Mineral Surface Hydroxyl Group Identity and Reactivity

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Mineral surfaces are reactive transformation centres and sinks for gases, solutes and solvents. These surfaces are populated by (hydr)oxo functional groups that can undergo protonation, ligand exchange, and form extensive networks of hydrogen bonds (Figure 1). Knowledge of the types, distributions and orientations of these groups is consequently essential understanding molecular-scale processes taking place at mineral surfaces.

This work is focused on the properties of hydroxo groups on important crystallographic planes of synthetic nano-sized (α, β, γ)-FeOOH particles exposed to vacuum, water vapor and carbon dioxide. Vibration spectroscopic signatures of isolate and hydrogen bonded hydroxo groups on these minerals will be presented alongside predictions from molecular dynamics simulations. This body of work forms the basis for a molecular-scale understanding of reactions taking place at surfaces of geochemically relevant mineral particles.

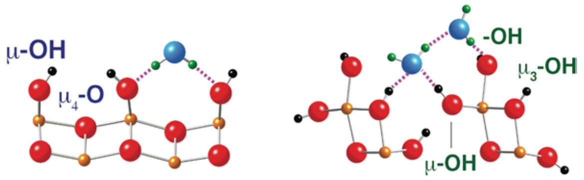

Figure 1. Schematic representation of dominant configurations of gaseous water molecules (blue) adsorbed on the (010) (left) and the (001) (right) planes of γ-FeOOH.

[1] Song X., Boily J.-F (2013) *Chem. Phys. Lett.*, ***560***, 1-9. [2] Song X., Boily J.-F (2012) *Phys. Chem. Chem. Phys.* ***14***, 2579-2586. [3] Boily J.-F (2012) *J. Phys. Chem. C.* ***116***, 4714-4724.

Reaction chain modeling of denitrification reactions during a push–pull test

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Field quantitative estimation of reaction kinetics is required to predict biogeochemical reactions in aquifers. We extended the analytical solution developed by Haggerty *et al.* [1] to model an entire 1st order reaction chain and estimate the kinetic parameters for each reaction step. We then evaluated the ability of this solution to model experimental results from a push pull test in a fractured crystalline aquifer (Ploemeur, Brittany). Nitrates were used as the reactive tracer, since denitrification is a sequential reduction of nitrates to nitrogen gas occuring in a chain reaction ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) under anaerobic conditions. The kinetics of nitrate consumption and by-products formation (NO_2^- and N_2O) during autotrophic denitrification were quantified by using a reactive tracer (NO_3^-) and a non-reactive tracer (Br-). Comparison of the Br^- and NO_3^- breakthrough curves showed that 10 % of the injected NO_3^- molar mass was transformed during the 12 hour experiment. Similar results, but with slower kinetics, were obtained from laboratory experiments in reactors. The good agreement between the model and the field data shows that the complete denitrification process can be efficiently modeled as a sequence of first order reactions. The variability of biogeochemical reactivity in the field will be also discussed.

[1] Haggerty *et al.* (1998), Ground Water **36 (2)**, 314–324.

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