

Oxygen Isotope fractionation

The term “kinetic fractionation” applies to change of state processes (evaporation/condensation), and that is mostly what we are dealing with in the application of oxygen isotopes to climate studies.

“Kinetic fractionation” does also apply to chemical reactions.

Oxygen has two main isotopes:

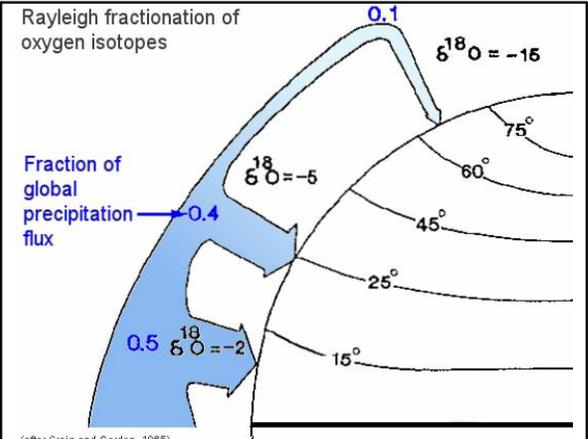
^{16}O which accounts for 99.8%
and
 ^{18}O which accounts for most of the remaining 0.2%

For our purposes, kinetic fractionation refers to the process whereby the heavier isotope is concentrated in the liquid as compared to the gas on evaporation or condensation.

The lighter isotope (^{16}O) tends to move more quickly and react at a faster rate than the heavier isotope (^{18}O).

When water evaporates, the water vapor becomes enriched in the lighter isotope and the water left behind becomes “heavier”.

When water vapor condenses the water becomes enriched the heavier isotope, and the water vapor becomes “lighter”



On earth most evaporation takes place in the tropics, and the general trend is for that evaporated water to move towards the poles.

The result is that equatorial waters are relatively heavy
 $\delta^{18}\text{O} \sim 0$

while temperate and near-polar waters are lighter
 $\delta^{18}\text{O} -5 \text{ to } -15$

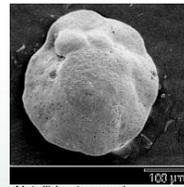
and polar ice is very light
 $\delta^{18}\text{O} -20 \text{ to } -55$

As the water vapour in the atmosphere is gradually condensed into water on its journey north or south, the rain produced is isotopically heavier than the vapour left behind, and this means that the water vapour becomes lighter and lighter as it moves towards the poles.
This is known as Rayleigh fractionation.

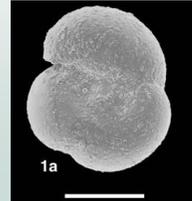
Oxygen isotope fractionation is more pronounced at low temperatures, so the equator-to-pole isotope gradient is greater under cool conditions.

Oxygen isotope data from ice cores show low $\delta^{18}\text{O}$ values for glacial periods.

Under glacial conditions, a greater than normal proportion of the earth's water is locked up in glacial ice, which is mostly situated near to the poles, and is isotopically very light. This means that the remaining sea water will be isotopically heavier than normal.
(i.e., $\delta^{18}\text{O}$ values are higher than normal)



Nutalides truempyi



Cibicides sp.

In foraminifer shells the ratio of ^{16}O and ^{18}O in the carbonate records that ratio that is present in seawater, modified by the temperature of the sea water (through fractionation of the ^{18}O and ^{16}O isotopes).

Both are benthic foraminifers.

Oxygen isotope measurements of marine sediments or of organisms in equilibrium with sea water are more strongly affected by the volume of ice than the temperature.

Biological processes fractionate oxygen isotopes during metabolism.
(organisms 'like' the light isotope better)

and the degree of fractionation is TEMPERATURE DEPENDENT.

The temperature dependence of this biological fractionation is:

1 ‰ decrease in $\delta^{18}\text{O}$ for each 4.2°C increase in water temperature

or... ^{18}O becomes less abundant in the carbonate shells of forams when the temperature increases.

or... $\delta^{18}\text{O}$ levels drop as temperature increases

Nevertheless, oxygen isotopes can be used as a measure of temperature.

Glacial ice has not always been present, and where necessary the volume of ice can be corrected for.

This is the opposite to what we see in ice-core records, where low $\delta^{18}\text{O}$ values are associated with cold periods.

In foram data from marine sediment cores low $\delta^{18}\text{O}$ values are associated with high temperatures.