

## Rock-water ratios and the stability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate materials

One generalization commonly made by isotope geochemists is that  $\delta^{18}\text{O}$  values of carbonate rocks and their components can be altered relatively readily, whereas  $\delta^{13}\text{C}$  values of the same materials are much less likely to be altered. The reason for this generalization lies in the relative abundance of O and C in limestone and in water. Limestones, as  $\text{CaCO}_3$ , are obviously rich in O and C. Natural waters, as  $\text{H}_2\text{O}$  with minor solutes, are obviously rich in O, but they have far less C than the rocks through which

they pass. If one accepts that most alteration of limestone occurs via dissolution-reprecipitation reactions with natural waters (rather than via solid-state processes), the ability of waters to deliver much "new" O but little "new" C dictates that such waters can change the O isotope compositions of limestones readily, but not the C isotope compositions of those limestones.

The plot and table below quantify these generalizations. The plot shows, for differing values of porosity, the ratio of the moles of O in

calcite to the moles of O in the water in the pores (the black curve). It shows the same ratio for C in two different cases, for a C-poor natural water (riverwater) and a C-rich water (an  $\text{HCO}_3^-$ -rich brine). The water delivers more than 300 times as much O than C for even the most C-rich solution.

Note that this plot says nothing about the actual re-equilibration that will take place between water and calcite if some amount of water passes through the pores of a limestone. Re-equilibration may vary from maximal to negligible, depending on a variety of other factors (temperature, crystal size, permeability, etc.).

The one setting where bulk C isotope signatures of limestones are commonly altered is in soils developed on recently-deposited carbonate sediments. Three factors are critical to this process: the instability of minerals in the newly-formed sediment, the extensive passage of rain water through the limestone beneath the soil (lots of "flushing" in the terminology used here) and the very low  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$ , so that a little carbon can have a large effect on the limestone's  $\delta^{13}\text{C}$ .

