Calcite growth rate and solution stoichiometry, implications for biomineralizations.

G. Nehrke (1,2), P. Van Cappellen (2), and J. Bijma (1)

(1) Alfred Wegener Institute of Polar and Marine Research, Division of Biogeosciences, Bremerhaven, Germany

(2) Faculty of Geosciences, Department of Earth Sciences – Geochemistry, Utrecht University, Utrecht, The Netherlands

The ion activity product is an entity describing the saturation state of a solution with respect to a solid phase. In kinetic descriptions of crystal precipitation the crystal growth rate is often linked to this saturation state, but do not take into account that the ions attaching to the surface of a growing crystal are of different kind, e.g. an anions and cations. To investigate the effect of the anion to cation ratio on the calcite growth rate, seeded calcite growth experiments were conducted at fixed pH (10.2) and two degrees of supersaturation ($\Omega = 5, 15$), while varying the Ca$^{2+}$ to CO$_3^{2-}$ solution ratio over several orders of magnitude. The calcite growth rate and the incorporation of Sr into the growing crystals strongly depended on the solution stoichiometry. At constant degree of supersaturation, the growth rate was highest when the solution concentration ratio, $r = [\text{Ca}^{2+}] / [\text{CO}_3^{2-}]$, equaled one, and decreased symmetrically with increasing or decreasing values of $r$. This behavior is consistent with the kink growth rate theory for non-Kossel crystals, assuming that the frequency factors for attachment to kink sites are the same for the cation and anion. Measured Sr partition coefficients, $D_{Sr}$, ranged from 0.02 to 0.12, and correlated positively with the calcite growth rate. These findings are interpreted in the context of the calcite formation of marina calcifying organisms used in paleo climate reconstruction. Both saturation state and solution stoichiometry at the site of calcite formation are modulated by cellular processes in the calcifying organisms, and may therefore contribute to the “vital effect” on Sr/Ca ratios.