## BaSO<sub>4</sub> crystallization in the presence of polymers: Evidence of barite crystallization via non-classical pathways

CRISTINA RUIZ AGUDO<sup>1</sup>, ALEJANDRO BURGOS-CARA<sup>2</sup>, ENCARNACIÓN RUIZ-AGUDO<sup>2</sup>, CHRISTINE PUTNIS<sup>1</sup>, CARLOS RODRÍGUEZ-NAVARRO<sup>2</sup> AND ANDREW PUTNIS<sup>13</sup>

<sup>1</sup>Institut für Mineralogie, Correnstrasse 24, 48149 Münster, Germany (c\_ruiz02@uni-muenster.de)

<sup>2</sup>Department Mineralogía y Petrología, Universidad de Granada; Fuentenueva s/n, 18071 Granada, Spain (encaruiz@ugr.es)

<sup>3</sup>The Institute of Geoscience Research (TIGeR), Curtin University, Perth, Australia. (Andrew.Putnis@curtin.edu.au)

Barite is widely known for being a problematic and costly scale-forming mineral in industrial processes. A common strategy aimed at reducing scale formation is the addition of organic of additives. Thus a better understanding of the mechanism of barite formation from aqueous solutions and the role of organic macromolecules on such a process is relevant for the design and optimization of treatments to prevent scale formation. Here, we investigate the initial stages of BaSO<sub>4</sub> precipitation from pure and polymer-containing aqueous solutions. Barium sulphate was precipitated by combining equimolar solutions of Ba-bearing and SO<sub>4</sub>-bearing compounds. 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 XRD, TG/DSC, FESEM, and TEM. As well, precipitation experiments (with and without polymers) were performed by the slow addition of 10 mM BaCl<sub>2</sub> solution to a 1 mM Na<sub>2</sub>SO<sub>4</sub> solution. During these experiments, Ba2+ potential, pH, conductivity and turbidimetry were monitored. 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 steps 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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