



Effects of Mg:Ca, temperature, and water agitation on CaCO₃ polymorph formation – implications for CaCO₃ depositional environments

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CaCO₃ forms as one of two main polymorphs: aragonite and calcite. The Mg:Ca ratio of the solution and temperature are widely recognised as two of the main factors that determine CaCO₃ polymorph type. While previous work has shown that increasing Mg:Ca ratio and temperature moves the CaCO₃ polymorph balance towards aragonite, little is known if this gradual shift is equally driven by nucleation and/or growth of crystals and if water movement influences the outcome. Separating out the effect of Mg:Ca ratio and temperature on nucleation and crystal growth has potentially important implications for interpreting the impact of aragonite-calcite sea conditions on biomineralisation and the formation of geological CaCO₃ deposits.

To address this, we carried out CaCO₃ precipitation experiments using continuous addition of bicarbonate to induce crystal formation under a range of Mg:Ca ratios (1, 2, and 3), temperature (20 and 30° C), and the absence or presence of water agitation (induced by an orbital shaker). Resulting crystals were nucleated on glass plates and photographed in an SEM. For each experiment at least three SEM images (with an area of 0.22 mm²) were analysed resulting in an average of ca. 500 crystals per experiment for which size, mineralogy, and the number of crystals was recorded. Each experiment was replicated 3-5 times.

Our results allow us to separate out the effects of Mg:Ca ratio, temperature, and water agitation on the number of nucleations and crystal growth for aragonite and calcite. While our results corroborate earlier findings of increasing aragonite proportions with increasing Mg:Ca ratio and temperature, we find that water agitation dramatically shifts the system in favour of aragonite. The main contribution of this prominent shift is due to decreasing calcite nucleations when the solution is shaken. We also find that the influence of temperature on the balance between aragonite and calcite affects crystal growth more strongly than nucleations.

Our results suggest that the same starting conditions of Mg:Ca ratio and temperature will result in different proportions of aragonite and calcite depending on the degree of water agitation. This implies that the proportions of aragonite and calcite will be different in quiet pore-water environments than in agitated sea-floor environments such as expected for ooid formation.