

## ESS 312 Geochemistry Stable Isotopes

Concepts you should understand after the next few lectures:

- (i) The isotopic compositions of most light elements, particularly H, C, N, O and S vary among natural materials. For example, the relative abundance of  $^{13}\text{C}$  to  $^{12}\text{C}$  in an organic compound such as methane or cellulose is different to that of an "inorganic" material such as  $\text{CO}_2$  or calcite. We call the enrichment or depletion of an isotope such as  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ , in one compound relative to another "isotopic fractionation". The degree of separation of isotopes between compounds is generally quite small – less than a few percent. In fact, it is usually described in units of "per mil", equivalent to parts per thousand or tenths of percent, written "‰".
- (ii) Why do isotopic compositions vary? Isotopic fractionation of an element such as C or O among compounds at equilibrium occurs due to differences in the bond strengths (vibrational energies) of the sites occupied by C or O atoms in the compounds. For example, when calcite and water are at equilibrium at  $25^\circ\text{C}$ , oxygen in the calcite, closely bonded to carbon atoms in  $\text{CO}_3^{2-}$  groups, is enriched in the heavy isotope  $^{18}\text{O}$ , by  $\sim 29\text{‰}$  (2.9%) relative to oxygen in the water (which is bonded to H atoms). The substance with stronger bonds (higher vibrational frequencies) tends to concentrate the heavier isotope.
- (iii) The degree of equilibrium isotopic fractionation among minerals, fluids and gases depends on temperature. Isotopic fractionation is greatest at low temperatures, and approaches zero (i.e. coexisting substances have the same isotopic composition) at high temperatures. Thus, by measuring the stable isotope compositions of a pair of compounds (such as the minerals quartz and magnetite in a rock, or rainwater and atmospheric water vapor) we can determine the temperature at which the substances last equilibrated. Stable isotope compositions, like trace element ratios and mineral assemblages, can be used for *geothermometry*. However, because isotopic substitution has no effect on molar volume, stable isotopic thermometers are not affected by pressure.
- (iv) Incomplete and/or unidirectional processes such as evaporation and diffusion can also separate stable isotopes, because light isotopic compounds move with higher velocities than heavy isotopic compounds. The effects of these processes are referred to as "kinetic" or non-equilibrium fractionation.
- (v) Together, equilibrium and kinetic fractionation processes give geological and biological materials distinctive isotopic signatures. For example; diamonds formed in subduction zones contain  $\sim 2\%$  less  $^{13}\text{C}$  than diamonds formed in the sub-continental mantle, and rainfall in Florida contains  $\sim 1\%$  more  $^{18}\text{O}$  than rainfall in North Dakota. These signatures can be used to "fingerprint" the source materials of everything from rocks and fluids to "corn-fed" beef and Scotch whiskey. For example, carbon dioxide released by fossil fuel burning contains  $\sim 3\%$  less  $^{13}\text{C}$  than  $\text{CO}_2$  produced from limestone in cement manufacturing.

You should also become familiar with the representation of stable isotope compositions as "delta" values, or deviations in parts per thousand from a standard isotopic composition. For example:

$$\delta^{18}\text{O}_{\text{sample}} = 1000 \left( \frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} - 1 \right)$$

Likewise, the representation of isotopic fractionation factors:

$$\alpha_{a-b}, \quad \delta_a - \delta_b, \quad \text{and} \quad 1000 \ln \alpha_{a-b}$$