

Alkali and alkaline earth metal adsorption to goethite

LOUISE J CRISCENTI^{1*}, DAVID HART², AND KIDEOK KWON³

¹Sandia National Laboratories, Geochemistry, ljcrisc@sandia.gov
(*presenting author)

²Sandia National Laboratories, National Security Applications,
dbhart@sandia.gov

³Sandia National Laboratories, Geochemistry, kkwon@sandia.gov

The adsorption of metals to Fe-hydroxides such as goethite influences contaminant migration in the subsurface environment. Many surface complexes have been proposed for cation adsorption to goethite. In this study, we use classical molecular dynamics (MD) simulations to investigate the specific location of surface species with respect to both the mineral surface and to the structured water at the interface. Simulations are conducted for a range of NaCl, MgCl₂ and BaCl₂ concentrations to evaluate the impact of ion adsorption on the interfacial water structure, and to evaluate how surface speciation might change with increased surface loading.

Figure 1 illustrates preliminary results for the (100) and (101) surfaces of goethite in a 5 M NaCl solution. Interfacial water at the (100) surface exhibits more ordered arrangements of interfacial water and more hydrogen bonding with surface hydroxyl groups than at the (101) surface. The overall water structure is not affected by Na⁺ and Cl⁻ adsorption. Sodium binds as an inner-sphere complex in 1 M NaCl solutions, but in a 5 M NaCl solution, it adsorbs both as inner and outer-sphere complexes. In 1M – 5 M NaCl solutions, the Cl⁻ ion adsorbs strictly as an outer-sphere complex.

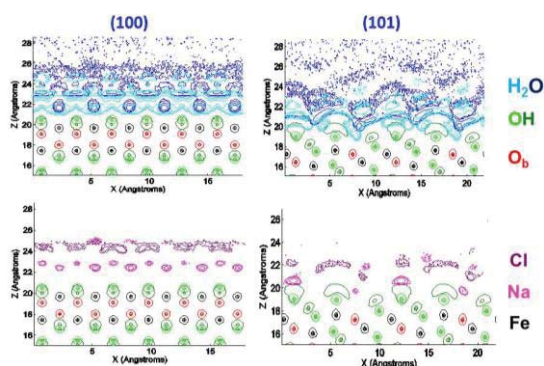


Figure 1: Water, Na⁺, and Cl⁻ adsorption on goethite surfaces.

Comparisons will be made between the adsorption of Na⁺, Mg²⁺, Ba²⁺ from NaCl, MgCl₂ and BaCl₂ solutions of different concentrations. Atomic density profiles, partition coefficients, statistics on the types of species formed on the surfaces (i.e., inner- vs. outer-sphere, ion-pairs), and water dipole orientation data will be presented. Differences in the electric double layer formed at the (100) and (101) surfaces will be discussed.

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Negative C-isotope excursion in carbonates during 2.0 Ga Shunga Event

ALENKA E. ČRNE^{1*}, VICTOR A. MELEZHNIK¹, AIVO LEPLAND¹,
ANTHONY E. FALICK², ANTHONY R. PRAVE³, AND
ALEXANDER T. BRASIER²

¹Geological Survey of Norway, Trondheim, Norway,
alenka.crne@ngu.no (* presenting author), victor.melezhnik@ngu.no,
aivo.lepland@ngu.no

²Scottish Universities Environmental Research Centre, East
Kilbride, UK, t.fallick@suerc.gla.ac.uk, alex.brasier@glasgow.ac.uk

³University of St. Andrews, St. Andrews, UK,
ap13@st-andrews.ac.uk

The ~2.0 Ga Shunga Event (SE), characterized by worldwide accumulation of extraordinary amounts of organic material, was among several global Paleoproterozoic events associated with the rise of atmospheric oxygen that were targeted by ICDP Fennoscandia Arctic Russia – Drilling Early Earth Project (FAR-DEEP). The SE appears to be linked to major disturbances in the C-cycle during the Paleoproterozoic, and follows or transitionally overlaps with the Lomagundi-Jatuli positive isotopic excursion of carbonate carbon at ~2.3-2.1 Ga. Four FAR-DEEP drillholes intersecting 670 m of sedimentary and volcanic rocks of the Zaonega Formation (ZF) offer a unique opportunity to study the C-cycle during the SE. Compositionally heterogeneous carbonate phases with δ¹³C values ranging from -22 to +8 ‰ indicate a complex, multistage formation and alteration of sedimentary carbonates. In order to make a distinction between primary and secondary phases and their compositional signatures, a suite of samples was characterized by SEM-BSE imaging and geochemical investigations (major and trace elements, C- and O-isotopes).

The lowermost part of the drilled succession, where sedimentary rocks are sandwiched between mafic lavas and sills, contains one carbonate phase. This is patchy calcite, with relatively constant, low δ¹³C values around -10 ‰. As the calcite is overgrowing previous mineral phases (e.g. pyrite), it is interpreted as a secondary carbonate phase unrelated to depositional or early diagenetic environmental conditions. The middle part of the drilled succession contains carbonate beds consisting of dolomite in the middle and calcite associated with talc in the outer parts of the beds. The talc-calcite association, which overgrows dolomite, indicates a metamorphic origin of the calcite through dolomite-silica reaction in marginal parts of the carbonate beds. Samples containing nearly pure dolomite, which is the earliest preserved carbonate phase, have highest δ¹³C values, between +3 and +8 ‰. Samples with a mixture of calcite and dolomite have δ¹³C values as low as -10 ‰ depending on the relative amount of the two mineral phases. Dolomite-dominated samples in the upper part of the succession are isotopically lighter with values from -2 to -5 ‰.

Even though the C-isotope composition of the carbonates of the ZF has been affected by post-depositional alteration, a negative C-isotope shift of 10 ‰ is recognized in best preserved dolomite samples with δ¹³C values from +8 to -2 ‰ over a 260-m thick stratigraphic interval. This shift may reflect a global change in isotopic composition of atmospheric/oceanic CO₂ [1], but local factors related to petroleum generation and spilling together with volcanic activity might have also influenced δ¹³C of the ambient seawater.

[1] Kump et al. (2011) *Science* **334**, 1694-1696.