

Electrolyte adsorption to goethite-water interfaces

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Adsorption onto goethite surfaces is a critical process influencing trace metal migration in the environment. This study investigates interfacial water structure and the adsorption of electrolyte anions and cations on different goethite surfaces to develop a better appreciation of the local environments that favour trace metal adsorption. The impact of different electrolytes (e.g., NaCl, Na₂SO₄, Na₂SeO₃) over a range of concentrations on water structure and surface loading will be presented.

Two goethite surfaces, the (100) and (101) surfaces as defined in the Pnma space group are under investigation. The (100) surface has three types of surface sites (5-fold Fe, Fe₂O_{1H}, Fe₃O_{1H}) and the (101) surface has four types of sites (Fe₁O_{1H}, Fe₂O_{1H}, Fe₃O_{1H}, and Fe₃O_{1H}). To date, molecular dynamics (MD) simulations have been performed to investigate the impact of 1M – 5M NaCl concentrations on interfacial water structure and surface loading. Each surface slab contains 192 Fe atoms and is protonated to create a neutral slab. The density of the bulk solution is maintained at 1.0 g/L regardless of salt concentration. A Leonard-Jones wall is imposed at both the top and bottom of the simulation cell. A natural surface of water is allowed to form at the top of the cell through an NPT simulation. Then, a vacuum gap three times the cell height is added to prevent interactions between periodic cells in the Z direction. Production runs were performed using the NVT ensemble at 298K for 10 ns.

Water layers at the (100) surface exhibit more structure and more hydrogen bonding with surface hydroxyl groups than at the (101) surface. Na⁺ adsorbs as inner-sphere complex to both surfaces; Cl⁻ adsorbs as an outer-sphere complex. From atomic density profiles, the introduction of 5M NaCl does not change the overall interfacial water structure, reinforcing previous MD studies that also suggest that the electric double layer is dominantly formed by interfacial water structure rather than ions at the surface.

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Deglacial NW Atlantic ventilation from paired deep-water coral radiocarbon and Nd isotopes

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Sequestration of carbon in the deep ocean during glacials and its subsequent release during deglaciation undoubtedly play a role in glacial/interglacial variation of atmospheric CO₂, although concrete evidence of the ocean's role has yet to be established. One route of investigation is to determine ocean ventilation rates. To do so requires combining dynamic tracer data, such as radiocarbon, with a conservative tracer to identify the water masses involved and their mixing ratios.

We describe the use of deep sea corals as an archive material providing same-sample U/Th ages, radiocarbon data and conservative water mass tracer data in the form of Nd isotope compositions. The majority of corals in this study are deglacial in age and span a water depth of 1000 to 2600 m in the NW Atlantic, where changes in the water column structure were pronounced across the last glacial/interglacial cycle [1]. Additional coral samples are located in the NE Atlantic and the northernmost parts of the North Atlantic to provide a broader picture of change.

This study builds on existing coral work, which has identified radiocarbon age reversals within single specimens [2] and rapid changes in radiocarbon content of the NW Atlantic water column [1]. By pairing the Nd isotope data to the radiocarbon data, we are able to identify the water masses present in the NW Atlantic during the deglaciation, the extent of mixing between these, and ultimately to translate the radiocarbon data into ocean ventilation rates.

[1] L.F. Robinson, *et al.* (2005), *Science* **310**, 1469-1473.

[2] J.F. Adkins, *et al.* (1998), *Science* **280**, 725-728.