Non-stoichiometric mineral surfaces: *Ab initio* phase diagrams

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We present recent work applying *ab initio* electronic structure methods based on DFT to model non-stoichiometric surfaces of minerals in equilibrium with a vapour consisting of different gases. The stability of surfaces of different stoichiometry are compared in terms of general surface phase diagrams, initially as a function of the oxygen and hydrogen chemical potentials, which are themselves dependent on temperature and partial pressures of oxygen and hydrogen. Thus, the stable structures and compositions can be evaluated at specific experimental conditions. The major dificulty of applying this approach is the large amount of computer time required to simulate the different surface configurations. We will show how atomistic methods can be used to aid in the search of different surface configurations and to model the surface lattice dynamics, thus giving a good representation of the free energies involved.

We will describe three recent applications. First, we will report the surface compositions of the low index surfaces of Alumina in contact with oxygen, hydrogen or water. In each the results are in good agreement with experimental data. Secondly, we will discuss the predictions of the surface behaviour of the (10.0) and (11.0) surfaces of ZnO again in equilibrium with both the bulk structure and partial oxygen and hydrogen pressures. At ambient temperatures, we predict that molecular water will be present on the surface of the (10.0) whereas a hydroxide layer is favoured for the (11.0). A prediction also duplicated using atomistic, potential based, methods. The final application is where we begin to include other gases such as carbon dioxide in contact with mineral surfaces. The results on the (10.4) and (00.1) surfaces of calcite in the presence of water and carbon dioxide not only show that the surface stoichiometries are highly dependent on the partial gas pressures, and predicts new surface structures not previously considered.

Observing the chemical composition and the point of zero charge of mineral surfaces *in situ* under water by nonlinear optics

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The properties of mineral/electrolyte interfaces are controlled by the surface functional species. In order to model surface reactivity and adsorption/desorption processes a large number of functional groups has been postulated. In most cases, however, a direct proof for the existence of these species in real aquatic environment is lacking because it is difficult to obtain chemical in situ information with interface selectivity. Here we apply interface selective sum frequency (SF) vibrational spectroscopy to study the speciation of the (001) surface of sapphire (α-Al_2O_3) under water between pH 4 and 12. The technique allows us also to measure the absolute polar orientation of the water molecules adjacent to the mineral surface. The inversion of the molecules' polar orientation upon the alteration of the pH indicates the point of zero charge (pzc). We use sapphire as a simple model for natural clay minerals and related iron phases. The data are required in order to reliably predict the migration of actinide ions in the aquifer. These studies are an essential part of our research on the safety of repositories for nuclear waste.

In the O-H stretch region of the infrared spectrum between 2800 and 4000 cm^{-1}, we observe a surprisingly large number of 7 SF bands in total. Two of them are due to the polar ordered water film near the mineral surface which is well known from various aquatic interfaces. At high pH, we observe the water dipoles to point into the direction of the mineral surface. This is consistent with a negative surface charge. The dipoles' orientation is reversed near pH 6 indicating that we have crossed the pzc. The other 5 bands originate from up to 5 different aluminol species or from specifically bound water molecules. The main peak with the SF intensity maximum at 3690 cm^{-1}, we attribute to an OH group bridging two aluminium atoms. A peak at 3450 cm^{-1} corresponds to a species with its O-H bond almost in the surface plane. Its SF intensity increases considerably below pH 6 indicating a strong increase of its concentration. At pH 4, we additionally observe a water species whose dipole points into the direction of the mineral surface. The oxygens of the in-plane OH species might act as hydrogen bond acceptors for these water molecules.