SIO 115: Ice in the Climate System

$\delta^{18}O$ as a Palaeoclimate Proxy in Ice Cores

Philipp Arndt

January 2020

This is a rather informal discussion of the topic. There is many more complicated things going on, but after reading this you should be able to have a decent grasp on why and how $\delta^{18}O$ *changes in ice cores represent past changes in global temperature.*

1 General concepts

1.1 Fractionation

Oxygen comes in two main stable isotopes. About 99.8% of oxygen on Earth is found in form of the lighter ^{16}O, and about 0.2% in form of the heavier ^{18}O. Whenever there is a slow phase change, the molecules that are isotopically heavier prefer the energetically more stable phase. In particular, this means that:

- during **evaporation**, the heavier ^{18}O preferentially stays in the liquid phase (i.e. the ocean).
- during **condensation**, the heavier ^{18}O will preferentially go from the gaseous into the liquid phase, so precipitation is isotopically heavier than the water vapor that remains in the atmosphere.

This process of fractionation *always* happens, regardless of whether the climate is cold or warm.

1.2 Rayleigh Distillation

A lot of evaporation happens at lower latitudes (closer to the equator). Water vapor in the atmosphere is transported all the way to the polar regions to form the precipitation

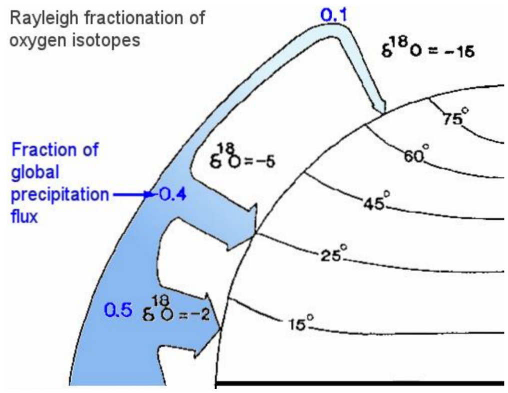

Figure 1: Rayleigh Distillation, after Craig et al. [1965]

that falls onto an ice sheet (and slowly forms the ice we find in ice cores). Since the polar regions are very cold, the air holding this water vapor needs to cool down during its way towards the poles. In general, cold air can hold much less water vapor than warmer air (this is the Clausius-Clapeyron relation, if you've heard of it). Thus on the way towards the poles, isotopically relatively heavier (^{18}O) water is continuously removed from the air, in the form of precipitation. Hence, the further we go towards the poles, the isotopically lighter the remaining water vapor in the air. When precipitation finally falls onto an ice sheet, the resulting precipitation is strongly depleted in the heavier ^{18}O. This process is known as Rayleigh Distillation.

2 Things that change in a changing climate

The colder the climate, the stronger the process of fractionation. There is lots of complicated things happening on the molecular level that affect this, but let's just have a quick look at evaporation as an example.

For any one molecule to go from the liquid to the gaseous phase, it needs to

- be close to the surface, and
- have a certain minimum velocity to escape the liquid.

But because molecules with ^{18}O are heavier, this means they need an even higher kinetic energy (than the lighter molecules with ^{16}O) to reach that particular velocity. Molecules in the liquid phase constantly bump into each other, so their velocities are randomly distributed around some mean value. This mean value loosely represents temperature. If temperature is low, molecules are on average moving quite slowly. If temperature is high, molecules are on average moving faster. Hence, at low temperatures there will be very few heavier molecules that happen to reach the escape velocity by pure chance. Thus, the vast majority of molecules that escape cold water are the lighter ^{16}O ones. When the water is warmer, many more molecules will attain the escape velocity, including also more of heavier ^{18}O ones. Now it becomes relatively more important whether the molecules are close to the surface, which happens by chance. Therefore, relatively more heavy ^{18}O will escape the liquid when it is warmer.

- First, think of boiling water. Most molecules have a high enough velocity to escape the liquid, so whichever molecules happen to be close to the surface by chance will become vapor. So there is essentially no fractionation: ^{18}O/^{16}O in the vapor is the same as in the liquid.
- Now, think of cold water. Molecules continuously bump into each other in the liquid phase, but only the very fastest ones will escape the liquid. The lighter ones need less energy to be accelerated to be fast enough to escape. So now mostly the lighter molecules will form vapor. This means fractionation is stronger: ^{18}O/^{16}O in the vapor is lower than in the liquid.

The colder the climate, the stronger the process of Rayleigh Distillation. This is due to polar amplification: the temperature difference between the tropical/temperate regions and the poles are larger in colder climates. Thus, on the way from mid latitudes to the pole, a larger fraction of water vapor is removed by precipitation when the climate is cold. This means that the precipitation that falls on ice sheets in the polar regions is more strongly depleted in the heavy ^{18}O when the climate is cold. Therefore, ^{18}O/^{16}O at the poles will be lower in a colder climate than it would be in a warmer climate.

3 What this means for ice cores

Both the strength of fractionation itself and the strength of Rayleigh Distillation contribute to a change in ^{18}O/^{16}O in the ice that is formed near the poles!

When the climate becomes colder:

- fractionation becomes stronger. So the ^{18}O/^{16}O ratio in vapor that forms at low/mid latitudes becomes lower as it gets colder.
- Rayleigh Distillation also becomes stronger. So more of the heavy ^{18}O is removed before water vapor reaches the poles. Hence, in a cold climate the ^{18}O/^{16}O ratio decreases even more before the water finally falls onto the ice sheet as snow than it would have decreased in a warmer climate.

Now δ^{18}O is a measure of how much the ^{18}O/^{16}O ratio deviates from a constant standard value. It is defined as

$$\delta^{18}\text{O} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{ice core sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{fixed standard}}} - 1 \right) \times 1000 \text{ ‰}.$$

Both the strength of Rayleigh Distillation and fractionation itself contribute to the following effect: The colder the climate is, the lower the ratio of ^{18}O/^{16}O in the ice that forms from snow accumulation during that time. Therefore, **$\boldsymbol{\delta^{18}}$O decreases when the climate gets colder, and increases when the climate gets warmer.**

If we can determine the age of the ice in an ice core, this *positive correlation between* δ^{18}O *and temperature* at the time when the ice had formed lets us reconstruct past temperatures.

Note: the value of δ^{18}O in the *ocean* is *negatively* correlated with the amount of glaciation. Why is that?

References

[1] Harmon Craig, Louis Irwin Gordon, et al. Deuterium and oxygen 18 variations in the ocean and the marine atmosphere. 1965.