Stable water isotopes and the physical environment

Les isotopes stables de l’eau et l’environnement physique

Roland Souchez, Réginald Lorrain and Jean-Louis Tison
Stable water isotopes and the physical environment

Les isotopes stables de l’eau et l’environnement physique

Roland Souchez, Réginald Lorrain and Jean-Louis Tison

This paper partially derives from lectures given by the first author in the framework of a «Francqui Chair» he obtained at the Université Catholique de Louvain during the academic year 1999-2000.

Introduction

1. The use of stable water isotopes for studying the physical environment can be extremely helpful. Two of the most important environmental issues that will affect human development in the course of the twenty first century, namely water resources and man-induced climatic changes, can be dealt with successfully by analysing the isotopic composition of the water molecule.

2. Atoms having the same number of protons, i.e. also the same number of electrons, are from the same chemical species. They can however differ from each other by the number of neutrons. In this case, they are isotopes from the same element and have identical chemical properties but different physical properties since their masses are different.

3. Among the isotopes making up the water molecule, the most abundant are two isotopes of hydrogen (1H or H, with one proton, and 2H or D, called deuterium, with one proton and one neutron) and two stable isotopes of oxygen 16O and 18O. This gives rise to the following most abundant water molecules: H216O, by far the most abundant, H218O and HDO. Their proportions vary in the different terrestrial reservoirs: atmosphere, ocean, ice sheets, lakes, rivers, groundwaters or sea ice. This results from isotopic fractionations that are mainly due to phase changes.
Isotopic fractionation during phase changes

When evaporation of water occurs, water vapour contains at equilibrium less molecules of $H_{2}{^{18}}O$ or HDO in proportion to $H_{2}^{16}O$ than the liquid water from which it derives. The partition is given by an equilibrium fractionation coefficient which is the ratio of the heavy to the light isotope in the liquid phase to the same isotopic ratio in the vapour phase. Such coefficients, either for deuterium or oxygen 18, have values higher than one because vapour pressures of the different water molecules are inversely related to their mass.

The isotopic composition of water is generally expressed in reference to a standard called SMOW or Standard Mean Ocean Water. The isotopic composition is given in $d$ units in per mil so that

$$\delta^{18}O = \frac{{^{18}O}({\text{sample}}) - {^{18}O}({\text{SMOW}})}{{^{18}O}({\text{SMOW}})} \times 1000$$

And

$$\delta D = \frac{D/H({\text{sample}}) - D/H({\text{SMOW}})}{D/H({\text{SMOW}})} \times 1000$$

The isotopic composition of standard sea water is thus $\delta^{18}O = \delta D = 0\text{‰}$.

Since, during evaporation of sea water, water vapour is impoverished in heavy isotopes (D or $^{18}O$), its $d$-values are negative. By contrast, condensation in the atmosphere results in an enrichment of heavy isotopes as compared with vapour. Therefore, after the condensed water is removed by a first precipitation event, the residual water vapour becomes more negative and further successive precipitation events are thus more and more impoverished in heavy isotopes. There is thus a reservoir effect (Clark and Fritz, 1997) giving rise to more negative $d$-values in precipitation as distance from the vapour source increases. Water vapour is mainly produced by evaporation of oceanic water in dry tropical regions where high temperatures and low relative humidity of the air favour this phase change. As a result, there is thus a latitude effect: snow in the polar regions will be more depleted in heavy isotopes ($\delta^{18}O$ values around -20 to -50‰) than precipitation in the temperate regions ($\delta^{18}O$ values around -5 to -10‰) which are, in turn, more depleted in heavy isotopes than rain in the tropics ($\delta^{18}O$ values between 0 ‰ and -5‰). The most negative $d$-values in precipitation are thus found in the Polar regions. Similarly, there is an altitude effect, precipitation at higher altitude representing a later stage in the evolution of an air mass forced to climb a mountain slope than precipitation at lower altitude. Therefore the $d$-values of precipitation are more negative at higher altitude.

The equilibrium fractionation coefficient, either for deuterium or oxygen 18, is inversely related to the temperature, being higher at lower temperature. This effect can be used for
palaeoclimatic reconstruction since the isotopic composition of the ice layers present in polar ice sheets represent past precipitation which has occurred at different temperatures.

10 A further step can be made if, instead of considering the water isotopic composition either in oxygen or in hydrogen, a co-isotopic study, both in δD and δ18O, is undertaken. In a δD-δ18O diagram, rain water samples are aligned on a straight line with a slope of about 8 called the Meteoric Water Line (MWL) which is given by the equation δD = 8 δ18O + d. From one specific region to another, this equation only differs by the value of the independent term d. This d value is called the deuterium excess. If the temperature in the region of the vapour source is higher and/or the relative air humidity lower, the deuterium excess has a higher value. For instance, deuterium excess in rain water from the eastern Mediterranean region is about 22‰ while it is roughly 13-15‰ in the western Mediterranean basin and about 10‰ in the Atlantic Ocean region, west from Portugal. As a result, when circumstances are favourable, the origin of precipitation can be determined from the deuterium excess value.

11 Now, let us take a water sample that plots on the local Meteoric Water Line and let this water partly evaporate. A kinetic isotope effect will appear during this phase change due to differences between diffusivities in air of the different isotopic water molecules. This kinetic effect is more effective when the temperature is higher and the air relative humidity lower. The points representing residual water samples will then be aligned in a δD-δ18O diagram on a straight line with a slope lower than 8, called the evaporation line. The distance along this line of a residual water sample to the intersection with the local MWL is a function of the amount of evaporation (Clark and Fritz, 1997).

12 The phase change from liquid water to ice also gives rise to isotopic fractionation. The ratio of the enrichment factors for deuterium and for oxygen 18 respectively is however less than 8. It can thus be thought that samples of ice resulting from freezing of liquid water will be aligned on a straight line with a slope lower than the MWL. Experimental work has shown the real existence of this line called a freezing slope (Jouzel and Souchez, 1982; Souchez and Jouzel, 1984). In the course of freezing of a finite reservoir, selective incorporation of heavy isotopes into the ice occurs and the residual water becomes progressively impoverished in heavy isotopes. Hence, successively formed ice layers show progressively more and more negative d-values along the freezing slope. This freezing slope is also dependent on the initial isotopic composition of the water, being lower is initial water has more negative d-values.

13 The example given below will show how the isotopic characteristics described above can be used as powerful tools for the study of the physical environment.

Use of water isotopes in the hydrological study of a drainage basin

14 In a drainage basin pollutants, like nitrates or phosphates, circulate either in ground- or surface water. A direct relationship between discharge and nitrate concentration is often a clear indication of the prominent role of runoff waters which are relatively more important at high discharge. By contrast, an inverse relationship between discharge and phosphate concentration could indicate the prominent role of groundwater in transporting these compounds, groundwater contribution to river discharge being
dominant or even exclusive at low discharge. It is thus worthwhile to know precisely during a specific time interval the relative contribution to the river discharge of groundwater and runoff water, either in the form of surface runoff or hypodermic runoff just below the soil surface. After subtracting the amount of rain water falling directly into the river, it is very often possible by the use of water isotopes to deduce such contributions in the river discharge at a gauging station.

Infiltration allows rain water to reach groundwater from the soil surface into the soil via fissures and soil pores. This process is responsible for damping the seasonal $\delta^{18}O$ signal with depth. A critical depth exists below which groundwater has a constant isotopic composition in the course of time. This critical depth is usually about 10 m. The absence of isotopic variations below this depth is due to the relatively high residence time of water in the soil and in the groundwater. For example, the attenuation of seasonal $\delta^{18}O$ signal at various depths during infiltration in an alluvial deposit near Munich in Germany has been reported by Eichinger et al. (1984) and is clearly visible in figure 1.

Figure 1. Attenuation of seasonal $\delta^{18}O$ signal at various depths during infiltration through an alluvial deposit near Munich.

In the case concerning the drainage basin of a small river ending into lake Erie in North America (Fig. 2) the groundwater has a constant $\delta^{18}O$ value of -11.5‰ (Clark and Fritz, 1997). A summer flood was recorded at the gauging station, due to heavy rain with a $\delta^{18}O$ value of -6.8‰. This isotopic composition is also that of the runoff waters because of the low residence time involved. Within the fifteen days considered for the study, the river had a maximum value of -9.3‰ during the peak discharge and reached a $\delta^{18}O$ value of -10.8‰ during the flood decrease. A simple isotope mass balance allows to estimate runoff and groundwater contribution at peak discharge and at the moment when the $\delta^{18}O$ of the river reached -10.8‰. Such contributions were respectively 53% and 85% groundwater contribution to the river discharge. As seen in figure 2, a groundwater discharge curve can be drawn and the storm or runoff flow can be evaluated at each time (Clark and Fritz, 1997).
Evaporation, transpiration and salinization in an arid area

Depending on the physical conditions prevailing in the air above the water and the importance of the derived kinetic isotopic effect during evaporation, residual water samples are aligned in a $\delta^D - \delta^{18}O$ diagram on an evaporation line, with a slope lower than that of the local MWL. Such an evaporation line can be established for a specific environment from the result of a pan experiment in which evaporation takes place in a limited water reservoir and successive $d$-values are measured in the residual water. Since evaporation is conducive to a salinity increase, it is worth to plot the $\delta^D$ values of the residual waters versus their respective chlorine content. Such a procedure was used for a region of irrigated fields in the Nile Delta (open circles in figure 3). By contrast, transpiration from the vegetation does not lead to apparent isotopic fractionation. Indeed, it can be shown that the limited water reservoir present in the leave is enriched in heavy isotopes and a steady state is reached by which the water vapour produced has the same isotopic composition as soil water. Therefore transpiration can be taken as a process without apparent isotopic fractionation. Water having been subjected to transpiration thus shows the same isotopic composition in the course of time but an increase in its chlorine content. Now, water samples from these Egyptian irrigated fields present such a behaviour (Fig. 3) indicating the prominence of transpiration in the increase in dissolved chlorine. In this case, salinization of the soil consecutive to water losses to the vapour phase is mainly the result of plant transpiration rather than direct evaporation of the water in the irrigation canals (Simpson et al., 1987). Water isotopes have thus been used with success for analysing the processes responsible for soil salinization in this arid area.
Figure 3. $\delta D (= d^3H)$ versus chlorine for Nile Delta agricultural drainage and evaporation pan experiment in the same region. Inset plot shows the slope of the evaporation line for the pan data.

Recharge of aquifers

Aquifers in mountainous regions have an isotopic composition that can be affected by the altitude effect described above. Such an aquifer is exploited by the company producing the mineral water of Evian in the French Alps, south of the town of the same name. This aquifer is recharged by precipitation from water vapour rising along the steep slopes fringing the southern shore of Lake Geneva.

One parameter of utmost importance for a mineral water is its low content in nitrates. It is critical to forecast the influence of certain human activities such as pastoralism on groundwater quality. Excluding areas where the groundwater is recharged from adverse human economic developments is thus a high priority for this company. By a careful mapping of the $\delta^{18}O$ distribution in precipitation, recharge zones have been localised and afforested so that nitrate producing pastoral activities have been excluded from these critical areas.

Another example of successful use of stable isotope analyses in the study of aquifers can be found in a completely different environment: the Negev region in the Middle East. Deuterium excess of rain in this region, like in other eastern Mediterranean countries, is about 22‰. Deuterium excess in the aquifer is however about 10‰. Rains having such a low deuterium excess are extremely rare at present but occur only by strong south westerly winds bringing Atlantic water vapour ($d = 10‰$) in the area. Such meteorological situations were much more frequent during the Last Ice Age. The aquifer is considered as having been formed at that time and it is thus largely composed of fossil water. In this case, this isotopic study shows that there is a high risk for this aquifer to be overexploited.
Antarctic ice as climatic archive

Polar ice is a remarkable archive of our environment. This is notably the consequence of the following features.

First, the oxygen or hydrogen isotopic composition of the ice crystals is dependent on the temperature of their formation. Since the equilibrium fractionation coefficients for deuterium or oxygen 18 are temperature dependent, a seasonal effect is displayed in polar precipitation. Winter snow has more negative d-values than summer snow. This, incidentally, can be used for dating the ice by counting the annual fluctuations of the d-values. At larger time scales a colder climatic period is thus conducive to more negative d-values while a warmer period is characterised by less negative d-values. Since, in polar regions, there is an excellent correlation between surface temperature and d-values of the snow precipitated, it is possible to reconstruct the precise temperature of a past period from the d-values of an ice layer which derives from the snow of that period. The isotopic composition of an ice layer is thus the equivalent of a palaeothermometer.

Secondly, during ice formation, air initially present in the pores of the snow cover is progressively entrapped as gas bubbles within the ice. The composition of these bubbles gives the composition of the atmosphere at the time of their formation. As ice sheets contain ice from successive glacial and interglacial periods, the composition of the air present in an ice layer, either in the form of gas bubbles or in the form of gas hydrates (in the high pressure deeper parts of the ice sheet), thus reflects the composition of the atmosphere of the corresponding period. Analysing the gases extracted from an ice layer, for instance greenhouse gases, gives therefore the opportunity to reconstruct the atmospheric composition of the past.

The Vostok ice core is the result of a deep drilling conducted in East Antarctica near the Russian Vostok station. This station is located on the ice plateau, far from coastal areas, at an altitude of about 3500 m above sea level. The ice thickness at the drilling site is about 3700 m. From the surface to 3310 m depth, where the ice is 420 000 years old, the climatic record in the ice is of very good quality. The time scale is dependent on the annual snow accumulation rate. Since it is very low at Vostok, the time span is very large. Annual ice layers are thinned at depth because of ice deformation so that one year accumulation near the ice surface corresponds to a 25 mm thick ice layer while, at 3000 m depth, one year accumulation corresponds to a 3 mm thick ice layer. Therefore it is not possible to obtain a fine resolution of climatic events at depth. The Vostok ice core records the main climatic events in the last 420 000 years but no climatic variation of low periodicity can be detected.

A striking feature of the climatic record given by the Vostok ice core in the last 420 000 years is the close correspondence between the temperature deduced from the isotopic composition of the ice and the concentration in greenhouse gases (CO₂ and CH₄) present in the ice (Fig. 4). The climate system oscillates with a periodicity of about 100 000 years between an interglacial state with a temperature close to present-day values (or 1 to 2°C higher) and a glacial state with temperatures 8 to 10°C lower than today. This oscillation corresponds to the periodicity of the earth’s orbit eccentricity around the sun which produces insolation changes. Orbital forcing causes major climatic variations at the scale of 100 000 years but it is not the only factor to consider. Greenhouse gases indeed act as a strong amplifier. Between glacial and interglacial periods, the composition of the
atmosphere in greenhouse gases oscillates between two well defined values: about 180 ppmv CO$_2$ at each glacial period and 280-300 ppmv CO$_2$ at each interglacial period while for CH$_4$ the typical values are 320-350 ppbv and 650-770 ppbv (Petit et al., 1999). A sawtooth record is displayed either in temperature or in greenhouse gases: the decrease towards the minimal values of glacial times is slower than the increase towards interglacial levels. As seen from the results of the Vostok ice core, greenhouse gases are clearly influencing earth’s climate.

The present-day CO$_2$ concentration in the atmosphere (about 365 ppmv) was never reached in the past 420 000 years. There is thus little doubt that Man, by his activities, is conducting an experiment in the atmosphere which was never realised in Nature during this time period.

Figure 4. The isotopic temperature, the CO$_2$ and CH$_4$ records in the Vostok ice core from the surface to 3310 m depth. The temperature deduced from the d-values is given as the temperature difference with the present-day temperature arbitrarily fixed at 0°C.

Subglacial Lake Vostok

Lake Vostok is a subglacial lake situated at the ice-bedrock interface in the vicinity of the Russian station cited above. It has been discovered by airborne radio-echo-sounding. Ice is transparent to radar radiation of certain wavelengths. Using these wavelengths allows to define the subglacial topography and to detect subglacial water masses like Lake Vostok. The area of this lake is approximately 14 000 km$^2$, nearly half the size of Belgium, and is about 700 m deep. It can be compared in dimensions with Lake Ontario, one of the American Great Lakes. It is elongated in a north-south direction; its ice ceiling is tilted, being at 750 m below sea level under 4300 m of ice in the north and only at 250 m below sea level under 3750 m of ice in the south near Vostok Station.

Below 3310 m depth, the Vostok ice core does not show an undisturbed climatic and environmental record anymore. Our research team has been involved in the study of this deepest part of the ice core. From 3310 m to 3539 m depth, there are arguments indicating intense ice deformation modifying the isotope climatic signal. This is the reason for the damping of isotope variations ($\delta$D in this case) in this depth interval (Fig.
5). Below 3539 m depth, there is a sudden change in ice properties (Jouzel et al., 1999). Among others, gas content decreases to near zero values, d-values increase sharply at the transition and deuterium excess values shift from 14‰ to 7 or 8‰. The sharp decrease in deuterium excess at 3539 m depth and the other characteristics mentioned above indicate that the ice below this depth results from freezing of Lake Vostok waters. Indeed, as indicated above, the deuterium excess of an ice sample is its δD value minus eight times its δ18O value. In a δD - δ18O diagram samples of ice due to water freezing, and not from dry metamorphism of snow, are aligned on a freezing slope rather than on the MWL on which ice layers resulting from snow precipitation at the ice sheet surface are aligned. Since the freezing slope has a value lower than 8, ice samples enriched in heavy isotopes (showing higher d-values), due to refreezing of water in a large reservoir like Lake Vostok, have all a lower deuterium excess. Moreover, freezing of water gives rise to ice nearly devoid in gases. It has been calculated that more than 200 m of lake ice is present above the liquid water of the lake. Water circulation in the lake involves melting at the base of the ice sheet where the ice ceiling of the lake is lower i.e. where the pressure is higher. The meltwater produced rises along the tilted ice-water interface and becomes supercooled. Frazil ice crystals are produced within the water plume and accrete at the bottom of the ice sheet. This produces lake ice where the ceiling is higher, i.e. the pressure lower, which is the case underneath Vostok Station (Souchez et al., 2000). As soon as it was demonstrated that lake ice was present, a thorough examination began to detect if micro-organisms which could thrive in the lake water had been incorporated into the lake ice. At this stage, only contradictory results have been obtained by different teams.

Figure 5. Change in ice properties at 3539 m depth in the Vostok ice core between ice of meteoric origin and lake ice (mbs = meters below the surface).
Conclusion

The theory of stable water isotopic fractionation summarized in this paper and the examples given make clear that such a scientific approach could be a powerful tool to understand many processes active in various physical environments.

BIBLIOGRAPHY


NOTES

1. The ratio of the enrichment factors for deuterium and oxygen 18 respectively, enrichment factors being equilibrium fractionation coefficients minus one (for SMOW).
ABSTRACTS

This paper presents the characteristics of the fractionation of water isotopes which occurs during evaporation and freezing of water. It shows how these characteristics can be used for studying some aspects of the physical environment, namely hydrological and glaciological issues. On the one hand, case studies regarding the hydrological cycle are considered. They deal with the relative contributions of runoff and groundwater to the discharge of rivers, of plant transpiration and direct evaporation in the arid regions atmosphere and of different water sources in aquifer recharge. On the other hand, the paper explains how the water isotopes are used in the study of the Antarctic Ice Sheet as climatic archives as well as how they allow to understand the formation of more than 200 m of lake ice present above the liquid water of subglacial Lake Vostok in East Antarctica. This case study approach demonstrates that stable water isotopes can be an ideal tool to account for many processes active in the physical environment.

INDEX

**Mots-clés:** isotopes stables, hydrologie, glaciologie, archives climatiques, Antarctique, environnement aride, environnement alpin, Lac Vostok

**Keywords:** stable isotopes, hydrology, glaciology, climatic archives, Antarctica, arid environment, Alpine environment, Lake Vostok

AUTHORS

ROLAND SOUCHEZ

Département des Sciences de la Terre et de l’Environnement, Université Libre de Bruxelles, rsouchez@ulb.ac.be