Why no Aragonite? Polymorph selection in the early stages of calcium carbonate nucleation

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Aragonite and calcite are the two most commonly observed calcium carbonate polymorphs found naturally and synthetically. Thermodynamic analysis of the two phases has shown that calcite is slightly more stable than aragonite [1], which favours the presence of calcite in geological systems. Recent simulations, however, show that, in water, aragonite may have more stable surfaces than calcite [2] suggesting that growing nuclei of aragonite may be more stable than their calcite counterparts and therefore we would expect to see aragonite crystals forming in the early stages of crystallisation. A further issue is the so-called calcite-aragonite transition whereby aragonite becomes the dominant observed polymorph at temperatures above ~70°C [3] despite the lack of a change in thermodynamic stability between the phases.

We have used computational molecular dynamics to study the interfacial energies of calcium carbonate polymorphs in a variety of aqueous and amorphous calcium carbonate environments. These simulations, coupled with other literature data, demonstrate the similarities in the stabilities of aragonite and calcite nuclei. We have extended these simulations to study the early stages of calcium carbonate nucleation and analyse the structure of clusters forming in solution. We examine the features of the potential nuclei and how they may grow to form crystals. Our analysis suggests that kinetic rather than thermodynamic effects may be controlling the polymorph selection within the calcium carbonate system. We extend our methods to examine the influence of temperature on the formation of these potential nuclei and comment on how temperature may affect polymorph selection

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