O 5: Focus Session: Mineral-water interfaces I

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: Monday 10:30–12:30 Location: HSZ/0403

Invited Talk O 5.1 Mon 10:30 HSZ/0403

Can the mineral-water interface save the world? Mineral carbonation, enhanced weathering and negative emissions — •Philip Pogge von Strandmann — Johannes Gutenberg University, Mainz

The rising atmospheric CO2 concentrations are clearly having a significant impact on the climate, and will continue to do so. The currently only foreseeable method by which anthropogenic climate change will not be completely catastrophic (i.e. limited to 1.5-2°C warming), is if we implement global "negative emissions" technologies, that is the artificial removal of CO2. Two such technologies directly rely on the mineral-water interface: mineral carbonation and enhanced weathering. Both require the dissolution of silicate minerals in mildly acidic water, and the subsequent precipitation of carbonate secondary minerals, but without too much precipitation of silicate secondary minerals, which hinder the reaction. In fact, the reaction is more complex than that, because numerous reactions occur at the mineral-water interface: dissolution, sorption, exchange, co-precipitation and incorporation into interstitial sites in mineral lattices. Each of these reactions has significant consequences for the efficiency of the reaction and the CO2 drawdown. This presentation will examine these reactions, including the aspects we currently understand and can measure, and those where our knowledge and analytical abilities are still lacking.

O 5.2 Mon 11:00 HSZ/0403

Reconstruction of calcite (10.4) manifests itself in the tip-assisted diffusion of water — •Klausfering Lea, Schneider Florian, Bechstein Ralf, and Kühnle Angelika — Bielefeld University, 33615 Bielefeld, Germany

Calcite is the most common carbonate in the Earth*s crust and plays a fundamental role in environmental and industrial processes. The most stable cleavage plane of calcite is the (10.4) plane. This surface has already been extensively studied in liquid environments as well as under ultra-high vacuum (UHV) conditions. Under UHV conditions, the surface exhibits a (2 x 1) reconstruction. Due to this reconstruction, there are two energetically different adsorption sites for adsorbates, such as water. Here, we present an atomic force microscopy (AFM) study in which the diffusion of individual water molecules on the calcite (10.4) surface was investigated under UHV conditions at a temperature of 140 K. The positions of individual water molecules could be precisely determined in several consecutive atomically resolved images, allowing the diffusion of the water molecules to be observed. We found that the AFM tip has an influence on the diffusion of the water molecules, but that diffusion only occurs between one type of adsorption positions.

O 5.3 Mon 11:15 HSZ/0403

Nanoscopic insights on ice nucleation on microcline (001) — •Florian Schneider[1], Rasmus Väinö Erik Nilsson[2], Ralf Bechstein[1], Bernhard Reischl[2], Thomas Koop[1], Angelika Kühnle[1], and Tobias Dickbreder[3] — [1]Bielefeld University, Bielefeld, Germany — [2]University of Helsinki, Helsinki, Finland — [3]University of Vienna, Vienna, Austria

Heterogeneous ice nucleation plays a crucial role in various environmental and technological processes. An in-depth understanding of the nucleation at the atomic scale can greatly enhance our capability to create materials with particular ice-nucleating properties and improve our climate models. In the atmosphere, a particularly active ice nucleating particle is dust from the feldspar mineral microcline [1]. However, why microcline outperforms other mineral dust particles in its ice-nucleating ability still remains a puzzle. Here, we present atomic force microscopy images of ice crystals growing from the vapor phase on the (001) surface of microcline at low temperature. In contrast to the prevailing view of active sites such as step edges or cracks being responsible for ice nucleation, we observe ice growth at random positions on the bare terrace. For the closely related feldspar sanidine, in contrast, ice nucleation is prevalent at step edges as expected. This comparison underscores the exceptional ice nucleating ability of microcline as it demonstrates ice nucleation even in the absence of surface defects and raises important questions regarding the different ice nucleation mechanisms on these two feldspar mineral surfaces.

[1] Harrison, A. D. *et al.*, Atmos. Chem. Phys., 16, 2016.

Invited Talk O 5.4 Mon 11:30 HSZ/0403

Machine learning exploration of water binding and ice nucleation at silicate and carbon surfaces — •Mie Andersen — Department of Physics and Astronomy, Aarhus University, Denmark

Mineral-water interfaces play a central role in environments ranging from the interstellar medium to Earth's surface and subsurface. In astrochemistry, the chemical evolution of star-forming regions is controlled by gas-grain interactions on dust grains that may be partially or fully covered by water ice. A key quantity underlying these processes is the binding energy (BE) of adsorbates, which determines desorption and diffusion rates and controls chemical kinetics.

In this contribution, we explore computational strategies to quantify BE distributions at complex, partially ice-covered mineral surfaces. Using graphene and forsterite as model grain substrates, we combine atomistic simulations with machine-learning interatomic potentials to generate realistic surface structures and to efficiently sample BEs. The modelled ice structures range from amorphous structures generated by low-temperature molecular dynamics simulations to highly stable crystalline structures generated by global structure optimization. The resulting BE distributions are analyzed in terms of surface heterogeneity, ice coverage and hydrogen bonding.

While motivated by astrochemical applications, the presented methodology is broadly transferable to mineral-water interfaces under terrestrial conditions. The approach offers a general framework for linking molecular-scale interfacial structure to macroscopic transport and reaction models across disciplines.

O 5.5 Mon 12:00 HSZ/0403

Chiral water structures on dolomite(104) surfaces — •Jonas Heggemann[1], Paul Laubrock[1], Jie Huang[2], Adam S. Foster[2,3], and Philipp Rahe[1] — [1]Institute of Physics, Osnabrück University, Osnabrück, Germany — [2]Department of Applied Physics, Aalto University, Helsinki, Finland — [3]Nano Life Science Institute (WPI NanoLSI), Kanazawa University, Kanazawa, Japan

The formation mechanisms of dolomite ($CaMg(CO_3)_2$), an abundant rock-forming carbonate mineral with rhombohedral structure [1], are still poorly understood in the earth's crust [2]. The lack of replicating mineral growth under geological conditions in the laboratory is a further characteristic of the "dolomite problem" [2]. Consensus could be reached that dolomite formation only occurs in the presence of water [3] and it is further known that (104) is the most stable surface [4].

Here, we unravel a chiral character of dolomite(104) surfaces from non-contact atomic force microscopy data acquired with CO terminated tips. Backed by density functional theory and probe-particle model calculations, the presence of two surface enantiomers is identified. We further investigate water adsorption, with coverage ranging from single molecules to a full monolayer. Preferred water adsorption is found at calcium and magnesium surface sites; yet, the geometries carry a clear chiral property.

[1] L. S. Land, AAPG **24**, 1 (1982)
[2] J. A. Roberts, Nature Geoscience **17**, 716 (2024)
[3] S. E. Kaczmarek *et al.*, Sedimentology **61**, 1862 (2014)
[4] N. H. De Leeuw, Am. Mineral. **87**, 679 (2002)

O 5.6 Mon 12:15 HSZ/0403

Atomically Resolved Imaging of the Gypsum (010) surface — •David Kugler, Andrea Conti, Tun Sinner, Florian Mittendorfer, Michael Schmid, Gareth S. Parkinson, Ulrike Diebold, and Jan Balajka — Institute of Applied Physics, TU Wien, Vienna, Austria

Gypsum ($CaSO_4 \cdot 2H_2O$), the dihydrate of calcium sulfate, is the most abundant sulfate mineral in Earth′s crust and it is widely used as a fertilizer and as a construction material. Its bulk crystal structure consists of alternating calcium sulfate bilayers and bilayers of crystal water. While the water in the bulk has been extensively studied, a comprehensive understanding of surface processes is still missing. Water is, however, present on all surfaces in ambient environment and influences surface chemistry. Because the adjacent layers are linked only by hydrogen bonds, gypsum cleaves readily along the (010) plane, exposing large, atomically flat terraces. In this work, noncontact atomic force microscopy (nc-AFM) with a qPlus sensor was used to resolve the atomic structure of the cleaved gypsum (010) surface and to visualize the configuration of adsorbed water. Our results indicate that one of the surface crystal water molecules rotates into a lower energy orientation, forming a hydrogen bond with the second crystal water molecule within the unit cell. Preliminary ab-initio modeling suggests that the first adsorbed water layer preserves the periodicity of the bulk structure by forming hydrogen bonds with the surface crystal water.