

# **Physics of aquatic systems**

## **Part II: Isotope Hydrology**

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# 1 Introduction to Isotope Hydrology

## 1.1 Introduction to Isotopes and Tracers

"Isotope Hydrology" is a relatively young scientific discipline (or rather an interdisciplinary field), that evolved since around the 1950s, when it was first realised that the methods of nuclear physics for the detection of isotopes could have useful applications in hydrology. The classical tools of isotope hydrology are the isotopes of the constituents of the water molecule ( $\text{H}_2\text{O}$ ) itself, namely the rare stable isotopes of hydrogen and oxygen ( $^2\text{H}$ ,  $^{18}\text{O}$ ) and the radioactive tritium ( $^3\text{H}$ ). These were soon complemented by radio-carbon ( $^{14}\text{C}$ ), which enabled water dating via the decay of  $^{14}\text{C}$  in the carbon dissolved in the water.

Later on, many more methods were added to the toolbox of the isotope hydrologists, some of which are not really isotope methods at all. For example, dissolved gases such as noble gases and certain anthropogenic trace gases are very useful markers to "trace" the fate of water in some parts of the hydrological cycle. Such substances are thus called tracers, or more precisely "environmental tracers" to distinguish from substances that are added purposefully to the water (e.g. dyes). From a modern point of view, isotope hydrology may therefore be defined as the application of "environmental isotopes and tracers" to study (parts of) the hydrological cycle.

Isotope hydrology is a truly interdisciplinary science. It emerged from the application of methods developed in physics (analytical techniques) to problems of Earth and environmental sciences. This combination proved very successful not only in hydrology but also other branches of Earth sciences, leading to the related fields of isotope geology and isotope geochemistry. Hydrology, the science of water, on the other hand, is in itself a very diverse and segmented field. Some parts are covered by engineers (hydraulics, water supply and waste water), others by geologists (groundwater: hydrogeology), and still other experts of special disciplines such as oceanography (water in the oceans), meteorology (water in the atmosphere), and limnology (water in lakes and rivers). Isotope methods have become important in physical oceanography and limnology, but the term isotope hydrology is most often used in relation to the study of groundwaters.

A central role in the development of isotope hydrology and its worldwide application has been played by the International Atomic Energy Agency (IAEA) in Vienna. This at first sight maybe surprising link grew out of the monitoring of radioactive fallout from the bomb tests, which added large quantities of tritium to the water cycle. This effort resulted in the establishment of the "Global Network of Isotopes in Precipitation" (GNIP), which is now run jointly by the IAEA and the WMO (World Meteorological Organisation). GNIP-stations measure stable isotopes and tritium in precipitation, pro-

ducing an invaluable basic data set for the science of isotope hydrology. The IAEA runs itself an isotope lab, which distributes international isotope standards to the research laboratories worldwide. The IAEA also organises regular conferences on isotope hydrology since 1963. As a result, much literature on isotope hydrology has been edited by the IAEA, including the volumes by Mook [1], that are recommended for further reading.

Problems studied in isotope hydrology may be classified in two large clusters:

- a** Determination of the origin of water masses and the conditions during formation
  - Identification and separation of water components
  - Determination of groundwater recharge areas, flow paths, mixing
  - Determination of the origin of contaminants
  - Reconstruction of recharge temperatures for palaeoclimate studies
- b** Determination of the residence time of water in the system ("water age")
  - Calculation of flow velocities, assessing mixing and dispersion
  - Determination of water fluxes, recharge rates, and exchange rates
  - Study of transport and degradation of contaminants

### 1.1.1 Environmental tracers

A tracer is a substance, which is present only in trace concentrations ("Spurenstoff") and marks a trace in a natural system (marker). In hydrology, it ideally marks the water itself or dissolved substances therein, and moves passively with the water or the solutes. Isotopes are often nearly ideal tracers, e.g.:

- Isotopes of H and O mark the water molecule
- Isotopes of C, N, S etc. mark dissolved substances
- Conservative solutes (e.g. noble gases) are good tracers

Environmental tracers are isotopes or other tracers that are widely distributed in the environment, especially the hydrosphere. They can be both of natural or anthropogenic origin. They can be further classified into

- a** Transient tracers: Anthropogenic substances with an input to the environment (hydrosphere) that varies with time. Typical examples are tritium, CFCs, SF<sub>6</sub>, and <sup>85</sup>Kr.
- b** Geochemical tracers: Tracers of natural origin with a (more or less) constant input, e.g. stable isotopes, <sup>14</sup>C and noble gases.

The term "environmental tracers" is mainly used to distinguish them from "artificial tracers", both of which are often simply called tracers but are used in quite different settings and usually by different researchers. Artificial tracers are released deliberately into the investigated system, in local tracer experiments (e.g., dyes, chemicals, also isotopes, SF<sub>6</sub> and so on). The essential difference is that environmental tracers can be applied for studies on large spatial and temporal scales, whereas artificial tracers are suitable for targeted studies of small scale processes.

## 1.2 Introduction to isotopes

Nuclei of atoms consist of protons and neutrons (= nucleons)

- $Z$  = number of protons (atomic number)
- $N$  = number of neutrons
- $A = Z + N$  = number of nucleons (mass number)

$Z$  determines to which element a nucleus belongs and is equal to the number of electrons in a neutral atom. The number of electrons determines the chemical properties of the elements.

As a general term for the type of nucleus determined by  $Z$  and  $N$  we use the word nuclide. Isotopes are nuclides of the same element (same  $Z$ ), with a different number of neutrons (thus varying  $N$  and  $A$ ). The term is derived from the Greek iso topos = same place (in the periodic system).

There are two forms of notation for isotopes:

**a** Full notation:  ${}^A_Z\text{X}_N$  e.g.  ${}^{14}_6\text{C}^8$

**b** Short notation:  ${}^A\text{X}$  e.g.  ${}^{14}\text{C}$

The full notation is rarely used, because the short notation contains all information, if one knows the number of protons ( $Z$ ) of the elements.

### 1.2.1 The Chart of the Nuclides

The chart of the nuclides provides an overview of the existing isotopes and is an important source of basic information for isotope sciences. The isotopes are mapped in plot of neutron number  $N$  versus proton number  $Z$ . Isotopes of a single element stand in rows (Fig. 1.1). Stable isotopes of the light elements align roughly along the 1:1 diagonal, for heavier elements, there is always an excess of neutrons over protons (Fig. 1.2). The chart contains usually a lot of information on the nuclides, such as exact mass or half-life and decay mode for the radioactive isotopes. Nuclide charts and the related information can be found on the web, e.g. at the Korea Atomic Energy Research Institute (<http://atom.kaeri.re.kr/>).



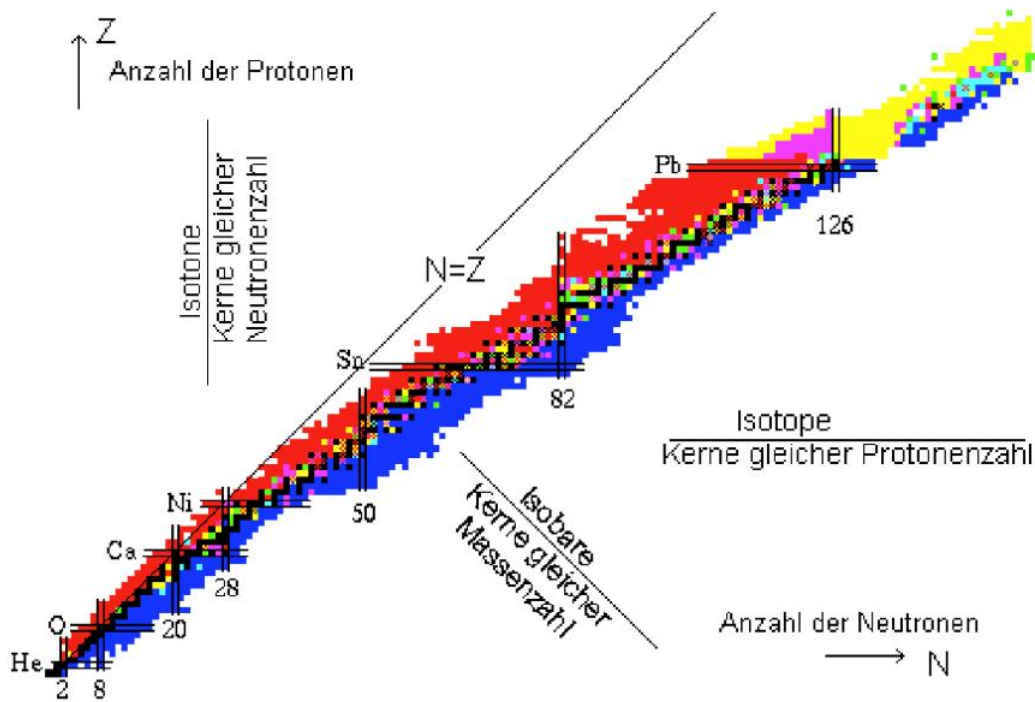


Fig. 1.2: The entire chart of the nuclides. Black squares correspond to stable isotopes, all coloured squares to radioactive isotopes. Colours indicate different decay modes. The highlighted proton and neutron numbers are the so-called "magic numbers" (see text).

elements are particularly important. As expected, symmetric ( $Z = N$ ) and (doubly) magic nuclides are most abundant (e.g.  ${}^4\text{He}$ ,  ${}^{12}\text{C}$ ,  ${}^{14}\text{N}$ ,  ${}^{16}\text{O}$ ,  ${}^{20}\text{Ne}$ ), whereas isotopes with uneven  $Z$  or  $N$  are rather rare (e.g.  ${}^3\text{He}$ ,  ${}^{13}\text{C}$ ,  ${}^{15}\text{N}$ ,  ${}^{17}\text{O}$ ).

### 1.2.3 Radioactivity

Most nuclei are actually unstable and undergo radioactive decay. There are many very short-lived isotopes, which have no practical importance, but some longer-lived isotopes are of great use in Earth and environmental science and especially in isotope hydrology (e.g.  ${}^3\text{H}$ ,  ${}^{14}\text{C}$ ). We therefore look a bit closer at the phenomenon of radioactivity. There are several different modes of radioactive decay (Fig. 1.4). Particularly important for the isotopes that are applied in hydrology are the  $\alpha$  and  $\beta^-$  decay. In an  $\alpha$ -decay an  $\alpha$ -particle, which is nothing else than the tightly bound  ${}^4\text{He}$  nucleus, is emitted. The proton and neutron numbers of the decaying nuclide are thus both reduced by 2, and the mass number is reduced by 4. In a  $\beta^-$ -decay a  $\beta^-$ -particle, which is nothing else than an electron, is emitted, and a neutron is converted to a proton. Consequently, the proton number is enlarged by 1 while the neutron number is reduced by 1, and the mass number remains the same. The effects of radioactive decays on the position of an isotope in the chart of nuclides is shown in Fig. 1.3. This figure also contains additional decay

Tab. 1.1: Isotopic abundance (ratio of the abundance of a given isotope to that of all isotopes of the element) of the stable isotopes of the light elements. There is always one dominating light isotope, and one or two rare, usually heavier isotope(s) with higher neutron number.

Element	Abundance of stable isotopes (%)					
Hydrogen	$^1\text{H}$	99.985	$^2\text{H}$	0.015		
Helium	$^4\text{He}$	99.9999	$^3\text{He}$	0.0001		
Carbon	$^{12}\text{C}$	98.89	$^{13}\text{C}$	1.11		
Nitrogen	$^{14}\text{N}$	99.63	$^{15}\text{N}$	0.37		
Oxygen	$^{16}\text{O}$	99.758	$^{18}\text{O}$	0.204	$^{17}\text{O}$	0.038
Neon	$^{20}\text{Ne}$	90.51	$^{22}\text{Ne}$	9.22	$^{21}\text{Ne}$	0.27

modes such as neutron (n) and proton (p) emission, electron capture (EC), and the  $\beta^+$  decay. The latter two of these modes are illustrated in Fig. 1.4.

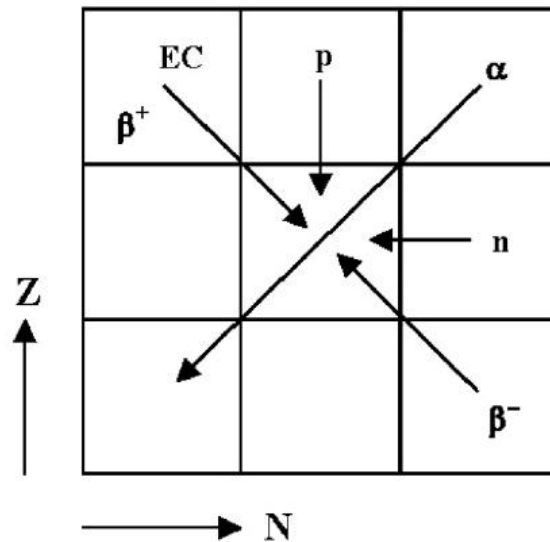


Fig. 1.3: Effects of radioactive decay modes in the chart of the nuclides.

Radioactive decay is a purely statistical process, with constant decay probability. The number of decays in a given time interval is proportional to the total number of nuclides:

$$\frac{dN}{dt} = -\lambda N \quad (1.1)$$

where  $\lambda$  [ $\text{T}^{-1}$ ] is the decay constant, i.e. the decay probability per unit time. The decay constants of the different radioisotopes are characteristic material constants. They are in principle well-known, although the precision of the values for long-lived isotopes is not always very high.

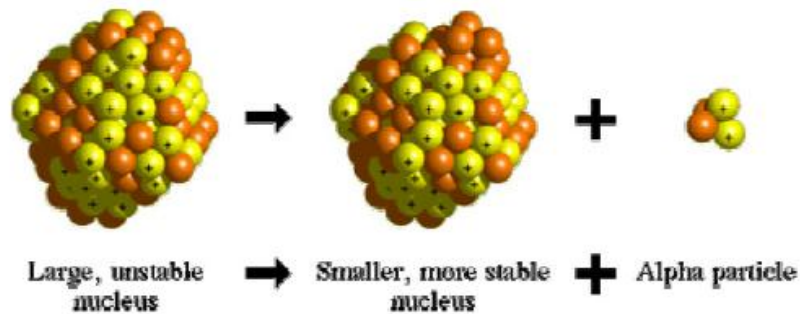
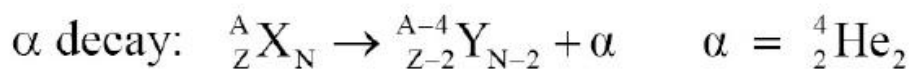
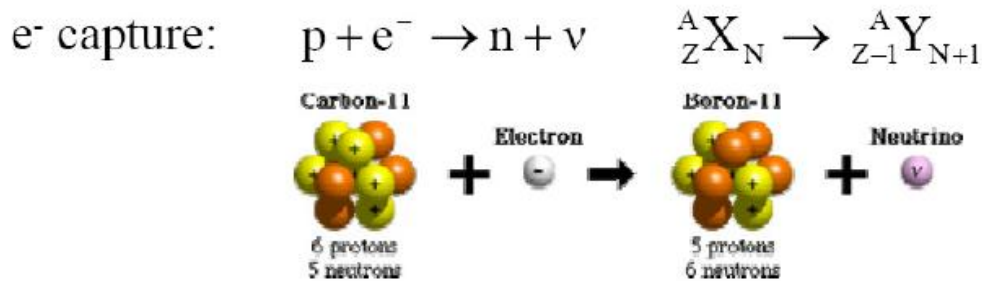
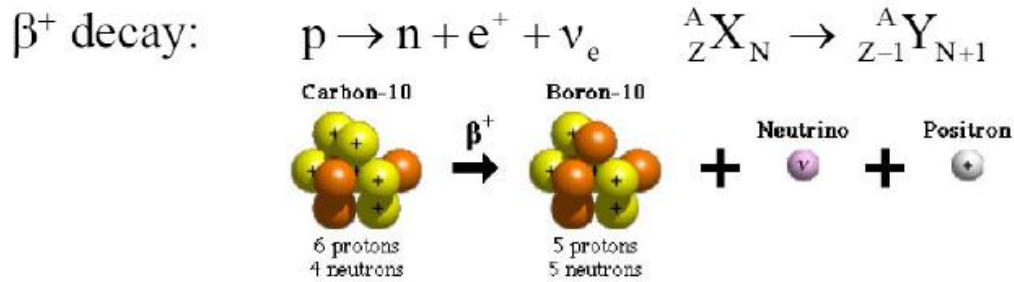
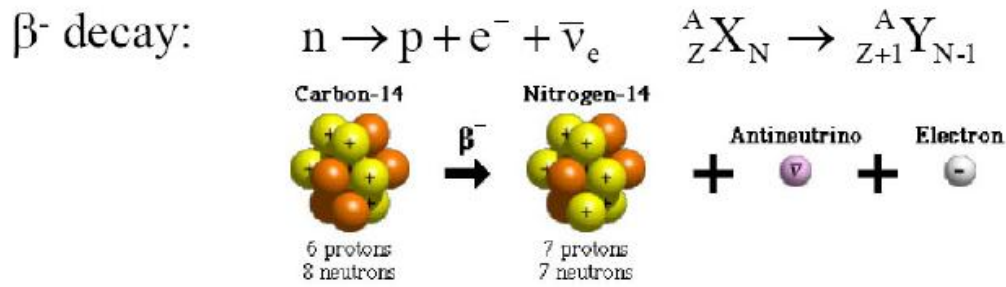


Fig. 1.4: Radioactive decay modes.

Integration of eq. 1.1 with the initial condition  $N(0) = N_0$  yields

$$N(t) = N_0 \cdot e^{-\lambda t} \tag{1.2}$$

This is the well-known equation of an exponential decay (Fig. 1.5). The time dependence of this decay is entirely characterized by the decay constant  $\lambda$ . Instead of  $\lambda$ , it may be

more convenient to use its inverse  $\tau = 1/\lambda$ , which has the dimension of a time.  $\tau$  corresponds to the time when the number of nuclides has declined by a factor of  $1/e$  and it equals the expectation value for the lifetime of the nuclides. It is thus called the mean life (mittlere Lebensdauer) of the isotopes. Although mathematically less elegant, a much more customary measure of the characteristic time of a radioactive decay process is the half-life (Halbwertszeit)  $T_{1/2}$ , which is the time when the number of nuclides has declined to half of its initial value. It can easily be seen that the half-life is linked to  $\tau$  by a factor of  $\ln 2$ :

$$T_{1/2} = \frac{\ln 2}{\lambda} = \tau \cdot \ln 2 \quad (\text{follows from } N(T_{1/2}) = N_0 \cdot e^{-\lambda T_{1/2}} = \frac{N_0}{2}) \quad (1.3)$$

Eq. 1.3 is a simple but very useful relationship! It may even be worthwhile to remember that  $\ln 2$  is about 0.7, thus the half-life is about 70% of the mean life. (Remark: A related useful rule of thumb is that the doubling time of the money in your bank account is 70 yr divided by the interest rate in %. The interest rate corresponds to  $\lambda$ , if expressed in % we have to multiply  $\ln 2$  by 100, leading to the 70 yr constant. The same is true for the doubling time of population and the yearly growth rate, e.g. the population of Egypt with a current growth rate of 2% per year will double in 35 yr if nothing changes).

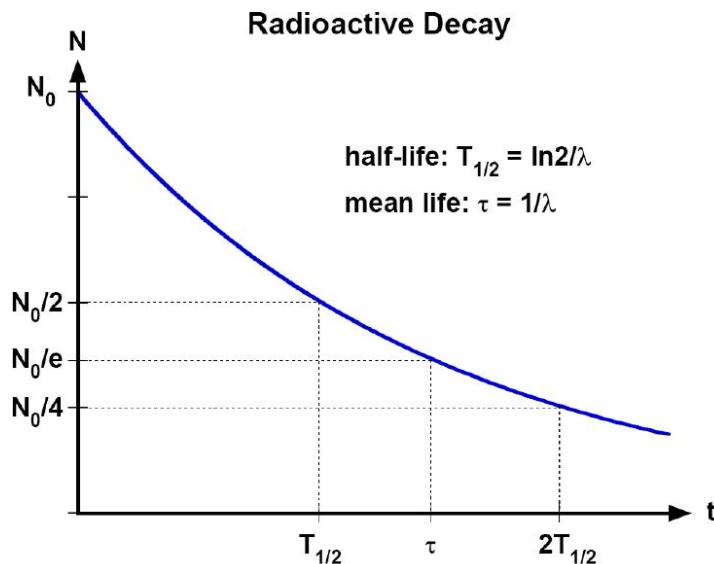


Fig. 1.5: Radioactive decay curve, and definition of some characteristic times.

Radioactive isotopes can yield time information (age), if  $N(t)$  and  $N_0$  are known (the  $\lambda$ 's are known constants). The age is obtained simply by solving eq. 1.2 for the time:

$$t = -\frac{1}{\lambda} \ln \left( \frac{N(t)}{N_0} \right) = \tau \ln \left( \frac{N_0}{N(t)} \right) \quad (1.4)$$

In applications of this equation for dating, time zero is some unknown date in the past, whereas time  $t$  is usually the present time or more precisely the time of analysis.  $N(t)$

is thus directly measured, the problem is to know  $N_0$ ! We will address this problem and possible solutions in some detail later on in the discussion of individual methods. The basic idea is usually that  $N_0$  is assumed to be a known constant value. Another very important approach is to measure the product of the decay (the so-called daughter isotope) in addition to the decaying radioisotope itself (the mother isotope).

Radioisotopes are usually rather rare (because they constantly disappear), but the fact that they decay offers an opportunity to detect them even at very low abundance. Thus, in practice, often not  $N$  (number of atoms, abundance) is measured, but the activity, which is the number of decays per unit time:

Definition of **activity**:

$$A \equiv \frac{dN}{dt} = -\lambda N \quad (1.5)$$

Units for  $A$  are:

- Becquerel (Bq) =  $s^{-1}$  (decays per sec)
- Curie (Ci):  $1 \text{ Ci} = 3.7 \cdot 10^{10} \text{ Bq}$  (activity of 1 g Ra)

The modern SI-unit is of course the Bq, which we will use. The Curie is a historical unit, derived from the early experiments of Marie Curie with radium as a source of radioactivity. The Curie is a rather large unit, environmental activities are often in the range of pCi.

It should be noted that activity is a measure of the mass (number of atoms) of a radioactive substance. Their concentrations are often given as activity concentrations (e.g. Bq/m<sup>3</sup>).

### 1.2.4 Radioisotopes, their abundance and production

Radioactive isotopes can only occur in nature if they are either very long lived (i.e., the half-life is comparable to the age of Earth) or if they are constantly produced by nuclear processes. Radioisotopes can be classified according to their origin:

- Primordial (remnants from the formation of the solar system, when supernova-produced radioisotopes must have been present)
- Cosmogenic (produced by interactions with cosmic rays in the Earth atmosphere or near the Earth's surface)
- Subsurface-produced (produced by nuclear reactions in the solid Earth)
- Anthropogenic (produced by technical processes)

Most radioisotopes have very low isotopic abundances, except for some very long-lived primordial isotopes (Tab. 1.2). Some heavy elements occur in nature, although they have no stable isotopes: Uranium, thorium, and isotopes produced in the U/Th-decay series (Fig. 1.6).

Radioisotopes can be produced by nuclear reactions induced by irradiation of nuclides. Sources and types of irradiation are:



- In the atmosphere, near the Earth’s surface: Cosmic rays (CR, protons, neutrons, etc.)
- In the subsurface: U/Th-decay series and fission ( $\alpha$ ’s and neutrons)
- In the anthroposphere: Nuclear bombs, reactors, accelerators, etc. (mainly neutrons)

Tab. 1.2: Isotopic abundance, half-life, and decay mode (EC: electron capture, SF: spontaneous fission) of long-lived primordial radioisotopes. The half-life of  $^{238}\text{U}$  is quite close to the age of Earth (about 4.55 Gyr), some others are much longer.

Isotope	Abundance (%)	Half life (yr)	Decay mode
$^{40}\text{K}$	0.0117	$1.28 \times 10^9$	$\beta^-$ , EC
$^{50}\text{V}$	0.25	$1.4 \times 10^{17}$	EC, $\beta^-$
$^{87}\text{Rb}$	27.83	$4.75 \times 10^{10}$	$\beta^-$ , EC
$^{144}\text{Nd}$	23.8	$2.29 \times 10^{15}$	$\alpha$
$^{148}\text{Sm}$	11.3	$8.0 \times 10^{15}$	$\alpha$
$^{178}\text{Lu}$	2.59	$4.0 \times 10^{10}$	$\beta^-$ , EC
$^{174}\text{Hf}$	0.162	$2.0 \times 10^{15}$	$\alpha$
$^{232}\text{Th}$	100	$1.45 \times 10^{10}$	$\alpha$ , SF
$^{235}\text{U}$	0.72	$7.038 \times 10^8$	$\alpha$ , SF, Ne
$^{238}\text{U}$	99.27	$4.468 \times 10^9$	$\alpha$ , SF

An example of a nuclear reaction that produces radioisotopes is spallation, where a high-energy particle of the cosmic radiation breaks a nucleus apart, forming a radioisotope and some smaller fractions, e.g.:



Another example is thermal neutron capture, where low-energy neutrons react less violently with nuclides, e.g.:



Which isotopes are produced in the atmosphere (by cosmic rays) or the subsurface (by particles from the U/Th chains) depends mainly on the nuclides that are available for reaction. Main target elements are

- In the atmosphere: N, O, Ar
- In rocks: Li, O, Na, Mg, Al, Si, Cl, K, Ca, Fe

Some possible reactions are listed in Tab. 1.3. Very important for environmental isotope science is the production of radioisotopes by cosmic radiation. Cosmic rays (CR) are divided in two types:

Tab. 1.3: Examples of nuclear reactions producing radioisotopes in the atmosphere and in the subsurface.

Atmosphere	Subsurface
$^{14}\text{N}(\text{n,p})^{14}\text{C}$	$^6\text{Li}(\text{n},\alpha)^3\text{H}$
$^{14}\text{N}(\text{n},^3\text{H})^{12}\text{C}$	$^{35}\text{Cl}(\text{n},\gamma)^{36}\text{Cl}$
$^{40}\text{Ar}(\text{p},3\text{n}2\text{p})^{36}\text{Cl}$	$^{40}\text{Ca}(\text{n},2\text{n}3\text{p})^{36}\text{Cl}$
$^{40}\text{Ar}(\text{n},2\text{n})^{39}\text{Ar}$	$^{39}\text{K}(\text{n},\text{p})^{39}\text{Ar}$
$^{40}\text{Ar}(\text{p},\text{sp})^{26}\text{Al}$	$^{40}\text{Ca}(\text{n},\alpha)^{37}\text{Ar}$

- primary CR: 87 % protons (p), 12 %  $\alpha$ -particles, 1 % heavier nuclei
- secondary CR: mainly neutrons

Primary cosmic rays are important in the upper atmosphere, below the secondary radiation dominates. Fig. 1.7 shows the cascades of cosmic rays occurring in the atmosphere.

Production rates by cosmic radiation (Tab. 1.4) are very low, hence cosmogenic isotopes are very rare, e.g.:

- $^{14}\text{C}/^{12}\text{C} \sim 10^{-11}$
- $^{36}\text{Cl}/^{35}\text{Cl} \sim 10^{-15}$
- $^3\text{H}/^1\text{H} \sim 10^{-18}$ , global natural  $^3\text{H}$  inventory: 3.6 kg

Tab. 1.4: Production rates of some cosmogenic isotopes of environmental importance.

Radioisotope	Prod. Rate [atoms $\text{cm}^{-2} \text{s}^{-1}$ ]
$^3\text{H}$	0.28
$^7\text{Be}$	0.035
$^{10}\text{Be}$	0.018
$^{14}\text{C}$	2
$^{36}\text{Cl}$	0.0019

Another important source of radionuclides is anthropogenic production (Tab. 1.5). Major sources of anthropogenic radionuclides are

- Tests of nuclear weapons in the atmosphere ( 1950s - 60s)
- Accidents of nuclear power plants (esp. Chernobyl, 1986)
- Normal releases of nuclear power and reprocessing plants

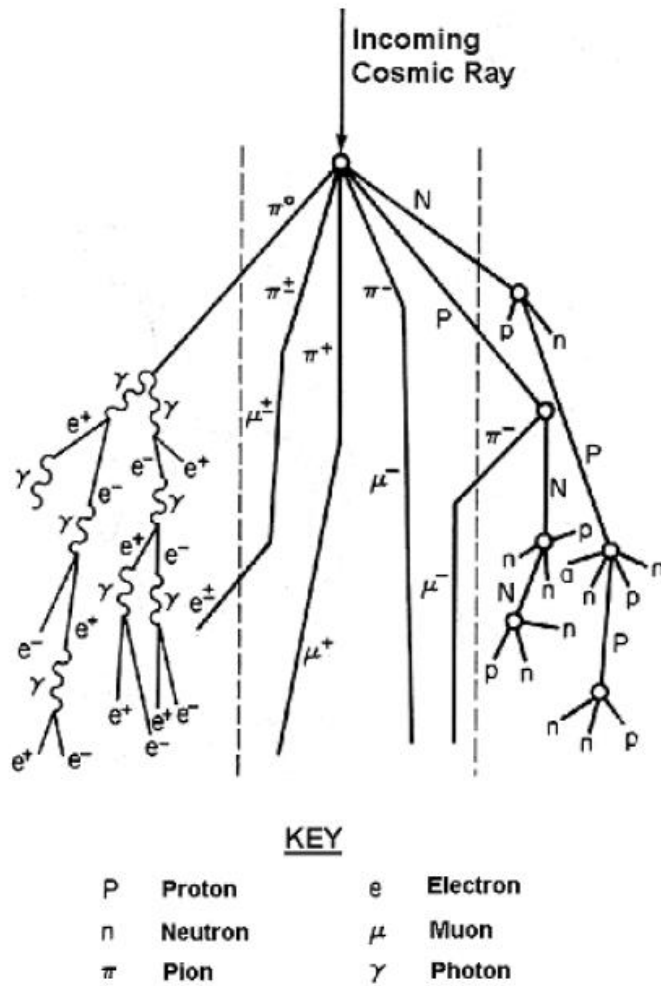


Fig. 1.7: Cosmic ray shower in the atmosphere, by reaction with nuclei of gases in the air.

- Waste from other applications (medical, science, etc.)

Anthropogenic nuclides of importance for isotope hydrology are listed in Tab. 1.5. The primary example of such nuclides is of course tritium, which along with the stable isotopes of H and O is the classical tool of isotope hydrology. The input history of tritium into the hydrosphere via precipitation is illustrated by Fig. 1.8, showing the prominent peak resulting from atmospheric nuclear bomb testing, the so-called "bomb peak" that occurred in 1963. Further details on tritium see chapter 3.

Tab. 1.5: Anthropogenic nuclides of importance for isotope hydrology.

Isotope	Half-life [yr]	Origin
$^3\text{H}$	12.32	bomb tests
$^{14}\text{C}$	5730	bomb tests
$^{36}\text{Cl}$	308000	bomb tests
$^{85}\text{Kr}$	10.7	fuel reprocessing

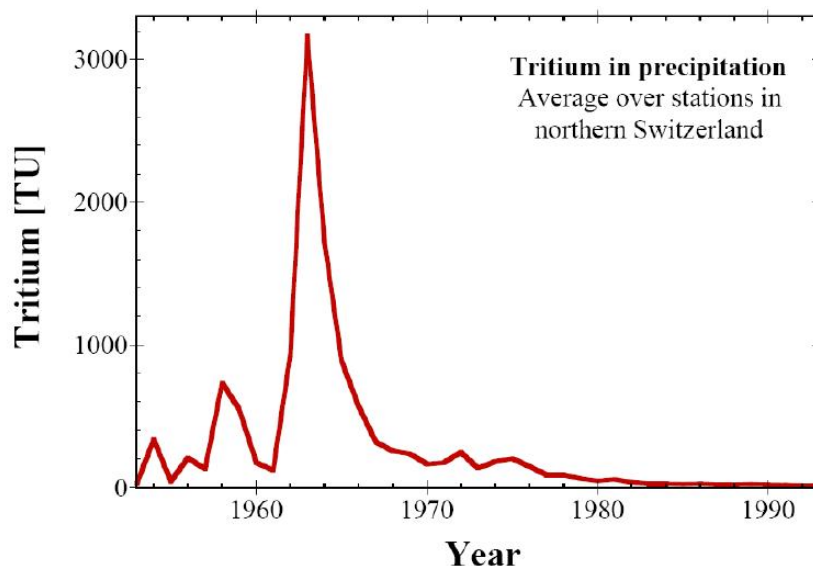


Fig. 1.8: Tritium in precipitation of northern Switzerland. The shape of the curve with the pronounced "bomb peak" in 1963 is typical for the entire northern hemisphere.

### 1.3 Overview of isotopes and tracers in hydrology

Tab. 1.6 summarises the isotopes that are applied in hydrology and related fields. The stable isotopes deuterium and  $^{18}\text{O}$  (see chapter 2) as well as the radioactive tritium (see chapter 3) are direct markers of the water molecule. All other isotopes are related to some dissolved substance, such as dissolved inorganic/organic carbon (DIC, DOC), sulphate ( $\text{SO}_4$ ), or dissolved (noble) gases.

The half-lives of the radioisotopes cover a wide range from the short-lived  $^{222}\text{Rn}$  (3.8 days) to the long-lived  $^{81}\text{Kr}$  (210 kyr) and  $^{36}\text{Cl}$  (308 kyr). Consequently a wide range of ages is at least in principle accessible for dating by radioisotopes in water. We will discuss the classical  $^{14}\text{C}$ -method in some detail in chapter 5. Dating is not only possible through the observation of the radioactive decay, but also by using the time-dependent input of some radioisotopes ( $^3\text{H}$ ,  $^{85}\text{Kr}$ , see chapters 3 and 4) or the steady accumulation of radiogenic stable isotopes ( $^4\text{He}$ ,  $^{40}\text{Ar}$ , see Fig. 1.9). A special case among the dating methods is the mother-daughter pair  $^3\text{H}$ - $^3\text{He}$  (see chapter 3).

In addition to dating, many (stable) isotopes can be used as markers and to obtain information about the conditions during the formation of a water mass.

Tab. 1.6: Isotopes that are used in hydrology.

Isotope	Phase	Half-life	Use
Deuterium ( $^2\text{H}$ , D)	$\text{H}_2\text{O}$ (HDO)	stable	Marker, formation
Tritium ( $^3\text{H}$ , T)	$\text{H}_2\text{O}$ (HTO)	12.32 yr	Dating (input)
Helium-3 ( $^3\text{He}$ )	dissolved He	stable	Dating ( $^3\text{H}/^3\text{He}$ )
Helium-4 ( $^4\text{He}$ )	dissolved He	stable	Dating accumulation
Carbon-13 ( $^{13}\text{C}$ )	DIC, DOC, ...	stable	Marker
Carbon-14 ( $^{14}\text{C}$ )	DIC, DOC, ...	5730 yr	Dating (decay)
Nitrogen-15 ( $^{15}\text{N}$ )	diss. $\text{N}_2$ , $\text{NO}_3$ , ...	stable	Marker
Oxygen-18 ( $^{18}\text{O}$ )	$\text{H}_2\text{O}$ ( $\text{H}_2^{18}\text{O}$ )	stable	Marker, formation
Sulfur-34 ( $^{34}\text{S}$ )	$\text{SO}_4$ , ...	stable	Marker
Chlorine-36 ( $^{36}\text{Cl}$ )	$\text{Cl}^-$	308000 yr	Dating (decay)
Chlorine-37 ( $^{37}\text{Cl}$ )	CHCs, ...	stable	Marker
Argon-39 ( $^{39}\text{Ar}$ )	dissolved Ar	269 yr	Dating (decay)
Argon-40 ( $^{40}\text{Ar}$ )	dissolved Ar	stable	Dating (accumulation)
Krypton-81 ( $^{81}\text{Kr}$ )	dissolved Kr	210000 yr	Dating (decay)
Krypton-85 ( $^{85}\text{Kr}$ )	dissolved Kr	10.7 yr	Dating (input)
Radon-222 ( $^{222}\text{Rn}$ )	dissolved Rn	3.8 d	Dating (accumulation)
U-series ( $^{238}\text{U}$ , $^{234}\text{U}$ )	Dissolved $\text{UO}_2$	variable	Dating (disequilibrium)

Another category of environmental tracers in hydrology are dissolved conservative gases (Tab. 1.7), especially the noble gases He through Xe, which in particular can be used to determine the temperature that prevailed during the infiltration of groundwater (see chapter 6). The transient gas tracers CFCs (chlorofluorocarbons, Freons) and  $\text{SF}_6$  (sulfurhexafluoride) are used for dating young groundwater (see chapter 4).

A final category of environmental tracers are such simple properties or constituents of the water as temperature and dissolved ions. Dissolved ions can be looked at individually or as a sum parameter such as salinity or TDS (total dissolved solids), which often is parameterised through the more easily measurable electrical conductivity. These properties, or at least temperature and conductivity, should always be measured in applications of tracer methods in aquatic systems. Temperature and conductivity enable the calculation of density (see part I of this lecture) and thus form the basis of any assessment of the physical state of the system. Moreover, they can very often be used as quasi-conservative tracers that are very simple, quick and cheap to measure. When more sophisticated tracer methods are applied, one should not forget that sometimes a lot of useful information can already be gained from these simple tools. Nevertheless, we will not discuss these basic tracers in much detail in this lecture.

Tab. 1.7: Gases and other tracers that are used in hydrology.

Gases			
Tracer	Phase	Half-life	Use
He, Ne, Ar, Kr, Xe	dissolved	stable	Formation (temp.)
Nitrogen (N <sub>2</sub> )	dissolved	stable	Formation (temp.)
CFCs (11, 12, 113)	dissolved	stable (oxic)	Dating (input)
SF <sub>6</sub>	dissolved	stable	Dating (input)
Others			
Tracer	Phase	Half-life	Use
Temperature	bulk	stable	Marker
Conductivity (TDS)	bulk	stable	Marker
Ions (Cl <sup>-</sup> , Li <sup>+</sup> , ...)	dissolved	stable	Marker

### 1.3.1 Dating methods and ranges

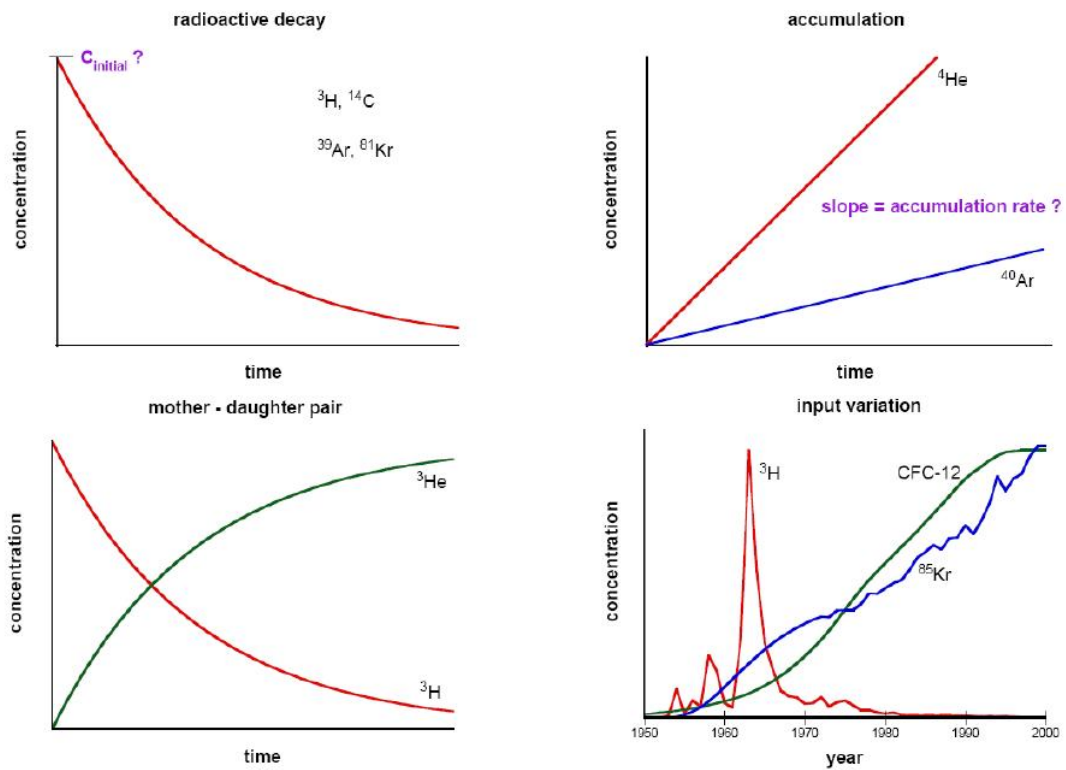


Fig. 1.9: The four basic principles of the dating methods in hydrology.

Among the many applications of environmental tracers in hydrology, water age dating, i.e. the determination of the residence time of a water mass in a particular system, is

probably the most important. As seen above (Tab. 1.6), there is a large variety of dating tracers. These can be classified in four categories with respect to the basic principle of the dating methods (Fig. 1.9):

- Radioactive decay: Direct use of the decay law (eq. 1.4) with the difficulty of knowing the initial (activity) concentration  $C_0$ . The classical example is  $^{14}\text{C}$ , but  $^{36}\text{Cl}$ ,  $^{39}\text{Ar}$ , and  $^{81}\text{Kr}$  also belong to this category.  $^3\text{H}$  actually usually works via input variation.
- Mother-daughter pair: Combined determination of the decaying radioisotope and its accumulating stable daughter, solving the problem of  $C_0$  (which equals the constant sum of mother and daughter). The only relevant example is  $^3\text{H}$ - $^3\text{He}$ .
- Accumulation: Observation of only the accumulation of a stable radiogenic daughter isotope, with the problem of knowing the production and accumulation rate. Examples are  $^4\text{He}$  and  $^{40}\text{Ar}$ , where the mother isotopes (U/Th and  $^{40}\text{K}$ ) are so long-lived, that accumulation can assumed to be linear with time.
- Input variation: Using the time information in the variable input history of transient anthropogenic tracers. Examples are  $^3\text{H}$ ,  $^{85}\text{Kr}$ , CFCs, and  $\text{SF}_6$ .

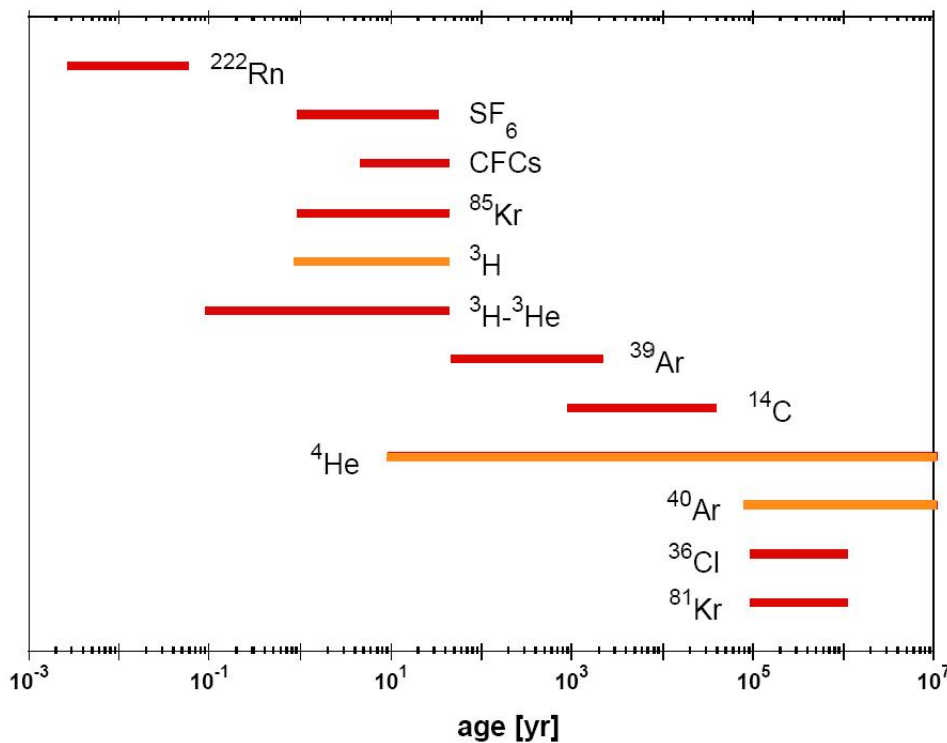


Fig. 1.10: Dating ranges of the different tracer methods. Quantitative methods are indicated in red, whereas orange bars refer to methods that usually give only qualitative age information.

As already mentioned, the dating methods cover a wide dating range, which is shown in more detail in Fig. 1.10. Obviously, the temporal range of methods based on radioactive isotopes is determined by the half-life of the isotope in question. As a rule of thumb, the dating range extends at most up to 10 half-lives, when it becomes very difficult to detect the small remaining concentrations. The transient tracers are also clearly limited to the period when their input variation took place, which is essentially the last 50 years. This limit also applies for  $^3\text{H}$  and the  $^3\text{H}$ - $^3\text{He}$  method. The accumulation of stable daughters of very long-lived mother isotopes in principle allows dating on very long time scales. In practice, however, the  $^4\text{He}$  and  $^{40}\text{Ar}$  accumulations rarely work as quantitative dating tools, because the accumulation rates are not known sufficiently well.

## 1.4 Basics of stable isotopes and fractionation

The fact that the water molecule occurs in different isotopic forms (so-called isotopomers), due to the various isotopes of its constituent elements hydrogen and oxygen, constitutes of course the very basis of isotope hydrology. It has turned out that by observing the small variations of the isotopic composition of natural waters a great deal can be learned about the functioning of the global water cycle as well as sub-systems thereof on all scales. In this section we treat first the fundamentals of stable isotope hydrology (most of which are also valid for many other fields of stable isotope geochemistry). We then discuss in some detail the theory of isotope fractionation, including the Rayleigh process, which is fundamental for the understanding of stable isotopes in the global water cycle. The distribution of stable isotopes in this cycle is described by the global meteoric water line (GMWL) and a variety of isotope effects, which we will discuss in chapter 2. Finally, it will be shown how all these effects can be applied in studies of surface and groundwater hydrology as well as for paleoclimate reconstruction.

We focus here on the isotopic composition of the water itself, i.e. on the isotopomers of the water molecules. We will use the term "stable isotopes" synonymous to stable isotopes of hydrogen and oxygen. However, many of the basic facts are also applicable to stable isotopes of many other elements. For applications in environmental sciences, the stable isotope geochemistry of some quite abundant and relatively light elements is of most interest. Such elements are mainly hydrogen, carbon, nitrogen, and oxygen (see Tab. 1.8), but also boron, sulfur, chloride and others.

### 1.4.1 Isotope abundance, isotope ratios, and $\delta$ -notation

In section 1.2 (Tab. 1.1) we have already seen that most light elements have several stable isotopes, which usually group into one dominating light isotope (e.g.  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{14}\text{N}$ ,  $^{16}\text{O}$ ), and one or two rare, heavier isotope(s) with a higher neutron number (e.g.  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ). Some also have a super-heavy radioactive isotope ( $^3\text{H}$ ,  $^{14}\text{C}$ ). In the following, we will concentrate on the rare heavy isotopes  $^2\text{H}$  (also called deuterium or D) and  $^{18}\text{O}$  (which is heavier and more abundant than  $^{17}\text{O}$ ). In stable isotope geochemistry, natural variations of the ratios between rare and abundant isotopes are studied. Thus,

the central quantities are the isotope ratios  $R$ , which are defined as:

$$R \equiv \frac{\text{abundance of rare isotope}}{\text{abundance of common isotope}} = \frac{\text{abundance of heavy isotope}}{\text{abundance of light isotope}} \quad (1.6)$$

Another useful quantity that is sometimes reported in tables (e.g. Tab. 1.1) is the isotope "concentration" or mixing ratio. It is the fractional abundance of a given isotope relative to all isotopes of the element (often reported in ‰). Tab. 1.8 lists the typical isotope ratios and concentrations of the most important light elements in nature.

Tab. 1.8: Isotope concentrations or mixing ratios (ratio of the abundance of a given isotope to that of all isotopes of the element, see Tab. 1.1) and isotope ratios (ratio of the abundance of two isotopes of the same element, see Eq. 1.6) of the stable isotopes of the light elements.

Element	Isotope	mixing ratio (%)	Isotope ratio
Hydrogen	$^1\text{H}$	99.985	$^2\text{H}/^1\text{H}$ 0.00015
Carbon	$^{12}\text{C}$	98.89	$^{13}\text{C}/^{12}\text{C}$ 0.011
Nitrogen	$^{14}\text{N}$	99.63	$^{15}\text{N}/^{14}\text{N}$ 0.0037
Oxygen	$^{16}\text{O}$	99.785	$^{18}\text{O}/^{16}\text{O}$ 0.0020
Oxygen	$^{16}\text{O}$	99.785	$^{17}\text{O}/^{16}\text{O}$ 0.00038

As can be seen from Tab. 1.8, the isotope ratios of interest are quite small numbers. In fact, we are not so much interested in these ratios themselves, but rather in the their variations between different reservoirs in the environment. Moreover, the usual measurements do not directly yield absolute isotope ratios, but are conducted relative to a reference material or standard with a more or less well-known ratio. For these reasons, it is practical to report not the absolute ratios but the deviation relative to the standard. This is achieved by the so-called  $\delta$ -notation, which is very generally used in isotope science. This notation is defined by:

$$\delta \equiv \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \quad (\cdot 1000\text{‰}) \quad (1.7)$$

Applying this general definition to the isotopes of interest in hydrology, we obtain

$$\delta^2\text{H} = \frac{(^2\text{H}/^1\text{H})_{\text{sample}}}{(^2\text{H}/^1\text{H})_{\text{standard}}} - 1 \quad (\cdot 1000\text{‰})$$

and

$$\delta^{18}\text{O} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} - 1 \quad (\cdot 1000\text{‰})$$

It has to be noted and stressed that the  $\delta$ -values are in the first place dimensionless and usually small numbers. Because they are so small, it is convenient to multiply them by 1000 and report them in ‰. In many texts, the convention that  $\delta$ -values are reported

in ‰ is taken as fixed, implying that in many calculations they have to be divided by 1000. For simplicity and elegance, but also for reasons of logical strictness, we follow the convention of Mook [1], in which the factor of 1000 (used to convert to ‰) does not occur in equations. This means that if the qualifier ("unit") ‰ is not used, the  $\delta$ -values are understood to be small dimensionless numbers. For example, the following statements are correct and equivalent:  $\delta^{18}\text{O} = 3 \text{ ‰} \Leftrightarrow \delta^{18}\text{O} [\text{‰}] = 3 \Leftrightarrow \delta^{18}\text{O} = 0.003$ .

As the  $\delta$ -notation is defined relative to a standard, such a standard has of course to be defined. Since we are interested in water, it is logical to use some particular water as a standard. The by far largest reservoir of water on Earth is the ocean, and it is quite homogenous. This is why ocean water forms the basis of the standard for stable isotope hydrology. Harmon Craig, a pioneer of stable isotope geoscience, first defined a standard that he mixed from deep ocean samples, and called it "Standard Mean Ocean Water" or short SMOW. In principle, this is still the standard that is used, but it had to be prepared in larger quantities and distributed worldwide. The task of preparing and distributing an internationally accepted standard was thus taken over by the IAEA (International Atomic Energy Agency) in Vienna. For this reason, the current water standard is often referred to as Vienna-SMOW or V-SMOW.

Geoscientists studying the carbon and oxygen isotopes in carbonate ( $\text{CaCO}_3$ ) minerals and rocks introduced a different standard, which is simply some piece of carbonate rock, called "Pee-Dee Belemnite" or short PDB. The name refers to a location in the US called Pee-Dee, and a certain type of rock containing certain fossils called belemnite. This standard is nowadays also distributed by the IAEA and often referred to as Vienna-PDB or V-PDB. It is used generally for  $\delta^{13}\text{C}$ , whereas for  $\delta^{18}\text{O}$  both scales (SMOW and PDB) are in use, depending on the type of samples. This can sometimes cause confusion, but in isotope hydrology SMOW is exclusively used for the water isotopes.

For the nitrogen isotopes, atmospheric air is usually used as reference standard, which has the advantage that every lab has easy access to the globally well-mixed reservoir of air. For oxygen isotopes, very small variations may be present in air, due to the photosynthesis - respiration cycle. Furthermore, as oxygen isotopes are usually measured on samples in the form of  $\text{CO}_2$ , direct comparison with  $\text{O}_2$  from the air is not easily possible.

Tab. 1.9: Standard materials used in isotope geochemistry and their reference isotope ratios.

Element	Ratio	Standard	Ref. value
Hydrogen	$^2\text{H}/^1\text{H}$	VSMOW	$1.5575 \cdot 10^{-4}$
Carbon	$^{13}\text{C}/^{12}\text{C}$	VPDB	$1.1237 \cdot 10^{-2}$
Nitrogen	$^{15}\text{N}/^{14}\text{N}$	atmospheric N <sub>2</sub>	$3.677 \cdot 10^{-3}$
Oxygen	$^{18}\text{O}/^{16}\text{O}$	VSMOW	$2.0052 \cdot 10^{-3}$
		VPDB	$2.0672 \cdot 10^{-3}$

The different reference materials used in isotope geochemistry are listed in Tab. 1.9,

along with the reference value for the isotope ratios of these materials. These standards are distributed internationally to assure that data produced in different laboratories are comparable. In reality, the laboratories usually have their internal working standards, which are well calibrated against the international reference.

## 1.4.2 The origin of isotope fractionation

The central fact that makes the study of isotope ratios so useful is that many natural processes cause slight changes of these ratios. The reason for this so-called isotope fractionation is that the physical and chemical properties of different isotopes (or compounds containing different isotopes) are slightly different. As a result of fractionating processes, slight variations of the isotope ratios occur in natural materials. Two major differences that cause fractionation can be identified:

### 1 Mobility

Rare heavy isotopes are slightly less mobile than the light isotopes, because the thermal velocity of an isotope or molecule is inversely proportional to the square-root of its mass:

$$kT \propto \frac{1}{2}mv^2 \Rightarrow v \propto m^{-\frac{1}{2}} \quad \text{for a given } T \quad (1.8)$$

As a result of the lower thermal velocity, the diffusivity of the heavy isotopes or compounds is slightly lower. Thus heavy species diffuse slower, and diffusion can create isotope fractionation.

### 2 Reactivity

Molecules containing the rare heavier isotope generally are slightly less reactive than molecules with the abundant light isotopes, because they have higher binding energies. The reason for the higher binding energy of the heavy molecules is their lower zero-point energy. This can easily be seen for the case of a diatomic molecule, such as H<sub>2</sub> or HD, respectively. Because normal hydrogen (<sup>1</sup>H) and deuterium (<sup>2</sup>H, D) both have one proton and one electron, the electrostatic potential that the atoms in the molecule see is the same for both isotopomers (Fig. 1.11). However, the energies of the vibrational and rotational states in this potential differ because of the different reduced mass of the two molecules.

The rotational energy states are given by

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) \quad (1.9)$$

with the moment of inertia  $I = \mu R^2$ . It follows that these energies are inversely proportional to the reduced mass  $\mu = m_1 \cdot m_2 / (m_1 + m_2)$ , which is larger for HD than for H<sub>2</sub>. The vibrational energies are given by

$$E_{vib} = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad \text{with} \quad \omega_0 = \sqrt{\frac{D}{\mu}} \quad (1.10)$$

These energies are inversely proportional to the square-root of the reduced mass. In particular, the zero-point energy of  $\frac{1}{2}\hbar\omega_0$  is lower for the heavy isotopomer, thus leading to a larger dissociation energy for the HD molecule.

As a result of the higher binding energy, the heavy molecules react slightly lower. Thus chemical reactions as well as biological transformations can create isotope fractionation.

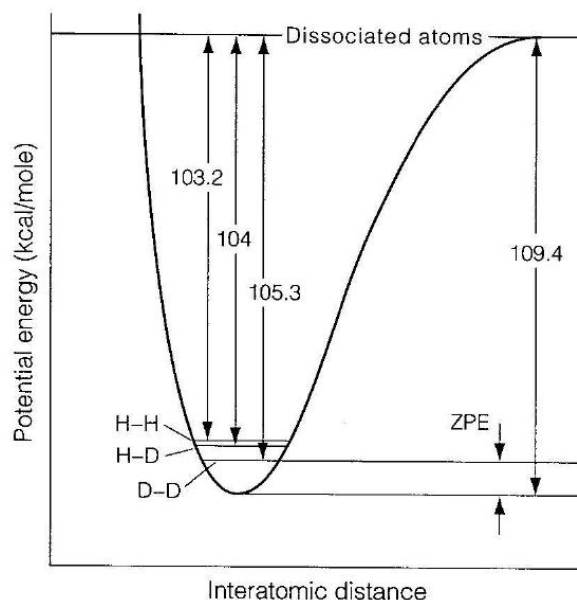


Fig. 1.11: Interatomic potential and zero-point energy of the isotopomers of  $\text{H}_2$ .

The different masses of the isotopomers of course also influence the density of the substances that are made up of them. Moreover, such physical properties as melting and boiling points are also influenced by the mass of the molecules, because heavier molecules require more thermal energy to be able to escape from the binding potentials in solids or liquids (see point 1 above). Tab. 1.10 lists the density, melting and boiling

Tab. 1.10: Physical properties of pure isotopic forms of water (not present in nature).

Property	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$	$\text{H}_2^{18}\text{O}$
Density at 20°C [ $\text{g cm}^{-3}$ ]	0.9982	1.1051	1.1106
Melting point [°C]	0	3.81	0.28
Boiling point [°C]	100	101.42	100.14

points for different types of water (normal and heavy water). Of course these are extreme examples, as natural water will always be essentially normal light water. But it shows that the heavy isotopomers will behave significantly different under phase transitions.

As a result, the heavy water molecules tend to be enriched in the condensed phase. This is a very basic effect for isotope hydrology, which we will discuss in more detail later.

### 1.4.3 Description of isotope fractionation

Isotope fractionation occurs in physical, chemical, or biological transitions/reactions between two phases or compounds A and B. Conceptually, two types of fractionating processes have to be distinguished.

#### 1 Equilibrium fractionation

Equilibrium fractionation occurs in reversible reactions or transitions  $A \leftrightarrow B$ . Examples are the chemical equilibrium between two compounds or the phase equilibrium between e.g. a liquid and its vapour. At equilibrium, the forward and backward reaction rates equal, not only for the transition as such, but also for the different isotopic species. Thus, constant isotope ratios are attained in both states A and B.

#### 2 Kinetic fractionation

Kinetic fractionation occurs in irreversible, unidirectional reactions or transitions  $A \rightarrow B$ . Examples are chemical reactions with isolated reaction products, or phase transitions with phase separation. An important special case is diffusion, which is an irreversible stochastic process. Kinetic effects are usually stronger than equilibrium fractionation.

The mathematical description is identical for both types of fractionation. The isotopic effect of a transition or reaction  $A \leftrightarrow B$  or  $A \rightarrow B$  is described by the fractionation factor  $\alpha$ :

$$\alpha_{B/A} = \frac{R_B}{R_A} \quad (1.11)$$

The fractionation factor  $\alpha_{B/A}$  expresses the isotope ratio  $R_B$  in state B relative to the ratio  $R_A$  in state A. In the literature, often only  $\alpha$  without an index is used, when the states A and B are clear from the context. Sometimes  $\alpha_k$  is used for kinetic fractionation factors, or other notations are used to distinguish kinetic and equilibrium fractionation factors.

Fractionation effects are usually small, in the sense that the isotope ratios in the two states are only slightly different, and their ratio  $\alpha$  is close to unity. To highlight the effect of the fractionation, often the deviation of  $\alpha$  from 1 is used:

$$\epsilon_{B/A} = \alpha_{B/A} - 1 \quad (1.12)$$

The quantity  $\epsilon$  is simply called fractionation or sometimes enrichment factor (although in contrast to  $\alpha$  it is not a factor!). Since the values of  $\epsilon$  are usually small, as the  $\delta$ -values, the  $\epsilon$ 's are usually multiplied by 1000 and reported in ‰.

Often  $10^3 \cdot \ln \alpha$  is tabulated, which is nearly the same as  $\epsilon$  in ‰, because for small  $\epsilon$  the following approximation holds (first order Taylor expansion):  $\ln \alpha = \ln(1 + \epsilon) \approx \epsilon$

In the following, a few useful rules of the isotope calculus are summarised. From the definition of the  $\delta$ -value we obtain an important relationship to express the isotope ratios in terms of  $\delta$ -values:

$$\delta_A = \frac{R_A}{R_{st}} - 1 \Leftrightarrow R_A = R_{st}(1 + \delta_A) \quad (1.13)$$

Using this relationship, we obtain an equation that relates the fractionation factor  $\alpha$  to the  $\delta$ -values of the two involved states:

$$\alpha_{B/A} = \frac{R_B}{R_A} = \frac{R_B/R_{st}}{R_A/R_{st}} = \frac{1 + \delta_B}{1 + \delta_A} \quad (1.14)$$

From  $\alpha$  we easily obtain  $\epsilon$ , but when expressing  $\epsilon$  in terms of the  $\delta$ -values, it is convenient to make an approximation based on the fact that the  $\delta$ -values are much smaller than 1. As above for  $\ln \alpha$ , these approximations are always simply first order Taylor expansions around  $\delta$  (or  $\epsilon$ ) = 0. Note that  $(1 + x)^{-1} \approx 1 - x$  for  $x \ll 1$ . This way we obtain the following simple relationship between  $\epsilon$  and the  $\delta$ -values:

$$\epsilon_{B/A} = \alpha_{B/A} - 1 = \frac{1 + \delta_B}{1 + \delta_A} - 1 \approx \delta_B - \delta_A \equiv \Delta_{B/A} \quad (1.15)$$

Here, a new quantity  $\Delta$ , called the isotopic separation (of the states A and B) has been introduced. It is rarely used as it essentially equals  $\epsilon$ . The meaning of eq. 1.15 is that we can simply add  $\epsilon$  to the initial  $\delta$ -value  $\delta_A$  in order to obtain the final  $\delta$ -value  $\delta_B$ .

The next expression relates the fractionation factor of the reverse process B  $\rightarrow$  A (sometimes denoted as  $\alpha^*$ ) to that of the original process A  $\rightarrow$  B:

$$\alpha_{A/B} = \frac{R_A}{R_B} = \frac{1}{\alpha_{B/A}} \quad \text{or} \quad \alpha^* = \frac{1}{\alpha} \quad (1.16)$$

Not surprisingly, the fractionation factors of reverse processes are simply each others inverse. We can also derive  $\epsilon$  for the reverse process and find that it simply has the inverse sign of the original value, although this again is only approximatively valid:

$$\epsilon_{A/B} = \alpha_{A/B} - 1 = \frac{1}{\alpha_{B/A}} - 1 = \frac{1}{1 + \epsilon_{B/A}} - 1 = \frac{-\epsilon_{B/A}}{1 + \epsilon_{B/A}} \approx -\epsilon_{B/A} \quad (1.17)$$

To summarise, we can express the change of the isotopic composition in the process A  $\rightarrow$  B in two ways:

$$R_B = R_A \cdot \alpha_{B/A} \quad \text{or} \quad \delta_B \approx \delta_A + \epsilon_{B/A} \quad (1.18)$$

Note that  $R$  and  $\alpha$  are multiplicative, whereas  $\delta$  and  $\epsilon$  are approximately additive. In principle, the notation system with  $R$  and  $\alpha$  might look preferable as it allows exact calculations. However, the system with  $\delta$  and  $\epsilon$  is very intuitive and allows simple estimations of isotopic effects. Therefore, experts in isotope science have gotten used to think in these terms.

A few notes should be made about terminology, as many different wordings are often used to express certain observations on isotope compositions and their changes, which

can be confusing. The terms usually refer to the (change of) abundance of the rare, heavy isotope with respect to the abundant, light isotope.

A process with  $\epsilon > 0$  is said to induce an enrichment (Anreicherung), whereas a process with  $\epsilon < 0$  leads to a depletion (Abreicherung) of the rare isotope. If for two states  $\delta_A > \delta_B$  holds, it can be said that A is enriched in the rare (heavy) isotope relative to B, or that A is "heavier" than B. Alternatively, one can say that B is depleted relative to A, or B is lighter than A. The terms enriched or depleted should always be used relative to another state, as there is no absolute scale of "enrichment". E.g., it is not customary to speak of "depleted" for all materials with negative  $\delta$ -values (i.e., to use the standard as an absolute reference). This would make little sense in isotope hydrology, as then almost all water in the hydrological cycle would be "depleted", as we will see later. The fact that we often encounter negative  $\delta$ -values is also a cause of confusion. One has to be a bit careful with words like "larger" or "higher" for negative values. This is why isotope experts often use expressions like heavier/lighter or more positive/negative to avoid misunderstandings. For example,  $-10\text{‰}$  is higher or more positive or heavier than  $-20\text{‰}$ .

An important conclusion from the above discussed isotope calculus is that mixing of two water masses 1 and 2 with different  $\delta$ -values leads to an approximately linear behaviour of the  $\delta$ -value of the mixed water with the mass mixing parameter  $f = m_1/(m_1+m_2)$ . It is left to the reader as an exercise to show that the following relationship holds:

$$\delta_{mix} \approx \delta_1 f + \delta_2(1 - f) \quad \text{with } f = m_1/m_{tot} \quad (1.19)$$

Fig. 1.12 shows an example of this relationship in a case where river water mixes into seawater, e.g. in an estuary near the mouth of a big river. Here, the salinity or chlorinity of the water is a direct measure of the mixing parameter and one can observe that  $\delta$ -values and Cl concentrations follow a mixing line.

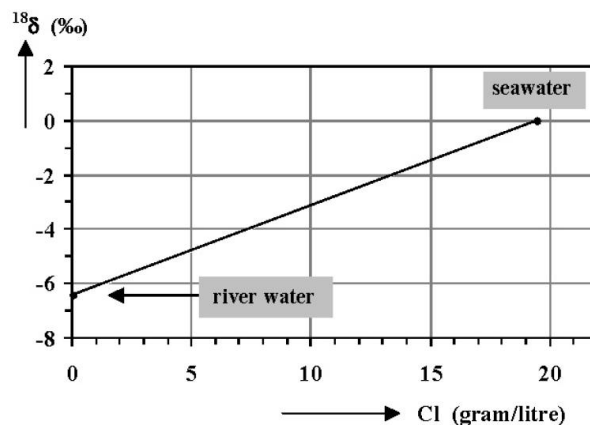


Fig. 1.12: Mixing line of  $\delta$ -values and Cl-concentrations near the mouth of a river. From Mook, [1].

### 1.4.4 Theoretical treatment of isotope fractionation

Fractionation factors can be understood in terms of reaction rates, i.e. the theory of reaction kinetics. We only give a brief overview of this topic. We first consider equilibrium fractionation in a reversible processes  $A \leftrightarrow B$ . In the isotope exchange reaction, a rare heavy isotope which is present in state (phase, compound) A is transferred to state (phase, compound) B, and vice versa. Thus, by distinguishing the light and heavy isotopes in both states, we can write the reaction as  $A_h + B_l \leftrightarrow A_l + B_h$ .

Denoting concentrations (actually activities) of the different isotopomers in brackets we can write

$$\alpha_{eq} = \frac{R(A)}{R(B)} = \frac{[A_h]/[A_l]}{[B_h]/[B_l]} = \frac{[A_h][B_l]}{[A_l][B_h]} = K \quad (1.20)$$

Here,  $K$  is the equilibrium constant of the isotope exchange reaction, as defined in reaction kinetics by the law of mass action.

**Examples of exchange reactions** Water/vapour isotope exchange:

The exchange between liquid water and vapour,  $H_2O(liq) \leftrightarrow H_2O(vap)$  gives rise to the isotope exchange reaction  $H_2^{18}O(liq) + H_2^{16}O(vap) \leftrightarrow H_2^{16}O(liq) + H_2^{18}O(vap)$ . This reaction is very important for isotope hydrology.

The reaction between water and  $CO_2$  to form carbonic acid,  $H_2O + CO_2 \leftrightarrow H_2CO_3$ , leads to water/ $CO_2$  isotope exchange:  $H_2^{18}O + C^{16}O_2 \leftrightarrow H_2C^{18}O^{16}O_2 \leftrightarrow H_2^{16}O + C^{18}O^{16}O$ . This reaction is the basis for measuring the  $^{18}O$  content of water via equilibration with a small quantity of  $CO_2$  which is then analysed in a mass spectrometer.

Now we consider a one way reaction, which involves kinetic isotope fractionation. The reaction  $A \rightarrow B$  divides in  $A_l \rightarrow B_l$  and  $A_h \rightarrow B_h$  with reaction rates

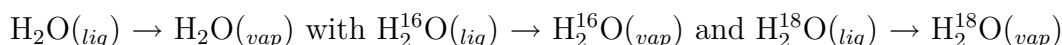
$$r_l = k_l[A_l] \quad \text{and} \quad r_h = k_h[A_h] \quad (1.21)$$

where  $k_i$  are the reaction rate constants for the light and heavy isotopomers. The isotope ratio of the (instantaneous) product  $\Delta B$  is:

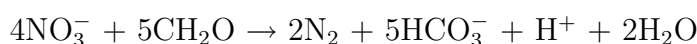
$$R(\Delta B) = \frac{r_h}{r_l} = \frac{k_h[A_h]}{k_l[A_l]} R(A) = \alpha_k R(A) \quad (1.22)$$

Thus, the kinetic isotope fractionation factor can be related to the ratio of the reaction constants for the isotopomers.

**Examples of kinetic reactions** Evaporation with removal of vapour:



Biologically mediated reactions:



Finally, we derive a relationship between kinetic and equilibrium fractionation. The equilibrium reaction  $A \leftrightarrow B$  divides in two pathways  $A \rightarrow B$  and  $B \rightarrow A$  with the following isotope ratios of the products:

$$R(\Delta B) = \alpha_k R(A) \quad \text{and} \quad R(\Delta A) = \alpha'_k R(B) \quad (1.23)$$

$$\text{with } \alpha_k = \frac{k_h}{k_l} = \frac{k(A_h \rightarrow B_h)}{k(A_l \rightarrow B_l)} \quad \text{and} \quad \alpha'_k = \frac{k'_h}{k'_l} = \frac{k(B_h \rightarrow A_h)}{k(B_l \rightarrow A_l)}.$$

Using equations 1.22 and 1.23, the equilibrium fractionation factor can be expressed as

$$\alpha_{eq} = \frac{R(A)}{R(B)} = \frac{R(\Delta B)}{\alpha_k R(\Delta A)} = \frac{\alpha'_k r_h r'_l}{\alpha_k r_l r'_h}. \quad (1.24)$$

At equilibrium reaction rates are equal:  $r_l = r'_l$ ;  $r_h = r'_h$ . Thus follows

$$\alpha_{eq} = \frac{\alpha'_k}{\alpha_k}. \quad (1.25)$$

**Fractionation by diffusion** Molecular diffusion is an important mechanism of kinetic fractionation. From eq. 1.8 we know that the mean velocity  $\bar{v}$  of molecules in thermal equilibrium is inversely related to the square-root of the mass. Remembering that the diffusion coefficient is proportional to the mean velocity ( $D = \frac{1}{3}\bar{v}\lambda$  with the mean free path  $\lambda$ ), it follows that  $D$  is also proportional to  $m^{-1/2}$ . The transport by diffusion is proportional to  $D$  (Fick's first law), thus the fractionation induced by diffusion is given by

$$\alpha_{k,dif} = \frac{D_h}{D_l} = \sqrt{\frac{m_l}{m_h}} < 1 \quad (1.26)$$

The heavy isotopomers diffuse more slowly than the light ones and are therefore depleted in the diffusing flux.

For diffusion of gas A through gas B, it can be derived from the kinetic theory of gases that  $m$  has to be replaced by the reduced mass  $\mu$ :

$$\mu_l = \frac{m_{A,l} \cdot m_B}{m_{A,l} + m_B}; \quad \mu_h = \frac{m_{A,h} \cdot m_B}{m_{A,h} + m_B}$$

**Temperature dependence of fractionation** The equilibrium fractionation factor depends on temperature and usually decreases with increasing temperature. The dependence of fractionation on temperature  $T$  is often described by:

$$\ln \alpha = aT^{-2} + bT^{-1} + c \quad (1.27)$$

As an example, the temperature dependence of the water - vapour fractionation factors  $\alpha$  for  $^{18}\text{O}$  and  $^2\text{H}$  are shown in Fig. 1.13 and the fractionations  $\epsilon$  for the inverse process are listed in Tab. 1.11.

Tab. 1.11: Vapour-(liquid) water equilibrium fractionation  $\epsilon_{v/l}$ , from Mook [1].

T (°C)	$^2\epsilon_{v/l}$ (‰)	$^{18}\epsilon_{v/l}$ (‰)	$^2\epsilon_{v/l}/^{18}\epsilon_{v/l}$
0	-101.0	-11.55	8.7
5	-94.8	-11.07	8.5
10	-89.0	-10.60	8.4
15	-83.5	-10.15	8.2
20	-78.4	-9.71	8.1
25	-73.5	-9.29	7.9
30	-68.9	-8.89	7.7
35	-64.6	-8.49	7.6
40	-60.6	-8.11	7.4

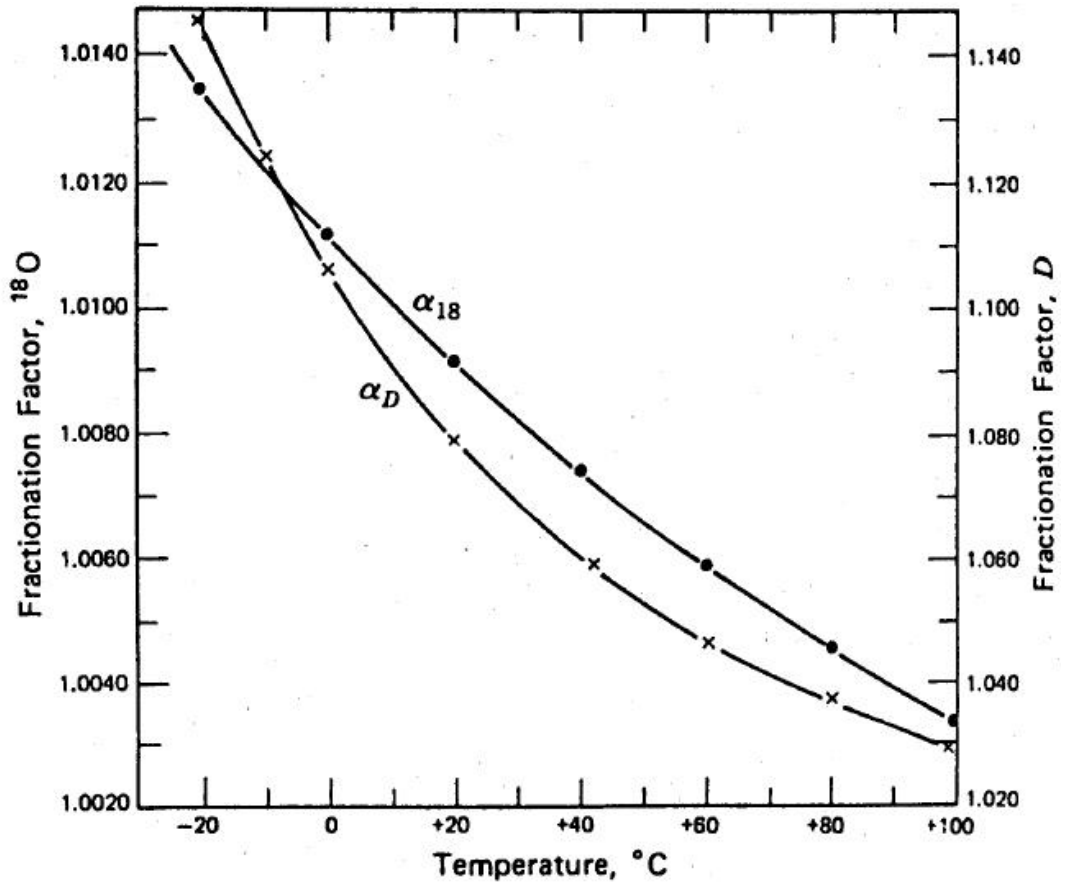


Fig. 1.13: Water-vapour equilibrium fractionation factors  $\alpha_{w/v}$ , from Faure [2].

**Rules of thumb on fractionation** Some generally valid statements on fractionation are listed in the following:

- Light elements fractionate stronger than heavy elements
  - ${}^2\text{H}/{}^1\text{H}$ :  $\Delta m/m_l = 1$ ,  ${}^{18}\text{O}/{}^{16}\text{O}$ :  $\Delta m/m_l = 1/8 \Rightarrow \epsilon({}^2\text{H}) \approx 8\epsilon({}^{18}\text{O})$
- Multiple isotopes: Fractionation scales with mass difference
  - $\epsilon({}^{18}\text{O}) \approx 2\epsilon({}^{17}\text{O})$ ,  $\epsilon({}^{14}\text{C}) \approx 2\epsilon({}^{13}\text{C})$
- Fractionation decreases with temperature
- Heavy isotopes are generally enriched in the
  - denser phase ( $\delta_{solid} > \delta_{liquid} > \delta_{gas}$ )
  - chemically more strongly bound form
  - compound with the higher molecular weight

### 1.4.5 The Rayleigh Process

A very important case of isotope fractionation is the continuous depletion of a reservoir through a fractionating process. This case is often referred to as Rayleigh distillation or more general as the Rayleigh process. Rayleigh fractionation frequently provides an adequate description of the isotopic composition and evolution of a limited amount of any substance in some compartment of the environment. Fig. 1.14 shows the principle of the process. Some examples:

- A terminal lake losing water by evaporation
- An air mass losing water vapour by condensation and rainout
- A water film on a stalagmite losing  $\text{CO}_2$  by outgassing
- A contaminant in groundwater being continuously degraded

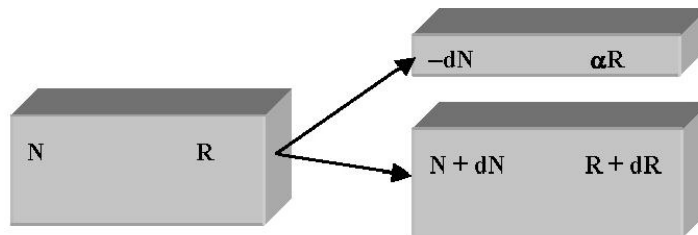


Fig. 1.14: Scheme of the Rayleigh process. The reservoir initially containing  $N$  molecules with an isotope ratio  $R$  is continuously losing mass, and the mass  $-dN$  being lost in each step is isotopically fractionated by the factor  $\alpha$  relative to the reservoir (substrate).

For the derivation of the equation for Rayleigh fractionation we first find an expression for the number of heavy (rare) isotopes (or isotopomers)  $n_h$  in terms of the total number  $N$  and isotope ratio  $R$ :

$$R = \frac{n_h}{n_l} ; \quad N = n_h + n_l \quad \Rightarrow \quad n_h = Rn_l = R(N - n_h) \quad \Rightarrow \quad n_h = \frac{RN}{1 + R} \quad (1.28)$$

A mass balance for the heavy (rare) isotope between the two states shown in Fig. 1.14 then yields:

$$n_h = \frac{RN}{1 + R} = \frac{(R + dR)(N + dN)}{1 + R + dR} - \frac{\alpha R dN}{1 + \alpha R} \quad (1.29)$$

Now we make an important approximation. We neglect the small differences of the denominators in the terms of eq. 1.29. Note that we do not need to make the assumption that  $R$  is small compared to 1 (although this usually holds), but only that  $dR$  is small and  $\alpha R$  is close to  $R$  ( $\alpha \approx 1$ ). I.e., we set the denominators equal to  $(1 + R)$  and multiply 1.29 by this common factor to obtain

$$RN \approx (R + dR)(N + dN) - \alpha R dN = RN + R dN + N dR + dR dN - \alpha R dN \quad (1.30)$$

Neglecting the product of infinitesimal changes  $dR dN$  and rearranging the terms we find

$$R dN (\alpha - 1) \approx N dR \quad \Rightarrow \quad \frac{dR}{R} = \frac{dN}{N} (\alpha - 1) \quad (1.31)$$

Integration with  $R = R_0$  at  $N = N_0$  yields:

$$\frac{R}{R_0} = \left( \frac{N}{N_0} \right)^{\alpha-1} \equiv f^{\alpha-1} = f^\epsilon \quad \text{with} \quad f \equiv \frac{N}{N_0} \quad (1.32a)$$

This is the equation describing the evolution of the isotopic composition of the diminishing reservoir as a function of the remaining mass fraction  $f = N/N_0$ . Using eq. 1.13 we can also write the Rayleigh equations in terms of  $\delta$ -values:

$$\frac{1 + \delta}{1 + \delta_0} = f^\epsilon \quad \text{or} \quad \delta = (1 + \delta_0) f^\epsilon - 1 \quad (1.32b)$$

The equations 1.32a and 1.32b describe the isotopic evolution of the substrate on which the Rayleigh process operates. Next we look at the isotopic evolution of the product, i.e. the substance that is being lost from the reservoir.

At every moment, the isotopic composition of the formed compound is at equilibrium with the substrate:

$$R_P = \alpha R \quad \text{or} \quad \delta_P \approx \delta + \epsilon \quad (1.33)$$

The instantaneous product is therefore always directly linked to the substrate, which is described by the Rayleigh equations. More interesting is the isotopic composition of the accumulated product, i.e. the sum of all the fractions lost in each step. The mass of this summed up product is given by  $N_{\Sigma P} = N_0 - N$  and its isotope ratio can be derived by

integration (weighted mean of the isotope ratios  $\alpha R$  of the steps  $dN$ ). Using eq. 1.32a we obtain:

$$R_{\Sigma P} = \frac{1}{N_0 - N} \int_N^{N_0} \alpha R \cdot dN = \frac{1}{N_0 - N} \frac{\alpha R_0}{N_0^{\alpha-1}} \int_N^{N_0} N^{\alpha-1} \cdot dN \quad (1.34)$$

Carrying out the integration yields

$$\int_N^{N_0} N^{\alpha-1} \cdot dN = \frac{1}{\alpha} (N_0^\alpha - N^\alpha) \quad (1.35)$$

and thus

$$R_{\Sigma P} = \frac{N_0^\alpha - N^\alpha}{N_0 - N} \frac{R_0}{N_0^{\alpha-1}} = R_0 \frac{N_0 - N(N/N_0)^{\alpha-1}}{N_0 - N} \quad (1.36)$$

Dividing both the numerator and denominator by  $N_0$  and using the definition of  $f$  finally yields:

$$R_{\Sigma P} = R_0 \frac{1 - f^\alpha}{1 - f} \quad (1.37a)$$

Again, this can also be written in  $\delta$ -notation:

$$\delta_{\Sigma P} = (1 + \delta_0) \frac{1 - f^\alpha}{1 - f} - 1 \quad (1.37b)$$

Note in particular that for  $f = 0$  (complete conversion of the substrate into the product) we obtain  $R_{\Sigma P} = R_0$  (or  $\delta_{\Sigma P} = \delta_0$ ), as it has to be due to mass conservation.

Fig. 1.15 illustrates the evolution of the isotopic compositions of a diminishing water reservoir and the water vapour being formed as a function of the remaining water mass fraction  $f$ .

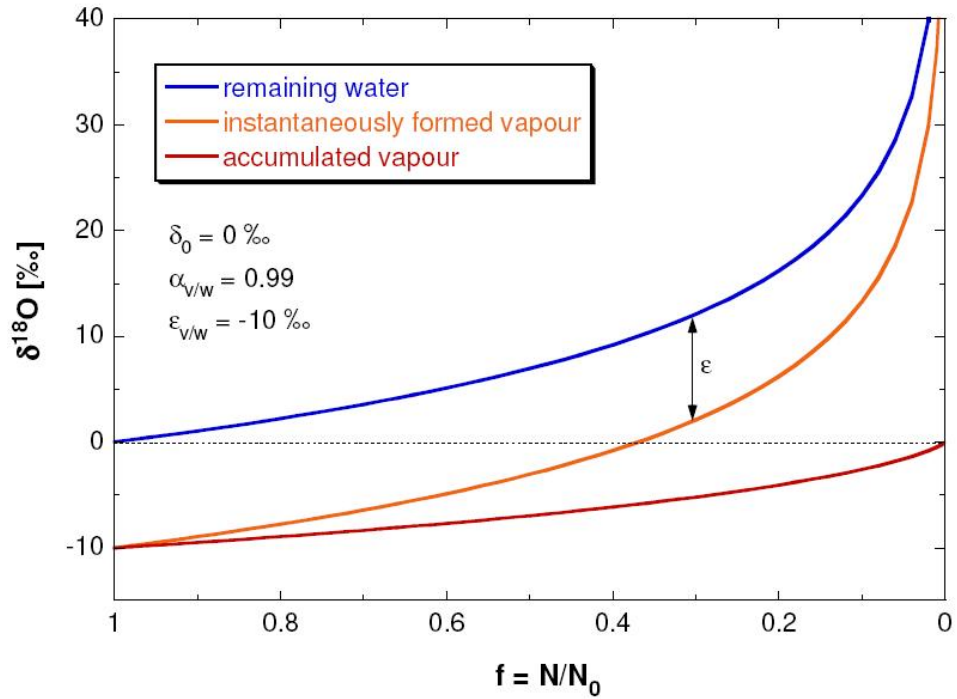


Fig. 1.15: Rayleigh fractionation during evaporation. The isotopic composition of the remaining water fraction  $f = N/N_0$  increases according to the Rayleigh equation as the vapour being lost is always lighter (by  $\epsilon = 10\text{‰}$  in this example) than the water. The isotopic composition of the accumulated vapour also increases and equals the initial composition of the water when the transformation process is complete.

# 2 Stable Isotopes of Water

## 2.1 Stable isotopes in the hydrological cycle

### 2.1.1 The Global Meteoric Water Line (GMWL)

A fundamental empirical finding in isotope hydrology was first described by Harmon Craig (1961): The isotopic composition of precipitation from all over the world, plotted in  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  graphs, is strongly correlated according to the equation:

$$\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10 \quad (2.1)$$

The line described by this equation is called the global meteoric water line (GMWL). It is the general reference with which the isotopic composition of any water samples should be compared.

The slope of the GMWL of 8 is similar to the ratio of the equilibrium fractionations of  $^2\text{H}$  and  $^{18}\text{O}$  and is due to the fact that precipitation is formed by equilibrium fractionation from atmospheric water vapour. The intercept of the GMWL of 10 ‰ is called deuterium excess (d-excess). It is due to the fact that isotope fractionation during the evaporation from the ocean into the atmosphere is partly kinetic and it is related to the relative humidity during evaporation, as will be explained below. Both values are not exact constants, different data compilations yield slightly different values (see Figs. 2.1 and 2.2).

Often, regional or local precipitation data are plotted in the same way and the resulting regression line of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  is then called the local meteoric water line (LMWL). LMWLs usually differ slightly from the GMWL.

### 2.1.2 Non-equilibrium fractionation during evaporation

The first step to explain the GMWL is evaporation from the ocean. From chapter 6 of the first part of this lecture we know that evaporation is proportional to  $(1 - h)$ , with the normalised (to the water temperature) relative humidity  $h$  (equations 6.31, 6.32). A net evaporation occurs if  $h < 1$  (which is usually the case). Because then there is a net flux from the water into the atmosphere, this is not an equilibrium process, but a kinetic effect due to the diffusive vapour transport through the atmospheric boundary layer plays a role.

The situation to describe isotope fractionation during evaporation is depicted in Fig. 2.3. The water vapour immediately at the interface is assumed to be in isotopic equilibrium with the water. A kinetic fractionation occurs as this vapour diffuses through the

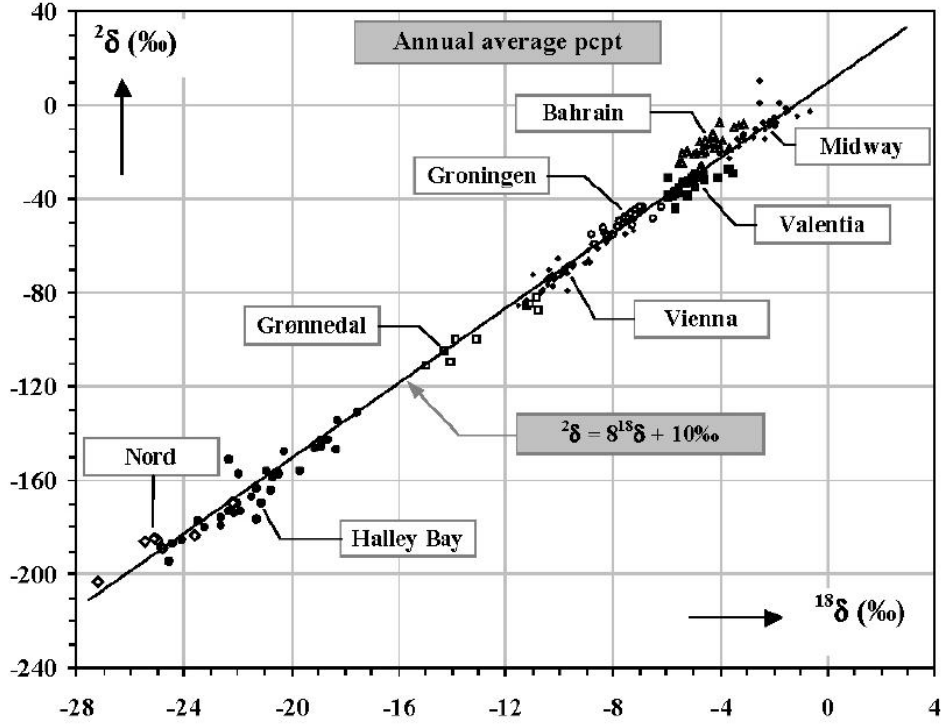


Fig. 2.1: The GMWL (from Mook [1]).

boundary layer into the free atmosphere. The details of this mixed process of equilibrium and kinetic fractionation are described by the famous Craig-Gordon model, which is not treated in detail here. The interested reader is referred to the literature (e.g. Mook [1], Vol. 2, chapter 3.2 or Clark and Fritz [3]). Only the main result is given here.

While there is isotopic equilibrium at the surface ( $\delta_v = \delta_l - \epsilon_{l/v}$ ), the total fractionation is given by  $\epsilon_{tot} = \epsilon_{l/v} + \epsilon_{dif}$ , where the diffusive effect depends on  $h$ . The  $\delta$ -value of the evaporation flux is found to be

$$\delta_E = \frac{\delta_l - h\delta_a - \epsilon_{tot}}{1 - h} \quad (2.2)$$

From this follows the slope of the so-called evaporation line in the isotope plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$ :

$$S_E = \frac{[h(\delta_a - \delta_l) + \epsilon_{tot}]_{2\text{H}}}{[h(\delta_a - \delta_l) + \epsilon_{tot}]_{18\text{O}}} \quad (2.3)$$

This slope depends on the environmental conditions ( $h$ ,  $\delta_a$ ) and the total fractionation. For  $h = 0$  (or  $\delta_a = \delta_l$ ) it equals the ratio of the total fractionation constants, which in turn depends on the parameterisation of the gas exchange (vapour exchange) coefficient as a function of molecular diffusivity. Assuming a dependence with  $D^{1/2}$ , the slope is found to be about 3.8. If the system were closed and allowed to reach equilibrium, the slope of the evaporation flux would have to equal that of the condensation and both would be given by the ratio of the equilibrium fractionations of  $^2\text{H}$  and  $^{18}\text{O}$ , which is about 8 (depending on temperature).

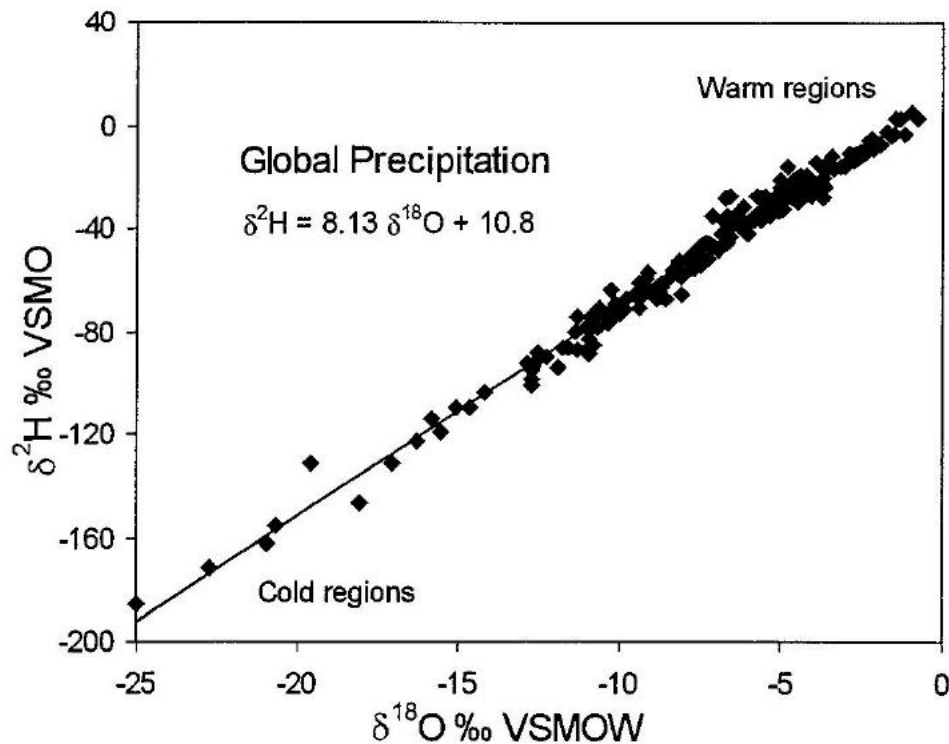


Fig. 2.2: Another representation of the GMWL (from Clark & Fritz [3]).

In summary, evaporation produces vapour whose isotopic composition in the isotope plot lies along a line with slope  $S_E$  which is generally smaller than 8 and depends on humidity. Such a line is called evaporation line (Fig. 2.4). The vapour is of course depleted relative to the water reservoir, and the remaining water shifts in opposite direction. The shift of the water reservoir is important for limited reservoirs such as (surface layer of) lakes, rivers, or groundwater, but not for the ocean as a whole.

### 2.1.3 Equilibrium condensation of atmospheric vapour

The second step leading to the GMWL is condensation of water vapour in the atmosphere to form precipitation. In the clouds, water droplets can continuously exchange with the surrounding moisture, thus the fractionation between raindrops and atmospheric moisture can be assumed to be in equilibrium. This gives rise to the slope of about 8 of the GMWL, as the equilibrium fractionation of  $^2\text{H}$  is about 8 times larger as that of  $^{18}\text{O}$ .

As the initial amount of water vapour in the air is continuously diminishing (rainout of atmospheric moisture), a Rayleigh-type fractionation occurs during condensation in clouds. Because the precipitation is always enriched relative to the vapour, the moisture becomes continuously more depleted, following a Rayleigh equation (Fig. 2.5). The fraction  $f$  of remaining water vapour is given by the ratio of the actual vapour pressure to the initial vapour pressure. Rainout occurs when air is cooled, so that the saturation

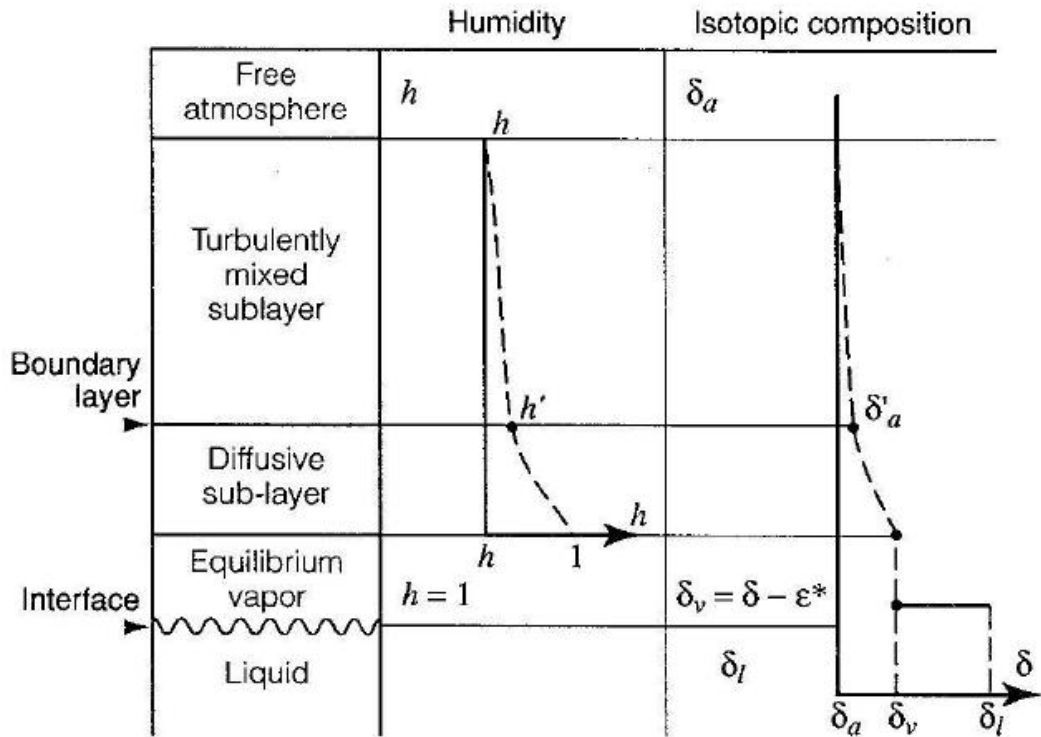


Fig. 2.3: Vertical profiles of the normalized humidity  $h$  (relative humidity referred to the water temperature) and the isotopic composition of water vapour above a water surface, used to derive a model for isotope fractionation during fractionation (Craig-Gordon model). Subscripts: l = liquid (water), v = vapour, a = atmosphere. From Clark and Fritz [3].

vapour pressure diminishes and the moisture is forced to condensate.

### 2.1.4 Explanation of the GMWL

Combining the two steps from above, we finally obtain an explanation of the GMWL. In the first step, evaporation from the (tropical) ocean forms then initial vapour content of the air. As the mean value of  $h$  is less than 1 (about 0.85), this first step contains a kinetic isotope effect and does not follow a slope of 8. As a result, the first water vapour lies to the left of a line with slope 8 through the origin of the isotope plot (seawater, Fig. 2.6). This shift explains the deuterium excess, as a line with slope 8 through the first vapour formed at  $h = 0.85$  yields a  $\delta^2\text{H}$ -intercept of  $\tilde{10} \text{‰}$ . The deuterium excess depends on humidity, with a higher excess indicating dryer conditions during evaporation (Fig. 2.7). The d-excess of  $\tilde{10} \text{‰}$  of the GMWL thus indicates that the mean relative humidity during evaporation from the ocean is about 85%. Regionally, the d-excess of precipitation can deviate from the global value, indicating different conditions in the moisture source regions. Starting from the first vapour, precipitation is formed by equi-

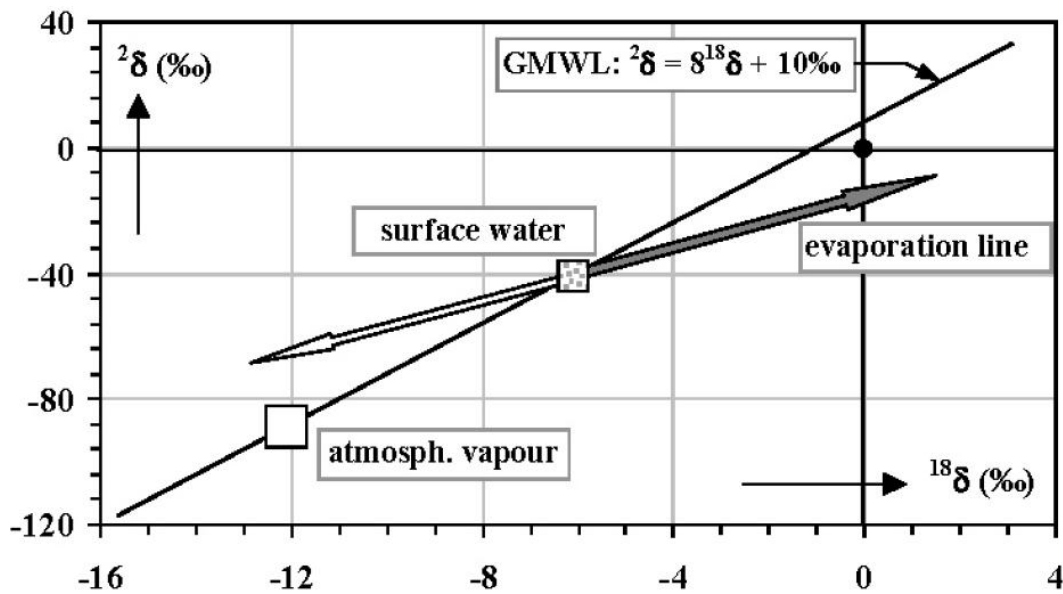


Fig. 2.4: Evaporation line originating from evaporation of surface water. Both the original water and the atmospheric moisture are assumed to lie on the GMWL. The slope of the evaporation line is smaller than 8 (the slope of the GMWL). From Mook [1].

librium condensation in the clouds. This shifts the isotopic composition of both the rain and the residual vapour along a line with slope 8, which is the GMWL. The first rain is almost back to the origin, but slightly more depleted in  $^2\text{H}$  than in  $^{18}\text{O}$ . The remaining vapour becomes ever more depleted as the rainout continues. Condensation and precipitation are forced by cooling, as the saturation vapour pressure drops rapidly with lower temperature. Continuous condensation steps define a Rayleigh process, during which the atmospheric vapour and consequently the precipitation formed from it become increasingly depleted. Both vapour and precipitation move downwards along the GMWL. This is why precipitation in cold regions plots on the lower left in the isotope plot (Fig. 2.2).

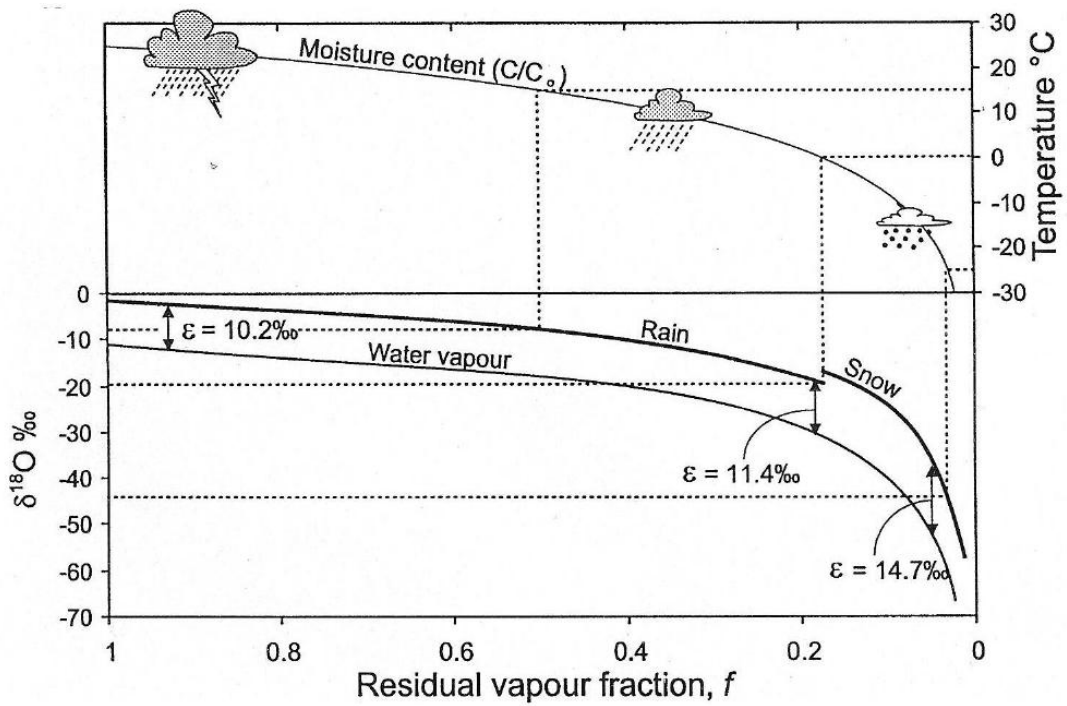


Fig. 2.5: Evolution of the isotopic composition of the atmospheric water vapour and the resulting precipitation as a function of the residual vapour fraction  $f$  (from Clark & Fritz [3]).

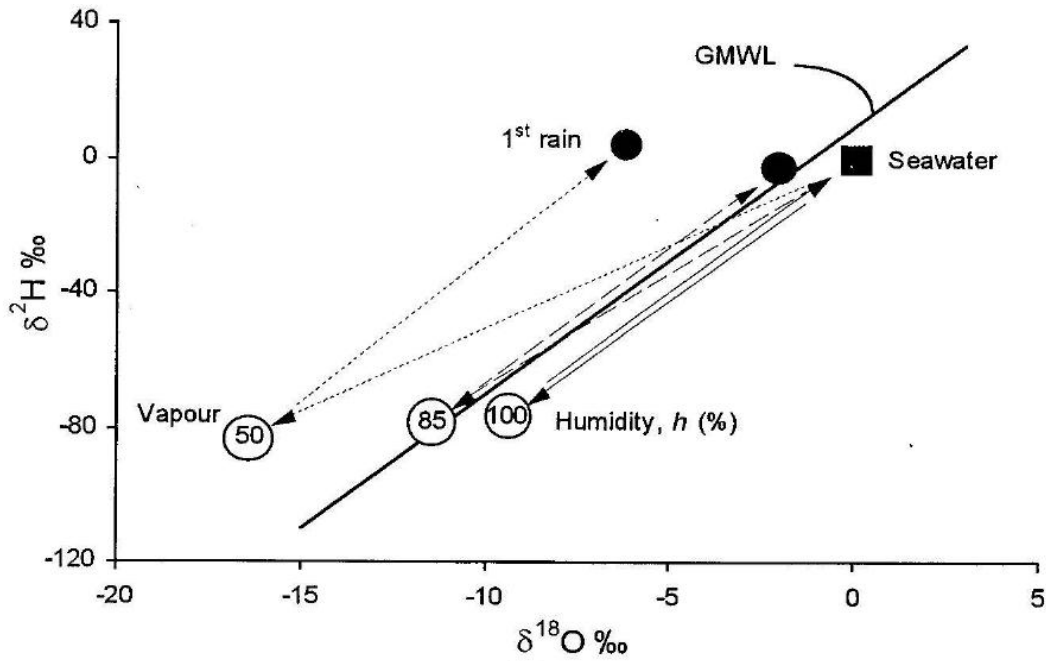


Fig. 2.6: Evolution of the isotopic composition of the atmospheric water vapour and the resulting precipitation in the isotope plot. An initial non-equilibrium evaporation step (at  $h = 0.85$ ) followed by equilibrium fractionation during the subsequent condensation steps explains the GMWL (from Fritz & Clark [3]).

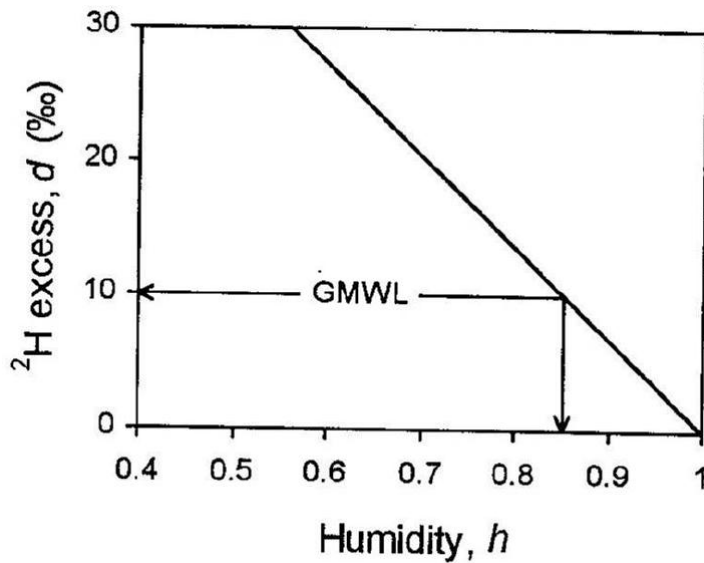


Fig. 2.7: D-excess resulting from the initial non-equilibrium evaporation as a function of the normalised humidity  $h$ . The empirical value of the GMWL of 10‰ indicates a mean relative humidity of 85% during evaporation from the ocean (from Fritz & Clark [3]).



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- [2] Faure, 1986: Principles of Isotope Geology
- [3] Clark & Fritz, 1997