

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 CaCO_3 , are obviously rich in O and C. Natural waters, as H_2O with minor solutes, are obviously rich in O, but they have far less C than the rocks through which

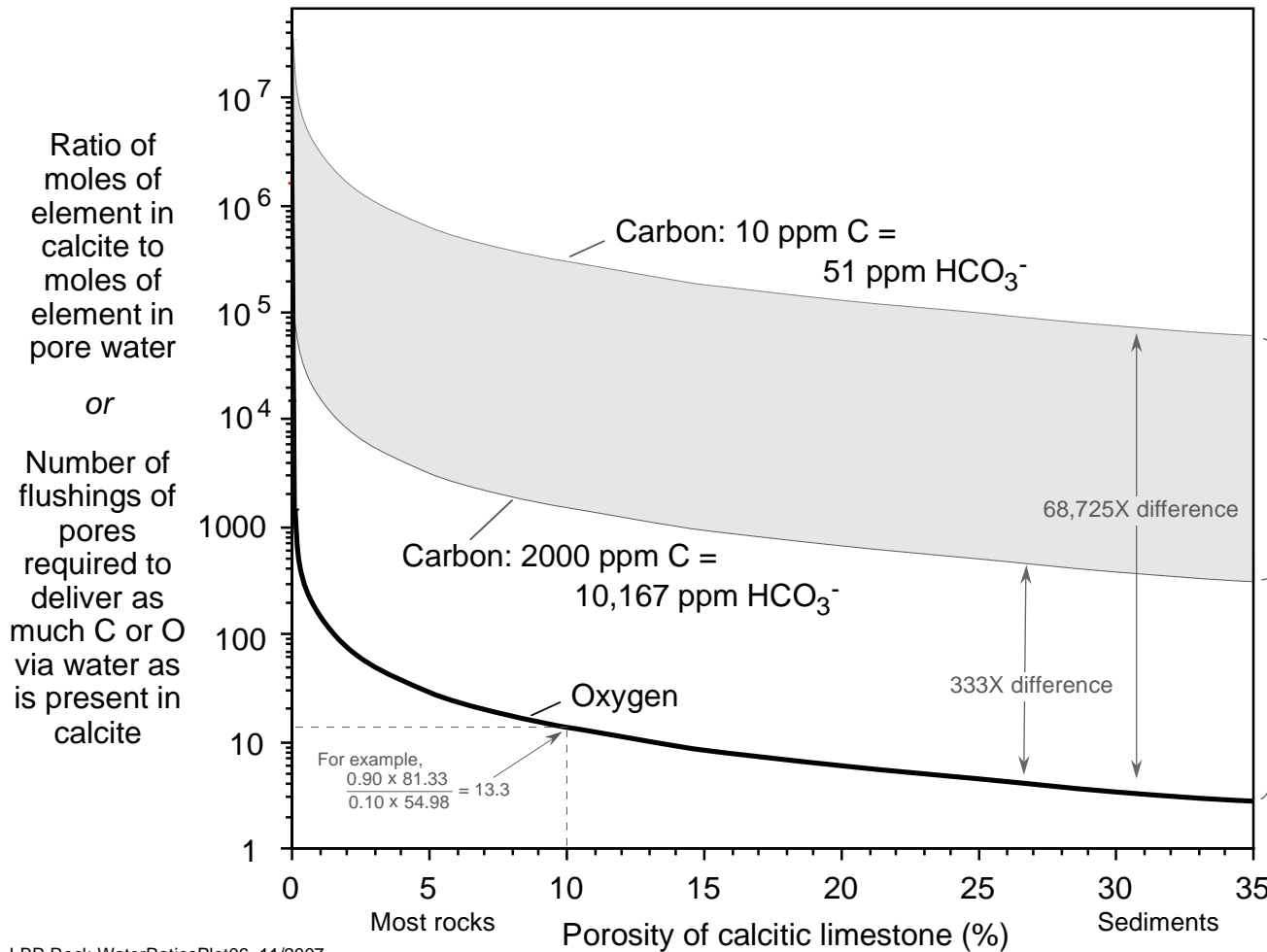
they pass. If one accepts that most alteration of limestone occurs via dissolution-reprecipitation reactions with natural waters (rather than via solid-state processes), the ability of waters to deliver much "new" O but little "new" C dictates that such waters can change the O isotope compositions of 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 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 CO_2 , so that a little carbon can have a large effect on the limestone's $\delta^{13}\text{C}$.



Element	ppm in water (mg/kg)	moles L of water	moles L of calcite
C	10 (riverwater)	0.0008	27.08
C	2000 (brine)	0.165	27.08
O	888105	54.98	81.33

$\frac{16}{18} \times 10^6$

This is a very simple treatment of the issue of interaction between rocks and waters. For a much more thorough treatment, see Banner, J.L., and Hanson, G.N., 1990, Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis: *Geochimica et Cosmochimica Acta*, v. 54, p. 3123-3137. The C concentrations above come from that paper.