

## The effect of temperature on switching between calcite and aragonite seas

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During the Phanerozoic oscillations in seawater composition are believed to have controlled the dominant inorganic carbonate mineral polymorph, leading to the concept of “aragonite” and “calcite” seas [1, 2]. These variations are important for understanding the evolution of marine calcifiers, the controls on the marine Ca isotope system and the vulnerability of the marine biodiversity to ocean acidification. Previous work has focused mainly on the Mg/Ca ratio as a primary driver. Recently, a quantification of the effects of SO<sub>4</sub> on calcium carbonate mineralogy [3] has indicated that at 21°C, an increase in dissolved SO<sub>4</sub> decreases the threshold at which the shift from calcite to aragonite occurs. Although recently temperature has been suggested as another important factor controlling calcium carbonate mineralogy [4], so far the relative influence and effects of temperature and solution chemistry in today's and past oceans is still poorly constrained. Therefore, we mimicked calcium carbonate precipitation in seawater at 5-35°C in constant addition experiments and at variable Mg/Ca and SO<sub>4</sub> contents spanning Phanerozoic ocean chemical conditions. Our results show that temperature has a significant influence on polymorph compositions. For example, at 5°C, the Mg/Ca ratio at which calcite is destabilized and aragonite becomes the predominant polymorph is far lower than at 21°C, and at 5°C, vaterite is stabilized and the amount of magnesium and sulphate incorporated into the calcite structure is decreased. This in turn also decreases the growth rates of aragonite relative to calcite. Temperature also highly affects the morphology and crystal sizes of the formed polymorphs in that with at lower T crystal sizes increase. Thus, temperature in tandem with Mg/Ca and SO<sub>4</sub> are important parameters that should be included in any existing models relating seawater chemistry to CaCO<sub>3</sub> mineralogy throughout the Phanerozoic.

[1] Horita, J. *et al*, (2002) *GCA* **66**, 3733-3756; [2] Holt, N.M. *et al*, (2014) *GCA* **134**, 317-334; [3] Bots, P. *et al*, (2011) *Geology* **39**, 331-334; [4] Balthasar, U., Cusack, M., (2015) *Geology* **43**, 99-102.