

## Ion adsorption on nanocrystalline anatase surfaces: Integrating experimental and theoretical studies through surface complexation modeling

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Detailed experimental studies have been undertaken to quantitatively examine particle-size effects on proton-induced surface charge and accompanying ion adsorption phenomena on a suite of nanocrystalline anatase (TiO<sub>2</sub>) phases. Commercially available, crystalline, monodispersed anatase particles ranging in diameter from 3 to 40 nm were used in the study. Extensive characterization of these particles revealed that the [101] face predominates. Bulk surface titrations were completed in LiCl, NaCl, KCl, RbCl and NaCF<sub>3</sub>SO<sub>3</sub> (NaTr) electrolyte solutions, over a wide range of ionic strengths (0.0005 to 0.3 *m*). Additionally, the specific adsorption of divalent ions (e.g., Sr<sup>2+</sup>) has been investigated as a function of pH and loading in NaCl media.

Molecular simulation, DFT-MD, calculations were completed to complement the surface adsorption studies. Specifically, bonding geometries on the anatase [101] surface were predicted for the adsorption of cations and anions used in the experimental studies. The DFT-MD simulations show inner-sphere binding for all cations, with bidentate geometries predominating. Conversely, monovalent anions form outer-sphere complexes.

To integrate the experimental results with molecular-level insights gained from the simulation studies, surface complexation modelling (SCM) was performed. The CD-MUSIC model, coupled with a Basic Stern layer description of the electric double layer, was used to successfully provide a surface structural description of the ion adsorption data. All fitting parameters within the SCMs were constrained by the DFT simulation results. The resulting SCMs rationalize successfully the subtle differences observed in the surface reactivity of the anatase particles as a function of particle size. For example, the small decrease in pH<sub>ZnPC</sub> values with increasing particle diameter are accounted for by slight differences in protonation constants, K<sub>H</sub>. Similarly, binding constants for adsorbed ions and capacitance values for the EDL vary with particle size.

## Anaerobic oxidation of methane coupled to iron reduction in deep marine sediments

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Anaerobic oxidation of methane (AOM) is an important process in the global methane cycle and contributes to the regulation of methane release to the atmosphere. In sulfate depleted environments, methane can be oxidized anaerobically via microbial consortia tied to other electron acceptors.

Emphasizing the inorganic geochemistry, we explored the process of iron reduction coupled to AOM (Fe-AOM) in marine sediment samples from the Argentine Basin taken during RV Meteor expedition M78/3 (May – July 2009). The essential geochemical requirement for Fe-AOM is the juxtaposition of elevated methane concentrations and abundant reactive Fe(III) in anoxic sediments lacking reactive organic matter. These conditions are met in the Argentine Basin, where dynamic depositional conditions lead to the rapid burial of highly reactive metal phases. Additionally, reworked organic matter is delivered to deeper marine sediments resulting in the dilution by, and subsequent burial of, refractory organic carbon.

Our results show elevated dissolved iron concentrations in the pore water below the sulfidic zone accompanied by high amounts of highly reactive Fe (III) phases. This evidence indicates active iron reduction. In the same sediment, methane concentrations are high, while sulfate and sulfide are depleted. Low TOC contents (<0.8 wt%) throughout the sediment column and sulfate reduction rates close to or at the detection limit argue against the availability of highly reactive organic matter. This suggests that the refractory organic pool does not provide a sufficient energy source for dissimilatory iron reducing microorganisms in these deeper sediments. Thus, we propose that contributions from organo-clastic Fe reduction in these methane-rich sediments are minor. Instead, the concomitant occurrence of abundant methane and reactive ferric iron in the absence of sulfide argues for reduction of biologically available Fe(III) coupled to anaerobic oxidation of methane. The presence and release of dissolved iron and associated alteration of iron minerals in deep sulfate-depleted sediments has been observed in various marine environments, suggesting that Fe-AOM is important in the modern ocean, and, perhaps particularly so, in the sulfate-poor but highly methanic ancient ocean.