



BaSO₄ crystallization in the presence of polymers: evidence of barite crystallization via non-classical pathways

Cristina Ruiz-Agudo¹, Encarnación Ruiz-Agudo², Alejandro Burgos-Cara²,

Christine Putnis^{1,3}, Aurelia Ibáñez-Velasco², Carlos Rodríguez-Navarro² and

Andrew Putnis^{1,4}

¹Institut für Mineralogie, Corrensstrasse 24, 48149 Münster, Germany, c_ruiz02@uni-muenster.de

²Department of Mineralogy and Petrology, University of Granada, 18071, Spain, encaruiz@ugr.es

³Nanochemistry Research Institute, Department of Chemistry, Curtin University, 6845 Perth, Australia, putnisc@uni-muenster.de

⁴The Institute of Geoscience Research (TIGeR), Curtin University, Perth, Australia.

Andrew.Putnis@curtin.edu.au

Barium sulphate is widely known for being a problematic and costly scale-forming mineral in industrial processes. In oil recovery, barite forms when injection water which is sulfate rich and barium-containing formation water interact downhole. Scale minerals can clog formation pores near the wellbore reducing porosity and permeability of the reservoir and they also can form a thick deposit in production pipes. A common strategy aimed at reducing scale formation is the addition of organic additives (usually phosphonates or carboxylates) to the water injected into the reservoir (threshold treatment, *Shakkthivel et al.*, 2006).

Thus a better understanding of the mechanism of barite formation from aqueous solutions and the role of organic macromolecules on such a process may be relevant for the design and optimization of treatments to prevent scale formation. Here, we investigate the initial stages of barium sulphate precipitation from pure and polymer-containing aqueous solutions. Barium sulphate was precipitated at room temperature by combining equimolar Ba²⁺-bearing and SO₄²⁻-bearing solutions. The precipitation process was quenched at different times by the addition of ethanol or quick immersion in liquid nitrogen and subsequent freeze-drying, and the precipitates were studied by various analytical methods, XRD, TG/DSC, FESEM, ESEM and TEM. As well, precipitation experiments (with and without polymers) were performed by the slow addition of 10 mM BaCl₂ solution to a 1 mM Na₂SO₄ solution. During these experiments, the Ba²⁺ potential, pH, conductivity and turbidimetry were continuously monitored and allowed to get better insights into interactions between copolymers and prenucleation species before nucleation occurs (*Gebauer et al.* 2009).

AFM growth experiments were additionally carried out. Observations of the nanostructure evolution indicate that barite forms by two-levels of oriented aggregation of nanosized particles. In pure solutions, most of the porosity in the micron-sized aggregates formed in the second step is annealed, resulting in perfect single crystals. However, in the presence of polymers, this step is retarded and BaSO₄ mesocrystals are commonly observed. Furthermore, evidence supporting the existence of liquid and solid amorphous precursors that precedes the formation of the first solid (primary) particles is given.

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References

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