

The realtime kinetics and mechanisms of nucleation and growth of dolomite from solution

J.D. RODRIGUEZ-BLANCO*, S. SHAW AND L.G. BENNING

School of Earth and Environment. Univ. Leeds. Leeds, UK
LS29JT (*correspondence: j.d.rodriguez@see.leeds.ac.uk)

Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is a common sedimentary rock-forming mineral [1], yet virtually no quantitative information about its formation mechanism is available. Here we demonstrate how *in situ* and time-resolved synchrotron-based diffraction, combined with conventional imaging and spectroscopy were successfully applied to quantify the kinetics and mechanisms of crystallization of dolomite from solution.

Experiments were carried out by mixing equimolar aqueous Ca/Mg and CO_3^{2-} solutions ($\text{CO}_3^{2-}:\text{Ca}^{2+}:\text{Mg}^{2+}=2:1:1$) at 60° to 220°C and the crystallization was followed via synchrotron-based *in situ* and time-resolved Energy Dispersive X-ray Diffraction (ED-XRD).

Upon mixing of the two solutions a poorly ordered precursor (amorphous calcium-magnesium carbonate, ACMC) precipitated instantaneously. After a temperature dependent induction period ($t_0=45$ min and 10 min respectively at 60 and 220°C) dolomite nucleated and crystallized rapidly (2-3 min) forming nanocrystalline aggregates (Fig. 1A). The changes in Bragg peak areas over time for the dolomite (104) peak were fitted using the Johnson–Mehl–Avrami–Kolmogorov model [2]. The results suggest that dolomite crystallized following first order kinetics. The activation energies of nucleation (EA_{nucl}) and crystallization (EA_{cryst}) were derived from the Arrhenius equation (Fig. 1B and 1C).

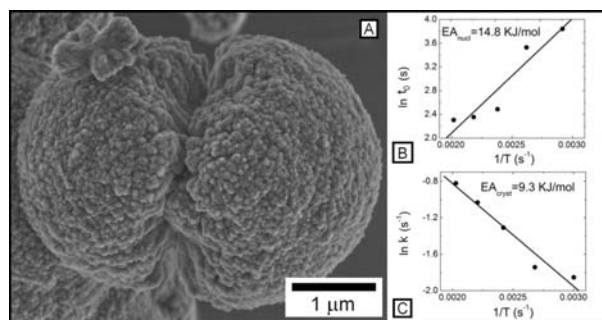


Figure 1: Photomicrograph of nanocrystalline (<100nm) dolomite aggregates formed at 60°C (A); Arrhenius plots for the dolomite induction time, t_0 (B) and growth rate, k (C).

[1] Reeder (1983) *Rev. Mineral* **11**. [2] Johnson & Mehl (1939) *American Institute of Mining Engineering, Technical Publication* **1089**, 1-27.

Nanoelectrophoresis studies of magnetite and silica in hydrothermal environments

V. RODRIGUEZ-SANTIAGO¹, M.V. FEDKIN¹,
S. VIDOJKOVIC¹, D.J. WESOLOWSKI² AND S.N. LVOV^{1*}

¹Penn State University, University Park, PA, USA
(*correspondence: lvov@psu.edu)

²Oak Ridge National Laboratory, Oak Ridge, TN, USA

Iron oxides and silica minerals are ubiquitous in aqueous geochemical environments, including hydrothermal solutions. These minerals are often present in nano-colloidal form and play important roles in biogeochemical and environmental cycles. The study of the surface properties of these oxides provides important information about their interaction and behavior, especially in hydrothermal regimes, where experimental data are scarce.

We have recently developed a nanoelectrophoresis apparatus for determining the electrophoretic mobility and zeta potential of nanoparticulate materials (particle size down to 80 nm) at temperatures up to 260 °C and pressures up to 70 bar [1,2]. In the past, we were successful in obtaining the zeta potential data for micron-size particles of ZrO_2 and TiO_2 at hydrothermal conditions [2,3], which helped to understand the effect of temperature on the interface reactions in the electrical double layer (EDL) on the oxide surface [4].

In this study, we obtained new zeta potential data for magnetite (Fe_3O_4) and silica (SiO_2) in hydrothermal solutions of KNO_3 and NaCl , respectively. The electrophoretic mobilities and zeta potentials of the studied materials were determined as a function of pH and temperature for different particle sizes. The isoelectric point (IEP) values – pH at which the zeta potential is zero – were determined by fitting the zeta potential data. Consideration of the particle size as well as kinetics of the aggregation processes in the system was found critical for correct calculation of the zeta potentials from the high temperature electrophoresis data.

[1] Rodriguez-Santiago *et al.* (2008) *Rev. Sci. Instrum.* **79**, 0933021-4. [2] Zhou *et al.* (2003) *Rev. Sci. Instrum.* **74**, 2501-2506. [3] Fedkin *et al.* (2003) *Langmuir* **19**, 3797-3804. [4] Machesky *et al.* (2006) in *Surface Complexation Modeling* **11**, 324-358.