Crystengcomm

Electronic Supporting Information

Exploring the effect of polyacrylic acid on pre- and post-nucleation $BaSO_4$ species: new insights into the mechanisms of crystallization control by polyelectrolytes

Cristina Ruiz-Agudo[1] (*), Encarnación Ruiz-Agudo[2], Alejandro Burgos-Cara[2], Christine V. Putnis[1,3], Aurelia Ibáñez-Velasco[2], Carlos Rodriguez-Navarro[2] and Andrew Putnis[1,4].

1. Calculation of sulphate bounded from conductivity measurements

Conductivity measurements in the control run were used to prove that prenucleation associates were neutral (e.g., the same amount of sulphate and barium are bounded in the prenucleation species). The amount of sulphate bounded could be assessed independently from ISE measurements assuming that ion associates are neutral (e.g., a 1:1 barium to sulphate ratio in the associates).

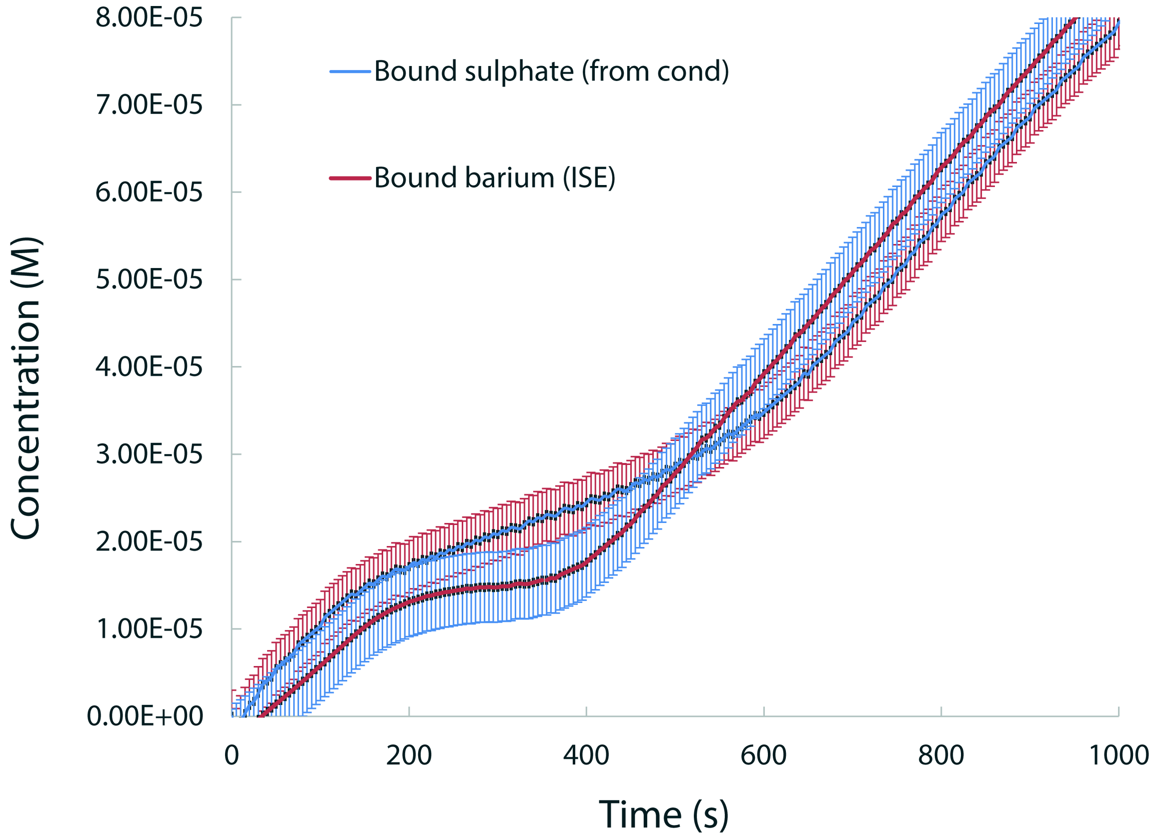
For the calculations, the "calculated" conductivity (k_{cal}) of the solution was estimated taking into account that the activity and molarity of all the ions present in solution was equivalent (e.g., activity coefficient equal 1) and that the bounded ratio of barium and sulphate is 1:1. The calculated conductivity is higher than the measured conductivity and this is due to the formation of ion pairs and/or clusters in solution prior to nucleation.

$$k = \sum_i c_i * \lambda_i = k_{cal} - c_{bounded} * \lambda_{BaSO_4}$$

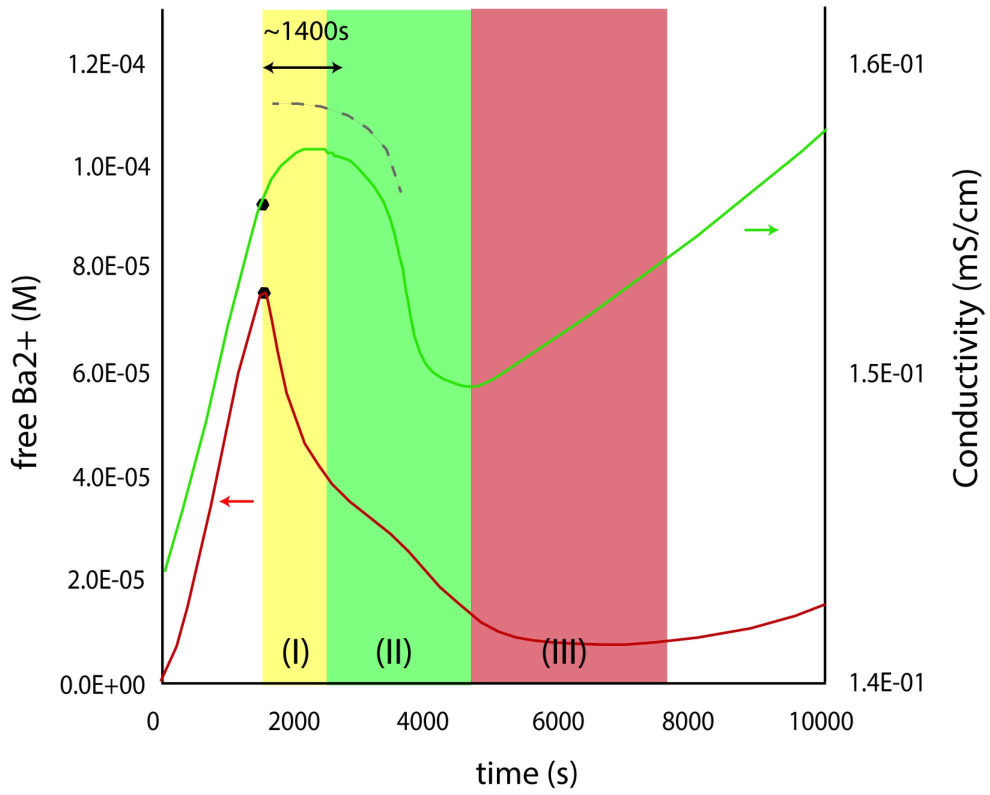
c_i (M) and λ_i (S cm^2 mol^{-1}) are respectively the concentration and the molar conductivity of ion "i"; k_{cal} is the calculated conductivity taking into account all the ions in solution; $c_{bounded}$ is the concentration of prenucleation species in solution and λ_{BaSO4} is the molar conductivity of $BaSO_4$ calculated with Kolhrausch law.

$$\lambda_{BaSO_4} = \lambda_{Ba^{2+}} + \lambda_{SO_4^{2-}}$$

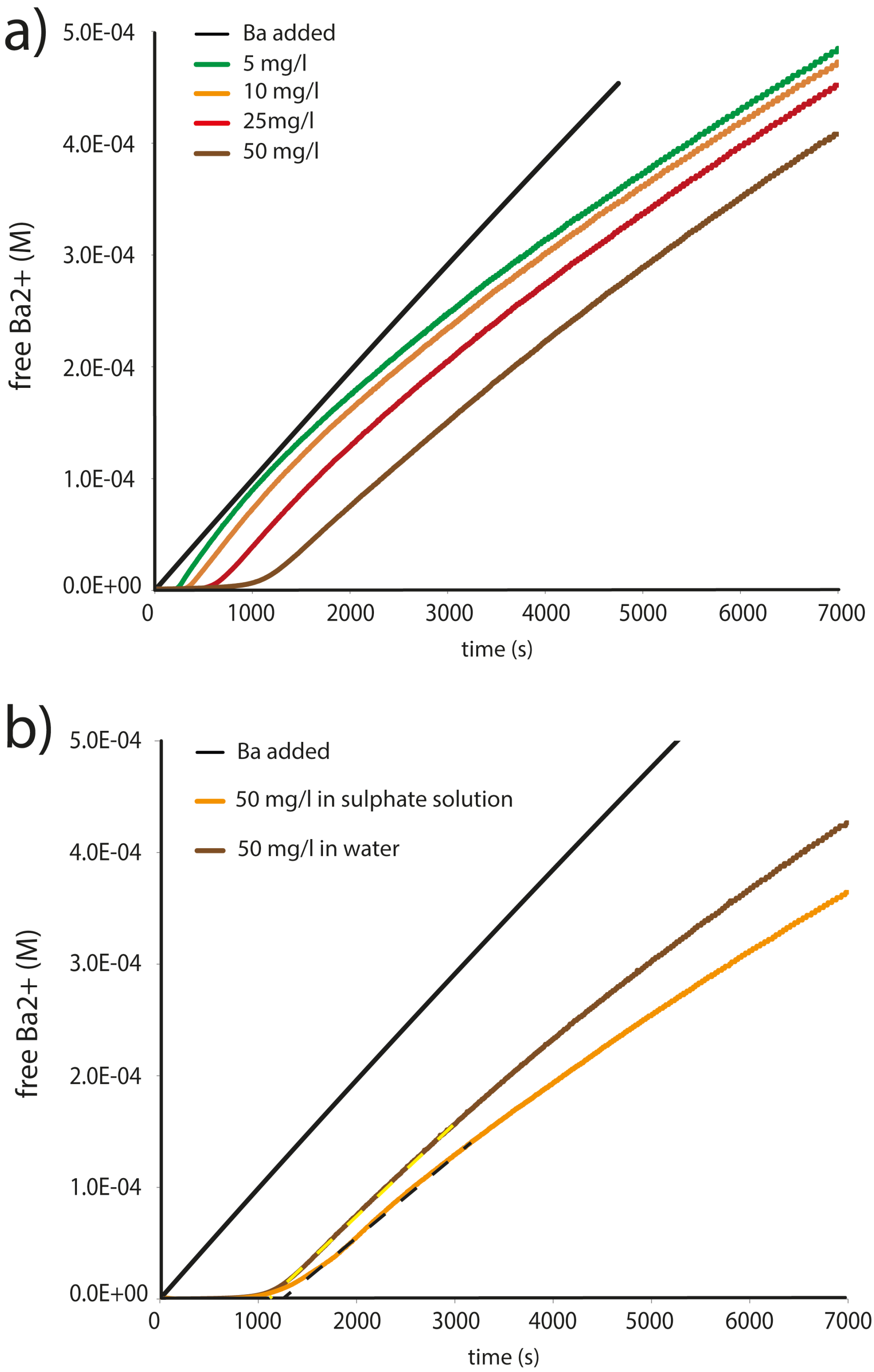
Bound sulphate (from conductivity measurements) agrees well within experimental error, with the bound barium (from ISE), thus indicating that prenucleation associates are indeed neutral as assumed for the calculations.



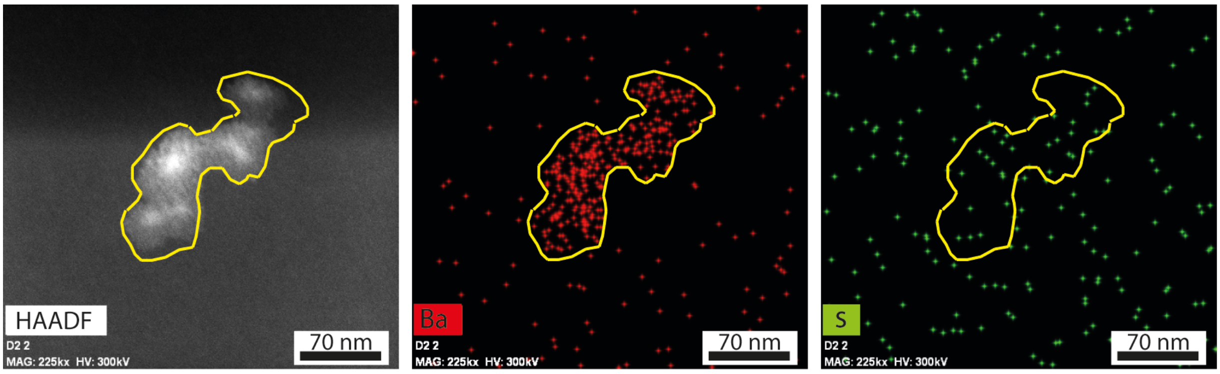
ESI 1. Bounded sulphate calculated from conductivity measurements and barium bounded calculated from ISE. Error bars correspond to the detection limit of the probes.



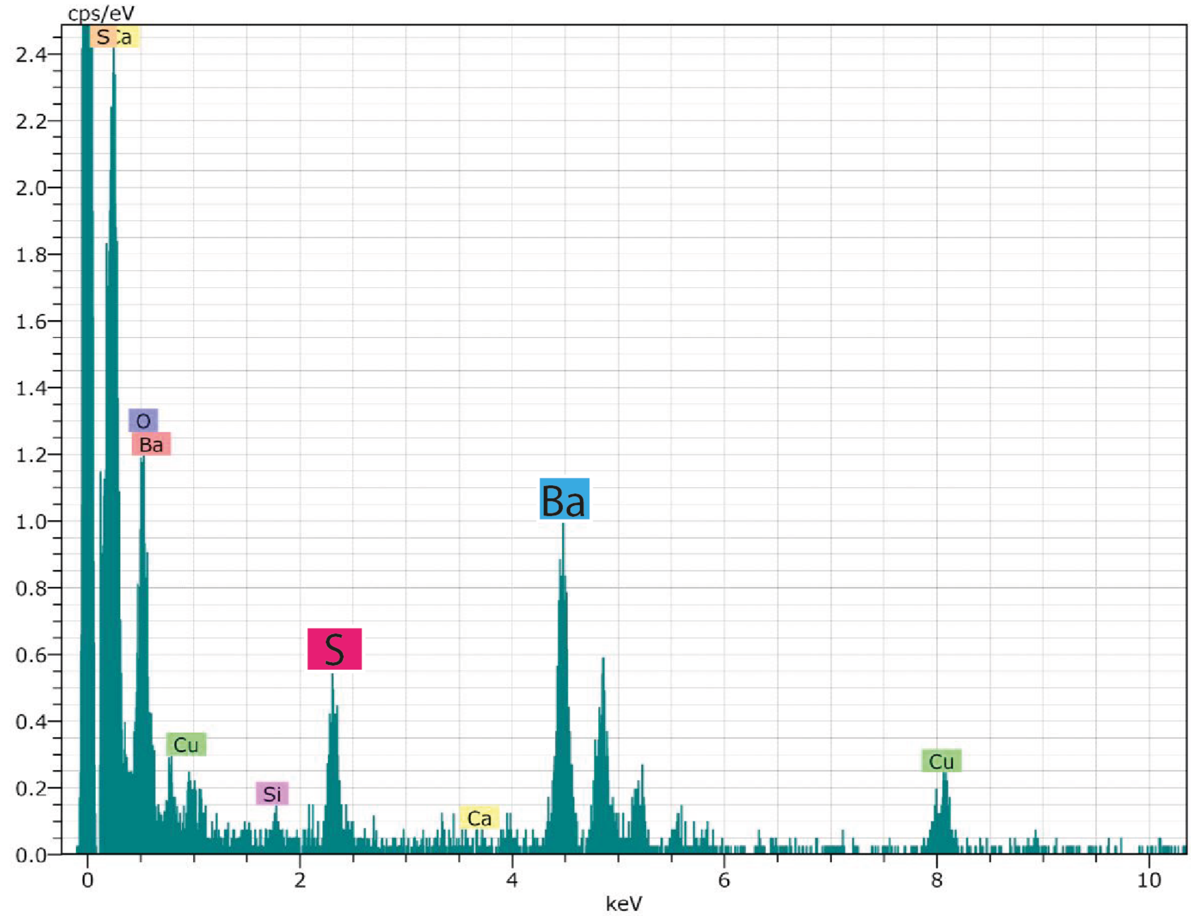
ESI 2. Evolution of free-Ba^{2+} and conductivity with time in the presence of 2.5 mg/l of PAA. Transmittance drop is included in discontinuous lines. Three regions have been distinguished in colours for clarity. In region (I) free-Ba^{2+} concentration decreases, conductivity curve bends and transmittance is not affected. In region (II) free-Ba^{2+} concentration decreases but slower than in the previous region, conductivity and transmittance curves drop. In region (III) free-Ba^{2+} concentration is constant and conductivity increases.



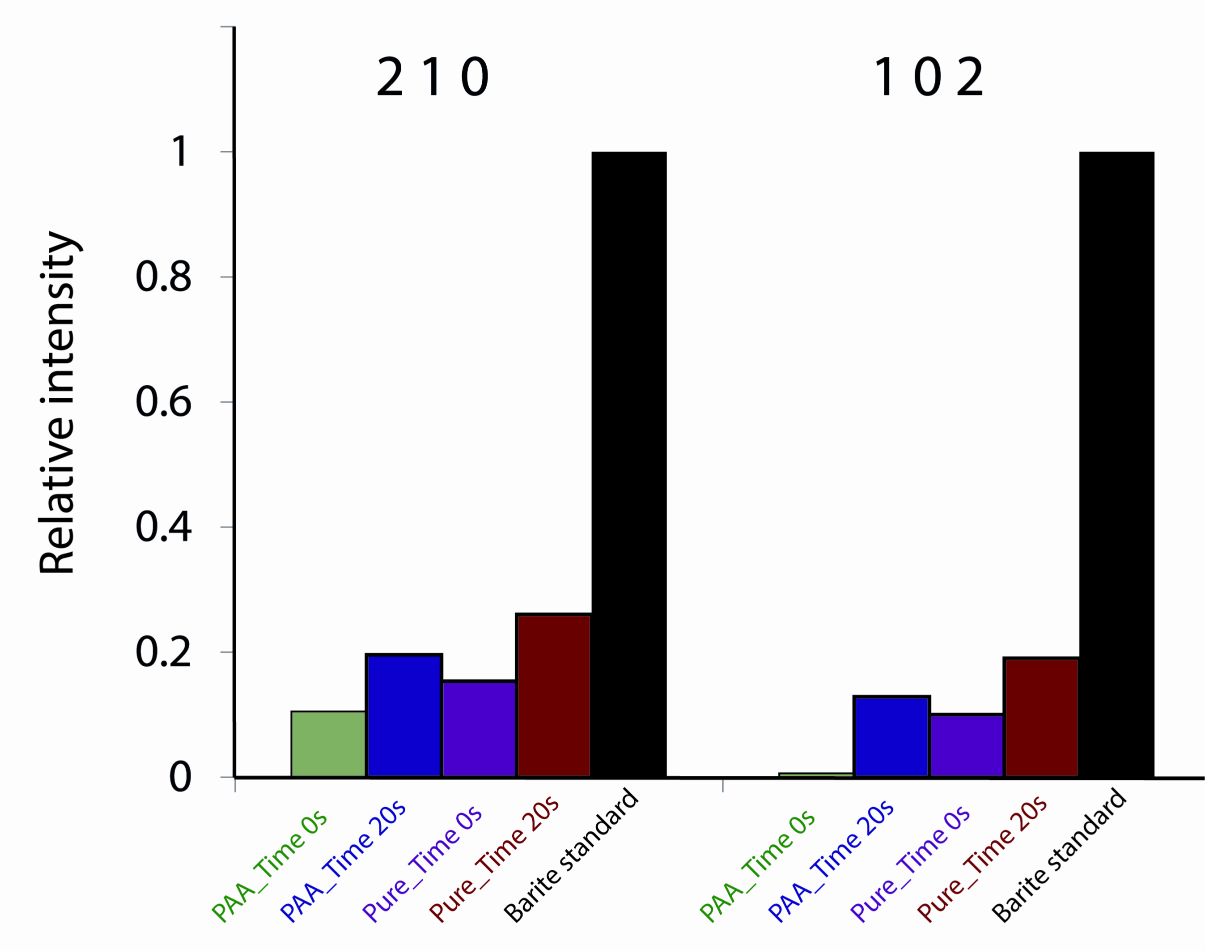
ESI 3. a) Barium binding capacities of PAA in water with 5, 10, 25 and 50 mg/l of PAA. b) Comparison between the binding capacity of 50 mg/l of PAA in water and in 1 mM Na_2SO_4 solution. The discontinuous lines mark the intersection of the barium curve lines with the x-axis. The black line refers to the amount of barium ions added.



ESI 4. a) STEM-HAADF image of a Ba-PAA globule (Fig. 4) with its contour area delimited by the yellow line. EDX maps of the area in STEM-HAADF images: b) barium, c) sulfur.

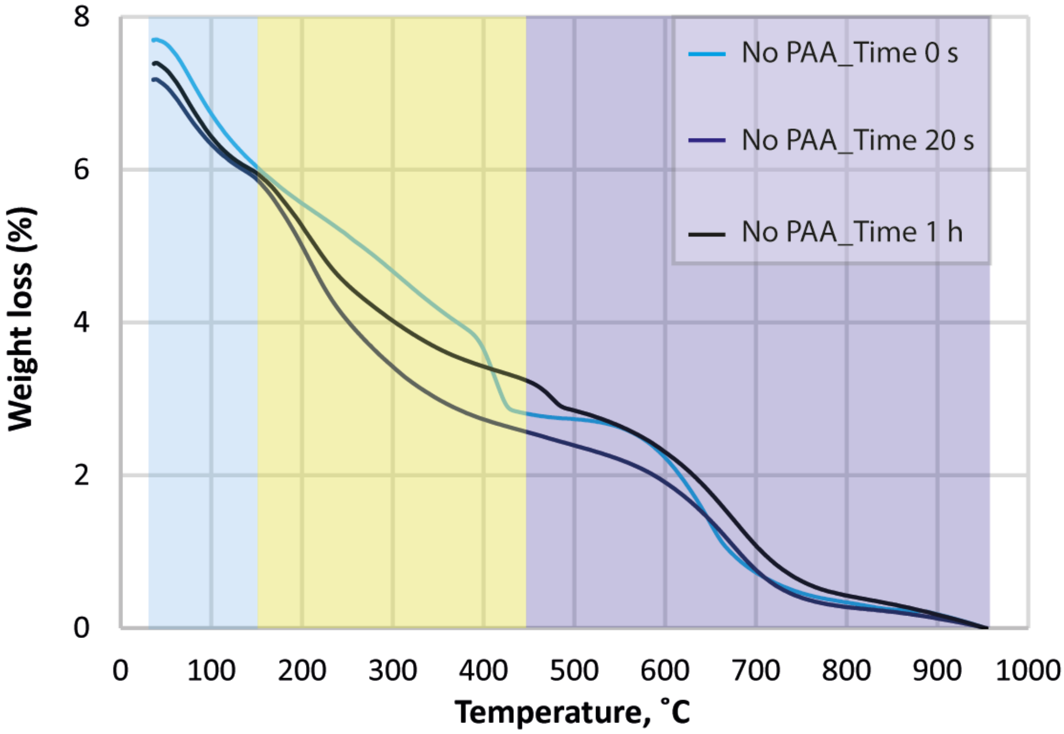


ESI 5. EDX spectra of the shapeless structures with poorly defined contours (Fig. 5b). EDX analysis show both barium and sulfur peaks.

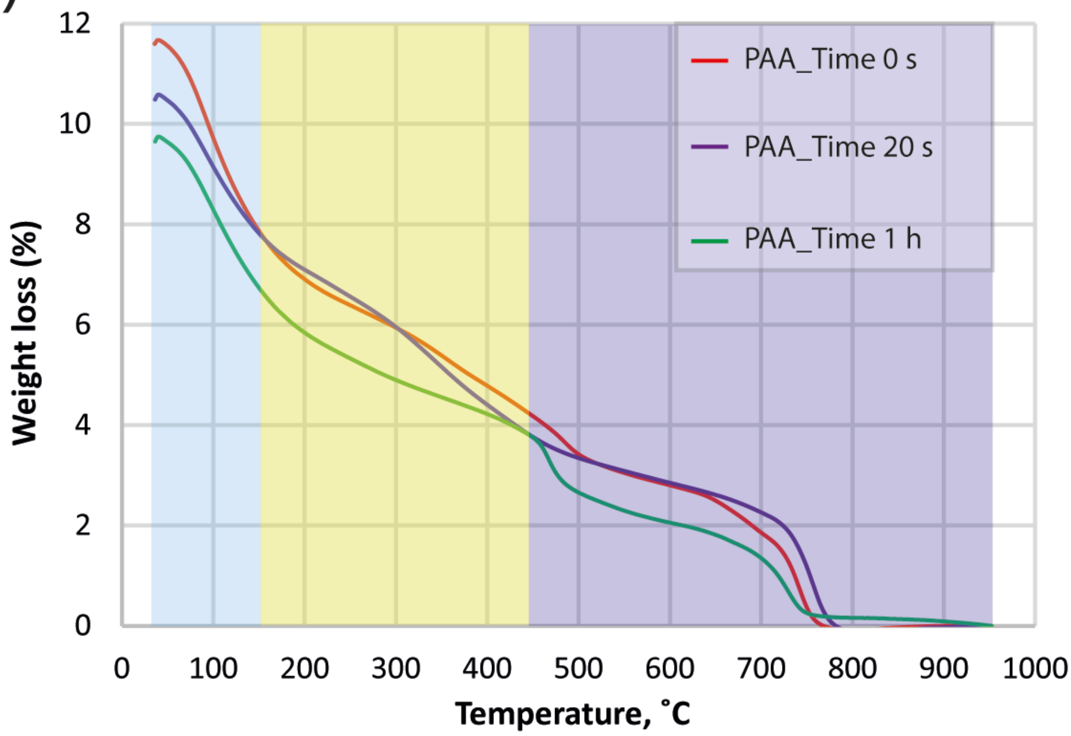


ESI 6. Average relative intensities of the 210 and 102 Bragg peaks of freeze-dried samples obtained by X-ray diffraction. XRD intensities can be compared with the barite standard. Error bars indicate standard deviation.

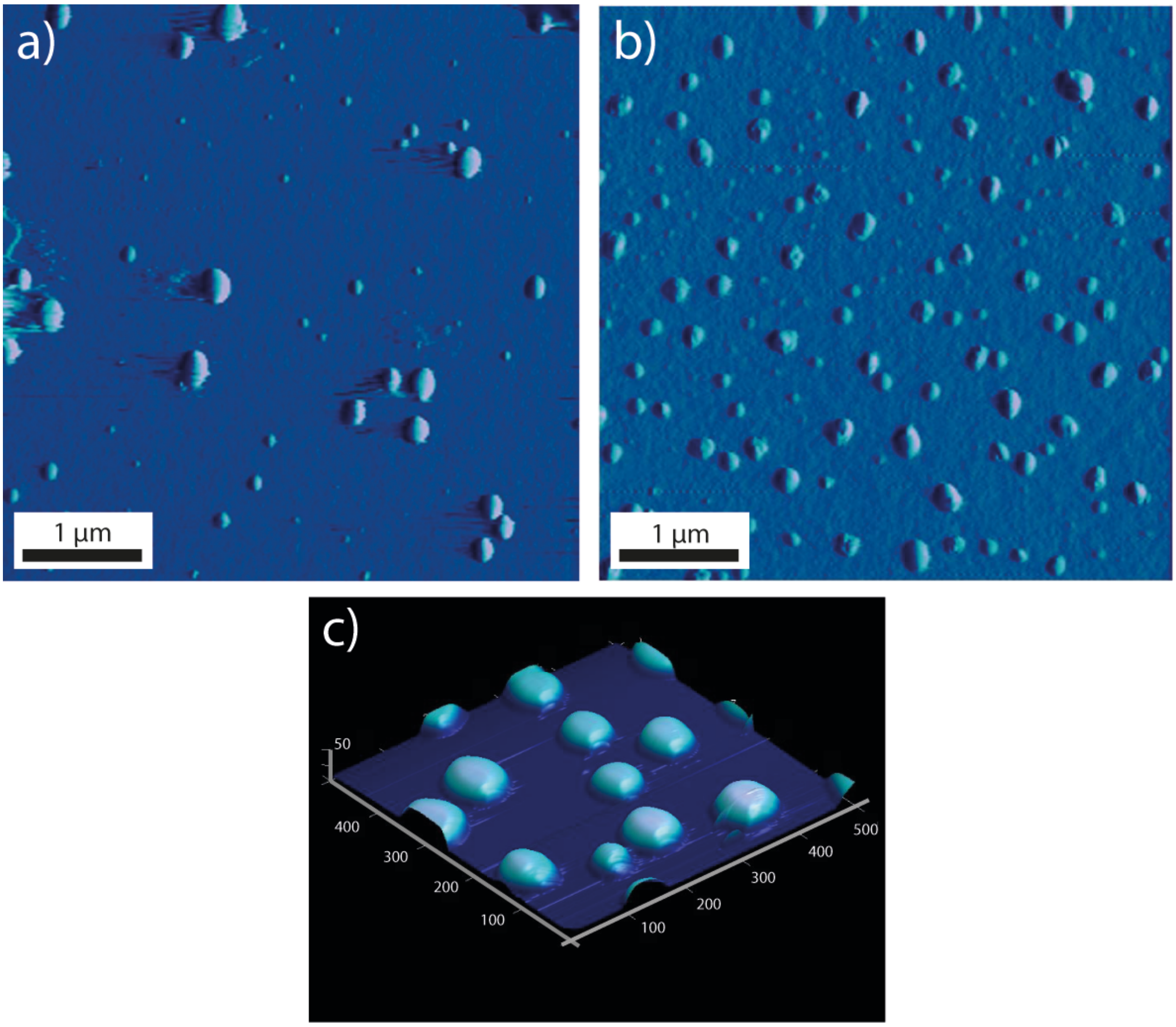
a)



b)



ESI 7. TGA plots of freeze-dried a) pure and b) PAA-bearing $BaSO_4$ samples collected at different times upon mixing of $Ba(OH)_2$ and H_2SO_4 solutions. The weight loss is expressed as grams lost per 100 grams of pure, dry $BaSO_4$.



ESI 8. a) and b) AFM deflection images of ethanol suspensions of freeze-dried powders on glass slides. c) AFM 3D image made combining deflection and height images. Graduation of the xyz axes is in nanometres.