Supplementary information

Capturing an amorphous BaSO\(_4\) intermediate precursor to barite

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1. Titration experiments

Titrations were performed using a Metrohm 836 Titrando auto titration unit, coupled with an 867 pH Module and controlled with the Tiamo 2.5 software package. Solutions were added using 800 Dosino units attached to 807 Dosing Units using tubes fitted with anti-diffusion tips. The pH was recorded with a combined pH electrode (Metrohm, 6.0256.100), referenced with 3M KCl solution (Merck) and calibrated with standard buffer solutions (Mettler-Toledo). The free barium concentration was measured using a Ba Ion Selective Electrode (Mettler-Toledo, DX337Ba), filled with the corresponding reference electrolyte. Turbidity was measured using a multiple wavelength Optrode (Metrohm, 6.1115.000) set to 610 nm wavelength. All probes and nozzles were set to the same immersion depth to ensure that all data was collected from the same level in the titration. The probes, vessel and nozzles were thoughtfully cleaned between experiments. First, the reactant vessel was filled with EDTA cleaning solution (0.01 M, pH 12) and the probes and nozzles were immersed for 30 min. Following, everything was rinsed with Milli Q water, then the vessel was filled with Milli Q water, and all probes and nozzles were immersed there for 30 min. Final rise with Milli-Q water was used to eliminate any remaining traces of EDTA.

A diagram of the titration setup is shown in Fig. S5. Double addition titrations were carried through by adding 2 mM BaCl\(_2\) and 2 mM Na\(_2\)SO\(_4\) into 75 mL water at 150 \(\mu\)L-min\(^{-1}\) for a maximum of 17 mL each. The
pH was kept constant by counter-titrating either NaOH or HCl (0.01 M). The Barium ISE was calibrated using the same parameters as above in the absence of sulfate. A nitrogen atmosphere was introduced through a port on the titration vessel lid in order to avoid the formation of any carbonate species (BaCO₃).

2. TEM characterization of the samples

For selected titrations, aliquots were removed from the vessel and prepared for transmission electron microscopy (TEM) analysis. Aliquots (1 mL) were taken and immediately quenched by using 20 mL of ethanol. Following, TEM samples were prepared by dipping the grid in the alcohol dispersion for 1 minute. The grids were then dried in air and storage at low humidity conditions. TEM and HRTEM analysis of the samples were carried out using a Zeiss Libra120, operated at 120 kV and a FEI Titan, operated at 300 kV. Energy dispersive X-Ray analysis were carried out in scanning transmission electron microscopy (STEM) mode using a Super-X EDX detector (FEI), formed by four SSD detectors with no window surrounding the sample. STEM images in the FEI Titan TEM of the areas analyzed by EDX were collected with a high angle annular dark field (HAADF) detector.

3. FTIR measurements

ATR-FTIR measurement were recorded on a Bruker 80 V spectrometer equipped with a diamond crystal heated golden gate ATR-unit (Specac). Milli-Q water was used as background and subtracted from each sample scan. Each aliquot pipetted out from titration vessel at different times (Fig. S3) was dropped onto the crystal and sealed with a volatile cover anvil from Golden gate. For each sample, 2000 scans were recorded at a speed of ~ 4 scans per second between 900 cm⁻¹ and 1900 cm⁻¹. Between each sample, the crystal surface was cleaned with acetic acid and Milli Q-water. A new Milli-Q background was measured before each sample.
4. **Figures**

**a)**

**Double addition**

**b)**

**Single addition**

Fig. S1. Comparison of the free and bound barium during the prenucleation regime for a) stoichiometric addition of barium and sulfate (double addition) and for b) barium addition to sulfate excess. Moles of barium added (black), free (blue) and bound (red) are represented for both experimental conditions.
Fig. S2. Comparison of IAP plateaus seen in titrations under conditions used to test if carbonate impurities are present in the system. The grey area illustrates the standard deviation of the experiments shown in Fig. 1 in the main text.
Fig. S3. IAP and transmittance evolution against time for a typical experimental run. Arrows mark the exact point from which IR spectra are displayed in Fig. 4 of the main paper.

Fig. S4. Proposed crystallization mechanism for barium sulfate after combining the insights gained in this study with our previous results. ¹
Fig. S5. Schematic of the titration setup with Barium ISE, pH electrode and optrode, and nozzles for addition of all chemical species. The setup was modified as required for the different experiments by removing or adding extra accessories and plugging the ports.

References