

## Surface Complexation Modelling of the Adsorption of Ca(II) and Nd(III) at the Rutile-Water Interface to 250 °C

Moira Ridley (moira.ridley@ttu.edu)<sup>1</sup>, Michael Machesky<sup>2</sup>, David Wesolowski<sup>3</sup> & Donald Palmer<sup>3</sup>

<sup>1</sup> Texas Tech University, Department of Geosciences, Lubbock, TX 79409-1053, USA

<sup>2</sup> Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820, USA

<sup>3</sup> Oak Ridge National Laboratory, Box 2008, Oak Ridge, TN 37831-6110, USA

Surface ion adsorption reactions may be studied at various levels, ranging from the macroscopic to molecular scale. Adsorption phenomena, however, are most realistically modelled when bulk macroscopic measurements are reconciled with molecular information from in situ spectroscopy. The charge distribution Multi Site Complexation (CD-MUSIC) model of Hiemstra and Van Riemsdijk (1996) successfully describes surface-complexes and the distribution of various surface sites (i.e., macroscopic and molecular data) in a single conceptual model. The CD-MUSIC model is an extension of Hiemstra et al.'s (1996) revised MUSIC model, which describes the proton affinity of various types of surface hydroxyl groups on a mineral surface. Machesky et al. (2000) have extended the revised MUSIC model from 25 °C to temperatures up to at least 300 °C. Consequently, the CD-MUSIC model may be used to describe surface ion adsorption reactions from 25 °C into the hydrothermal regime.

The CD-MUSIC model was used to rationalize the adsorption of Ca<sup>2+</sup> and Nd<sup>3+</sup> on the surface of rutile, which was studied using potentiometric titrations performed in NaCl media (ionic strength = 0.03 and 0.3 μM between 25 and 250 °C). Results of these studies show that relative to Na<sup>+</sup>, Ca<sup>2+</sup> and Nd<sup>3+</sup> significantly enhance the development of net proton-induced negative surface charge, and the extent of the enhancement increases with temperature. An increase in ionic strength suppressed the adsorption of Ca<sup>2+</sup>, whereas the adsorption of Nd<sup>3+</sup> was unaffected. In the Ca<sup>2+</sup> titrations performed above 150 °C and in all Nd<sup>3+</sup> titrations, the pH<sub>Znpc</sub> values of rutile were shifted toward lower pH values, suggesting that the two cations are specifi-

cally adsorbed onto rutile. Moreover, the Ca<sup>2+</sup> titrations exhibit a relatively constant proton stoichiometry ratio between 25 and 250 °C, implying that the mechanism involved in Ca<sup>2+</sup> adsorption (both chemical and electrostatic) is constant with temperature (Ridley et al., 1999).

The Ca<sup>2+</sup> adsorption data were modelled successfully with the CD-MUSIC model and the classic 1 pK<sub>a</sub> model. In both cases, the electrostatic effects were accounted for by a four-plane representation of the electrical double layer. In the CD-MUSIC model a bidentate association between Ca<sup>2+</sup> and rutile was considered, whereas a tetradentate bonding configuration was applied in the 1 pK<sub>a</sub> model. The tetradentate configuration was based on the results of a recent study by Fenter et al. (2000), in which X-Ray standing wave measurements of Sr<sup>2+</sup> adsorption by single-crystal rutile (110) revealed a tetradentate bonding configuration.

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