

Modelling Structure and Transport at Mineral Interfaces at the Atomic Level

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The aim of this presentation is to describe some recent developments in modelling the interaction of mineral surfaces with both solid and liquids. In the case of the latter focusing on mineral surfaces in contact with aqueous solutions. The basis of these techniques is to use the Born model of solids to specify the interatomic forces. Energy minimisation and molecular dynamics techniques are then applied to model mineral interfaces. Molecular dynamics gives the effect of temperature by assigning kinetic energy to the atoms in the simulation cell and thus allows us to follow the trajectory of the atoms and molecules with time. However, the energy barriers for atom and molecular transport near mineral interfaces even in solution are so high that there is not enough mobility. Thus constrained techniques, which force atoms to move must be employed. These techniques have the added advantage that free energies of migration can be evaluated.

We will illustrate the approaches by considering two types of mineral interfaces. The first is the mineral-mineral interface where we aim to model the development of microstructure and its influence on the transport processes. In addition, the comparison of the differences between corundum and cerianite allows us to explore how the oxygen stoichiometry can play a role in surface behaviour including surface diffusivity. In our second example we consider the mineral water interface focussing on iron oxides and calcite. We have modelled the free energy of dissolution of ions from the surface into aqueous solution as a function of ionic strength. The resulting double layers are highly structured near the surfaces, which makes a small but significant reduction to the dissolution free-energies. Finally, we have begun to probe the adsorption of organics at mineral surfaces. We find that for chlorine containing pollutant molecules, e.g. PCCDs that the adsorption energies are related to the chlorine content. Furthermore, by considering the adsorption in contact with aqueous solution we can begin to evaluate the distribution coefficients of both molecules and ions.

In summary, the results obtained to date demonstrate that molecular simulation is a viable tool for studying interfaces and gives us confidence to continue to apply these approaches to ever more complex interfaces.