthermore, it is probable that dispersive mixing and even molecular diffusion will smooth out initial differences in stable isotope and $^{14}C$ content between Holocene and pre-Holocene waters, giving rise to inconsistent palaeoclimatic reconstruction.

Over and above that, it has been seen from some field studies (e.g. in Argentina, Kalahari, Venice, and to some extent in England and France) that it
was not even sure that palaeowaters bear the isotopic fingerprint of a cold-type recharge. However, a conclusive investigation of changes in climatic and hydraulic conditions of recharge could be attempted in regions where the periods of the last deglaciation are very well established and where hydraulic gradients are too low to induce monogenization by dispersion along flow paths. In these regions (northern Europe, north-eastern America) one could expect to find distinct stable isotope contents in groundwaters: pre-glacial (pre-Würm or pre-Wisconsin) waters (isotopically 'warm' type), water from ice melting (isotopically 'cold' type), and post-glacial waters (progressive set-back to isotopically 'warm' type). At the same time a field calibration could be made on the $^{14}$C correction models of groundwater dating.

12.2.5. Palaeowaters in unconfined aquifers and related systems

The occurrence of palaeowaters in unconfined aquifers can be investigated in arid regions where recent recharge is small as compared with the discharge. The occurrence of palaeowaters can prove the stratification of waters within the aquifers and the existence of a deep zone of stagnant water overlaid by a shallow zone where groundwater is relatively mobile.

Groundwaters from the unconfined aquifer of the Tertiary limestones and sandstones of the Hamada du Guir in the north-western Sahara were found to contain old DIC (Conrad and Fontes, 1972), which can account for the low $^{18}$O content of the waters ($\delta^{18}$O $\approx -9.5\%$). The interpretation is that recharged occurred during the last Holocene humid period and that the aquifer is now discharging ancient groundwater resources (Conrad et al., 1966; Conrad and Fontes, 1970, 1972). This is in agreement with the observed decrease in the piezometric level which is marked by travertine layers in the Wadi Saoura valley. No tritium (<1 TU) was measured (Conrad et al., 1975) and therefore the discharge does not include any detectable contribution of the last 30 years.

In the Island of Schiermonnikoog in the Netherlands, Vogel (1967) found $^{14}$C age stratification from recent years (adjusted to 82.1\% of modern carbon) to about one thousand years. However, no significant variations were observed in the $^{18}$O content ($\delta^{18}$O = $-7.5\%$). For the semi-confined groundwaters from the lissemeer polder, $^{14}$C ages varying from recent years to more than 23,000 years were calculated assuming an initial $^{14}$C content of 85 pmc for DIC. Except for one location where $\delta^{18}$O is definitely lower ($\delta^{18}$O = $-8.4\%$) than that of recent recharge ($\delta^{18}$O $\approx -7.5\%$), no further evidence of a recharge process which occurred under cooler conditions was observed.

An interesting, but still preliminary, comparison has been made between noble gases, $^{14}$C and the stable isotope content of some hot springs in Swaziland (Mazor et al., 1974). The temperatures of recharge, deduced from noble gas ratios, deuterium and oxygen-18 contents, were similar to those of present day,
for ages of DIC ranging from some hundred to some thousand years, depending on the model adopted for $^{14}$C corrections. Further work is needed in this field, particularly on groundwaters with a stable isotope content quite different from that of present rains.

Another interesting attempt to use the stable isotope and $^{14}$C contents of groundwater in combination for palaeoclimatological reconstruction has been proposed by Sonntag et al. (1976, 1979a, 1979b). First, an isotope gradient of continentality is established for Western Europe in groundwaters and in winter
precipitation. The gradients are $-0.33\%$ and $-2.4\%$ per 100 km of distance from the Atlantic shore, for $^{18}O$ and $D$ respectively. Similar gradients are found for groundwaters from the Sahara (Algeria and Libya), although these waters show DIC with $^{14}C$ ages ranging from some thousand to more than 40 000 years (Fig.80). The conclusion is that past recharge in the Sahara occurred under similar meteorological patterns as exist nowadays in Europe, with depressions moving eastwards. The differences between the present-day gradient in Western Europe and the ‘ancient’ gradient in northern Africa (about $2\%$ in $^{18}O$) are assumed to reflect the differences in mean temperature during the recharge season. Using Dansgaard’s relationship, a difference of $-2$ to $-3^\circ C$ was proposed for ancient Saharan winter temperatures. Furthermore, considering all the available data on the stable isotopic content of groundwater and of rains at some African stations of the IAEA/WMO network, Sonntag et al. (1979a) propose that variations in deuterium excess can be correlated to the deficit of saturation (i.e. to the global climate) within the tropical zones of cloud formation at the recharge time. Thus they conclude that when the recharge took place between 40 000 and 20 000 BP, the atmosphere was relatively more humid and hence cooler than at present.

After the dry episode which took place between 20 000 and 14 000 BP, it is suggested by Sonntag et al. (1979a) that, between 14 000 and 10 000 BP, a short period of western drift followed, bringing winter rains. Then a regime of rains carried by convective winds is believed to have taken place since 10 000 BP. Convective winds would have been less active eastwards in the northern and central Sahara, as suggested by the less frequent values of $^{14}C$ ages of less than 10 000 years found in Egypt as compared with those found in Libya and Algeria.

The eastward depletion in heavy isotopes accompanied by low deuterium excess ($\approx +5\%$) can be observed as far as approximately $20^\circ$ northern latitude in old (regarding the $^{14}C$ content) waters (Sonntag et al., 1979b). In more southern latitudes, and especially in the Sahel, an opposite trend is found. Eastwards, the groundwaters become enriched in heavy isotopes, without any significant evaporation effect on the $\delta D-\delta^{18}O$ correlation. This enrichment, which thus cannot be due to evaporation, is attributed by Sonntag et al. (1979a) to an eastwardly increasing contribution of vapour evapotranspired from vegetal cover to the atmospheric vapour. Evapotranspiration is assumed to release vapour with the same isotope content as that of groundwater itself. Then, any further condensation stage would produce an enrichment in heavy isotopes of precipitation. Thus, in these regions rains (and recharge) are believed to show the influence of evapotranspiration from the tropical forest.

This approach, which may allow a palaeoclimatological reconstruction to be made, is not, however, exempt from criticism, especially with regard to some of the assumptions made (see, for instance, the discussion of the paper by Sonntag et al., 1979a). In particular, caution should be exerted in the promiscuous use of isotopic values of waters with presumably wide age differences.
FIG. 81. Stable isotope content of brines associated with oil fields. The lines corresponding to each field can be attributed to mixing and/or exchange processes. The intercept with the meteoric water line indicates that a simple marine origin is ruled out. (Clayton et al., 1966.)

12.3. PALAEOWATERS IN FORMATION FLUIDS

Isotopic compositions of relict fluids buried in sediments during diagenesis and lithification, or infiltrated into rocks during palaeogeographical events, can provide information on the origin of solutions and the mechanisms of sedimentation and diagenesis.

12.3.1. Formation waters\(^{20}\)

Degens et al. (1964) studied oil-field brines from Oklahoma, Colorado, Texas and Utah. They obtained positive correlations for \(^{18}\)O and salt contents and interpreted them in terms of mixing of old brine of marine origin, enriched in \(^{18}\)O by evaporation, with local, recent or ancient groundwaters of meteoric origin.

This interpretation was criticized by Clayton et al. (1966) who examined \(^{18}\)O, D and salt contents of oil field brines from Illinois, Michigan, Alberta and the Gulf Coast (Fig. 81), and also observed a correlation between salt and heavy

\(^{20}\) See also Section 10.5.
isotope contents which intercepts the local rain value for zero salinity. The origin of brines is thus mainly attributed to groundwaters recharged by precipitation in order to account for the low deuterium values; these are slightly increased towards the centre of the basins by hydrogen isotope fractionation which may occur during ultra-filtration processes through clay-rich levels which also concentrate the salts (Graf et al., 1965). It is proposed that exchange with rocks and chiefly with carbonates at the aquifer temperature is responsible for the $^{18}\text{O}$ enrichment. As in the previous study the authors interpreted low heavy isotope contents as belonging to Pleistocene waters, but they argue that this distinction should rather be made on the basis of deuterium content, since deuterium does not undergo exchange with rocks because of the lack of significant amounts of hydrogen in the solid phase. However, the $^{18}\text{O}$ contents of samples suspected to be palaeo-groundwaters are also low ($\delta D = -82\%$, $\delta^{18}\text{O} = -10.2\%$ in Illinois; $\delta D = -109\%$, $\delta^{18}\text{O} = -13.1\%$ in Michigan) and the representative points fall close to the meteoric water line. The conclusion was that the initial formation water had been expelled by compaction phenomena and washed out by the subsequent supply of groundwater, some of which infiltrated during cold periods.

Hitchon and Friedman (1969) studied brines from Alberta and made a synthesis of previous interpretations, assuming that mixing of waters enriched in heavy isotopes with groundwaters occurs, as well as exchange with rocks. They assume that the component enriched in heavy isotopes is similar to present-day sea-water (i.e. SMOW). Thus, an interpretation of any value greater than zero either in $^{18}\text{O}$ or D would imply complex processes of exchange with rocks (chiefly carbonates) for the oxygen shift and of exchange with fluids (H$_2$S or possibly hydrocarbons) for the hydrogen shift. Furthermore, the deuterium content of these waters can be depleted by ultra-filtration processes.

In the thermal springs of the Wilbur Springs mercury district in California, White et al. (1973) found large enrichments in stable isotopes ($\cong 13\%$ in $^{18}\text{O}$ and $\cong 40\%$ in D) as compared with local meteoric waters. They attribute these values to a large contribution of old marine connate waters which reacted with sediments before being expelled by geopressure and mixing with shallow waters.

In deep-sea cores performed in the Gulf of Mexico, Manheim and Sayles (1970) found brackish waters (13.3 g/l TDS) in the cap rock of a salt dome which was supposed to have been buried by marine sediments and sea-water at least since the Miocene. Low deuterium content (−6.7%) was attributed to inorganic oxidation of H$_2$S produced by gypsum reduction on top of the cap rock. For four moles of gypsum which are reduced at least three moles of water are produced:

$$3\text{CaSO}_4 + C_{16}H_{22} \rightarrow 3\text{H}_2\text{S} + C_6\text{H}_{14} + 3\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

$$\text{SO}_4^{2-} + 3\text{H}_2\text{S} \rightarrow 4\text{S}^0 + 2\text{H}_2\text{O} + 2\text{SH}^+$$
FIG. 82. Stable isotope contents of waters from the Upper Silesian Coal Basin. The points describe a mixing line between recent local recharge and a hypothetical old brine. (Różkowski and Przewlocki, 1974.)

FIG. 83. Mineralization versus oxygen-18 content of thermomineral waters from the Carpathians. The total mineralization remains lower than that of sea-water, whereas the $^{18}O$ content reaches $+6\%$. 
However, the authors could not explain a few values showing enrichment in deuterium (+ 18.8‰).

Rózkowski and Przewłocki (1974) measured the isotopic content of brines from Polish mines, which lies on a mixing line between local groundwaters (D = −72‰ and 18O = −10.1‰) and a remnant water which is similar to SMOW. This remnant water is assumed to be representative of Miocene sea-water (Fig. 82). Also in Poland, Dowgiallo (1973) reports that mineral water from the Carpathians shows an enrichment in 18O and deuterium, but in this case the enrichment attains high positive values for both 18O and deuterium. If this phenomenon is due to mixing, this would imply that one of the end-members has a heavy isotope content significantly higher than SMOW (Fig. 83). This salty and heavy-isotope-rich solution may be a remnant of a Miocene brine.

12.3.2. Interstitial waters of sediments

The first data for interstitial waters of sediments were reported by Friedman (1965). In waters extracted from deep-sea sediments cored at variable depths below the sea floor (30–130 m) he found a depletion in deuterium as compared with SMOW (−0.9 to −5.6‰). No correlation existed between the different degrees of depletion and either the depth or the mineralogical composition of the solid phase.

Numerous cores obtained from the Deep-Sea Drilling Programme (DSDP) provided a large amount of samples of interstitial waters from sediments for chemical and stable isotope studies. As a rule, these interstitial waters exhibit variations (generally depletion) in 18O as compared with present-day sea-water.

Several explanations can be proposed according to local conditions of physiography, environment and sedimentology. In Red Sea sediments (Lawrence, 1974) the decrease in 18O with depth ranges from + 1.6‰ at 6 m in Pleistocene oozes to −3.3‰ at 306 m in late Miocene sediments. Hypotheses are: (i) influx of meteoric waters through the sea bottom; (ii) residual Red Sea water with lighter isotope content; (iii) diagenetic effect with uptake of heavy oxygen in authigenic minerals; and (iv) deep diffusional supply of water depleted in 18O as a result of basalt alteration into clay minerals or zeolites. Since, besides the depletion in 18O, the deuterium contents is also markedly decreased (Friedman and Hardcastle, 1974), explanations (i) and chiefly (ii) can be invoked and partially account for the range of total variation. At 50 m depth an enrichment in both isotopes is attributed to a stagnation of waters at about 10 000 BP. The enrichment mechanism (iii) does not seem to play a major role in Red Sea sediments since no variations appear in the 18O content of bulk silicate which could be related to an uptake of heavy oxygen with depth. But explanation (iv) seems able to account for 18O variations as a general mechanism when the sea floor is made of basalts,
**FIG. 84.** Relationship between Mg and $^{18}$O contents in interstitial waters from two sites in the Norwegian Sea (DSDP).

The neogenesis of clay minerals is reflected by an uptake of Mg and $^{18}$O from the solution. (Randall et al., 1979.)

e.g. at sites 149, 148, 157, 336, 348, 386, 387 of DSDP (Lawrence, 1974; Lawrence et al., 1975; Gieskes et al., 1978; Randall et al., 1979).

An exemplary case of the influence of basalt alteration and subsequent neogenesis of hydrated silicates on the change in $^{18}$O content of water is given by the profiles of sites 336 and 348 of DSDP in the Norwegian Sea sediments (Randall et al., 1979). The content in $^{18}$O diminishes with depth and correlates perfectly with the loss of magnesium. At 491.5 m at site 348 the $^{18}$O and Mg$^{2+}$ contents are $-8.3\%$ and 0.8 mmol/l respectively (Fig. 84). A confirmation that this simultaneous decrease is really due to crystallization of magnesium and $^{18}$O-rich silicates is given by the chloride profile, which does not show any decrease (as would be expected in the case of dilution by continental water percolating per ascensum through the sediment column).
12.3.3. Validity of formation fluids as palaeohydrological indicator

From the above examples it clearly appears that old fluids entrapped in lithified formations as well as in sediments are subject to chemical and isotopic reactions. These reactions, which can proceed at low temperatures, are of several kinds:

(a) Exchange reactions with minerals generally tend to increase the $^{18}$O content of water without modification of the deuterium content

(b) Crystallization of neogenetic minerals (mainly clays and zeolites) leads to a decrease in $^{18}$O and an increase in deuterium contents because of respective fractionations

(c) Exchange with fluids generally affects hydrogen ($H_2S$, hydrogen, hydrocarbons) and tends to increase the deuterium content of the water, whereas the $^{18}$O content is not affected, except in the case of an exchange with large quantities of $CO_2$ which will lower the $^{18}$O content of water (Ferrara et al., 1965)

(d) Ultrafiltration phenomena would slightly lower the deuterium content, but they are difficult to distinguish from other causes of variations.

Taking into account other phenomena which can also modify the stable isotope content of formation waters (diffusion and mixing), it appears that genetic interpretations are delicate and require not only $^{18}$O and deuterium analyses but also detailed hydrochemistry. Furthermore, it is expected that even groundwater of pure meteoric origin may undergo such a type of change in stable isotope content, even at low temperature when circulating very slowly in highly reactive chemical environments (e.g. weathered silicates and clay minerals). In this case, any further change in $^{18}$O and deuterium of pore water will depend upon the ratio of available atoms for reactions in the water and in the solid phase at any time (i.e. porosity and permeability).

12.3.4. Crystallization waters

When a hydrated mineral has reached saturation and precipitates from a solution, the isotopic composition of crystallization water reflects that of the mother water, which can therefore be computed, provided that: (i) the fractionation factors (and possible temperature dependences) between mother water and crystal water are known; and (ii) no further exchange between environmental and crystal water has occurred after deposition.

Fractionation factors have been determined for several hydrated minerals from evaporitic sequences: gypsum (Gonfiantini and Fontes, 1963; Fontes and

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical composition</th>
<th>δ¹⁸O (25°C)</th>
<th>αD (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gypsum</td>
<td>CaSO₄ · 2H₂O</td>
<td>1.004</td>
<td>0.985</td>
</tr>
<tr>
<td>mirabilite</td>
<td>NaSO₄ · 10H₂O</td>
<td>1.0015</td>
<td>1.0188</td>
</tr>
<tr>
<td>gaylussite</td>
<td>Na₂CO₃ · CaCO₃ · 5H₂O</td>
<td>n.d.</td>
<td>0.987</td>
</tr>
<tr>
<td>trona</td>
<td>Na₂CO₃ · NaHCO₃ · 2H₂O</td>
<td>n.d.</td>
<td>0.920</td>
</tr>
<tr>
<td>borax</td>
<td>Na₂BO₃ · 10H₂O</td>
<td>n.d.</td>
<td>1.000</td>
</tr>
</tbody>
</table>

\[ \alpha = \frac{R_{\text{cryst.water}}}{R_{\text{mother water}}} \text{ with } R = \frac{^{18}O}{^{16}O} \text{ or } D/H. \]

Except for gypsum, all these minerals are highly soluble and thus can be found only in evaporitic deposits from continental basins.

Since fractionation factors are quite independent of temperature and would thus provide an easy estimate of the mother water, several attempts have been made to use crystallization water of gypsum as an index of the isotopic content of palaeowaters (Fontes et al., 1963, 1967, 1973; Matsubaya and Sakai, 1973; Pierre and Fontes, 1978, 1979; Sofer, 1978). However, because of the low binding energy between crystal and water, isotopic exchange between percolating water and crystallization water seems to occur easily (Fontes and Gonfiantini, unpublished data; Sofer, 1978). Nevertheless, in some cases crystal water may have been preserved at least partially since the upper Miocene (see, for instance, Pierre and Fontes, 1978, 1979). In the Mediterranean area the water of crystallization of emerged gypsum with primary facies exhibits a heavy isotope content similar to that of deep-sea sediments of the same Messinian age, suggesting that crystallization had occurred from evaporated waters of continental origin. Furthermore, some gypsiums, either outcropping or cored in DSDP cruises in the Mediterranean, show obvious secondary facies (hydration of anhydrite or recrystallization). These secondary gypsiums have crystallization waters whose heavy-isotope content is close to that of present-day tropical rains (e.g. present-day first stages of monsoon condensations). These data are in agreement with other information drawn from stable-isotope investigations on carbonates and sulphates, and suggest: (i) the preservation of the isotopic content of crystallization waters for about eight million years; and (ii) the consistence with the palaeoclimatic and palaeogeographic reconstruction of a system of coalescent basins during the late Miocene desiccation of the Mediterranean sea.

In the Negev Desert, Sofer (1978) found a rather low heavy-isotope content for mother water of secondary gypsum of continental origin (hydration of an-
FIG.85. Fractionation (dashed lines) between isotopic compositions of free water and of constitutive water of a given clay mineral at various temperatures \( T_3 > T_2 > T_1 \). Line A represents the equilibrium with sea-water. (Savin, 1980.)

Hydrite. According to the model proposed by Matsubaya and Sakai (1973) (Rayleigh process of uptake from a finite reservoir of water with the appropriate fractionation factors) the hydration of anhydrite gives rise to an evolution of deuterium and \( ^{18}\text{O} \) contents which should describe a line with a slope of \(-5\) in the \( \delta D - \delta ^{18}\text{O} \) diagram. On samples from Negev, the local meteoric water line \( (\delta D = 8 \delta ^{18}\text{O} + 21) \) and the lines with a slope of \(-5\) intercept at values of \( \delta ^{18}\text{O} \) = \(-8\) to \(-9\)% and \( \delta D \) = \(-43\) to \(-51\)%o, which are much lighter than present-day precipitation in that area. Even further extrapolation to the global meteoric water line, \( \delta ^{18}\text{O} = 8 \delta D + 10 \), still gives low values, which are attributed to a period of cooler climate than today.

Further possibilities of estimating of the heavy-isotope content of groundwater or pore-water are provided by hydrated minerals like clays and cherts. An extensive review of fractionation mechanisms and consequent effects is given by Savin (1980). For instance, new minerals formed during weathering of rock show deuterium and \( ^{18}\text{O} \) contents which are closely related to the isotopic composition of local groundwater. Since each mineral has its own fractionation factor, several families of lines will exist on the \( \delta D - \delta ^{18}\text{O} \) diagram, e.g. for gibbsite lines, kaolinite lines and smectite lines (Savin and Epstein, 1970; Lawrence and Taylor, 1971). For each mineral, there is not a unique correlation with the mother brine; since fractionation factors are temperature-dependent, the heavy-isotope content of water in the crystal will depend both on the isotopic composition of the mother water and on the temperature (Fig.85). However, a rough correlation (Fig.86) is seen to exist between the heavy-isotope content of local meteoric waters and that of clay minerals and hydroxides (Lawrence and Taylor, 1971).
FIG. 86. Stable-isotope contents of water extracted from clay minerals and of related meteoric waters from several regions of North America. (Lawrence and Taylor, 1971.)
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Chapter 13

PRACTICAL APPLICATIONS OF STABLE ISOTOPES TO HYDROLOGICAL PROBLEMS

13.1. INTRODUCTION

Practical applications of stable isotope tracing to hydrological problems rely, in one way or another, on the features of the distribution of the heavy isotopes in the atmosphere and the surface waters and groundwaters, as described in previous chapters. The characteristic and distinctive isotopic composition of waters from different geographic origins or of a different hydrological nature, on the one hand, and the conservation of the isotope content of the water in the groundwater bodies, on the other hand, form the basis for these applications. As a rule, groundwaters change their isotopic composition only insofar as mixing with other waters takes place. Unlike radioactive environmental tracers, the stable isotope composition is not inherently time-dependent nor are time-scales established, except by means of seasonal variations which can, under favourable circumstances, be followed in the hydrological systems. We thus expect the stable isotopes to be called upon primarily wherever the water origin and the degree of mixing is being questioned. In this respect, their role is akin to chemical tracers, such as salinity. Isotopic tracers usually have practical advantages of a greater variability of composition and of lesser interactions with soil and rock material as long as temperatures are not too high. As a result, the isotopic evidence is less ambiguous and in conjunction with other data quite irrefutable.

The isotope method does not stand alone as an independent tool. Our aim is not the establishment of an isotope hydrology model, distinct from the hydrological picture. Rather, the method is used to greatest advantage where a clear definition of the problem in hydrological terms can be made. From the outline of the hydrological and hydrogeological setting (and of the geochemical background in cases where problems of salinity are involved) a number of hypotheses emerge; the compatibility of the isotope data with these hypotheses may then enable one to choose among them. At this stage, the quantitative aspects of the problem should also be formulated, such as the percentage of an admixture which should be detected.

After the statement of the hydrological problem an assessment of whether or not the isotope method can contribute to the problem at hand follows. This will be made on the basis of the general principles of isotope geochemistry, as discussed in earlier chapters, of an examination of stable isotope data which may be available from earlier studies in the area and of data from the IAEA/WMO
network of precipitation stations. Based on all of this, it is attempted to find out whether the water-bodies involved can be expected to have a distinct enough isotopic composition and to be different enough regarding the changes or degrees of mixing to be distinguished.

Except for the case where a very specific, limited objective has been defined, it is desirable at this stage to conduct a regional reconnaissance survey, extending in scope beyond the immediate study zone, to cover all possible water sources which might be involved. Ideally, such a survey would aim at a map of isotope contours for precipitation over the area or, more precisely, of the water effective in recharge; at a documentation of the isotope content of surface waters (rivers, lakes and reservoirs); and, finally, at obtaining representative values of the isotopic composition of aquifer units. For an interpretation, it would then be attempted to match the isotope data for groundwaters with those for recharge waters at appropriate locations or with those for surface waters, or to relate them to the geochemical processes expected to occur, for example in a geothermal system.

The regional map of the isotope content of precipitation may be based on regional precipitation surveys (using collection procedures of the IAEA/WMO network), taking into account that measurements over a number of years may be necessary before a statistically meaningful value can be established. Failing such a record, one can rely for this purpose on shallow water sources which are known to be locally recharged. As a last resort, one can attempt to interpolate between the world-grid data, taking local topography and altitude and temperature correlation into account. However, this may be misleading unless the meteorological patterns are recognized in great detail.

In sampling of surface waters the variability of the isotopic composition with time must be taken into account. In no way can a grab sample convey a representative impression, although a knowledge of hydrograph characteristics and/or water level measurements may help in interpolating (in time) between sampling points.

Estimation of the stable isotope index of an aquifer requires a selection of sampling points to provide a sufficiently representative coverage of the aquifer. When sampling from a borehole which is being pumped, the locations of the perforated sections must be known. Not infrequently, a borehole may tap two aquifers which are quite different in composition owing to different recharge areas or, when the recharge areas are similar, an age difference between the aquifer units may manifest itself in a changed $\delta$-value. Sampling from boreholes which have not been pumped for some time should be carried out only after operation of the pump for a sufficient time in order to ensure that formation water is being sampled.

Sampling from a borehole or a spring is best carried out at certain time intervals so as to check that there is no variation in composition with time.
This is particularly important for springs which may discharge a mixture of waters originating from different recharge areas. Seasonal variations of discharge may suggest such a possibility. In any case, a spring of variable discharge should be measured at different stages of discharge.

Having selected suitable sampling points exhibiting no significant variation with time as being representative of a component of the overall system, the representativity of the component area must be considered. Logically, this aspect would follow after the selection of representative sampling points but, in practice, time pressure demands that a sampling scheme be drawn up and the representativity of sampling points evaluated as the investigation proceeds. In theory, a sampling scheme can be designed to give adequate areal coverage, but the availability of wells and springs is the governing factor. A critical appraisal of published studies suggests that proper and adequate sampling is perhaps one of the weakest points of a number of studies.

Because of the great variety of hydrological situations, it is impractical to spell out a general scheme for the application of stable isotopes. We shall rather attempt to illustrate some of the principles through a set of case studies exemplifying successful employment of the method. The problems with which these studies were concerned are: the location of recharge zones; assessment of contribution of surface waters to a groundwater body; questions concerning the degree and mixing of different groundwater bodies; and determination of the origin of salinity in groundwaters. Specific examples, concerning hydrograph separation of surface flow and problems related to ice and snow hydrology, have already been given in the appropriate chapters.

In keeping with the subject of the monograph the following case studies deal specifically with the contribution of the use of stable isotopes to the problems at hand. However, it cannot be overemphasized that, as there must be a continuing dialogue between isotope specialists and hydrologists, there is also the necessity of employing other environmental isotopes, such as tritium and carbon-14, as well as water chemistry.

13.2. INTERRELATION BETWEEN SURFACE WATER AND GROUNDWATER

(a) Statement of the problem

Surface water systems, rivers, lakes or reservoirs are a potential source of recharge to groundwater. Infiltration of local precipitation is another possible source of recharge to the groundwater system. Thus the question may arise as to the relative importance of these two potential sources of recharge. Surface waters are, at best, (point) sources in a larger field and their influence is expected to be local, except for flow in fractured rock, such as in karstic
areas where leakage from the surface water system may occur along confined flow-paths. In that case the proportion of infiltrated surface water to locally infiltrated precipitation may remain high, even at a considerable distance away from the surface water.

(b) *Theoretical basis for the isotope approach*

The isotope approach to this problem is based on the fact that the surface water system has a stable isotope composition significantly different from that of recharge by infiltration of local precipitation. Lake waters undergoing partial evaporation are enriched in heavy isotopes along ‘evaporation lines’ so that they are double-labelled by comparison with local waters, in that they have an isotopic composition which is more positive and a lower deuterium excess. One must also consider that inflow waters into a lake may not be of local origin but from a distant source.

13.2.1. Contribution of a lake to groundwater recharge

13.2.1.1. Problem

Lake Chala is a volcanic crater lake located at an elevation of 840 m on the south-east slope of Mt. Kilimanjaro on the border between Kenya and Tanzania. The lake has an area of 4.2 km², a maximum depth of 100 m and an estimated volume of $3 \times 10^8$ m³. The lake has neither surface inflow nor outflow and in the early 1960s the feasibility of using the lake water for expansion of a nearby irrigation scheme was under consideration. However, the problem was to know whether lake water provided a significant proportion of the discharge of springs in the area, the waters of which were already utilized (Payne, 1970).

13.2.1.2. Sampling and data

Samples of the lake water from ten locations, taken on two occasions nine months apart, were analysed for their stable isotope composition. Samples were taken from the springs and in most cases the stable isotope composition was measured at different times over a period of about three years.

The stable isotope composition of the lake, the springs and the groundwater sample is given in Table XVIII. The analytical errors (one sigma) are 0.2‰ and 2‰ for δ¹⁸O and δD, respectively.

The data for the lake represent the mean values of the samples from ten different locations. There was no significant variation outside the analytical error so that the isotopic composition of the lake was considered homogeneous.
TABLE XVIII. STABLE ISOTOPE COMPOSITION OF LAKE CHALA AND GROUNDWATER

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{18}$O (%)</th>
<th>$\sigma^a$</th>
<th>$\delta^D$ (%)</th>
<th>$\sigma^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Chala, 1967</td>
<td>2.51</td>
<td>0.07</td>
<td>7.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Lake Chala, 1968</td>
<td>2.43</td>
<td>0.16</td>
<td>4.9</td>
<td>4.7</td>
</tr>
<tr>
<td>Homer Spring</td>
<td>−3.96</td>
<td>0.05</td>
<td>−20.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Kileo Spring</td>
<td>−4.72</td>
<td>0.08</td>
<td>−23.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Kitovo Spring</td>
<td>−4.56</td>
<td>0.21</td>
<td>−21.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Lenonya Spring</td>
<td>−4.11</td>
<td>0.43</td>
<td>−17.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Little Lumi Spring</td>
<td>−4.20</td>
<td>0.21</td>
<td>−18.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Magi ya Waleni Spring</td>
<td>−3.97</td>
<td>0.20</td>
<td>−17.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Njoro Kubwa Spring</td>
<td>−4.05</td>
<td>0.43</td>
<td>−19.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Njoro Ndogo Spring</td>
<td>−4.04</td>
<td>0.24</td>
<td>−18.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Latema borehole</td>
<td>−4.53</td>
<td>0.14</td>
<td>−22.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

* Standard deviation of an individual measurement.

This fact was confirmed by the tritium measurements which were part of another aspect of the overall investigation. Also, there was no significant difference in the stable isotope composition from 1967 to 1968, so the mean composition of the lake was taken to be 2.47‰ and 6.1‰ for $\delta^{18}$O and $\delta^D$, respectively.

13.2.1.3. Interpretation

The stable isotope composition of Lake Chala does not vary with time and, furthermore, its composition is markedly different from that of waters falling on the meteoric water line, which would be the other component in the case of mixing of lake-water and groundwater (Fig. 87). Furthermore, there is no evidence that the composition of the groundwater changes with time so that the conclusion that none of the groundwaters sampled receives any contribution of water from Lake Chala is very dependable. The maximum possible contribution of lake-water would not exceed a few per cent.
13.2.1.4. Discussion of other cases using a similar approach

A quantitative assessment of the relationship between a lake and a groundwater system is not possible with a small number of samples if there is variability in the isotopic composition of the lake-water and the groundwater. Mazor (1976) reports that the Ram Crater Lake has a $\delta^{18}$O composition varying between $-2.5\%$ and $+0.4\%$. It was suspected that the Borrias spring was fed by the lake. The $\delta^{18}$O-values of the spring were shown to vary between $-7.0\%$ and $-8.1\%$. The mean deuterium excess was $20\%$. The variability in the composition of the spring could be due to varying contributions from the lake or it could reflect changes in isotopic composition of the water recharging the spring. Since the Borrias spring has an isotopic composition similar to that of other springs located higher up on the slopes of Mount Hermon, it was concluded that the Borrias spring was not fed by the lake. On the other hand, it was concluded that groundwater sampled at the Masada well close to the lake was a mixture of lake-water and regional groundwater.

The $\delta^{18}$O of the regional groundwater had a variance outside analytical error, most probably due to variations in lake-water contribution. That lake-water does contribute is not in question — the deuterium excess ($10.8\%$) is distinctly different from that of the springs — but a quantitative estimate would require a relatively long time series of measurements of both the spring and the groundwater.

The deuterium excess parameter may be useful in studying lake/groundwater interactions. Dinçer and Payne (1971) used this approach in a study of the relation between lakes and groundwater in south-west Turkey. A plot of $\delta D$
against deuterium excess showed that the values for the base-flow of the Köprüçay river were between those of lakes Beyşehir and Eğridir and groundwater. This suggested that 31% of the base-flow could be attributed to lake-water.

Gonfiantini et al. (1962) published $\delta^{18}$O-data on groundwater in the region of Lake Bracciano in Italy. The average $\delta^{18}$O of groundwater was $-6.0\%_o$, that of the lake was $+0.69\%_o$, which demonstrated the independence of the two systems. The samples covered the period June 1960 to March 1961 and little or no variability outside analytical error was evident. No deuterium data were reported for the lake and the eight different groundwater sampling points. Since there were no significant differences in the $\delta^{18}$O-values of the different groundwater sampling locations, deuterium measurements were unnecessary.

Payne (1976) reports on groundwater data for the area between Lake Paralimni and the coast which show that wells and coastal springs are discharging water entirely of lake origin.

Fontes et al. (1970) studied the influence of water from Lake Chad on the groundwater system in the neighbourhood of the lake. The groundwater close to the north-east side of the lake has a stable isotope composition which is indicative of an appreciable contribution of lake-water. Moving away from the lake, the $\delta$-values become more depleted, owing to the contribution of infiltrating precipitation which also recharges the groundwater system.

13.2.1.5. Methodological comments

A quantitative assessment of the relationship between a lake and a groundwater system is not possible with a small number of samples if there is variability in the isotopic composition of the lake-water and the groundwater.

The seasonal variations of the isotopic composition of lake-water are usually the limiting factor in the sensitivity of the method. Given a variability of isotopic composition of the lake of $\pm \Delta(\%_o)$ and a difference of $\Lambda(\%_o)$ between lake-water and groundwater composition, the inherent limit of detection of surface water contribution to the groundwater samples is $\Delta/\Lambda$. As mentioned in the case of the Turkish lakes, the deuterium excess may be a more useful parameter in this respect, since the variability of 'd' of groundwaters is often less than that of the individual isotopic species. However, for such an application the analytical requirements for deuterium measurements should be better than is often the case, i.e. better than $\pm 1\%_o$.

The sensitivity of the method depends on isotope enrichment in the lake relative to inflow waters ($\Lambda$) and this relation would be expected to be maximum in arid regions. This advantage may be offset, however, by the evaporative enrichment of meteoric water input in the atmosphere or during recharge, resulting in a greater spread in isotopic composition of truly 'meteoric groundwaters'. 
13.2.2. Contribution of a river to groundwater recharge.

Case study: The river Chimbo in Ecuador as a potential source of recharge

13.2.2.1. Problem

The river Chimbo leaves the Andes mountains at Bucay, about 90 km west of Guayaquil. The area studied consists of a deltaic fan of sedimentary deposits in which the groundwater table is about 3 m below the surface. The problem was to ascertain the relative importance of infiltration from the river Chimbo and of local precipitation as potential sources of recharge to the groundwater (Payne and Schroeter, 1979).

13.2.2.2. Sampling and data

Shallow groundwater was sampled at the end of the dry season from 51 open and closed wells fitted with hand-pumps (Fig.88). Deeper groundwater was sampled from seven drilled wells, but in all cases the screens extended over almost the whole depth of the well, which was mostly about 80 m. The river Chimbo was sampled at Bucay, in November and December 1976, and at San Carlos, ~30 km to the west of Bucay. All samples were analysed for both their deuterium and oxygen-18 content.

In view of a certain variability in the stable isotope composition of the river system the index for this potential source of recharge was based not only on river data but also on some of the groundwater samples taken from wells close to the river which had similarly depleted delta values as the river. The estimate for the river index was $-7.34\%\pm 0.09$ and $-47\%\pm 0.7$ for $\delta^{18}O$ and $\delta D$, respectively.

The criteria adopted for the choice of samples for estimating the recharge index by infiltration of precipitation were: location in an area where the possible contribution of river-water is minimal, and samples having the most positive values if there was no evidence that this was due to partial evaporation. The estimate for this index was $-4.43\%\pm 0.07$ and $-24.1\%\pm 0.8$ for $\delta^{18}O$ and $\delta D$, respectively.

13.2.2.3. Interpretation

The variation in the stable isotope composition of the shallow groundwater extended over a range of about 4% and 30% for oxygen-18 and deuterium, respectively (Fig.89). This suggested that the shallow groundwater is a mixture of varying proportions of two sources, each having its own characteristic stable isotope composition.
**FIG. 88.** Location of sampled wells and δD-values of groundwater in the vicinity of the river Chimbo.

**FIG. 89.** Stable isotope composition of shallow groundwater from open (○) and hand-pumped wells (Δ) near the river Chimbo.
FIG. 90. Frequency distribution of $\delta D$-values of shallow groundwater near the river Chimbo.

Figure 90 presents a histogram of the frequency distribution of the $\delta D$-values of shallow groundwater, excluding two samples which exhibit a marked evaporation effect. The distribution is highly skewed, with the maximum frequency close to the estimated index for recharge by infiltration of local precipitation, while the lower frequency occurs at $\delta$-values close to the estimate of the river index.

Since the sampling may be considered reasonably representative, the mean $\delta D$-value, weighted for frequency of occurrence, indicates that about 73% of the shallow groundwater originates from precipitation falling directly on the area.

The mean stable isotope composition of samples from drilled wells was more depleted than that of the shallower groundwater. Since the wells are screened over their major length, this was interpreted as being due to the occurrence of more depleted water at depth. An estimate of the negative stable-isotope gradient with depth was used to show that in the aquifer as a whole, down to a depth of 80 m, infiltration from the river system is the dominant source of recharge.

13.2.2.4. Discussion of other cases using a similar approach

Morgante et al. (1966) studied the infiltration of water from the Isonzo river to the groundwater system in the Gorizia plain in north-eastern Italy.
The δ¹⁸O-values of groundwater from 32 wells were measured at different times between December 1963 and April 1965. The Isonzo river was also sampled between March 1964 and April 1965. No significant difference between the river sampling locations was observed, although there was some variation with time. The mean value was close to −10‰.

The δ¹⁸O-values of the groundwater samples were noted to become more positive with increasing distance from the river, which was interpreted as being due to infiltration of river-water to the west and south of the river. Figure 91 gives the frequency distribution of the δ¹⁸O-values of the groundwater samples, the location of which is representative of groundwater in the area. It will be noted that the highest frequency occurs between −7.0 and −7.5‰, which is a reasonable δ¹⁸O-index of recharge by infiltration of local precipitation. The low frequency occurs at a δ¹⁸O-value which is typical of that of the Isonzo river. The shape of the distribution is highly skewed and illustrates very well the infiltration of river-water to a groundwater system.

Bortolami et al. (1973) have studied the origin of groundwater in the plain of Venice. This investigation primarily focused on the groundwater below Venice itself, but it was also found that the phreatic aquifer in the middle and upper part of the plain was characterized by a δ¹⁸O-value of −10‰, which corresponded to that of the Brenta and Piave rivers.

In the context of a detailed study of environmental isotope composition of groundwater in the Winnipeg area, Fritz et al. (1974) report on river infiltration into particular wells. On the basis of water level and chemical data, two wells located close to the confluence of the Assiniboine and Red rivers were believed to receive infiltrated river-water. Oxygen-18 data showed that the Red river undergoes seasonal variations exceeding 10‰, while the values for the two
wells remained essentially constant. This suggested that little or no river-water enters the wells. On the other hand, another well located in the inlet structure of a major flood-way had a variable $\delta^{18}O$ composition. During high stage of the Red river, the $\delta^{18}O$ of the well was identical with that of the river, while in summer it was typical of groundwater in the area. In New Zealand, where the aquifer materials of the plains are composed of alluvial or fluvo-glacial (mainly in South Island) deposits, recharge by infiltration from rivers is of great importance. The vertically separated systems of gravel beds are fed largely by the rivers emerging from New Zealand's hills and mountains. Because of the altitude effect, appreciable isotopic contrasts exist between these rivers and water derived by recharge of precipitation on the plains, so that aquifers deriving from rivers are identifiable by their $\delta D$ or $\delta^{18}O$-values. This situation was used to advantage in a hydrogeological study by Brown and Taylor (1974) of the small alluvial Kaikoura Plain (150 km$^2$). Several sources of groundwater could be identified: (1) a flowing artesian aquifer deriving from the major Kowhai River which drains water from the Kaikoura mountains and exhibits uniform $\delta^{18}O$-values of about $-9.4\%e$; (2) a non-flowing artesian aquifer at approximately the same depth, fed mainly by the Kowhai River but containing some water of less negative $\delta^{18}O$; (3) unconfined groundwater, fed by stream seepage in the fan areas of hill-side streams but receiving some direct precipitation recharge, with $\delta^{18}O$-values ranging from $-6.0\%e$ to $-8.5\%e$ according to the proportion from each source; and (4) unconfined inter-fan water, receiving recharge only from direct precipitation ($\delta^{18}O$ about $-6.0\%e$).

An isotopic contrast sufficient for easy distinction of the respective water masses exists also between the Blue and White Nile Rivers near Khartoum, Sudan. The flow of the Blue Nile is sustained by orographic precipitation on the Ethiopian highlands originating from air masses moving inland from the Gulf of Aden and the Red Sea. The mean ($\delta^{18}O$, $\delta D$) composition of the Blue Nile was found to be (−1.92‰, −0.98‰). In contrast, the mean composition of the White Nile is (+1.19‰, +16.8‰); the relatively high values of the latter reflect the low latitude of the drainage basin in equatorial Africa. Both Nile rivers are enriched in D and $^{18}O$ relative to the ancient groundwater (−9.8‰, −72‰) near Khartoum. Their influence on local groundwater could therefore be determined by sampling wells near to the rivers and their confluence. Wells containing mixtures of river-water and groundwater exhibit isotope concentrations that are on a mixing line for the two end-members defined by the river-water and old groundwater. Between the two rivers, above and below the confluence, some groundwater samples lie on the mixing line for the two rivers. To some extent the river contribution can be demonstrated by tritium measurements, since the ancient groundwater contains no tritium and the rivers contain bomb tritium. However, tritium is detectable in these mixed waters only if the river component is younger than 25 years; the proportions
of river-water/groundwater cannot be determined using tritium. In this case the stable isotope contrasts provide a better tracing tool.

An increasing number of municipal water supplies are indirectly or directly linked to rivers. In many instances an improvement in water quality is possible if river-water infiltration is induced and if the water is collected once it has passed through river gravels and sands. However, if the pumping wells are far from the river, they draw not only river-water but also local groundwater. In a study of the water supply system of the city of Bern, Siegenthaler and Schotterer (1977) could show that the groundwater component increased with increasing distance from the river. The Aare river has an average and rather constant $\delta^{18}O$-value of $-12.9\%$ and mixes with local groundwater whose $\delta^{18}O$-values vary between $-9.5$ and $-10.0\%$. A linear positive correlation between distance and isotopic composition of these two end-members is observed over a distance of more than one thousand metres. Long-term monitoring of a single pumping well shows that the isotopic composition is always close to $-11.3\%$, which indicates that its water consists of a mixture of about 50% locally generated groundwater and infiltrated river-water.

13.2.2.5. Methodological comments

The resolution of the problem depends upon the accuracy of the estimates of the stable isotope composition of the two potential sources of recharge. Measurements of the river must be made at different times and river stages to ascertain whether there are any significant variations in stable isotope composition. If variations are evident, the mean value should be weighted for discharge. A quicker and often better estimate may be obtained from groundwater sampled close to the river where, on the basis of groundwater levels, recharge can be said to be derived from the river. However, even this approach is not completely infallible, as was found in the case of a hand-pumped well, about 10 m from the river Chimbo, in the case study cited above. From November to February there was a change of $0.78\%$ in oxygen-18.

The stable isotope composition of recharge by infiltration of precipitation is probably the easier of the two indices to estimate. Measurements of groundwater away from the influence of the river may be used, or even the peak value from the skewed frequency distribution of $\delta$-values.

Any conclusions regarding the origin of recharge are based on the groundwater sampled. If shallow groundwater is sampled, there is the possibility of partial evaporation from open wells and also of return irrigation water. In order to minimize interference from isotope enrichment due to evaporation, deuterium data should be used in preference to oxygen-18 data.

For sampling of deeper groundwater a knowledge of the location and length of the well screens is required for drawing valid conclusions.
13.3. ORIGIN OF GROUNDWATER

(a) *Statement of the problem*

Assessment of a groundwater resource requires information on its distribution, rate of replenishment and origin. Almost all groundwater of economic interest is derived originally from precipitation. Precipitation may recharge a groundwater system directly by local infiltration or indirectly by infiltration from a surface water system such as a river, as discussed in the previous section. However, even where there is no surface water system as a potential source of recharge, groundwater may be recharged not only by infiltration of local precipitation but also by groundwater originating at a higher elevation where the amount of precipitation may be higher. Also, in the case of fractured rock, such as karst, the limits of the recharge area may not be restricted to the water divide as defined by the topography. Questions may also arise concerning leakage between different aquifers and across fault systems.

(b) *Theoretical basis for the isotopic approach*

Many problems of the origin of groundwater depend on the altitude effect, whereby precipitation falling at higher elevations is more depleted in stable isotopes than precipitation falling at lower elevations. Differences in the stable-isotope composition of two groundwater sources may arise even if they were recharged at the same elevation. Such differences may occur if one of the systems was recharged some thousand years ago when a cooler climate prevailed, resulting in a composition more depleted in stable isotopes. Large-scale studies may profit from situations where one potential source of groundwater is recharged in a different geographical area, which gives rise to a difference in stable isotope composition.

13.3.1. Case study: The origin of groundwater in the Chinandega Plain, Nicaragua

13.3.1.1. *Problem*

The Chinandega plain (Fig. 92) covers an area of about 1100 km² between the Pacific Ocean and the drainage divide of the Cordillera de Marrabios. The topography rises gradually from the coast to 200 m at a distance of 20 km, after which the gradient becomes steeper, with maximum elevation at the crest of the Cordillera being 1745 m. As part of a project to assess the groundwater, environmental isotopes were used to estimate the relative importance of recharge by precipitation on the plain versus groundwater flow from the higher slopes of the Cordillera (Payne and Yurtsever, 1974).
13.3.1.2. Sampling and data

Samples of groundwater were collected from drilled wells at different times over a period of one year. A spring at 800 m elevation, a dug well and a stream were also sampled. Precipitation was sampled at different elevations. Most of the samples were also analysed for tritium as a qualitative indicator of age.

The repeated sampling of the drilled wells showed no variation in stable isotope composition outside that attributable to analytical error. The tritium concentrations were less than 7 TU. The shallowest drilled well (well No.3) exhibited a tritium concentration comparable to that of current precipitation (~25 TU), which suggested that this represented local recharge by infiltration of precipitation falling directly on the plain. Confirmation of this assumption was provided by the $\delta$-values of groundwater sampled from a dug well and of base-flow of a stream in the north-west of the project area where the influence of recharge from the slopes of the Cordillera was expected to be minimal.

13.3.1.3. Interpretation

The altitude effect was estimated on the basis of groundwater samples from the plain, samples from a well located at 280 m, and samples from a spring located at 800 m. The latter two samples were assumed to represent the integrated isotopic composition of infiltrating precipitation above the respective altitudes.
The isotopic composition of recharge at different elevations is weighted by amount of precipitation and land surface area at different elevations. Available data at the time of the study indicated no significant variation of precipitation with elevations above 300 m. Therefore, only the weighting factor for the different surface areas at different elevations was used to deduce a mean altitude of 1000 m for the area of recharge to the spring located at 800 m, and of 625 m for the well located at 280 m. Figure 93 shows the variation of $\delta^{18}$O of recharge with elevation. The magnitude of the altitude effect is $-0.28\%$o/100 m, as compared with the value of $-0.26\%$o/100 m estimated from precipitation data.

From the mean value ($-6.85\%$o $\pm$ 0.06) of the drilled wells it was concluded that the major source of recharge (75% $\pm$ 6) was from elevations above 280 m.

13.3.1.4. Discussion of other cases using a similar approach

Fontes et al. (1967) used oxygen-18 data for determining the area of recharge of the water from the Evian spring complex. The altitude effect of $-0.4\%$o/100 m for oxygen-18 was estimated on the basis of the gradient of monthly $\delta^{18}$O-data with temperature at Thonon-les Bains and the local gradient of temperature with altitude. Although this approach leads to uncertainty in the estimate of the altitude effect, the conclusion that the recharge area was located at an altitude of between 800 and 900 m was reasonable from the hydrogeological point of view.

Stahl et al. (1974) estimated the origin of groundwater discharged by artesian wells in the Sperkhios Valley in Greece on the basis of the altitude effect determined from measurements of 15 springs in the area. From a knowledge of
the hydrogeology the mean altitude of the springs was determined. The regression of oxygen-18 on mean altitude of recharge gave an altitude effect of $-0.18\%$/100 m. From the regression of mean altitude of recharge on oxygen-18 the mean elevations of recharge for the three different groups of artesian waters, based on geographical location, were estimated.

The altitude effect has also been used by Gonfiantini et al. (1976) to estimate the mean elevation of recharge of waters sampled in the island of Gran Canaria. They found that the $\delta D/\delta^{18}O$ relationship of groundwater was dependent upon whether the waters were recharged on the northern or the southern part of the island. Sites on the northern side showed a $\delta D/\delta^{18}O$ relation with a slope close to 8, while the sites to the south exhibited a slope of 4. The estimated altitude effects for oxygen-18 were $-0.13\%/100$ m and $-0.25\%/100$ m for the northern and southern sites of the island, respectively.

Zuppi et al. (1974) studied the origin of a number of springs in the neighbourhood of Rome. They also estimated different altitude effects for the Tyrrenian and Adriatic sides of the mainland. All springs, with one possible exception, exhibit marked variations in stable isotope composition, which the authors interpret as resulting from mixing of different waters. In such a situation it is therefore rather difficult to assign unique areas of recharge. A subsequent paper (Fontes and Zuppi, 1976), dealing with the same area, indicated that the variability in $\delta^{18}O$ of the Lavinio spring was due to geothermal exchange, thus underlining the necessity of making at least some check deuterium analyses in order to ascertain the reason for variability in $\delta^{18}O$.

13.3.1.5. Methodological comments

Care should be exercised when estimating the altitude effect solely from precipitation data. Estimates based on data of limited duration may differ appreciably from long-term values. In the case of the study in Nicaragua the altitude effect differed by over 30% from one year to the next and, even more important, the $\delta^{18}O$-value at a given elevation differed by more than 1.5%. Therefore it is advisable to deduce the change in stable isotope composition with elevation from groundwater data for which estimates of the area of recharge can be derived from the hydrogeology of the area.

Very often the system under study may result from a mixing of different sources of recharge. For example, in the study in Nicaragua it was concluded that the major source of recharge was from elevations in excess of 280 m. This implies that the minor component is infiltration of precipitation falling directly on the plain. In this case, there should be a gradient in stable isotope composition to more positive values, moving away from the mountains as precipitation becomes increasingly dominant as a source of recharge. The limited number and distribution of wells in the cited case study did not permit such an assessment.
In the Mediterranean region there are many examples of coastal springs which are brackish. Often the recharge area of the fresh-water component has to be established in order to intercept it before it is contaminated with sea-water. In principle, stable isotope techniques may be applied here (Payne et al., 1978). However, it is conceivable that the recharge area is not unique but is made up of different areas, each at a different elevation. The isotope data will provide a mean altitude of recharge which may be the result of mixing of waters from two or even more areas, each differing in extent and elevation. The interpretation therefore demands a very close co-operation with the hydrogeologist who can define the different possibilities.

13.3.2. Case study: The origin of groundwater in the region of El Hamma and Gabès in Tunisia

13.3.2.1. Problem

The Continental Intercalaire aquifer is the largest in the Northern Sahara. The piezometric gradient suggested that water from this system discharges into the Complexe Terminal aquifer in the region of the Gulf of Gabès. A major fault system is aligned in a NNW-SSE direction from El Hamma to Médénine. As part of an overall study of the Continental Intercalaire and its relation to other aquifers, Gonfiantini et al. (1974a) studied the influence of this fault system on groundwater movement.

13.3.2.2. Sampling and data

The eastern Continental Intercalaire aquifer is characterized by the following homogeneous stable isotope composition: \( \delta^{18}O = -8.4\% \pm 0.4 \) \( \delta^D = -61\% \pm 3 \). In the region of the Gulf of Gabès the water samples from the Complexe Terminal have an isotopic composition which falls on a line below the meteoric water line (Fig.94).

13.3.2.3. Interpretation

The groundwater samples from the Complexe Terminal fall on a line with the mean compositions of the Continental Intercalaire and the aquifer of Zarzis-Djerba as end-points. This is interpreted as the groundwater being the result of a mixing between these two components. Furthermore, in the region of El-Hamma the \( \delta^{18}O \)-values of the Complexe Terminal are characteristic of water from the Continental Intercalaire. Moving eastwards, the values become more positive, indicating a decreasing influence of the water from the Continental Intercalaire and therefore an increasing contribution of locally recharged water.
with an estimated composition of $-6.1\,\%_o \pm 0.1$ and $-44\,\%_o \pm 3.5$ for $\delta^{18}O$ and $\deltaD$, respectively. The interpretation was supported by carbon-14 data, albeit limited in number, which tend to increase in an easterly direction, from 0\% $^{14}C$ in the region of El-Hamma. Further to the southeast the fault system acts as a barrier to groundwater movement, as indicated by the groundwater values not being significantly different from the value estimated for local recharge.

13.3.2.4. Discussion of other cases using a similar approach

Some quite large variations in the oxygen-18 content of groundwater in the Winnipeg area have been reported by Fritz et al. (1974). The regional distribution of $\delta^{18}O$-values of several groundwater flow systems in a single confined carbonate aquifer varies between about $-11\,\%_o$ and $-22\,\%_o$. However, the variation within a particular flow system is much less and rarely exceeds 3\%. The authors suggest that the differences in isotopic composition are related to the physical characteristics of the recharge areas of the different flow systems. In particular they suggest that changes in vegetation have taken place during the last hundred years as a result of the clearance of the bush and forest for the purpose of cultivating the land. This may explain part of the variation in stable isotope composition, but it is probable that changes in climate may also have been responsible for an appreciable part of the variation. However, no matter what the reason for these differences in stable isotope composition, the characteristic labelling of the different flow systems provides a very useful investigational tool.

Payne et al. (1979) also report on groundwater samples in the Mesa de San Luis area of the Mexicali Valley, where the oxygen-18 content extends over a range of 6.5\%_o for a series of wells located perpendicular to the direction of
FIG. 95. Location of sampling points in the Mexicali Valley.

into the Presa Morelos from 1960 to 1972. The Wellton-Mohawk drain conveys poor-quality drainage water from the Wellton-Mohawk irrigation district, about 50 km upstream of the Presa Morelos. The estimates of the stable isotope composition of these two systems, based on samples of surface water, were as follows:

Presa Morelos \[ \delta^{18}O = -12.14\% \pm 0.10; \ \delta D = -99.0\% \pm 0.7 \]

Wellton-Mohawk drain \[ \delta^{18}O = -11.03\% \pm 0.16; \ \delta D = -90.2\% \pm 0.6 \]

All groundwater samples from the two areas were found to be more depleted in stable isotopes than indicated by these two indices; the variability in stable isotope composition suggested that this resulted from mixing between water
from the Presa Morelos or the Wellton-Mohawk drain and a water which was
more depleted than either of these two sources. This depleted water was
identified by its stable isotope composition as that of the Colorado river before
the construction of the dams along the river which commenced in the 1930s.
The reservoirs which have been created behind the dams have resulted in recent
Colorado river water having a stable isotope composition typical of an evaporation
effect. This suggested that the variation in stable isotope composition of
groundwater may have resulted from mixing of recent Colorado river water
infiltrating from the canal system with older Colorado river water. A more
detailed examination of this and other possible mechanisms of salinization
was made, as described below.

13.4.1.3. Interpretation

For each of the two areas a partial correlation coefficient matrix for the
stable isotope and ionic species was computed in order to determine which
parameters were responsible for most of the variance observed. For the N.E.
and E. area, which includes samples fairly close to and along the course of the
Colorado river, the partial correlation coefficients were high for \( \delta^{18} \text{O} \) with \( \delta^2 \text{H} \),
\( \text{Cl}^- \) and \( \text{SO}_4^{2-} \). Data for these three pairs of variables are plotted in Figs 96–98.
The following regression for the stable isotope data was found to fit the
mixing line defined by the indices for the old Colorado river water and
Wellton-Mohawk drain water:

\[
\delta D(\%) = (6.08 \pm 0.14) \delta^{18} \text{O} - (23.12 \pm 1.89)
\]

\[
r^2 = 0.99 \quad S_{y,x} = 0.7
\]

Although the slope of this regression is indistinguishable from an evaporation
process, it was concluded to be the result of a mixing process on the evidence
of the tritium data. Some groundwater samples contained appreciable tritium
which could only have been introduced via the surface-water system. Further
evidence for the mixing model is provided by the chloride data in Fig.97 which
indicate that most of the groundwater samples fall on a mixing line between
old Colorado river water and Wellton-Mohawk drain water. Some samples
(e.g. 3, 19) indicate mixing with water from Presa Morelos instead of water
from the Wellton-Mohawk drain. The sulphate data in Fig.98 are in general
agreement with mixing with the surface-water system. However, most of the
samples more depleted in oxygen-18 have an excess of sulphate above what
can be expected by mixing between old Colorado river water and water from
the Presa Morelos or the Wellton-Mohawk drain. This suggests that while the
increase in salinity is mainly due to infiltration of water of poor quality, the
samples less affected by this process have an excess of sulphate resulting from
leaching of evaporitic deposits.
FIG. 96. Stable isotope composition of groundwater in the N.E. and E. area of the Mexicali Valley.

FIG. 97. Chlorinity versus $\delta^{18}O$ in the N.E. and E. area of the Mexicali Valley.
FIG. 98. Sulphate versus $\delta^{18}$O in the N.E. and E. area of the Mexicali Valley.

The hypothesis that the salinity could have arisen as a result of mixing with sea-water trapped in the alluvial sediments during their deposition was rejected, since the regression between deuterium and oxygen-18 did not pass through the isotopic composition of sea-water. Additional evidence against mixing with sea-water was provided by the correlation between chloride and oxygen-18. Again, the regression did not pass through the composition of sea-water.

In the second area (N.W. and W.) the partial correlation coefficients for $\delta^{18}$O with $\delta$D and $\text{SO}_4^{2-}$ were highly significant. The lack of correlation between $\delta^{18}$O and Cl$^-$ ruled out evaporation and mixing with sea-water as sources of salinity. The following regression fits a mixing model between old Colorado river water and the surface-water system. However, in this area the surface-water component is defined by the index for water from the Presa Morelos.

$$\delta D(\%o) = (4.86 \pm 0.35) \delta^{18}O - (40.48 \pm 4.86)$$

$$r^2 = 0.88 \quad S_y \pi = 1.0$$

The partial tritium data also provide qualitative support for this mixing model.

The partial correlation coefficients for Ca$^{2+}$ and SO$_4^{2-}$ are higher in this area, which suggests that leaching of gypsum may be more important. The sulphate data are plotted against oxygen-18 in Fig. 99. The mixing lines between old Colorado river water and water from Presa Morelos and the Wellton-Mohawk drain define the maximum sulphate concentrations which can be attributed to infiltration from the surface-water system. Although the surface-water system has transported mixtures of water from both the Presa Morelos and the Wellton-Mohawk drain, the former has been the dominant component. Therefore, the sulphate concentrations are considerably in excess of those predicted from the mixing model with water from Presa Morelos. Thus, dissolution of gypsum is concluded to be an additional mechanism of salinization in this area.
13.4.1.4. Discussion of other cases using a similar approach

Gat et al. (1969) studied the mineral waters in the Jordan Rift Valley which had been the subject of conflicting views as to their origin and mechanism of formation, based on some geochemical evidence and geohydrological inference. On the basis of stable isotope and salinity data they suggested that, at some time in the past, water from a slightly evaporated sea-water lake had mixed with the groundwater prevailing at that time to form different fossil brine pockets along the floor of the Rift Valley. Subsequently, at a second stage, these brines had mixed with present-day local groundwater and also, in some cases, with water from the nearby Lake Tiberias or Dead Sea.

Below the terminal lake Sebkha el Melah in the north-western Sahara there is a confined aquifer saturated with sodium chloride. Chemical analyses alone could not answer the question as to whether saturation occurs by leaching of salts from the sediments in the bottom of the Sebkha or whether the infiltrating water is already saturated as a result of evaporation. Conrad and Fontes (1970) answered this question on the basis of oxygen-18 data. At times of flood, part of the water immediately infiltrates into the permeable margin of the basin. The fact that the δ¹⁸O-value (−4.9‰) of the groundwater saturated in sodium chloride is that of the flood-water indicates that saturation in halite occurs by leaching of the sediments. To the south of the Sebkha the δ¹⁸O-value is more positive (+9.6‰), which implies that infiltration had occurred after partial evaporation. In the north of the Sebkha the δ¹⁸O-value has risen to +19.6‰, so that the evaporation is almost complete.

The importance of evaporation as the mechanism for increasing salinity down the piezometric gradient of an irrigated area in the Juarez Valley in Mexico is demonstrated by stable isotope data (Payne, 1976). Increasing salinity
corresponded to enrichment in both deuterium and oxygen-18 along a typical evaporation slope for the regression of the stable isotope data. The following model for the mechanism of salinization was proposed: In the irrigated area, part of the water is evaporated, thus increasing the salinity of the remaining water which infiltrates. This water moves down the piezometric gradient and the cycle is repeated. Repetition of this cycle results in the observed increase of salinity and enrichment in stable isotope composition moving down-gradient.

Evaporation as the mechanism of salinization of shallow groundwater has also been reported by Gonfiantini et al. (1974b) in the Hodna region of Algeria. Shallow (<1 m) groundwater sampled from Auger holes to the south of the Chott-el-Hodna exhibits an enriched stable isotope composition typical of an evaporation process and which is distinct from that of deeper groundwater. The shallow groundwater samples were also characterized by high salinities, of the order of tens of grams TDS, which were positively correlated with the oxygen-18 values.

Many of the coastal springs in the Mediterranean region discharge partially saline water. An example is the Almyros spring, with a maximum discharge of about 10 m$^3$/s, located to the west of Heraklion in Crete. Sea-water intrusion raises the chloride concentration to about 6000 mg/l at times of low discharge. Payne (1976) reported on the combined use of chlorinity and oxygen-18 data to answer the question as to whether the water of varying salinity pumped from test holes in the neighbourhood of the Almyros spring was also derived from the fresh water feeding the spring. From the varying oxygen-18 composition and chlorinity of the spring at different discharge rates it was possible to estimate the $\delta^{18}O$-index of the fresh water feeding the spring. The stable isotope composition of water from the test holes did not vary with changes in chlorinity and was about 1.6‰ more positive, indicating a lower elevation of recharge independent of the fresh-water system feeding the Almyros spring.

Since the stable isotope composition of the Sarvistan and Caspian Gates salt springs in Iran is the same as that of local groundwater, it was concluded (Zak and Gat, 1975) that the salinity originates through dissolution of rock salt beds by infiltrating recharge waters. In the same reconnaissance survey the Mahalru brines from a playa lake exhibited an enriched stable isotope composition, indicating evaporation as an important salinization mechanism.

Lake Giulietti, which is situated in the Danakil depression in Ethiopia, is fed by a number of cold and thermal (40–55°C) springs around the lake. Gonfiantini et al. (1973) found that for the springs with a chloride concentration of <4 g/l there was a variation of about 1‰ in $\delta^{18}O$, which correlated with the chloride content. As the stable isotope composition did not depart from the meteoric water line the authors concluded that the changes in chlorinity were due to mixing of waters having different isotopic composition and salinity.
PAYNE, B.R. (1970), Water balance of lake Chala and its relation to groundwater from tritium and stable isotope data, J. Hydrol. 11, 47.


ZAK, I., GAT, J. (1975), Saline waters and residual brines in the Shiraz-Sarvistan Basin, Iran, Chem. Geol. 16, 179.

BIBLIOGRAPHICAL NOTE

Books dealing with stable isotope variations of light elements in natural compounds and their applications to hydrology and geochemistry are rather limited. Chapters on this subject are included in the following books:


These two classical books cover only the years up to 1957 and therefore do not contain any of the modern developments and applications of isotope techniques to earth sciences.

A booklet which constitutes an introduction to stable isotope geochemistry is:


Chapters on the same subject are included in:


and (in German) in:


Pilot's book has been translated into French by R. Létolle, who also slightly modified and updated the text:


Another publication (in Russian) is:

FERRONSKY, V.I., Ed. (1975), Natural Isotopes in the Hydrosphere, Nedra, Moscow 207 pp.

(Author: Ferronsky, V.I., Dubinchuk, V.T., Polyakov, V.A., Seletsky, Y.R., Kuptsov, V.M., Yakubovsky, A.V.)

Books with chapters on stable isotopes in hydrology are:


(These editors are planning to publish a series of volumes on this subject; the first of these has appeared in 1980.)
Chapters dedicated to stable isotope variations in natural waters are included in:


This book has been translated into Russian (Nedra, Moscow, 1971). A new revised edition of this book is being prepared under the supervision of the IAEA/UNESCO Working Group on Nuclear Techniques in Hydrology of the International Hydrological Programme.


The following IAEA proceedings are probably the most important source of papers on the use of stable isotopes in hydrology:


Papers on hydrogen and oxygen stable isotope applications in hydrological and geochemical studies are published by many international scientific magazines. The journals which most frequently contain articles on these subjects are: Geochimica et Cosmochimica Acta, Earth and Planetary Science Letters, and, limited to hydrology, the Journal of Hydrology and Water Resources Research. Also Nature and Science publish frequently stable-isotope geochemistry articles.

Papers dealing with isotopic applications to specific fields of hydrology can be found in more specialized journals, such as, for instance, the Journal of Glaciology; Limnology
and Oceanography; and Geothermics. Chemistry journals, and especially those dealing with physical chemistry, should be consulted for articles on the theory and calculation of isotope fractionation.

Most of the Russian articles on isotope hydrology and geochemistry are reported in Geokhimiya, English translations of which appear in Geochemistry International.

Abstracts of papers on stable isotope variations in natural compounds are given in the Chemical Abstracts and the INIS Atomindex. Geotitles Weekly publishes the full references of many articles dealing with isotopes in earth sciences.

A number of bibliographical collections have been published, such as the following:


FIDEL, R. (1976), Bibliography of Hydrogen and Oxygen Stable Isotope Hydrology, Hebrew University, Groundwater Research Centre, Jerusalem (849 references).
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