

Variation in seawater $[\text{Ca}^{2+}]$ as a major driver for Na, K, S, and B incorporation in inorganic calcites

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In this study, inorganic calcite samples grown in simplified (Mg-free) artificial seawater¹ were utilized to examine the patterns of Na, K, S, and B incorporation (measured as Na/Ca, K/Ca, S/Ca, and B/Ca ratios, respectively) as a function of changes in pH, [DIC], $[\text{Ca}^{2+}]$ of the artificial seawater, and hence calcite precipitation kinetics. The samples were grown in 5 separate series of precipitation experiments, which involved (#1) changing pH only, (#2) changing [DIC] only, (#3) changing $[\text{Ca}^{2+}]$ only, (#4) changing pH and $[\text{Ca}^{2+}]$ concurrently but to opposing directions, and (#5) changing [DIC] and $[\text{Ca}^{2+}]$ concurrently but to opposing directions, from the same baseline condition. The series #1 to #3 led to changes in the degree of calcite saturation and the rate of precipitation “*R*”, whereas the series #4 and #5 were designed to perform calcite precipitation at a near-constant *R*.

Our new data show positive linear trends with $[\text{Ca}^{2+}]$ of the artificial seawater for all measured element/Ca ratios, irrespective of whether varying $[\text{Ca}^{2+}]$ induced changes in *R* or not (*i.e.*, series #3 vs #4 and #5). This suggests that Ca^{2+} ions, but not necessarily the kinetic effects associated with *R*, play a central role in incorporation of the elements studied here. Moreover, while the linear trend against $[\text{Ca}^{2+}]$ was particularly robust and more exclusive for K/Ca and S/Ca ratios, Na/Ca and B/Ca ratios showed additional positive responses to increasing pH and/or [DIC] (series #1 or #2). We propose that these disparate incorporation patterns largely arise from the different response of growth-kink formation dynamics to changes in $[\text{Ca}^{2+}]$ as opposed to $[\text{CO}_3^{2-}]$ as well as the size differences between the aqueous forms of these elements (Na^+ , K^+ , SO_4^{2-} , and $\text{B}(\text{OH})_4^-$ and/or $\text{B}(\text{OH})_3$) relative to Ca^{2+} and CO_3^{2-} that constitute the calcite structure.

1: Uchikawa et al. (2017) *Geochim. Cosmochim. Acta*, 218, 291-307