Computing the water dynamics for nonstoichiometric calcite surfaces

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We would like to implement two novel parameters in the pore network modelling, namely the contribution of (i) solution stoichiometry[1] (Ca:CO_3), (ii) surface roughness/pore geometries[2] on calcite growth and dissolution rates. It is expected that the long residence time of water in the inner sphere of calcium in the calcite surface is the rate limiting step in the reaction since it prevents other molecules to enter and react with the surface. The stoichiometry of the solution is partly taken care of in the “ion-by-ion growth model” but does not take into account the influence of the non-stoichiometric surface on the dynamics of the solution at the interface. Therefore, determining water exchange frequencies in relation to stoichiometry will improve understanding the different reaction rates observed.

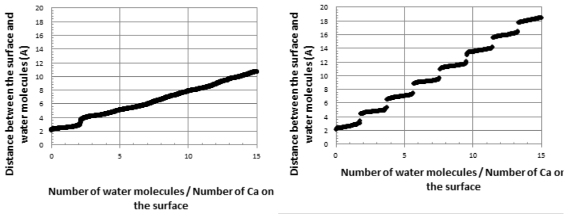

Figure 1 layering of water on top of a stoichiometric surface (left) and a non-stoichiometric surface (right)

To study the impact of different calcium to carbonate ratios at the calcite surface on the water dynamics, we simulated a calcium rich roughened surface and observed that the water is more layered compared to a Ca^{+2}/CO$_3^{2-}$ ratio of 1, Figure 1. This can be explained by the positive net surface charge generated by excess surface Ca^{+2-}. The oxygen atoms of the water molecules are oriented to the calcium in the surface and because of absence of hydrogen bonds between water and carbonate this creates a dipole in every single water layer. This triggers the next layer to keep the same orientation. So even after two times the cutoff distance of 8 A the layering is still observable. Further simulations should provide us the relation between the water mean residence time and the amount and distribution of charge over the surface.

[1] Wolthers et al. (2013) CrystEngComm 15, 5506. [2] Wolthers, M. et al. (2012) *Geochimica et Cosmochimica Acta*, 77, pp.121–134.