

Effects of Fe and Mn on stoichiometric characterization of dolomites by cell and Rietveld refinements

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Dolomite crystal lattice is subjected to change by cation substitutions through dissolution-precipitation reactions which impact on its stoichiometry (%CaCO₃). These transformations have consequences on dolomite stability/reactivity during diagenesis and are key factors for the study of the limestone petroleum reservoir properties. Iron and manganese are presents in dolomite and this contribution presents an extension of an approach developped by Turpin *et al.* [1] using the X-ray diffractometry (XRD) technique coupled with cell and Rietveld refinements on dolomitized rock samples.

Core-samples were investigated from Chatelblanc 1 well, representing the stratigraphic contact of the Upper Muschelkalk and Lettenkohle Formations (Middle Triassic). The investigated sequence covers an interval about 10m thick, consisting of limestones, dolostones and evaporites.

The analytical approach concerning dolomite stoichiometry analyses was achieved in two phases by bibliographic approach and XRD measurement. First, an abacus – with crystallographic data on dolomites – was built from a comprehensive literature review. Such data comprise cell parameters related to the lattice Ca percentage of various dolomites. Then, using the dolomite cell parameters determined by cell refinement and this abacus, dolomite stoichiometry could be calculated. The presence of Mn and Fe was measured by EMP and EDX analyses and is taken into account to assess the methodology.

[1] M. Turpin, F. H. Nader & E. Kohler (2009) A new approach for stoichiometric characterisation of carbonates based on cell & Rietveld refinements: Case study of Muschelkalk-Lettenkohle Triassic rocks in the French Jura, *ASF Congress*, 25–31 October, Rennes, France.

Imaging ion adsorption with total external reflection X-ray standing waves

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A long-standing challenge in understanding ion-mineral interactions is to be able to probe extended ion distributions. To this end, we report a new generalized model-independent approach that was developed for the analysis of long-period x-ray standing waves (XSW) data, which has sensitivity to probe extended structures at interfaces. The approach is applicable to various reflection geometries, including simple x-ray mirrors, and multi-layers, and is valid for XSW in an attenuating medium. The formalism allows direct extraction of the amplitudes and phases of the elemental structure factor from the measured long-period XSW data, leading to a fully model-independent recovery of the elemental distribution. The method is validated by extracting the vertical 1D Ti profile for a TiO₂/Si/Mo tri-layer sample on a Si substrate, using Ti-K α fluorescence yield measured in *ex situ* and *in situ* environments.

This approach was then applied to probe ion distributions at nm-thick titania films in contact with Rb and Sr-containing solutions at pH ~10. Titration studies reveal that these titania nanofilms (grown by atomic layer deposition on high surface area SiO₂ powders) exhibit significantly enhanced surface charge compared to single crystalline rutile surfaces. Additional long period XSW, X-ray fluorescence and X-ray reflectivity reveal this is expressed by a >2-fold higher total ion coverage on the nano-titania surface compared to rutile (110), and with a vertical ion distribution that is distinct from that observed on rutile.

[1] Kohli *et al.* *Physical Review B*, **81**, XXX (2010). [2] Kohli *et al.* in preparation (2010)..