Na incorporation into inorganic $CaCO_3$ and implications for biogenic carbonates

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Variations in the sodium content of field-collected and cultured foraminiferal calcite (Na/Ca) have been linked to varying seawater salinity [1] and calcium concentration [2]. However, wide inter- and intra-specimen variations in foraminiferal Na/Ca [3] suggest additional biological and/or environmental parameters at play. For example, variations in mineral growth rate and precursor phases could affect Na partitioning (DNa) during shell formation, but the magnitude of these effects remain unconstrained.

Here we present new Na/Ca results for inorganically precipitated calcium carbonate minerals (calcite, aragonite and vaterite), which can be used as a baseline to evaluate variations biogenic calcite Na/Ca. The effects of solution $[Na^+]/[Ca^{2+}]$, $[Na^+]$, calcite saturation state and $[Ca^{2+}]/[CO_3^{2-}]$ on carbonate Na/Ca were tested using two different experimental setups. We show that Na incorporation in calcium carbonate minerals mostly depends on growth solution $[Na^+]/[Ca^{2+}]$ and mineral growth rate (R), while polymorphism affects carbonate Na/Ca to a lower degree. Comparison of our results with published foraminiferal Na/Ca data could suggest foraminifers precipitate $CaCO_3$ at rates consistent with the coprecipitation of vaterite, in agreement with the observation of vaterite in foraminifer samples [4]. Our results suggest the use of biogenic-carbonate Na/Ca for reconstructing past variations in seawater salinity and $[Ca^{2+}]$ should be applied with caution, as both salinity and $[Ca^{2+}]$ have the potential to impact mineral growth rate.

[1] Wit et al. (2013) *Biogeosciences*
[2] Hauzer et al. (2018) *EPSL*
[3] Mezger et al. (2019) *Biogeosciences*
[4] Jacob et al. (2018) *Nature comm.*