# Theoretical investigation of the solvated corundum surface

R. POLLY*, B. SCHIMMELPFENNIG, M. FLÖRSHEIMER, R. KLENZE AND H. GECKEIS

Karlsruher Institut für Technologie (KIT), Campus Nord, Institut für nukleare Entsorgung (INE), Postfach 3640, 76021 Karlsruhe, Germany
(*correspondence: polly@kit.edu)

For the reliable long-term modelling of the actinide migration in geological formations, the adsorption/desorption properties and the reactivity of mineral surfaces must be understood at the molecular level. The adsorption of contaminants at mineral surfaces of the aquifer is an important process which leads to the retention/retardation of radio nuclides such as actinide ions. Methods of theoretical chemistry developed to reliable tools in recent years and are of great help to improve the understanding of experimental results and provide data experimental not accessible.

Here we present two completely independent theoretical approaches for this task. In our first approach we used $Al_{27}O_{75}H_{67}$ or $Al_{31}O_{60}H_{21}$ clusters as model systems for the corundum (110) and (001) surfaces, respectively. We found, that calculations on these clusters with Density Functional Theory (DFT) using the BP86 functional and the cc-pVDZ basis set provide accurate results in good agreement with ab initio methods. Experimental results at the INE (vibrational Sum Frequency Spectroscopy Generation and Time Dependent Laser Induced Fluorescence) and others (Crystal Truncation Rod Diffraction) experiments are reproduced very well by our calculations.

(1) The determination of the orientation and vibrational frequencies of the aluminol groups (Al-OH) at the corundum (001) and (110) surface.

(2) The interaction of bulk water with the surface. We study the accuracy of the model concerning the interlayer spacing between the first water layer to the corundum (0001) surface as well as the vibrational frequencies of the aluminol groups.

(3) Inner sphere complexes of trivalent lanthanide and actinide ions on the (001) surface. This is studied with the clusters mentioned above and, additionally, with $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ Keggin clusters as a model system for the (001) surface.

In an independent completely different theoretical approach, we use the plane-wave, supercell density functional theory (DFT) framework as implemented in the Vienna ab initio simulation package (VASP) to study the solvated corundum surface. The Perdew-Burke-Ernzerhof (PBE) functional is used together with the projector augmented wave (PAW) ansatz.

With this ansatz we study the surface aluminol groups (bond length, tilt angle) as well as their vibrational frequencies. These calculations complement the theoretical information already available from the cluster calculations.

# Endolithic habitats in shocked gneisses from Haughton impact structure, Devon Island, Canada

A. PONTEFRACT[1]*, G.R. OSINSKI[1], C.S. COCKELL[2] AND G. SOUTHAM[1]

[1]Dept. of Earth Sciences, UWO, London, ON N6A 5B7
(*correspondence: apontefr@uwo.ca)
[2]CEPSAR, Open University, Milton Keynes, MK7 6AA

Meteorite impacts are rarely thought of as agents promoting microbial growth: generating extreme temperatures and pressures, an impact may cause the target substrate to undergo deformation, vaporization, melting and shock metamorphism. These processes, however, can favourably change the availability and habitability of the substrate for lithophytic organisms, which are then able to (re)colonize microfractures and pore spaces created during the impact [1]. This study shows how shocked gneisses from the 39 Ma, 23 km diameter Haughton structure, Devon Island, Canada, offer significant refuge for lithophytic communities.

Macroscopic observations highlight an increase in the spatial distribution of the endolithic communities with shock level, up to approximately 50 GPa. As gneiss undergoes shock-metamorphism, porosity levels increase, as does the translucence of the rock [2]. These changes increase available surface area and allow in greater levels of photosynthetically active radiation (PAR), while simultaneously acting as a buffer against environmental stressors such as temperature, ablation and ultraviolet radiation. At shock levels greater than 50 GPa, subsequent growth decreases, correlating with the collapse of pore spaces and the creation of glass flows under such high pressures. Similarly, at low shock levels ($< 20$ GPa), porosity is low, restricting growth to near surface environments. Examination of these endolithic mm-scale habitats using scanning electron microscopy has highlighted the presence of a diverse community of microorganisms, including fungi, and organic coatings on mineral surfaces including evidence for bacterial growth as microcolonies. Culturing aerobic, heterotrophic bacteria using contact plates with R2A agar produced limited growth but highlighted the endolithic habitat as the dominant heterotrophic zone within the ecosystem. The increase in porosity created by this shock event appears to have created ideal physical and chemical endolithic habitats, where space and trace nutrients via weathering of glass, respectively, has enhanced the growth of microorganisms.

[1] Cockell *et al*. (2005) *Met. & Plan. Sci*. **40**, 1901-1914. [2] Cockell *et al*. (2002) *Met. & Plan. Sci*. **37**, 1287-1298.