

The effect of solution chemistry on Li elemental and isotopic fractionation during calcite growth

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The Li content and isotopic composition of seawater are potentially powerful proxies with which to study global chemical weathering and the long-term C-cycle. Carbonate rocks provide a potential record of seawater Li-chemistry if we understand the fractionations associated with calcite growth, and (especially) diagenesis, under varying conditions. In this study, the partition coefficient ($kd_{Li} = Li_{calcite}/Li_{solution}$) and isotopic fractionation factor for lithium between inorganic calcite and solution have been measured as a function of solution chemistry in mixed $CaCl_2$ - $NaHCO_3$ solutions spanning a range of pH from ~6 to ~9.5. Vaterite was added to solutions of variable composition and this slowly recrystallized to calcite with limited change in solution chemistry. The Li partition coefficient and Li-isotope fractionation factor increased from ~0.2 to ~3 and -6 ‰ to +2 ‰ respectively, with increasing pH (increasing Na/Ca). To better understand the role of diffusive Li-isotope fractionation a series of experiments were performed to determine the relative diffusivity of 6Li and 7Li in solutions with different pH. The results suggest little or no difference ($D^6Li \sim 0.998D^7Li$) across the range of solution chemistry considered (pH 4 to ~7.5). This implies that diffusive fractionation is not likely to be the main source of the observed fractionations and will generally lead to only small isotope fractionations in nature. The change in the kd_{Li} between calcite and solution is consistent with Li incorporation into calcite as $LiHCO_3$ and hence a dependence on solution H^+/Ca^{2+} . If this interpretation is correct, then the Li content of inorganic calcite precipitated from seawater at fixed calcite saturation state, and fixed Ca and Li concentrations, will increase with decreasing pH. These results have important implications for interpreting the Li content of inorganic calcite including any carbonate sediments that have undergone diagenesis. We hypothesise that diagenesis under variable conditions may provide an alternative explanation for Li-isotope excursions in carbonate sediment sequences that have been interpreted as indicating changing seawater Li isotopic composition.