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Carbonates reactivity in temperature and interactions with Fe-minerals

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The carbonate system is the one of most reactive in the mineralogical assemblages of clay-rocks. Consequently, pristine clay-rocks pore water compositions are expected to be at equilibrium with carbonate minerals. However, it is difficult to fully reconcile the concentration data obtained from seepage water sampled in equipped *in situ* boreholeswith the equilibrium concentrations obtained from pore water modeling (Pearson et al., 2011). It is especially true for dolomite whose solubility spans a large range of values in thermodynamic database as a function of crystallinity considerations, and for siderite/ankerite or other Fe-bearing carbonates whose compositions influence their solubility. The understanding of the carbonate system in clay-rock is necessary for a number of predictions including the effect of an increase of temperature on the pore water chemistry. In this respect, experiments were conducted to study the kinetics of equilibration of carbonate mineral assemblages as a function of temperature (25-80°C) in chemical conditions otherwise similar to those encountered in the Callovian-Oxfordian clay-rock.

Several authors reported higher Ca releases than Mg releases in solution during dolomite dissolution (*e.g.*Pokrowsky and Schott, 2001, Gautelier et al., 2007; Urosevic et al., 2012; Debure et al., 2013). However, others authors observed in their studies some experiments that displayed higher Ca release than Mg and some others that exhibitedonly small differences between Ca and Mg concentrations in solution (e.g. Pokrowsky et al., 2005; Zhang et al., 2007). Dolomite incongruent dissolution has been explained by the lower hydration energy of Ca^{2+}compared to $Mg^{2+}$and leading to a lower stability of Ca^{2+}at the dolomite/water interface and to aCa-depleted layer at the dolomite surface (Busenberg and Plummer; 1982; Pokrowsky and Schott, 2001; Zhang et al., 2007). More recently, Urosevic et al; (2012) evidence the formation of an $MgCO_3$ phase at the dolomite surface. However, the experimental data do not allow to quantitatively characterizing that phase. Such contradictory results underline the complexity of dolomite dissolution.In this study, dolomite dissolution in pure water wasinvestigated. Solution composition was monitored as a function of time and the mineralogy and surface chemistry was characterized before and after reaction (XRD, SEM, TEM and Raman analyses). Experiments were performed with powders (< 12 µm) and withmonocrystals. Mixed system such as dolomite/calcite and dolomite/calcite/goethite were investigated to quantify the Mg incorporation in calcite and the Fe incorporation in calcite and dolomite. Goethite was selectedfor those experiments in agreement with the presence of nanogoethite detected in COx samples (Gailhanou et al., 2012).These experiments were performed in a glove box with a 99%N_2/1%CO_2 atmosphere that is representative of the *in-situ* conditions (Gaucher et al., 2009) in order to preserve the systems from oxidizing perturbation and to buffer the pH.

For all the systems, high temperatures promoted high kinetic rate of dissolution and high concentrations in solution. Solution analyses did not evidence a large difference between Ca and Mg released in solution in the case of dolomite dissolution in pure water at 25°C and at 80°C. Nevertheless, TEM-EDX measurements showed the presence of incongruent Mg/Ca phases after reaction. SEM, Raman analysesdid not evidence Mg-bearing minerals precipitation but reveal the formation of hematite on the dolomite surface due to Fe impurities incorporated inside the crystals. In the calcite/dolomite systems, steady-state conditionswere quickly reached if solutions with composition closed to the expected equilibrium conditions were used as initial bulk electrolytes.

In the dolomite/calcite/goethite systems, steady state conditionswere quickly reached in solution as well (see Figure 1). TEM-EDX chemical analyses indicated a possible Fe incorporation in calcite and in dolomite. Further characterizations are in progress.

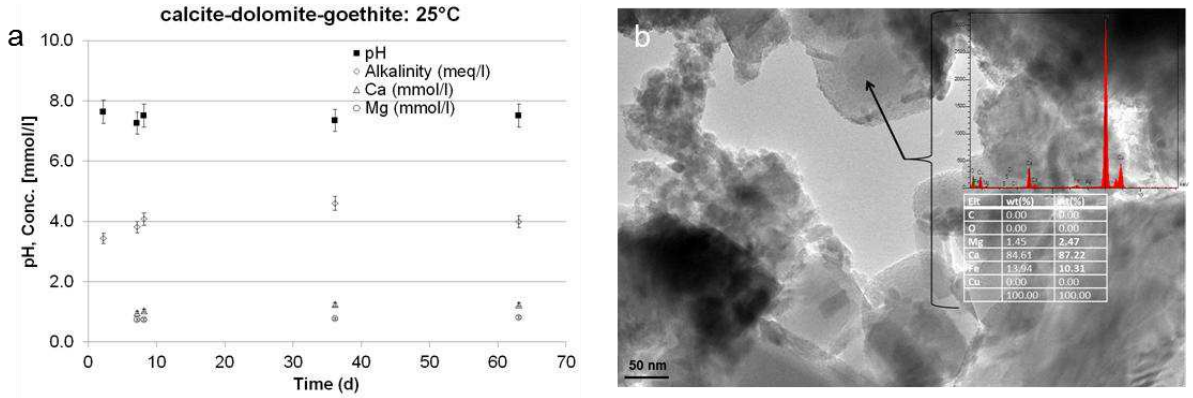

Figure 1.*Left :* evolution of pH in the batch solution and elements concentrations in solution over the time; *right:* TEM micrography showing a potential Fe incorporation in calcite in the case of calcite-dolomite-goethite experiment after 8 days of reaction at 80°C.

Finally,solution compositions at steady-state are mostly consistent with equilibrium calculations. The initially under-saturated solutions approach equilibrium with dolomite, calcite and/or magnesite,suggesting secondary phase's formation as observed by Urosevic et al. (2012).Additional analyses (*e.g.*Small-angle X-ray scattering) are foreseen to investigate dolomite crystal surface and to characterize secondary carbonates minerals.

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