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The surface chemistry of carbonatesM. WOLTHERS¹, L. CHARLET² AND P. VAN CAPPELLEN¹

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Carbonates play an important role in regulating the chemistry of aquatic environments from lakes to oceans, aquifers to hydrothermal systems, and soils to sediments under oxic to anoxic conditions. Through mineral surface processes such as dissolution, precipitation and sorption, carbonates affect the biogeochemical cycles of not only the major components of carbonates, such as Ca, Mg, Fe and C, but also H, P and trace metals.

In order to understand and describe the reactivity of the carbonate – water interface, Van Cappellen et al. [1] developed a surface complexation model. This model is based on experimental data from acid – base titrations and has been validated through correlating the model to carbonate dissolution kinetics and, more recently by different workers, through surface spectroscopic techniques. However, as Van Cappellen et al. stressed, their model represents an idealization of carbonate surfaces, not taking into account surface site heterogeneities.

An alternative model has been developed, describing the surface reactivity based on crystallographical data using the MUSIC model approach (e.g. [2]). This model will be presented and the advantages and draw-backs in comparison to the Van Cappellen et al. model will be discussed.

References

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A generalized surface complexation model for carbonate minerals in aqueous solutionsA. VILLEGAS-JIMÉNEZ¹, A. MUCCI¹, J. PAQUETTE¹, O.S. POKROVSKY² AND J. SCHOTT²

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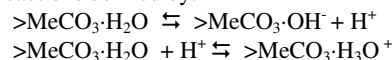
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A new generalized surface complexation model for carbonate minerals is presented. It predicts the surface electrical properties of these minerals in aqueous solutions. Bond valence, charge distribution and crystallographic concepts, previously applied to metal oxide surfaces [1], are combined with earlier results obtained from computer-assisted atomistic simulations [2] to construct a refined representation of the hydration layer at the calcite-water interface.

The model includes a large number of microscopic reactions that are re-formulated in terms of a single generic surface site for simple carbonates ($>MeCO_3 \cdot H_2O$) and binary solid solutions ($>Me_xMe_y(CO_3)_2 \cdot (H_2O)_2$), in order to limit the number of overall reactions and simplify the model.

The model was calibrated using surface charge data for magnesite and dolomite and applying evolutionary computation techniques to optimize the values of the intrinsic formation constants.

It is found that the acid-base properties of carbonate minerals can be reasonably explained by the generic acidity and protonation reactions defined by:



The values of the intrinsic formation constants of surface species are similar to those of equivalent aqueous species. In general, the model suggests that sorption of host ions on the carbonate surface is less important than previously proposed in determining the surface charge of these minerals.

Surface speciation predicted by the model is consistent with results obtained from spectroscopic studies [3,4].

References

- [1] Hiemstra T. and Van Riemsdijk W.H. (1996). *J. Colloid Interface Sci.* **179**,488-508.
 [2] de Leeuw N.H. and Parker S. C. (1997). *J.Chem. Soc., Faraday Trans.*, **93**(3),467-475.
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 [4] Pokrovsky O.S., Mielczarski J.A., Barres O. and Schott J. (2000). *Langmuir.* **16**(6), 2677-2688.