Geochemical investigations of saltwater intrusion into the coastal carbonate aquifer of Mallorca, Spain

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Coastal aquifers often display seawater intrusion resulting in the formation of a salty water wedge progressing inland. Complex geochemical processes are likely to occur in the freshwater – seawater mixing zone of carbonate aquifers where the water becomes in disequelibrium with the rock forming carbonates [1]. The induced diagenetic activity, such as calcite dissolution and/or dolomitization [2,3,4,5], may result in significant hydrodynamic changes [6,7].

This study investigates the mass tranfers in a current mixing zone located in the South-East part of Mallorca Island (Spain). Investigations were conducted in two boreholes, separated by 5 m, where repeated electrical conductivity logs of the formation and of the saturating fluid, as well as regular pore-water sampling and permanent downhole multi-parameters monitoring of the water were performed over a period of 9 years.

In the mixing zone, the significant acidification, the calcite saturation index profile and the calcium concentration profile cannot be explained by conservative mixing nor by dissolution-precipitation reactions only. Conversely, the analysis of organic carbon content and of the distinctly different time-resolved pH profiles measured in the two boreholes suggests the development of perennial biomass that enhances the calcite dissolution. Moreover, the presence of biomass seems to be correlated with the permeability and vertical connectivity at meter-scale. We speculate that the mechanism could be self-activated because the microbiological activity induces calcite dissolution and tends to increase porosity and permeability that favors biomass development.

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Proton behavior at water/silica interfaces: Reactions and proton transport

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A robust dissociative water potential has been used in molecular dynamics simulations to study water adsorption and reactions on silica surfaces, dissolution, and proton transport. This potential matches many structural and dynamic properties of bulk water and, when transferred to nanoconfined situations, shows the high thermal expansion of nanoconfined water. The simulations of water/silica interfaces show the appropriate dissociative chemisorption and silanol (SiOH) formation consistent with experimental data, enhanced H_3O^+ ion formation during surface reactions, and the location of weakly binding highly acidic proton adsorption sites on the silica surface, with results similar to ab-initio molecular dynamics simulations of small systems. The simulations also showed increased proton transport that is consistent with electrochemical studies that showed increased proton conductivity in mesoporous silica exposed to moisture.

In order to evaluate the proton transfer mechanisms seen at the water/silica interface, we studied proton transport in bulk water, where previous data exist. Without changing parameters used in our previous simulations mentioned above, the simulation results show proton transport in bulk water involving Eigen and Zundel complexes consistent with ab-initio calculations and H_3O^+ ion lifetimes consistent with experimental data and ab-initio calculations. H_3O^+ ion lifetimes in both the femtosecond regime and the picosecond regime are observed. The first is indicative of proton rattling between the H_3O^+ ion and an adacent water molecule while the second is indicative of the timescale for proton transport.

The activation barriers for proton transfer between the H_3O^+ ion and an adjacent water molecule in bulk water observed in the simulations are similar to the ab-initio calculations and also show the decreasing barrier height with decreasing O-O spacing between the interacting molecules.

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