O 36: Focus Session: Mineral-water interfaces II

The Focus Session discusses recent advances in the understanding of mineral-water interfaces. These interfaces are ubiquitous in nature, host of many geological and biological processes, intimately linked to the global carbon cycle, and therefore highly relevant for Earth*s climate. For example, silicate weathering removes carbon dioxide from the atmosphere on geological timescales, acting as a stabilizing feedback mechanism since weathering rates increase with temperature. In the oceans, carbonates dissolve and precipitate in response to changing atmospheric carbon dioxide concentrations, thus far mitigating part of the anthropogenic impact of CO_2 emissions. In addition, numerous industrial and technological processes involve mineral-water interfaces, including seawater desalination, scaling and incrustation prevention, as well as various biochemical applications. However, and despite their importance, many fundamental aspects of mineral-water interfaces remain poorly understood, including water binding and diffusion, structure formation, ice nucleation, growth, or desorption.

This DPG Focus Session will address these aspects at the molecular level, elucidating fundamental processes involving both single water molecules and bulk water in contact with mineral surfaces. The session brings together scientists investigating mineral-water systems under ultrahigh vacuum conditions as well as at mineral-water interfaces in bulk aqueous environments. We aim for a balanced Session with contribution from both renowned experts and young investigators active in the field.

Organized by Philipp Rahe (U Osnabrück), Angelika Kühnle (U Bielefeld), Jan Balajka (TU Vienna), Wolf Gero Schmidt (U Paderborn).

Time: Tuesday 10:30–12:30 Location: HSZ/0403

Invited Talk O 36.1 Tue 10:30 HSZ/0403

Acidity in nanoconfinement from ab initio and NNPs simulations — Anthony Baldo[2], Muhammad Saleh[1], Kevin Leung[2], and •Marialore Sulpizi[1] — [1]Department of Physics and Astronomy, Ruhr-University Bochum, Universitätsstraße 150, 44801 Bochum, Germany — [2]Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico, USA

Chemical and physical properties in nanoconfined systems may substantially differ from bulk, a phenomenon that can be exploited for the development of new industrial processes for energy generation and storage. Here we consider the specific behavior of acids within silica nanopores, a topic of relevance to the geochemistry and the nanofluids communities.

Starting from ab initio molecular dynamics simulations we develop neural network potentials (NNPs) capable of describing the solid/liquid interfaces and the nanoconfined liquids* behavior over a wide range of temperatures. These NNPs can capture the change in acidity constants when e,g acetic acid is confined in nanoscale slit or when it approaches the interface. Our approach can be further extended to more complex geometries and solution compositions.

O 36.2 Tue 11:00 HSZ/0403

Ab initio exploration of water clusters on CaF_2 — •Isaac Azahel Ruiz Alvarado[1], Wolf Gero Schmidt[1], Paul Laubrock[2], Jonas Heggemann[2], and Philipp Rahe[2] — [1]Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, Paderborn, Germany — [2]Institut für Physik, Universität Osnabrück, Osnabrück, Germany

The electronic and structural properties of the $CaF_2(111)$ surface-water interface are investigated from first-principles calculations. The energetic landscape for single molecular adsorption is calculated using standard DFT with London dispersion forces corrections. Single water molecules are found to preferentially adsorb on surface Ca atoms while large diffusion energy barriers are determined that restrict lateral movement of the water molecules. Additionally, the adsorption energies for the intact water molecule are compared to dissociative adsorption.

Multiple water molecules are included in the calculations to simulate the ice-like clusters observed experimentally by high-resolution AFM data acquired with CO-terminated tips. In order to understand the formation of these clusters, hexagonal rings similar to the ice I_h motif are modeled on top of the CaF_2 surface slab. The ice-surface incommensurability coupled with large diffusion barriers and preferred adsorption sites is suspected to limit the formation of a closed water monolayer. Complete water overlayers and additional structures are also calculated using molecular dynamics aided by machine learning force fields trained from ab initio calculations.

O 36.3 Tue 11:15 HSZ/0403

Surface Structure of Polar Silver Iodide (0001) in Various Liquids: No Indication for a Surface Reconstruction — •Kim Noelle Dreier, Annamaria Latus, Ralf Bechstein, and Angelika Kühnle — Physical Chemistry I, Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

Silver iodide (AgI) has long been known as a material that induces precipitation in clouds. The superior ice nucleation ability is commonly explained by the close lattice match between β-AgI(0001) and the basal plane of ice. However, this surface is polar, indicating that a stabilization mechanism should be present. Here, we investigate the Ag-terminated β-AgI(0001) and the I-terminated β-AgI(000-1) surfaces in water and compare the results with images recorded in n-dodecane, 0.1 M NaCl and 0.1 M KI aqueous solutions. Strikingly, high-resolution images consistently reveal a bulk-truncated structure. These findings align with observations at a larger scale, which neither indicate any surface reconstruction. Although the observed structures reveal a variety of features and depend on the surface termination, some general conclusions can be drawn. Firstly, in solvents with poor AgI solubility, only minor changes are observed. Secondly, the images taken in KI solution exhibit patterns that are characteristic of mineral dissolution and growth. Thus, even in a situation where AgI can and does dissolve, no indication for a surface reconstruction can be found. These results shed new light onto the surface structure of β-AgI(0001), challenging the expectation that a surface reconstruction is present under ambient conditions.

Invited Talk O 36.4 Tue 11:30 HSZ/0403

Living Interfaces: Dissolution and Precipitation Processes at Mineral-Brine Interfaces Revealed by AFM — •Igor Siretanu, Vincenzo Alagia, Saravana Kumar, Shilpa Mohanakumar, Max Nederstigt, Chinmay Shukla, Michel Duits, and Frieder Mugele — Physics of Complex Fluids Group and MESA+ Institute, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Mineral-brine interfaces are dynamic systems where dissolution and precipitation govern reactivity and morphology. Using in-situ Atomic Force Microscopy (AFM), we examine olivine ([Mg,Fe]2SiO4) and calcite. Olivine, a candidate for carbon mineralization, shows etch-pit-mediated surface retraction with morphology strongly dependent on solution chemistry. In H2SO4, pits are larger and deeper than in HCl, while oxalic acid induces anisotropic complexation, forming rectangular pits and stepped terraces aligned with crystallographic directions. These changes accelerate step retreat and Mg release, offering mechanistic insight into dissolution kinetics relevant for CO2 sequestration. At calcite-water interfaces near equilibrium, AFM force spectroscopy reveals two regimes: (A) DLVO-type forces with low surface potentials (<5 mV) and (B) long-range viscoelastic repulsion from a soft interfacial layer formed by coupled dissolution-precipitation. This dynamic interphase explains inconsistencies in reported surface forces and highlights how solution composition, crystallography, and transient phases control mineral reactivity, with implications for geochemistry, biomineralization, and carbon capture.

O 36.5 Tue 12:00 HSZ/0403

Water Organization and Speciation at the Calcite (10.4)-Water Interface at High pH — •Tobias Dickbreder[1], Frank Heberling[2], and Ellen H. G. Backus[1] — [1]Institute of Physical Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria. — [2]Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Calcite dissolution and precipitation are central for various environmental processes including the geological carbonate-silicate cycle, buffering of sea- and freshwater pH values and biomineralization. Since these processes take place at the calcite-water interface, the structure and properties of the interface between water and the most stable calcite (10.4) surface have been well studied. Despite this effort the protonation state of surface-bound water and interfacial carbonate groups remains poorly understood, because dissolution and carbonate buffering complicate studying calcite de-/protonation experimentally.

Here, we apply vibrational sum frequency generation (SFG) spectroscopy to directly assess the water species present at the calcite-water interface. As reported previously, the SFG spectrum at neutral pH is almost featureless due to the opposite orientation of the first two water layers [1]. At very high pH, however, we observe the emergence of spectral features suggesting surface charging and the presence of interfacial hydroxyl groups. Our study, thus, confirms the presence of hydroxyl groups at the calcite-water interface, facilitating the development of more-accurate models of the calcite-water interface.

[1] Söngen et al., J. Phys. Chem. Lett. 12 (2021), 7605 - 7611.

O 36.6 Tue 12:15 HSZ/0403

The mechanism of selenite incorporation into the calcite surface revealed by atomic-scale imaging — •Marie Luigs, Ralf Bechstein, and Angelika Kühnle — University of Bielefeld, Bielefeld, Germany

Selenium is an essential trace element for human health. However, the margin between its required and toxic intake is very narrow, making its distribution in soils and waters an important subject of research. Moreover, the interaction between the nuclear waste component 79Se and minerals in the Earth's crust is relevant for the selection of nuclear waste disposal sites. Selenium in the form of selenite can be incorporated into the mineral calcite by substituting for carbonate ions. However, the mechanism of selenite incorporation into calcite remains unknown. Here we demonstrate that selenite incorporation occurs at step edges during calcite crystal growth. Atomic-scale atomic force microscopy (AFM) images of the calcite surface exposed to a selenite-rich calcium carbonate growth solution shows that calcite layers grown in the presence of selenite displayed a significantly higher defect density than layers that were exposed to selenite only after their formation. These observations indicate that significant selenite incorporation into calcite, reflected by an increased defect density, does not occur via ion exchange on terraces but via step edge growth. Our results give further insights into the conditions required for selenite incorporation into calcite and present the first atomic-scale AFM images of a selenite-rich calcite surface.