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Kinetic influence of temperature and seawater composition on calcite crystal growth mechanisms and implications for Mg incorporation

P. Zuddas (1), O. Lopez (2), and D. Faivre (3)

(1) Departement Sciences de la Terre UMR5125 Université Claude Bernard Lyon1, France (pierpaolo.zuddas@univ-lyon1.fr), (2) Numericalrocks AS, Trondheim , Norway. (Olivier@numericalrocks.com), (3) Max Planck Institut für Kolloid, Wissenschaftspark 18 Golm, Potsdam, Germany (Damien.Faivre@mpikg.mpg.de)

The composition of carbonate minerals formed in past and present oceans is assumed to be significantly controlled by temperature and seawater composition. To determine if and how temperature is kinetically responsible for the amount of Mg incorporated in calcite, we quantified the influence of temperature and specific dissolved components on the complex mechanism of calcite precipitation in seawater. A kinetic study was carried out in artificial seawater and NaCl–CaCl2 solutions, each having a total ionic strength of 0.7 M. The constant addition technique was used to maintain [Ca2+] at 10.5 mmol/ kg while [CO3] was varied to isolate the role of this variable on the precipitation rate of calcite.

We find that, irrespective of the presence of Mg, SO4, and other specific seawater components known calcite reaction rate inhibitors, the partial reaction order with respect to carbonate ion concentration changes from 2 to 5 while the rate constant of the overall reaction, increases by 3–4 orders of magnitude when temperature varies from 5 to 70°C. The observed variations of the kinetic mechanism resulting from the temperature changes are correlated with the variable amount of Mg incorporated in the formed calcites. Moreover, at a given temperature, the increase in the saturation state enhances the rate of calcite precipitation without influencing the reaction mechanism and without changing the amount of Mg incorporated in the growing lattice.

Thus, the results of this experimental study are consistent with present-day abiotic marine carbonates where low-Mg calcite cements are mainly associated with cool water while high-Mg carbonates are dominantly found in warm-water environments. This suggests that the apparent inverse relationship between the global average paleo-temperature and the Mg/Ca ratio in past formed marine carbonate may correspond to major changes in seawater saturation state or (Mg/Ca) ratios that in turn should reflect significant changes in the relative seawater geochemical cycles of these cations.