

## Nanocrystalline anatase-electrolyte solution interface: A surface structural interpretation with the MUSIC and CD Models

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Mineral surface reactivity and pH-dependent charging in aqueous media is related to oxide surface structure and variations in the coordination of surface functional groups at mineral surfaces. Relatively little is known about how interface reactions affect the chemical and physical properties of nanoparticles. To develop a fundamental understanding of the surface reactivity of nanosized particles controlled studies with monodispersed crystalline anatase (TiO<sub>2</sub>) particles were performed. Bulk surface titrations were completed with commercially available anatase particles ranging in size from 200 to 3 nm diameter. The titrations were performed in NaCl media at ionic strengths from 0.005 to 0.3 molality.

The focus of this contribution will be our efforts to rationalize the bulk surface titration data utilizing surface complexation modeling (SCM) that incorporates all available molecular information (e.g., Ti-O bond lengths), with crystallographic information acquired from aberration corrected electron microscopy (ACEM). ACEM imaging revealed that the [100] face predominates on the 20 nm particles, and edges/facets include [010], [001], and [0-11]. A MUSIC model based description of surface protonation permitted rationalization of the experimentally observed decrease in pH<sub>znpc</sub> values with increasing particle size. The surface charging curves were fit with a charge distribution (CD) model and a three-plane description of the Stern layer. Moreover, the titration data suggested an innersphere species for the so-called "inert" Na electrolyte cations. From the SCM, a bidentate innersphere Na-surface species predominated, with the spatial charge distributed between the anatase surface (0-plane) and the 1-plane. Conversely, the best-fit for the Cl<sup>-</sup> ions was a monodentate outersphere complex. As conventional, the outersphere complex was treated as a point charge at the Stern layer (2-plane). The capacitance value of the Stern layer increased with increasing particle size, equating to a narrower compact layer; thus, reproducing the experimental data which showed an enhancement in positive surface charge for the larger nanoparticles (>20nm).

## Biogeochemistry of advective tidal flat porewaters

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Microbial life is abundant in marine sediments. Its activity has an impact on pore water chemistry and – on geological timescales - on sediment diagenesis. In open ocean sediments the limited supply of organic carbon and/or nutrients gives rise to low microbial activities at depth. Our studies on NW German tidal flat sediments have shown that advective systems are, in contrast, far more active than the diffusion controlled marine sediments.

For our studies we permanently installed 5 m long pore water samplers along a transect from the top of the tidal flat towards the low water line to monitor changes in pore water chemistry in space and time. During high tide the sediment at the top of the tidal flat is recharged with seawater and therefore with organic matter and electron acceptors such as oxygen, iron, manganese or sulfate. During the following low tide a deep pore water flow is established at the tidal flat margin. Flowing towards the low water line, the pore waters are strongly altered. Within about 30 to 40 m of flow path the pore water profiles show changing redox states from oxygenated to sulfate reducing. Close to the low water line, where pore water seeps are occurring, even methanogenesis can be detected. These seeps contribute to the trace metal and nutrient budget of the open water column. The quantification of this contribution is a major goal of this study and will help to understand trace metal and nutrient cycling in coastal systems affected by tides.

A modeling approach coupled with geophysical data shows that the residence time of pore waters in the tidal flat ranges between several days to a few weeks. This makes tidal flats an easily accessible small scale study site for the deep biosphere, which in this case is encountered at shallow depths, in contrast to sub-seafloor settings.