

Notes 13 Stable Isotopes (continued)

II. Nomenclature (continued)

III. Oxygen (and Hydrogen) isotope fractionation at the Earth's surface

IV. Carbon isotope fractionation and life

More nomenclature

α is called an “equilibrium fractionation factor” and its definition is very similar to that of equilibrium constant. α_{x-y} for oxygen isotopes, for example, would be

$$\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_x}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_y}, \text{ where } x \text{ and } y \text{ are coexisting phases}$$

Element-element exchange: $\Delta S_R \sim 20$ to 200 cal/mole

Isotope-isotope exchange: $\Delta S_R \sim 0.02$ to 0.2 cal/mole, and equilibrium constant $K \sim 1$.

For isotope exchange, $\Delta V_f \sim 0$

Hydrologic Cycle and Oxygen Isotopes

Imagine evaporation of seawater (with $\delta^{18}\text{O}$ of 0 per mil SMOW) in the tropics. More water vapor is soluble in air at high temperature, thus a large proportion of the water vapor in the atmosphere comes from evaporation in the tropical oceans. This water vapor is then transported through the atmosphere to higher latitudes (colder places), where it condenses as ice and water. When the water from the tropical ocean evaporates, it fractionates, usually by kinetic processes (as relative humidity is often less than 100%). The light isotope ^{16}O fractionates preferentially into the vapor so that $\delta^{18}\text{O}$ is about -10 per mil in the vapor. The air containing this water vapor moves poleward. As it does, temperatures fall and the air becomes saturated or supersaturated in H_2O . Water forms from the water vapor. This water initially has a $\delta^{18}\text{O}$ value of around 0 because ^{18}O fractionates preferentially into the water phase. Since ^{18}O has preferentially been enriched in the water and the water removed as rain, the remaining water vapor becomes more enriched in ^{16}O , i.e., its $\delta^{18}\text{O}$ becomes even less than -10 per mil. As the air moves further poleward, it cools further, becomes saturated/supersaturated again and more water forms from water vapor. Since the water forms from water vapor that has a lower $\delta^{18}\text{O}$ than -10, the water has a lower $\delta^{18}\text{O}$ than 0. The removal of this water, further depletes the remaining water vapor in ^{18}O , further lowering its $\delta^{18}\text{O}$. This process continues resulting in very light water vapor and very light precipitation at high latitudes. There is also a similar effect with altitude. To first order, this process can be modeled with a Rayleigh fractionation model, in which a scenario very similar to that just described is modeled:

$$R_v = R_o f^{(\alpha-1)}, \quad \alpha = R_l/R_v, \quad f = \text{fraction of vapor remaining (p. 307, Fig. 17.2).}$$

This process describes the present $\delta^{18}\text{O}$ patterns of modern precipitation and explains the correlation between modern precipitation and temperature. $\delta^{18}\text{O}$ from ice core records of ancient

precipitation have been used as records of past climate, and interpreted largely in terms of past temperature.

Because meteoric precipitation is generally enriched in ^{16}O (depleted in ^{18}O), when continental glaciers form (ultimately from sea water), they cause the ocean to acquire higher $\delta^{18}\text{O}$ values. When they melt, the $\delta^{18}\text{O}$ values drop, with the additional of low $\delta^{18}\text{O}$ water from the melting glaciers. This effect, along with one other is captured in the $\delta^{18}\text{O}$ of calcite foram shells. The second effect is the temperature dependent fractionation of oxygen isotopes when the calcite shells form from sea water: $\text{CaC}^{16}\text{O}_3 + 3\text{H}_2^{18}\text{O} = \text{CaC}^{18}\text{O}_3 + 3\text{H}_2^{16}\text{O}$. As it turns out, the lower the temperature, the more enriched the calcite becomes in ^{18}O . Thus, glaciation and low temperatures both result in higher ^{18}O in foram calcite, in very roughly equal proportions. Some of our best long-term records of the history of Quaternary glaciation come from the marine oxygen isotope record.

Carbon isotopes and organic carbon. In most cases, organisms favor molecules with lighter isotopes because they have weaker bonds which require less energy to break. Photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \Rightarrow \text{CH}_2\text{O} + \text{O}_2$ preferentially takes CO_2 with ^{12}C (and ^{16}O) so the sugars and starches and cellulose in plants have less ^{12}C than atmospheric CO_2 . For this reason, organic matter (C-H-O compounds produced by organisms) are very depleted in ^{13}C (have low $\delta^{13}\text{C}$ values - in the range of minus several per mil to minus several tens of per mil). Among plants, C_4 plants (generally grasses, also corn) are not as discriminating in carbon isotope uptake as C_3 plants (generally plants other than grasses), and therefore have higher $\delta^{13}\text{C}$ than C_3 plants. As cave calcite gets a good portion of its carbon from respired plant remains (in the soil), records of the $\delta^{13}\text{C}$ of cave calcite have been interpreted as measures of vegetation (grossly prairie (C_4 , relatively high $\delta^{13}\text{C}$) or forest (C_3 , relatively low $\delta^{13}\text{C}$)). Because organic matter is depleted in $\delta^{13}\text{C}$, a number of researchers have used the low $\delta^{13}\text{C}$ of carbon extracted from early Precambrian sediments as evidence that life was present very early in earth history.