



Impact of trace metals on the water structure at the calcite surface

Mariette Wolthers (1,2), Devis Di Tommaso (3), Nora De Leeuw (1,2)

(1) Department of Chemistry, University College London, U.K. (m.wolthers@ucl.ac.uk), (2) Department of Earth Sciences - Geochemistry, Utrecht University, Utrecht, Netherlands (m.wolthers@uu.nl), (3) School of Biological and Chemical Sciences, Queen Mary, University London, London, U.K. (d.ditommaso@qmul.ac.uk)

Carbonate minerals play an important role in regulating the chemistry of aquatic environments, including the oceans, aquifers, hydrothermal systems, soils and sediments. Through mineral surface processes such as dissolution, precipitation and sorption, carbonate minerals affect the biogeochemical cycles of not only the constituent elements of carbonates, such as Ca, Mg, Fe and C, but also H, P and trace elements.

Surface charging of the calcite mineral-water interface, and its reactivity towards foreign ions can be quantified using a surface structural model that includes, among others, the water structure at the interface (i.e. hydrogen bridging) [1,2] in accordance with the CD-MUSIC formalism [3]. Here we will show the impact of foreign metals such as Mg and Sr on the water structure around different surface sites present in etch pits and on growth terraces at the calcite (10-14) surface. We have performed Molecular Dynamics simulations of metal-doped calcite surfaces, using different interatomic water potentials. Results show that the local environment around the structurally distinct sites differs depending on metal presence, suggesting that metal substitutions in calcite affect its reactivity. The information obtained in this study will help in improving existing macroscopic surface model for the reactivity of calcite [2] and give more general insight in mineral surface reactivity in relation to crystal composition.

[1] Wolthers, Charlet, & Van Cappellen (2008). *Am. J. Sci.*, 308, 905-941.

[2] Wolthers, Di Tommaso, Du, & de Leeuw (2012). *Phys. Chem. Chem. Phys.* 14, 15145-15157.

[3] Hiemstra and Van Riemsdijk (1996) *J. Colloid Interf. Sci.* 179, 488-508.