

GLACIERS AS CLIMATE ARCHIVES – ICE CORE STUDIES WITH SPECIAL RELEVANCE TO ISOTOPIC APPLICATIONS

Thamban Meloth

Cryospheric Science Division
National Centre for Antarctic and Ocean Research
Headland Sada, Goa 403 804

1. Cryosphere - its components and significance

Cryosphere includes those portions of the Earth's surface where water is in solid form. This includes all kinds of ice, snow and frozen ground such as permafrost. The cryosphere is an integral part of the global climate system with important linkages and feedbacks generated through its influence on surface energy and moisture fluxes, clouds, precipitation, hydrology, atmospheric and oceanic circulation. It is strongly influenced by temperature, solar radiation and precipitation, and, in turn, influences each of these properties. It also has an effect on the exchange of heat and moisture between the Earth's surface (land or sea) and the atmosphere, on clouds, on river flow (hydrology), and on atmospheric and oceanic circulation. Changes in the ice mass on land have contributed to recent changes in sea level. The snow pack above the thick ice in these regions gives a wealth of information on the interactions between the cryosphere and atmosphere. Additionally, a plethora of microbial lives orchestrate some of the key chemical reactions in cryospheric regions governing the Earth's climate through various feedback mechanisms.

Snow cover has the largest areal extent of any component of the cryosphere, with a mean annual areal extent of approximately 26 million km². Most of the Earth's snow-covered area is located in the Northern Hemisphere, and temporal variability is dominated by the seasonal cycle; Northern Hemisphere mean snow-cover extent ranges from 46.5 million km² in January to 3.8 million km² in August (Robinson et al., 1993). Compared to this, ice sheets have the greatest potential source of fresh water, holding approximately 77% of the global in total. Fresh water in ice bodies corresponds to 71 m of world sea-level equivalent, with Antarctica accounting for 90% of this, Greenland almost 10%, and other ice bodies and glaciers less than 0.5%. Sea ice, formed by freezing of seawater, covers much of the polar oceans. It exhibits considerable seasonal, regional, and inter-annual variability in both hemispheres. Seasonally, sea-ice extent in the Southern Hemisphere varies by a factor of 5, from a minimum of 3-4 million km² in February to a maximum of 17-20 million km² in September (Gloersen et al., 1993). The seasonal variation is much less in the Northern Hemisphere where the confined nature and high latitudes of the Arctic Ocean result in a much larger perennial ice cover, and the surrounding land limits the equator-ward extent of wintertime ice. Northern Hemisphere ice extent varies by only a factor of 2, from a minimum of 7-9 million km² in September to a maximum of 14-16 million km² in March (Gloersen et al., 1993). Seasonally frozen ground, like snow, covers a large expanse of the globe. Its depth and distribution varies as a function of air temperature, snow depth and vegetation cover, ground moisture, and aspect. Hence it can exhibit high temporal and spatial variability. The area of seasonally frozen ground is not mapped annually. Permafrost (perennially frozen ground) may occur where the Mean Annual Air Temperature (MAAT) is less than -1°C and is generally continuous where MAAT is less than -7°C . Although not accurately known, it is estimated that permafrost underlies about 24.5% of exposed Northern Hemisphere land areas.

The cryosphere acts as both an indicator and integrator of climate variability and change. Snow and ice are not simply polar phenomena, but are global in occurrence. Majority of the world's ice volume is in Antarctica, principally in the East Antarctic Ice Sheet. In terms of areal extent, however, snow covers up to 60% of the Northern Hemisphere land area, about 80% of global fresh water is contained in ice sheets and glaciers, and permanently frozen ground underlies 25% of the global land surface (Robinson et al., 1993). The processes operating in the coupled cryosphere-climate system involve three time scales: intraseasonal-interannual, decadal-centennial, and millennial or longer. The inevitability of global warming as confirmed by the Intergovernmental Panel on Climate Change in its Fourth Assessment Report (IPCC, 2007), highlights the importance of monitoring and evaluation of climate change effects on glaciers and ice sheets of polar regions and elsewhere. Ice caps and ice sheets continuously record the chemical and physical nature of the Earth's atmosphere and often provide climate records with seasonal, annual, decadal and centennial resolutions. In order to understand these changes better, it is essential to evaluate the climate variability from a perspective provided by the long-term proxy climate records.

2. Main components of a glacier: snow, firn and ice

The glaciers and its various building blocks are made of water molecules that are composed of one oxygen and two hydrogen atoms (H_2O). In solid ice, the individual molecules are linked with one another through so-called hydrogen bonding, which is based on electrostatic forces; with each water molecule having two bonds available for sharing with neighbouring water molecules, the molecules form a crystal lattice that is composed of layers of molecules. Since these layers are easily separated and may glide against one another, ice offers little resistance to deformation forces, which is important for the way a glacier flows; within these layers molecules are arranged in a six-fold (hexagonal) symmetry which is also reflected in the appearance of individual snow flake crystals (Fig. 1).

Once snow crystals have been deposited on the ground, they are subject to a number of important changes. First, the delicate, highly branched dendritic crystals may be blown around by the wind such that breakage of crystals results in much smaller particles which can be compacted to a much larger degree (Fig. 1). Second, even if not redistributed, the highly branched crystals with a very high surface area in relation to their volume tend to change their shape (in a process called metamorphism) to a more compact spherical shape, which corresponds to a decrease in the surface area relative to the volume of ice; this process is driven by the tendency of substances to minimize their surface energy similar to the way small droplets of water tend to join into larger droplets, e.g. with rain flowing down a window pane. Further ageing and summer melt result in the transformation of snow into more compact, higher density firn. As layer upon layer of snow is deposited on a glacier or ice sheet, the firn is compressed under the weight of the overlying snow and ice (with the density increasing) until eventually the air space in between the grains of ice is compressed to individual small bubbles (Fig. 2).

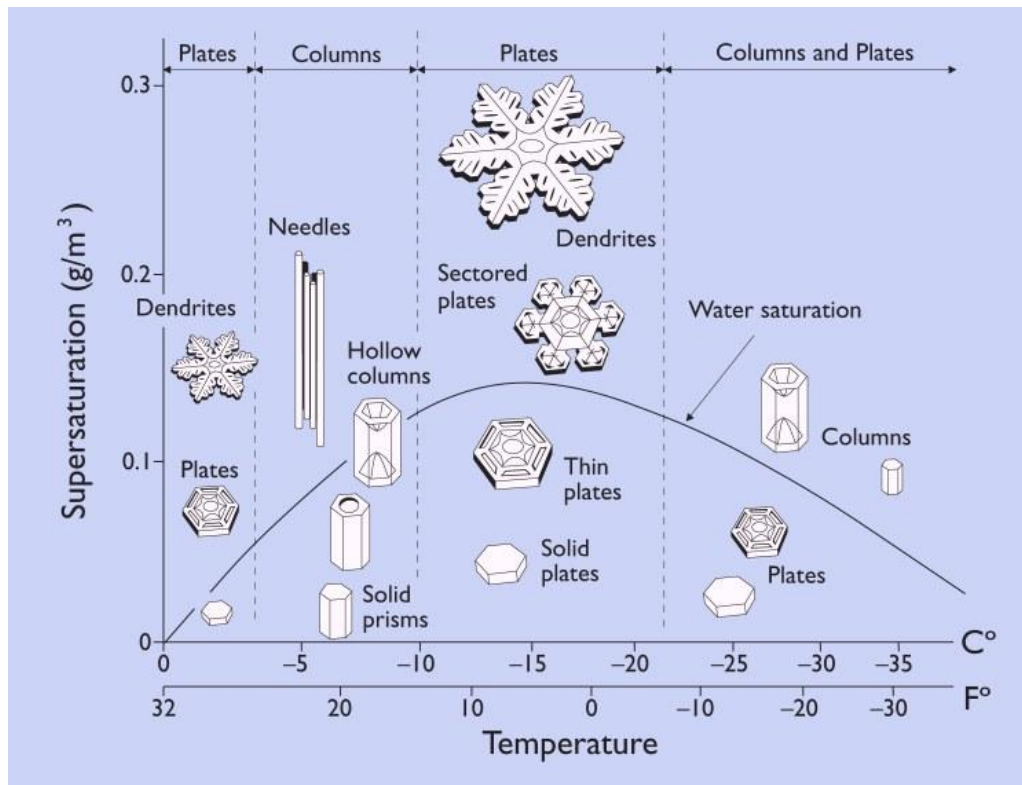


Fig. 1 Morphology diagram showing that ice crystal morphology is dependent on temperature and water vapor saturation over ice.

This transition from an open pore space, which is connected to the surface of the glacier (and hence the atmosphere), to isolated pores which are completely enclosed corresponds to the transition from firn (with an open pore space) to ice (with a closed pore space). The firn-ice transition usually occurs at an ice density of approximately 0.83 g/cm^3 (830 kg/m^3) (Table 1). With more and more snow layers deposited in the accumulation area of a glacier or an ice sheet, the transformation of snow to firn to ice takes place, with the ice preserving important information about the depositional history and the environmental conditions prevailing at the time the snow fell and was deposited.

Type	Density (g/cm^3)
Fresh snow (falling under calm conditions)	0.05 - 0.07
Damp new snow	0.1 - 0.2
Settled snow	0.2 - 0.3
Depth hoar	0.1 - 0.3
Wind-packed snow	0.35 - 0.4
Firn	0.4 - 0.83
Very wet snow and firn	0.7 - 0.8
Glacier ice	0.83 - 0.92

Table 1. Typical densities of snow, firn and ice at different stages of development (after Paterson, 1994).

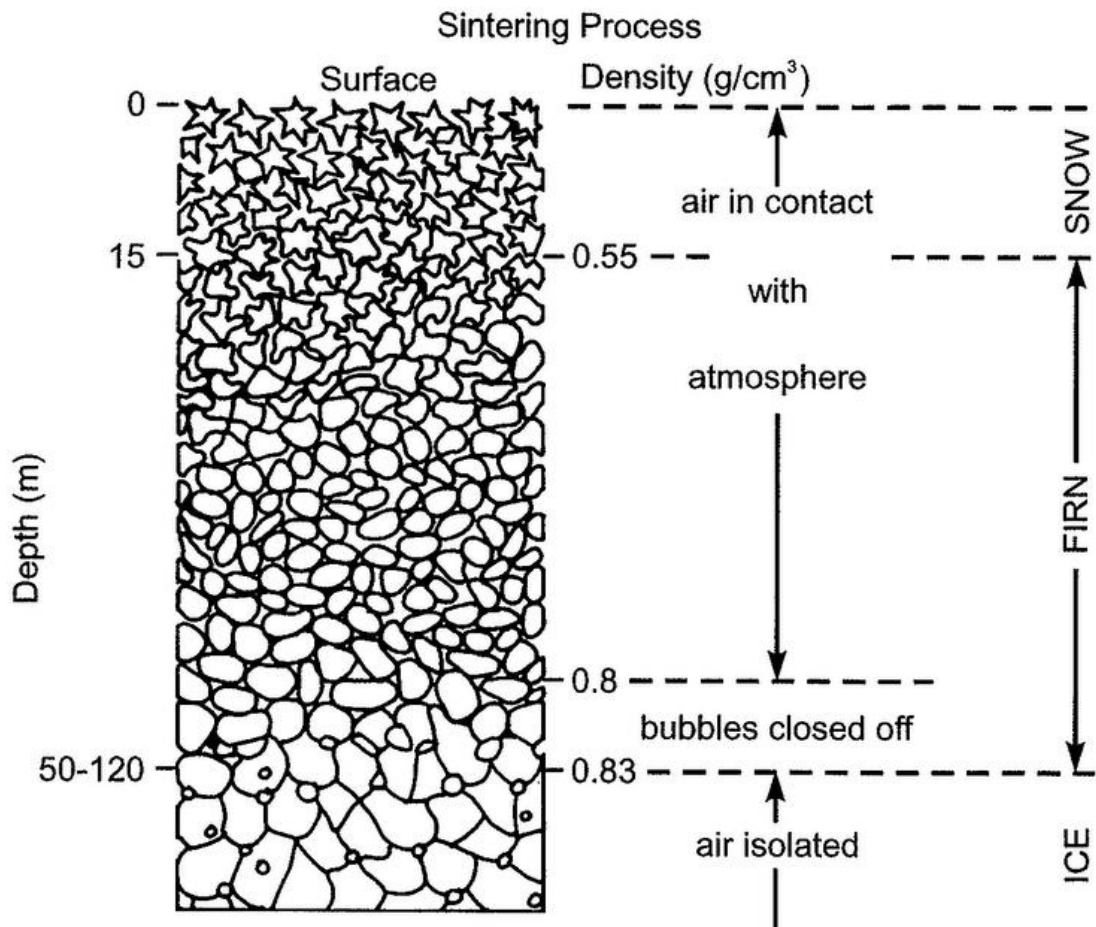


Fig. 2. Metamorphosis of snow to glacier ice and associated changes in density (Schwander, 1996).

3. Glaciers and ice sheets are climate archives

The major challenges in actual climate change research are the univocal detection of a possible current climate change due to human activities and to forecast the anthropogenic influence on the climate system. Evidently, the significance of any finding on current or future anthropogenic influence on climate has to be assessed against the background of natural climate variability operating on various spatial and temporal scales. Thus, in tackling the above tasks, historical climate information compiled from instrumental data sets and extended by various climate proxy data archives is urgently needed on the global and particularly on the regional scale. As our instrumental records extend back no more than ~100 years even in developed countries and are extremely limited in their spatial coverage researchers have found ways to extract climatic data from natural sources in order to reconstruct past climates. Some of these sources include ice cores, ocean and lake sediments, geomorphic surface features, tree rings, coral, stalactites and stalagmites, and others. The study and analysis of information contained in proxy data is called paleoclimatology, and the records themselves are called paleo-proxies. A paleo-proxy record is in most cases an indirect estimate of more standard meteorological parameters such as air temperature or annual precipitation. Many paleoclimate studies that examine time periods in the Quaternary (from ~2 million years ago until the present) have relied heavily on ice cores and ice cores have proven to contain some of the best paleo-proxy

records. Ice cores are perhaps the single most powerful means of tracking climate histories that indicates this. In addition to containing many chemical constituents that are deposited in snow, dust, or air bubbles, ice cores can record climatic variations as small as a few years, to much larger variations as long as hundreds of thousands of years.

The primary sources of ice cores have been the Antarctic and Greenland ice sheets due to their immense size, extreme thickness, and relatively undisturbed ice. More recently, very valuable cores have been obtained from smaller ice caps from around the world, many in tropical or subtropical latitudes. These ice caps reside at much higher altitudes making their drilling more dangerous and difficult. When ice cores are drilled, they are ~10 cm in diameter and cut in lengths of about 1 meter to be catalogued and stored for analysis. Although some of the physical and chemical analyses could be done at the drill site, most of the sophisticated analyses require cores to be shipped and stored in cold rooms. For scientists interested in reconstructing climatic histories, the chemical composition of the ice and dust contained in it allows for a wide variety of analytical techniques. This is a valuable characteristic of ice as it allows scientists to study many proxy parameters, enabling data comparisons from other ice cores and other paleo-proxy sources within the same ice core. This can be extremely useful in helping to determine age/depth relationships of ice cores (ice core dating) and test for data quality. Dating paleo-records is arguably the most important aspect of paleo-climatic reconstructions, since time series that cannot be placed in time are essentially useless.

Ice cores can contain several forms of paleo-proxy data that estimate standard meteorological parameters to help reconstruct past climates. Some of the more common meteorological data that can be reflected in ice include air temperature, atmospheric circulation variations, precipitation amount, atmospheric composition, solar activity, and records of volcanic eruptions (Table 2). These parameters can be represented by corresponding proxy records including stable isotopes, radioisotopes, dust composition, snow accumulation rate, air bubbles, and volcanic ash or sulfate. All of the modern analytical techniques used to extract these proxy records have been developed and honed over time, and with the assistance of better technology and new ideas more accurate methods of ice core analyses are being developed. Before scientists can begin reconstructing past climates from paleo-proxies derived from ice cores however, the ice must be drilled and analyzed.

Parameter	Proxy record
Temperatures Summer layers; Annual cycles	$\delta^{18}\text{O}$ ($^{18}\text{O}/^{16}\text{O}$), δD (D/H) Melt Layers
Humidity	Deuterium excess ($d = \delta\text{D} - 8 * \delta^{18}\text{O}$)
Paleo-accumulation	Seasonal signals, ^{10}Be
Volcanic activity	Electrical Conductivity (ECM), SO_4
Tropospheric turbidity	Dust content, trace elements
Wind speed	Dust size & concentration

Atmospheric composition	Greenhouse gases Glaciochemistry	content,
Atmospheric circulation	Glaciochemistry (anions & cations)	
Solar activity	¹⁰ Be	

Table 2. Potential climate parameters and proxy records in ice cores (after Bradley, 1999).

As mentioned earlier, ice cores taken from the world's glaciers and ice sheets have become a critical source of paleo-proxy data. In fact the ice core palaeoclimatology has revolutionized our view of the Earth system, and have become a cornerstone of research into climate and biogeochemistry. Ice cores from polar ice sheets have been used to address many fundamental and pressing questions about the earth system. For example, for the first time they provided clear evidence that greenhouse gases and climate have been tightly linked over the last 800,000 years (EPICA, 2004). Ice cores from the tropical mountains like Andes, Himalayas and Kilimanjaro revealed that the ice sheets in tropics are most vulnerable to the ongoing warming and the current warming at high elevations in the mid- to low latitudes is unprecedented for at least the last 2 millennia (Thompson et al., 2006). Some highlights of research findings from ice cores include: identification of abrupt changes in climate (Dansgaard *et al.*, 1989), the tight link between greenhouse gases in the atmosphere and surface temperature of the earth (Petit *et al.*, 1999), history of climate modes (Johnsen *et al.*, 1992), existence of somewhat regular changes in climate on millennial timescales (Alley *et al.*, 2003), and improved modeling of past and future response of ice sheets to climate change (Dahl-Jensen *et al.*, 1998).

Although the ice core records are best known for the valuable information they have provided of climate and climate forcing on long timescales, they are also of great use in studies of more recent and higher frequency climate variability. Such records are fundamental to the study of climate on the timescales (decadal to multi-decadal) that are of the greatest interest to climate dynamics studies, which are hampered by the relatively short period of direct instrumental climate observations. The timescales made accessible by these records are also of the greatest relevance to the formulation of climate policy, in the context of anthropogenic climate change. In the last decade, several initiatives have focused on obtaining ice cores records with significant spatial density: these include the multinational ITASE ("International Trans Antarctic Scientific Expedition") in Antarctica (Mayewski et al., 2005) and the collection of multiple cores in the Andes and Asia (Thompson, 2000). Results from these projects have demonstrated the utility of multiple ice core records in quantitative reconstruction of climate at annual resolution. Examples include new assessments of surface mass balance on both the Antarctic and Greenland ice sheets, and that even east Antarctic has warmed in the last century (Naik et al., 2010 a & b; Thamban et al., 2011). While some of these studies are mainly focused on the very recent past (last 100-200 years), they provide the necessary first step in understanding the longer time climate records, while retaining high resolution information.

A large network of ice core records are fundamental to the study of climate on the timescales (decadal to century) that are of the greatest interest to climate dynamics studies, which are hampered by the relatively short period of direct instrumental climate observations. Recent initiatives of SCAR like the IPICS (International Partnerships of Ice Core

Studies) have highlighted the importance of such high-resolution studies, especially in polar regions. However, one of the crucial requirements of such projects is the identification of high accumulation areas that are mostly restricted in the coastal areas. Considering the large scale ice flow and englacial dynamics, it is crucial to identify the ideal spots before the actual drilling could be carried out. The development and refinement of both airborne and sled-mounted ice-penetrating radars offer the potential to remotely extend ice-core accumulation measurements out from core locations, thereby efficiently measuring accumulation over large regions of ice sheets. Isochronous radar layers have been used as an established natural marker to examine glacial history, but ice flow models used for the interpretation usually assume simple ice rheology and bed properties. Assessing spatial variability in attenuation ultimately provides remote sensing means of thermal and chemical characteristics of the ice and of bed conditions, which can constrain ice flow models more realistically. A combined study of ground penetrating radar (GPR), seismic profiling and GPS studies are crucial for establishing a reliable glacial record for conducting deeper drilling and climate reconstruction.

4. Application of stable isotopes in glacier and ice core studies

One of the most common ice core proxies is the analysis of stable isotopic ratios, primarily deuterium (^2H) and oxygen 18 (^{18}O). Atoms are composed of protons, neutrons, and electrons. The number of protons determines what the element is, while neutrons and electrons can vary. An isotope is an atom with a different number of neutrons from the set number of protons. For example, oxygen, which contains 8 protons, usually has with it 8 neutrons creating oxygen 16. However, in some cases, there may be 9 or even 10 neutrons in the oxygen nucleus creating oxygen 17 and oxygen 18 respectively. Water, composed of hydrogen and oxygen, contains naturally occurring isotopes that combine into molecules of differing weights. Oxygen occurs naturally as three different stable isotopes with relative abundance in parenthesis - ^{16}O (99.76%), ^{17}O (0.04%), and ^{18}O (0.2%). Hydrogen can occur with two stable isotopes - ^1H (99.984%) and ^2H (0.016%). Together these combine to make up all water molecules, of which only two combinations are important for paleoclimatic research - $^1\text{H}^2\text{H}^{16}\text{O}$ and $^1\text{H}_2^{18}\text{O}$. As these water molecules are evaporated, primarily from the oceans, the lighter molecules, those having fewer neutrons, are preferentially evaporated over the heavier ones, due to a slight difference in vapor pressure caused by the extra neutrons. This causes the vapor to be depleted in heavy molecules but enriched in lighter ones. As the air mass cools and condensation occurs, the heavier molecules preferentially condense due to the same principle. The condensation is then assumed to fall out of the cloud as precipitation. Thus, the oxygen isotopic ratio of rain and snow is strongly related to condensation temperature. If the temperature of the air mass should continue to fall, the condensation will contain decreasing concentrations of the heavy molecules, resulting in a depletion of ^{18}O relative to precipitation that condensed in a warmer environment.

In the 1960's this principle was well understood by scientists and engineers; however for researchers around the world to study the relationship between isotopic ratios and air temperature a standard had to be developed to allow for intercomparisons of all samples. Developed in 1961, this is called Standard Mean Ocean Water (SMOW), and all oxygen isotopic deviations from it are denoted as $\delta^{18}\text{O}$; hydrogen isotopic deviations as δD . The long term records of water isotopes ($\delta^{18}\text{O}$, δD) from cold polar glacier fields have been shown to provide the most faithful atmospheric paleothermometer, which can be relatively well calibrated in terms of local temperature change, at least for the Holocene period.

Moreover, concurrent measurements of $\delta^{18}\text{O}$ and δD , providing the secondary quantity deuterium-excess may give insight into the water vapour source region of the stored precipitation. However, isotope signals in Greenland are strongly subdued during the recent Holocene and can thus hardly be distinguished from glacio-meteorological noise. Their weak isotope-temperature response to historical climate excursions (e.g. Little Ice Age, Medieval Optimum) makes them less useful therefore to infer the small scale climate variability at European level. On the other hand, isotope records from cold mountain glaciers are found to show relatively strong long term variations exceeding by far the range explainable by local temperature changes.

One of the fundamental processes in stable isotopes that make them so fundamentally important and useful is that the relative abundance of the various isotopes can be modified through different physical and biogenic processes. This is called fractionation and it is expressed by way of the fractionation factor (α), a ratio of the isotopic composition before and after the process occurred. For ^{16}O - ^{18}O , fractionation would be expressed as:

$$\alpha = R_1/R_2$$

Where $R_1 = ^{18}\text{O}/^{16}\text{O}$ of the product and $R_2 = ^{18}\text{O}/^{16}\text{O}$ of the starting material.

Stable isotopes are measured as the ratio of the two most abundant isotopes of an element. For oxygen, it is the ratio of ^{18}O , with an abundance of 0.204%, to ^{16}O which represents 99.796% of oxygen. Therefore the $^{18}\text{O}/^{16}\text{O}$ ratio is about 0.00204. Fractionation processes will modify this ratio in any given compound containing oxygen, but these differences are seen in the 5th or 6th decimal place. Doing this on a regular basis would be very difficult and impractical. The fractionation factor alone is insufficient to keep track of all this variation. So what labs do is measure an apparent or relative ratio. Isotopic values are expressed by relative ratio between the measured ratios of the sample and reference. The amount of ^{18}O compared to ^{16}O is expressed using delta notation:

$$\delta^{18}\text{O} \text{ ‰} = \frac{{}^{18}\text{O}/{}^{16}\text{O} \text{ of sample} - {}^{18}\text{O}/{}^{16}\text{O} \text{ of standard}}{{}^{18}\text{O}/{}^{16}\text{O} \text{ of standard}} \times 1000$$

Example: For a sample with $^{18}\text{O}/^{16}\text{O} = 0.00198$, $\delta^{18}\text{O} = [0.00198/0.00200 - 1] = -0.010$. Delta values are often expressed in units of permil (‰) by multiplying by a factor of 1000. In this example, ^{18}O is -0.010 (unitless) or -10‰.

Most meteoric waters have negative $\delta^{18}\text{O}$ and δD values. The 'meteoric water' with the lowest $\delta^{18}\text{O}$ and δD values is Antarctic ice with a $\delta^{18}\text{O} = -50\text{‰}$. The weighted mean value of $\delta^{18}\text{O}$ in meteoric water is -4.0‰ if the average groundwater is -7‰ and the average glacial ice is -30‰. During the last glacial maximum, when the ^{16}O -enriched continental ice sheets were at their greatest areal extent, the $\delta^{18}\text{O}$ of seawater was +1‰ based on mass balance considerations. If the present day continental ice sheets of Antarctica and Greenland were to melt, the $\delta^{18}\text{O}$ of seawater would *decrease* to about -0.6‰, and maybe down to -1.5‰ VSMOW. In the early days of stable isotope studies, oxygen and hydrogen isotopes were reported relative to the oxygen and hydrogen isotope value of seawater. The H and O isotope values of seawater are not perfectly uniform in the world's oceans. The $\delta^{18}\text{O}$ value ranges from -1.5‰ in Antarctic Bottom Water (AABW) to +0.5‰ in North

Atlantic Deep Water (NADW). In marginal marine environments like the Baltic Sea, $\delta^{18}\text{O}$ may be low as -5 to -7‰ , whereas in hot arid regions like the Red Sea, values as high as 1.8‰ are found. In practice nobody had ever used seawater as a genuine laboratory standard. Instead, NBS 1 (Potomac River water) was used, and Harmon Craig defined SMOW relative to NBS-1. This prompted the International Atomic Energy Association to prepare a large aliquot synthetic water standard with an isotope value close to seawater. The new standard was called Vienna SMOW, and all modern O and H isotope measurements are made relative to this standard.

The only way to produce precipitation is by cooling an air mass. This occurs by adiabatic expansion (no loss of enthalpy) as warm air rises to lower pressures, or by radiative heat loss. When the dew point is passed, water vapor condenses to maintain thermodynamic equilibrium, and it will rain or snow. If the temperature stabilizes or warms, condensation stops or is reversed and the humidity drops. As an air mass leaves its source (usually in the subtropics) it cools as it rises above the continents or as it moves to higher latitudes. This cooling induces precipitation that distills the heavy isotopes from the water vapor in the air mass. The remaining vapor becomes progressively depleted in ^{18}O and ^2H according to a Rayleigh-type distillation (Fig. 3). Precipitation with relatively high isotope values (compared to the air mass vapor) falls from the clouds. As precipitation continues however, the water vapor remaining attains lower and lower values resulting in precipitation attaining lower and lower values. This results in the so-called continentality effects and orographic effect that produces precipitation with very low values at high latitudes and altitudes. The relationship between isotope values and temperature allow us to estimate seasonal variability, altitude, latitude and past climate.

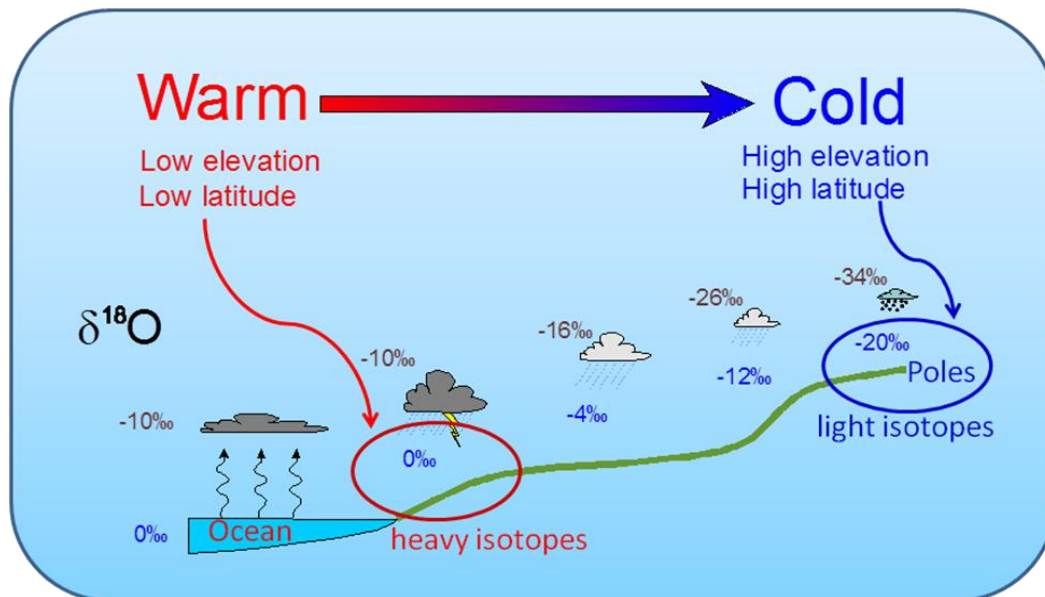


Fig. 3. Rainout and Rayleigh distillation of stable oxygen isotopes

The major factors controlling the isotope value of precipitation are:

- 1) Isotope value of source
- 2) Rate of evaporation of source
- 3) Isotopic evolution of air mass
- 4) Relative humidity during precipitation (raindrops may evaporate as they fall).

5) At high latitudes the amount effect becomes less pronounced as evaporation is lessened. Near the poles, isotope values are near those predicted by the low-altitude temperature. This is because precipitation often forms at low altitudes and consists of ice particles that are not as subject to exchange with environmental vapor.

Because glaciers are known to preserve the precipitation of the past in an unbroken sequence, it might seem that they are especially well suited for the study of the isotopic value of precipitation and its variation with time. This is however, not quite so simple. From the moment the snow has been deposited on the glacier surface, the isotope value of the snow pack begins to change owing to various processes. These processes not only affect the upper-most firn layers but may also affect the entire ice mass. Isotope studies of firn and snow have shown that, in every case, an appreciable isotopic modification is found to take place in glacier surface layers (accumulation) during firnification, *i.e.* when they undergo changes from snow to glacier ice. Epstein and Sharp (1959a) first showed that, under favorable conditions, the seasonal δ -variations can survive the firnification processes and are preserved in glacier ice. Such favorable conditions, however, exist mainly in the dry snow zones and occasionally also in the percolation zones, provided the percolation of meltwater is very small. In the percolation zones and especially in the soaked zones the seasonal δ -variations are always more or less smoothed out. Even in the dry snow zone the seasonal δ -variations do not always survive the firnification process. The obliteration of the seasonal δ -variation during firnification in the dry snow zones seems to be inversely related to the accumulation rate, but probably it also depends upon other parameters such as the windiness of the region. It is therefore vital to have a thorough knowledge of the prevailing climate conditions, physical processes and glacier dynamics for the application of stable isotopes in climate reconstruction using ice cores.

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