Effect of phosphonates on calcite-solution reactions

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Increasing amounts of anthopogenic phosphonates are entering the environment as a result of their use as chelating agents, herbicides or inhibitors of calcite scale formation in porous oil reservoirs [1, 2]. Phosphonates released into the environment may interact with minerals in rocks, soil or oil reservoirs. These compounds are also key components of the marine dissolved organic phosphorus. Recently, it has been proposed that an important source of phosphonates into the ocean is nitrogen-fixing cyanobacteria. These organisms bloom in warm, CO_2-rich environments, which suggests that phosphonate concentration in oceans may increase in the future [3]. Thus phosphonate interaction with carbonates may also be relevant for biomineralization processes taking place in marine environments. This study has used AFM *in situ* dissolution experiments on calcite in the presence of HEDP (hydroxy ethylene diphosphonic acid) at pH 8 in order to get insights into the kinetics and mechanisms of nanoscale processes occurring during the interaction of calcite-phophonate bearing solutions. Rhombohedral calcite etch pits appeared tear-shaped and dissolution rates were drastically reduced in the presence of phosphonate, although they increased with additive concentration. Stabilization of polar steps as well as increased frequency of water exchange in the hydration shell of Ca^{2+} (as shown by molecular dynamics simulations) may explain such observations. The nucleation and growth of a Ca-HEDP phase on calcite surfaces was also observed. The reaction must be controlled by a fluid boundary layer at the mineral-solution interface, which as a consequence of calcite dissolution, became supersaturated with respect to the phase that precipitated (although the bulk solution was undersaturated). The reaction stopped when the calcite surface was covered. However, when Na^+ is present in solution, a fibrous, highly porous Na-Ca-phosphonate phase which is loosely attached to the calcite surface, seems to be able to fully replace the parent crystal.

[1] Pairat *et al.* (1997) *Langmuir* **13**, 791-798. [2] Jonasson *et al.* (1996) *Chem. Geol.* 132, 215-225. [3] Dyhrman *et al.* (2009) *Nature Geoscience* **2**, 696–699.

Influence of MgO nanoparticle size on available surface area for carbonation

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It is widely accepted that anthropogenic carbon dioxide (CO_2) emissions are a leading cause of global warming and that there is an urgent need to develop methods for CO_2 capture and sequestration [1]. Metal oxides are an attractive material for CO_2 fixation. CO_2 reacts with metal oxides forming thermodynamically stable solid metal carbonates suitable for long term storage.

In this work we investigate the storage capacity of magnesium oxide nanocrystals as a function of particle size. Synthesis of spherical MgO nanocrystals with a narrow size distrubtion and tunable diameter has recently been reported [2]. Surface area is measured through N_2 adsorption [Figure 1] using the BET method. The small diameter of the particles studied (2 – 7 nm) results in large surface areas up to 2200 m^2/g. CO_2 physisorption and chemisorption capacities will be examined through alternate thermal cylcing of CO_2 and N_2 purge gases using a thermal gravimetric analysis (TGA) instrument.

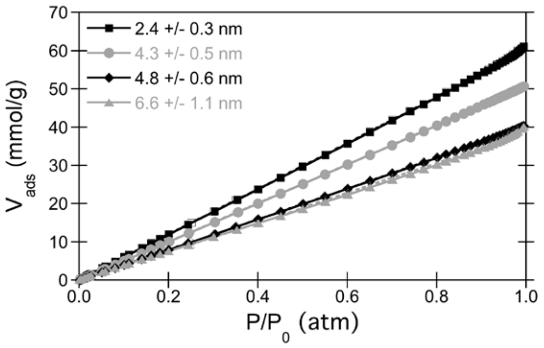

Figure 1: N_2 adsorption/desorption isotherms for MgO nanoparticles ranging from 2 to 7 nm in diameter.

[1] Metz et. al. (2005) *Special Report on Carbon Dioxide Capture and Stoarage, Intergovernmental Panel on Climate Change*. [2] Moon et. al. (2009) *Angew. Chem. Int. Ed.* **48**, 6278-6281.