

Water Ordering at Aqueous CaCO₃ Interfaces and the Interfacial Entropy of Formation

E. Armstrong, S. Yeandel, C. Freeman and J. Harding

Department of Materials Science and Engineering, University of Sheffield, UK

Calcite and aragonite are two of the most common forms of crystalline calcium carbonate. Despite only a small difference in thermodynamic stability, calcite is observed precipitating far more often than aragonite [1]. Although some methods are known to induce aragonite production over calcite (inclusion of Mg²⁺ ions or high temperatures [2]), the control over polymorph selection in calcium carbonate is still of significant concern. In particular, the reasoning and understanding of the environmental influence on polymorph selection in these systems [3].

By calculating the interfacial free energies of a variety of calcium carbonate surfaces, we can determine the expected morphologies of the polymorphs as well as obtain a greater thermodynamic understanding of the formation of calcite and aragonite. In this work we have used a novel method [4], taking the Einstein crystal as the reference value in thermodynamic integration, to calculate the interfacial energies of calcite and aragonite surfaces with water. Previous methods have calculated interfacial energies and morphologies based on enthalpy alone, however the current technique also includes the entropic contribution.

Our results indicate that the {104} faces significantly dominate the hydrated calcite structure and have a much lower free energy than any other calcite face. For aragonite, there is far less difference in energy between the surfaces, supporting the variety of structures observed experimentally. The entropic contribution varied greatly for the aragonite surfaces, indicating its importance when calculating free energies and its potential part in the polymorph selection of calcium carbonate.

[1] M. Ma et al., *Cryst. Growth Des.* **2019**, *19*, 6972-6988.

[2] U. Balthasar et al., *Geology*, **2015**, *43*, 99-102.

[3] A. M. Bano et al., *Langmuir*, **2014**, *30*, 7513-7521.

[4] S. Yeandel et al., *J. Chem. Phys.*, **2022**, *157*, 084117