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In-situ AFM study of the thermal dehydration of gypsumG. JORDAN¹ AND J.M. ASTILLEROS²

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Thermal dehydration of gypsum crystals is an important process for the formation of binders. The degree of dehydration and, therefore, the occurring phases depend among other parameters mainly on temperature and the presence of water in the system [e.g. 1]. However, only a certain range of mixtures of phases can be used as binders.

Dehydration in solutions

Hydrothermal AFM (HAFM) [e.g. 2] has been used to study the initial steps of the thermal dehydration reaction on gypsum (010) surface in solutions at different saturation states from 25 to 130 °C. HAFM enables the in-situ investigation of nano-scale changes of the morphology of gypsum surfaces and, therefore, permits an access to the molecular mechanism. Supersaturated solutions (beta = 1.8 - 5) caused gypsum growth in the entire temperature range, in near-saturated solution (beta = 1.02) a complex response of the gypsum surface could be observed. At 25 - 55 °C the surface did not undergo any significant changes. From 60 to ~120 °C growth could be observed. At ~120 °C a sharp transition to very fast dissolution took place suggesting a different phase being more stable than gypsum. Judging by literature data [e.g. 1], this transition is related to growth of hemihydrate, which was not found to be nucleating on the gypsum (010) surface.

Dehydration at low water vapor pressure

At low water vapor pressure, dehydration takes place via the nucleation and spreading of etch-pit like pattern. These thermal etch pits were found to nucleate even at positions that show no indications of screw dislocations making it likely that lattice strain induced by impurities or edge dislocations is sufficient to trigger the dehydration process. At the temperatures applied, no dehydration at monolayer steps on the (010) surface could be observed. Thus unlike growth or dissolution, surface energy related to kink sites is not sufficient to trigger dehydration.

References

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Computer modeling of the free energy of adsorption at the mineral - aqueous interface

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Atomistic simulation is a valuable tool for predicting the structure of surfaces. This poster considers some of our recent work aimed at applying the approach to mineral surfaces in contact with water. In general we use energy minimisation and molecular dynamics which are coupled with inter-atomic potentials. The use of such potentials enables the surface properties to be calculated rapidly and enables the study of complex systems. Therefore it is essential that we can derive and verify suitable parameters to describe these systems.

This is illustrated with in recent work where we combined techniques that use inter-atomic with electronic structure calculations using Density Functional Theory (DFT) to investigate the interactions of water with the surfaces of carbonate minerals. We first compared the two techniques for small model systems, namely the adsorption of a monolayer of water of the {10 $\bar{1}$ 4} surface of calcite, dolomite and magnesite. We then re-considered the potential model for the water-mineral interactions to improve agreement with the DFT calculations and enabled us to model with confidence the adsorption of water on the most significant low index surfaces and on growth steps. Finally, we performed classical molecular dynamics simulations of calcite surfaces in contact with bulk water to investigate the effect of temperature and kinetics on the calcite-water interface.

The need to simulate surfaces in contact with water is illustrated in recent work concerned with the surfaces of hematite (alpha - Fe₂O₃). It was found that the relative stability of the low index surfaces, and hence the morphology is highly dependent on whether water is present and to a lesser extent on whether the water layer consists of dissociated hydroxide ions or molecular water. This is further illustrated in work where the segregation of various iso-valent cations to the (00.1) and (0.12) surfaces of hematite where the presence of water significantly effects the segregation process.

Finally we highlight a key challenge for the future, which is not only to simulate at the interface between a mineral surface and a water layer, but also consider the interaction when the water layer contains charged species.