

Modelling the hydration, dissolution and crystallisation of alpha-quartz

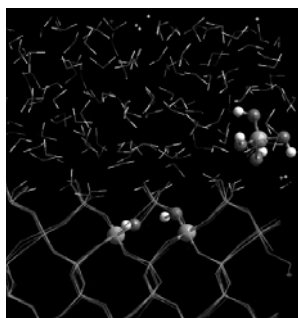
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A combination of Density Functional Theory (DFT) calculations and interatomic potential-based methods have been employed to investigate hydration, dissolution and crystallisation processes at the α -quartz (0001) surface.

DFT calculations and static energy minimisations techniques both agree that when under-coordinated surface silicon and oxygen atoms are present, water adsorbs dissociatively at the surface, thereby annihilating dangling bonds by the formation of surface hydroxy groups. However, when the surface species are linked by Si-O-Si bridges and fully coordinated, water adsorbs associatively.

Further Molecular Dynamics simulations (MD) in liquid water show that the structure of the water layers near the surfaces is affected by the nature of the substrate surface and by temperature. Ordered mono-layers of interfacial water molecules form in the region of the substrate where the surface is highly charged and built up of Si-O-Si bridges. As the temperature is increased this ordered mono-layer structure is gradually lost. When the surface is terminated by silanol groups, the water retains liquid-like properties even at low temperature and the molecules are distributed in a random manner, without the formation of distinct ordered mono-layers of water molecules near the surface.



Taking into the account the entropy of the system, the calculated energies of stepwise dissolution of a silicon species from the surface suggest that on thermodynamic grounds the complete dissolution of silicon atoms from the quartz surfaces in a liquid water environment is an endothermic process, but that the formation of a $-\text{Si}(\text{OH})_3$ species at the surface would be possible. In addition, if the $\text{Si}(\text{OH})_4$ species were to be dissolved, it would remain near the surface, and re-deposition at the defect-free surface is thermodynamically preferred, although there is an activation enthalpy to the first step in the process of nucleation of $\text{Si}(\text{OH})_4$ at the perfect surface.

Mine-related pollution in the Guadiana Estuary (SW Iberia)

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The Guadiana River drains the western part of the Iberian Pyrite Belt (IPB), one of the most important metallogenic massive sulphide provinces of the world, where the exploitation of sulphide deposits dates back to the Third Millennium B.C.[1]. Associated with the exploitation of these sulphide deposits, highly polluted acidic leachates with high concentrations of metals, metalloids and sulphates are being originated. These leachates are responsible of the pollution and water quality degradation of part of the river basin and, consequently, of the estuarine marshes which act as the ultimate continental filters before the discharge to the Gulf of Cadiz.

The main aim of this work is twofold: a) to evaluate the environmental quality of the most recent sediments through the comparison with the local background of Holocene sediments, and b) to assess of the influence of upstream human activities on the estuarine system. For this purpose, a sedimentological and geochemical characterization of the sediment samples recovered from boreholes have been made. All normalized concentrations have been calculated for the most important metals and metalloids in order to obtain local background levels. By using these background levels, enrichment factors (EF) have been calculated for the superficial sediments of the Guadiana estuary.

Our results show a conspicuous covariance of the studied elements in two groups; Group I of natural origin (Al, Fe, Mn, Co, Cr and Ni), and Group II of anthropogenic origin (As, Cd, Cu, Pb and Zn). The distribution of enrichment factors for the elements of Group II within the estuary suggests the existence of a diffuse mining pollution associated with the AMD forming processes in the Guadiana watershed [2]. The pollution which is inherited from 5 millennia of mining activities in the IPB, peaked during the last 150 years [3]. Other local sources of metal and metalloid pollution have been found near the villages of Ayamonte (Spain) and Villa Real de Sto. Antonio (Portugal) with high EF values for As, Cd and Zn.

[1] Nocete *et al.* (2005) *JAS* **32**, 1566-1576. [2] Delgado *et al.* (2008) *WASP* DOI: 10.1007/s11270-008-9882-x. [3] Álvarez-Valero *et al.* (2008) *Env. Geol* **55**, 1797-1809.