

Origin and significance of the age dependence of calcite recrystallization rates in deep sea sediments

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Understanding the rate of carbonate diagenesis in calcite-rich deep sea sediments is key in interpreting isotopic and elemental ratios recorded in calcite sediment and understanding their implications for paleoclimate and global elemental cycles. We have used available pore fluid Sr and Ca concentration data from ODP archives for 20 drill sites in nearly pure carbonate sections to systematically estimate the calcite dissolution/precipitation rates. The concentration-depth curves are fit with a simple reactive transport model to retrieve reaction rate versus depth assuming an exponential depth dependence. The Sr data provide the exchange rate, or the rate of dissolution (R_d) and precipitation (R_p), where rates are expressed in units of fraction reacted per unit time (Myr^{-1}). The pore fluid Ca concentration data provide the difference ($R_d - R_p$), which we refer to as the net reaction rate (R_{net}). When the model R_d ($\approx R_p$) values are plotted against the average age of sediments to which they apply, an approximate $1/\text{age}$ relationship is obtained, with $R_d \approx b/\text{age}$ and $b = 0.03$ to 0.1 . The larger data set conforms with a previously noted $0.1/\text{age}$ relationship found for a smaller number of sites [1] and silicate weathering in soils [2]. We show using both closed system and reactive transport models that the approach of pore fluid to equilibrium could come close to explaining the observed rate patterns in deep sea carbonates if calcite- pore fluid reaction rate is a function of $(1-Q/K_{\text{eq}})^{1+n}$, and n is between 1 and 1.5. This higher order rate dependence is consistent with most laboratory calcite dissolution experiments [3], but our results require that it apply to exceedingly small departures from equilibrium ($1 - Q/K_{\text{eq}} < 0.0001$, a regime that is not accessible through laboratory experimentation).

[1] Fantle & DePaolo (2007), *Geochimica et Cosmochimica Acta*, 71(10): 2524-2546.

[2] Maher, DePaolo & Lin (2004), *Geochimica et Cosmochimica Acta*, 68(22): 4629-4648.

[3] Adkins, Naviaux, Subhas, Dong & Berelson (2021), *Ann Rev Mar Sci*, 13: 57-80.