Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.15813

Determining the free energy of aqueous mineral interfaces

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The strong interactions between mineral ions and water molecules can change the structure and properties of water profoundly at aqueous interfaces[1]. Strong ordering produces density fluctuations, particularly for very flat interfaces (such as mica and calcite)[2]. Diffusion rates of water molecules are greatly reduced from the bulk, leading to the hypothesis that ice-like structure is present. The water often stabilises the mineral surface and configurational interfacial energies obtained from classical molecular dynamics simulations are used to interpret this, despite the fact that this ignores entropic effects. Our new methods for calculating interfacial free energies[3], based on using Einstein crystals as a reference state, demonstrate that these effects contribute significantly to the thermodynamics of these interfaces.

In this work we examine the surfaces of a range of minerals and polymorphs: calcium carbonate (calcite, aragonite), calcium sulphate (gypsum, bassanite) and halite. We quantify the entropic contributions at these interfaces and link this to the structuring and dynamics of the water molecules. This allows us to build a detailed understanding of the enthalpic and entropic contributions to the total energy of these interfaces. New insights into the transformation mechanisms between different polymorphs may also be obtained[4]. We will also discuss effects due to the presence of solute ions close to the interface which can alter the activity of interfacial water, induce electrical space charge layers or change the relative stability of different surfaces by disrupting the ordering of the solvent and thus altering the entropic contribution to the free energy of the aqueous interface.

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[4] M. Ilett, H.M. Freeman, Z. Aslam, J.M. Galloway *et al*; *J. Microsc.* **288** (2022) 155.