Electronic Supplementary Material (ESI) for CrystEngComm.
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Electronic Supplementary Information

$BaCO_3$ and NH_3SO_3 as precursors for the hydrothermal synthesis of $BaSO_4$

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Synopsis

This document contains:

1. *the specifications for the PTFE lined stainless steel high pressure reactor employed to carry out the $BaSO_4$ hydrothermal syntheses presented in the present work;*
2. *supplementary SEM micrographs of the powders synthesized;*
3. *DLS distributions;*
4. *details of the models employed to extract information from the experimental design of barite syntheses starting from NH_3SO_3;*
5. *References.*

1. Specifications for the PTFE lined stainless steel high pressure reactor

The syntheses were carried out in a 200 mL Teflon lined stainless steel high pressure reactor mod DAB3 (Berghof, Tuebingen, Germany, Figure S1). The heating/stirring was carried out with an heating mantle mounted on a magnetic stirrer/heater (Heidolph, Germany, mod MR-HEI standard) and a temperature controller/programmer mod BTC-3000 (Berghof, Germany) equipped with a type K thermocouple (see Figure S1 for the complete assembly). In Table S1 all the relevant conditions and dimensions of the high pressure reactors are reported.

Figure S1. Berghof DAB3 Teflon lined stainless steel high pressure reactor.

Table S1. Characteristics of the high pressure reactor and of the magnetic stirrer.

High pressure reactor description	
internal height (mm)	100.5
internal diameter (mm)	51.5
volume of liquid (mL ± 1 mL)	150
Magnetic stir bar	
length (mm)	30
diameter (mm)	6
stirring speed (rpm)	750

2. Supplementary SEM micrographs of the powders synthesized

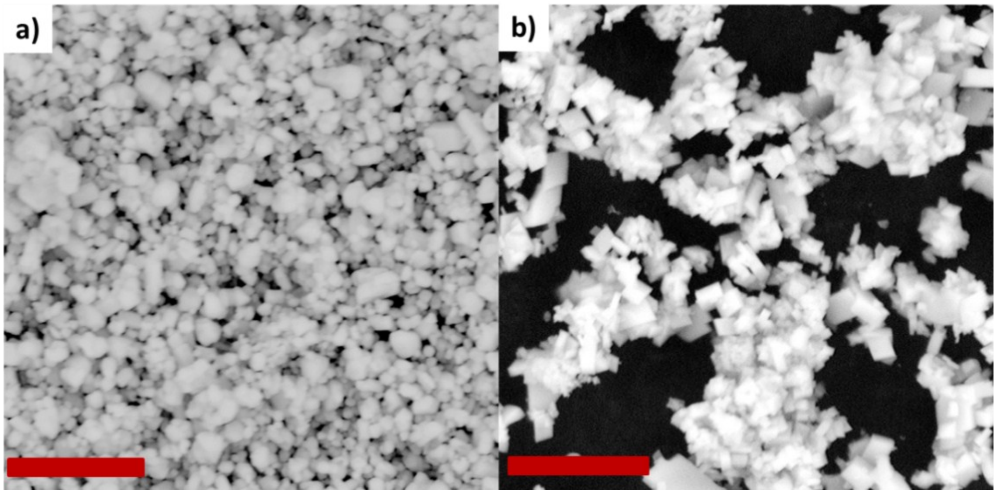

Figure S2. a) commercially available $BaCO_3$; b) $BaSO_4$ prepared from $BaCO_3$ and 50 mM Na_2SO_4 with reaction time 48 h, and T = 150°C. Scale bars are 5 µm in both panels.

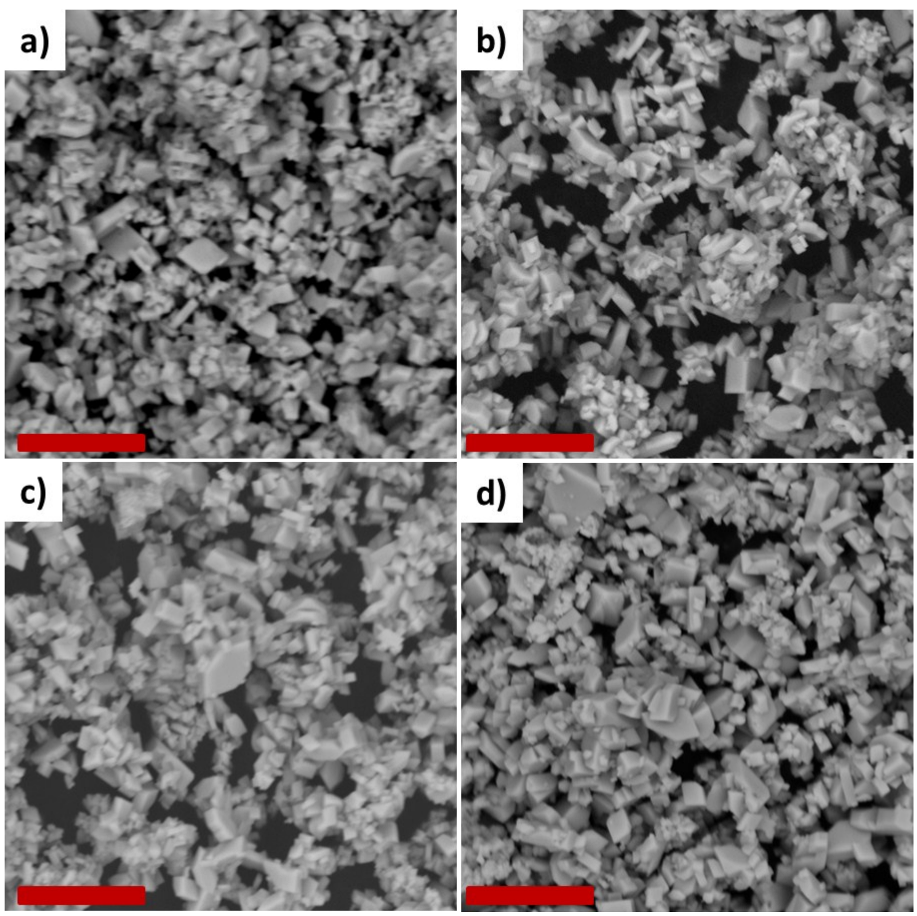

Figure S3. $BaSO_4$ prepared from $BaCO_3$ in the presence of 25 mM K_2SO_4, kept at T = 200°C for a) 6 h, b) 24 h, c) 48 h, d) 96 h. Scale bars are 5 µm in all the panels.

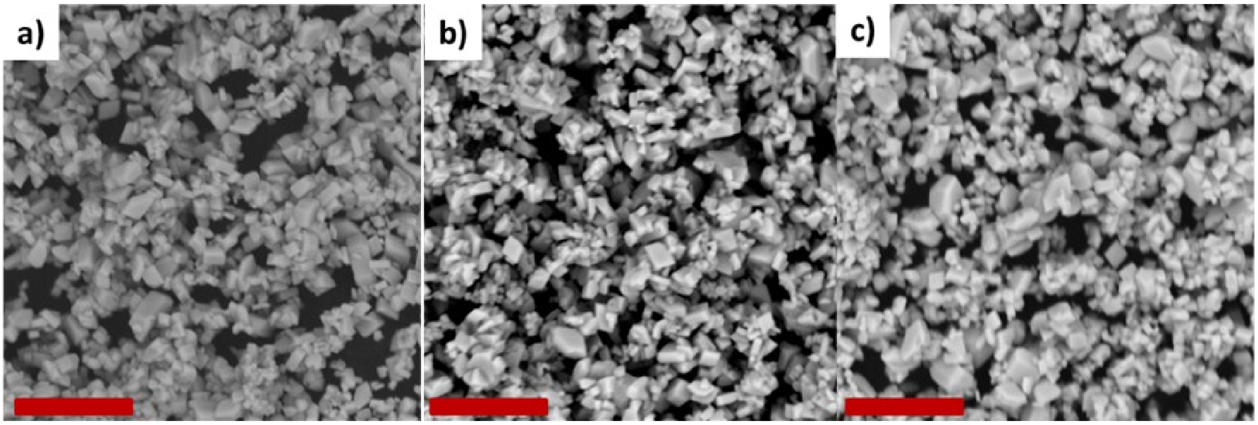

Figure S4. $BaSO_4$ prepared from $BaCO_3$ in the presence of 25 mM K_2SO_4, kept at T = 250°C for a) 24 h, b) 48 h, c) 96 h. Scale bars are 5 µm in every panel.

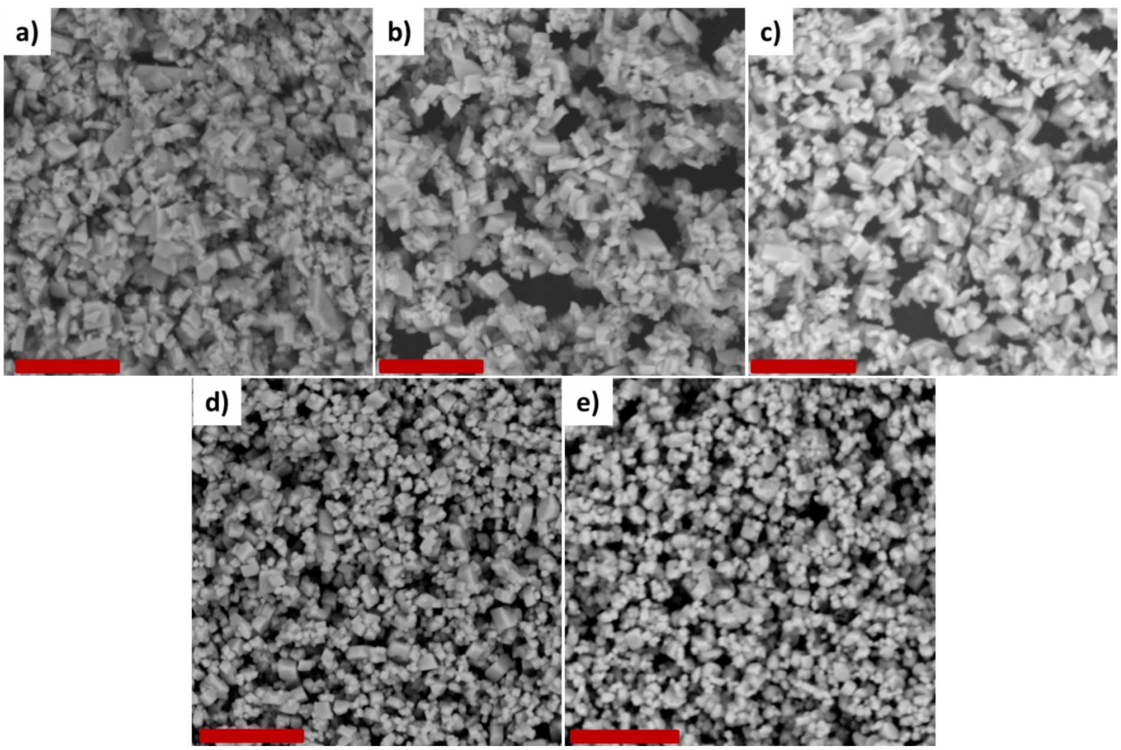

Figure S5. $BaSO_4$ prepared from $BaCO_3$ in the presence of sulfate with concentration a) 10 mM, 25 mM, c) 50 mM, d) 100 mM, e) 200 mM, with K as counter ion. Reaction time 48 h, T = 200°C. Scale bars are 5 µm.

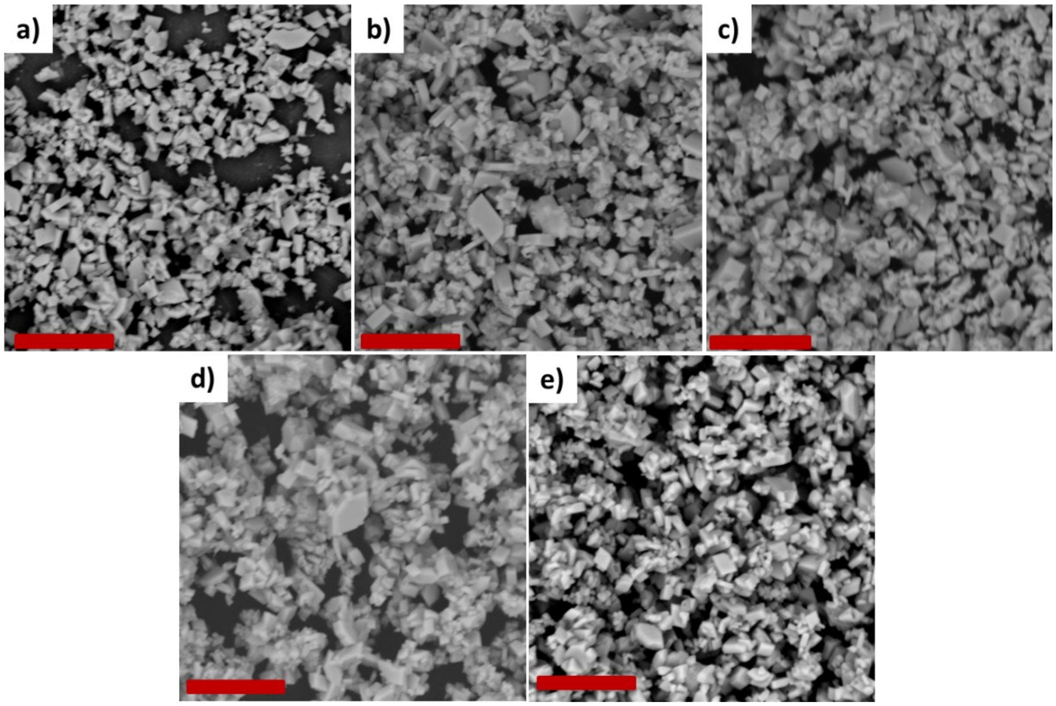

Figure S6. $BaSO_4$ prepared from $BaCO_3$ in the presence of 25 mM K_2SO_4, t=48 h at a) 25°C, b) 120°C, c) 160°C, d) 200°C, e) 250°C. Scale bars are 5 μm.

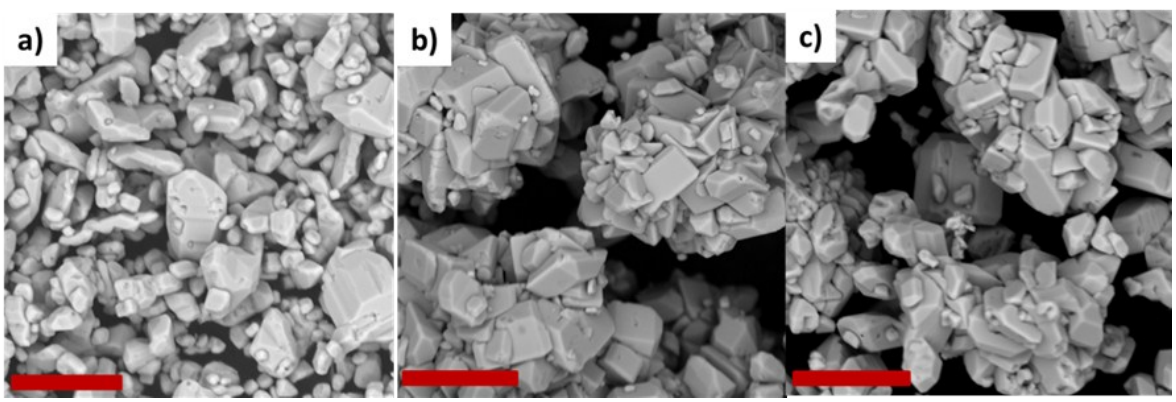

Figure S7. Barite from 100 mM $BaCl_2$ and 100 mM NH_3SO_3: a) 100 °C, pH 1.2, 48 h; b) 100 °C, pH 1.2, 48 h, 10 mM NTA; c) 100 °C, pH 1.2, 48 h, 1 mM Brij 35. Scale bars are 8 μm in every panel.

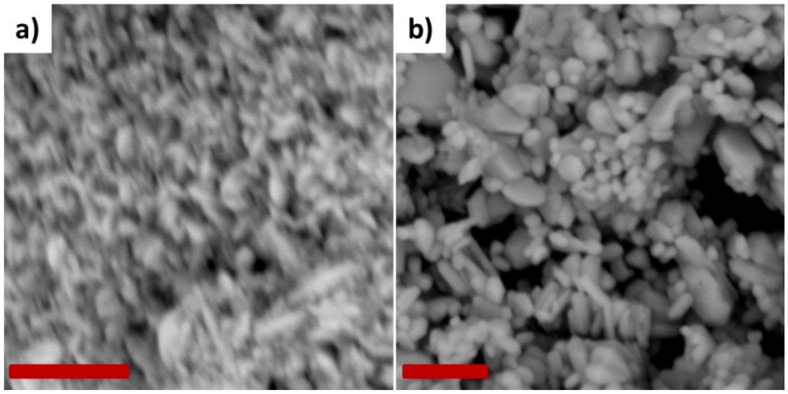

Figure S8. a) $BaSO_4$ obtained from 25 mM $BaCl_2$, 25 mM NH_3SO_3, with 100 mM NTA, kept for 48 h at 200°C; b) $BaSO_4$ obtained from $BaCl_2$ 10 mM, NH_3SO_3 10 mM, in the presence of NTA 100 mM, kept for 24 h at 200°C. Scale bars 2 µm.

3. DLS Distributions

In this section are reported the hydrodynamic distributions of the synthetized materials. The measurements were carried out using the CILAS Nano DS instrument with an angle of 90°. An ammonia (0.1 M) suspension (20 mg L^{-1}) was analyzed for each sample, after a sonication of 30 min (at least) in an ultrasound bath and in a closed vial to avoid NH3 evaporation (suggested 95 W, 37 kHz). The reported dimensions were obtained through the fit of the (decay times) distribution function to the integral equation relating the field correlation function and the said distribution function using a constrained regularization method (CONTIN DP algorithm) developed by Provencher.[1] The intensity distribution function is then obtained.

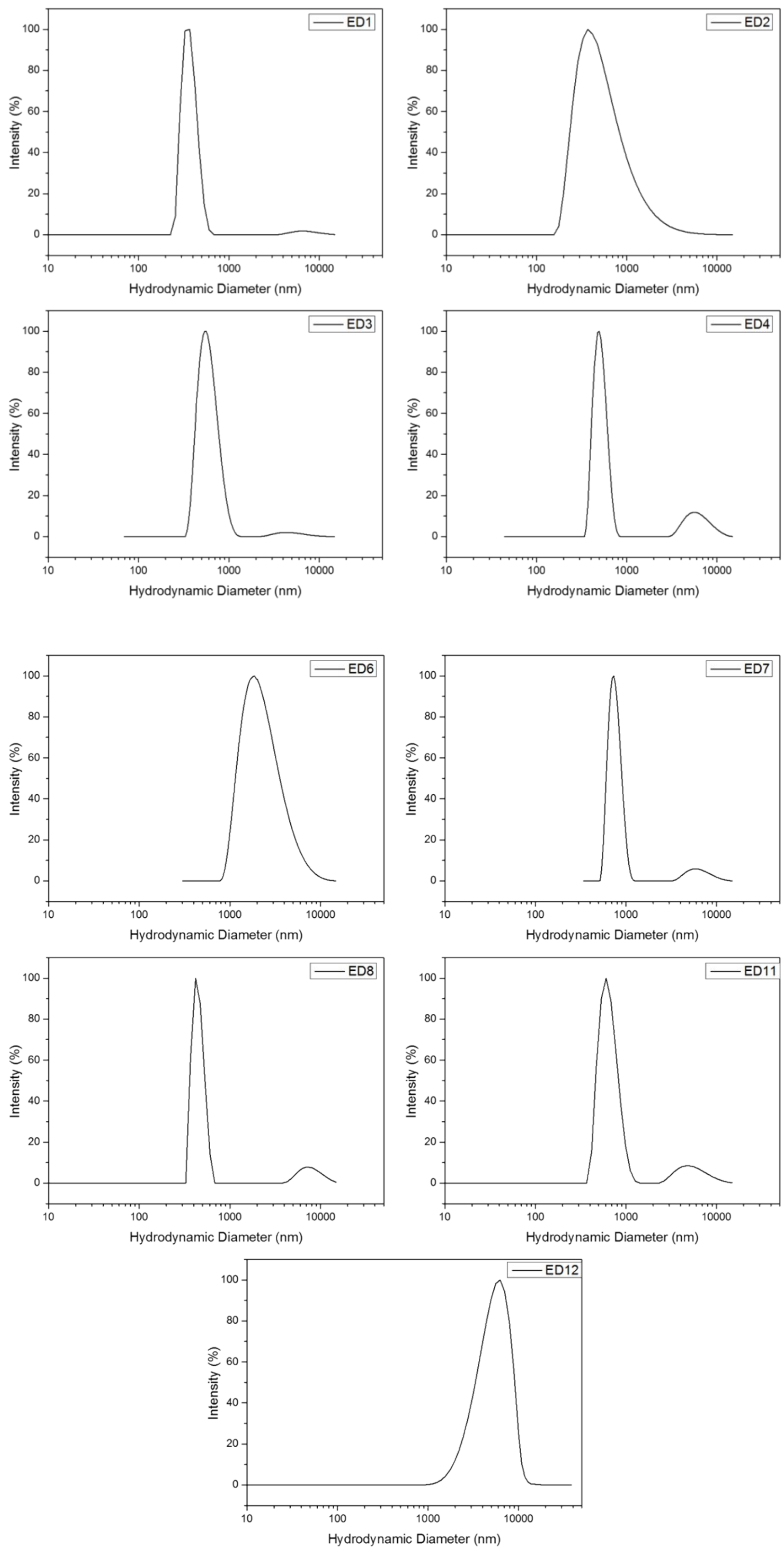

Figure S9. Hydrodynamic Diameter distributions obtained by DLS measurements on the Experimental Design materials.

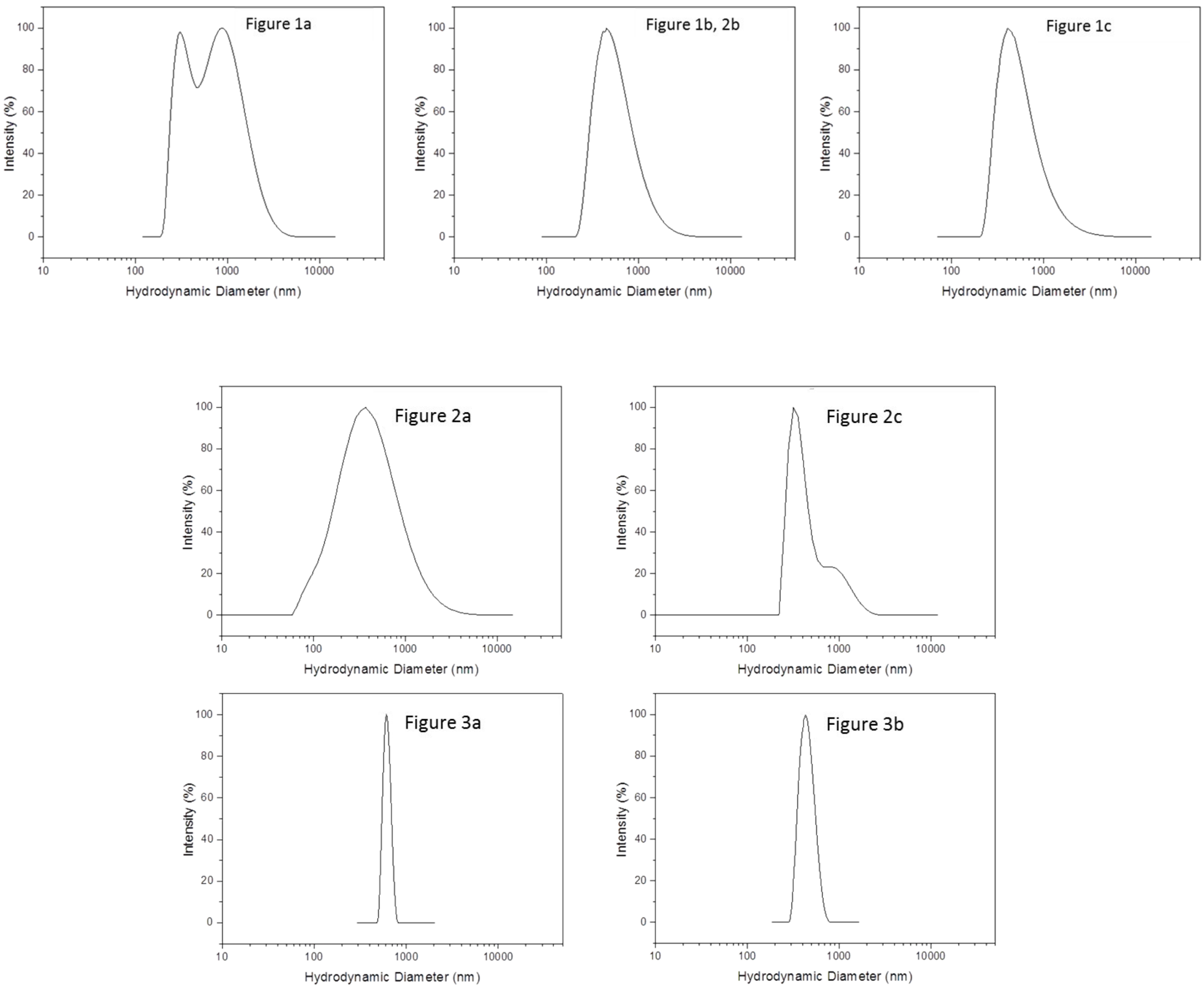

Figure S10. Hydrodynamic diameter distributions obtained by DLS measurements on the materials described in Table 1 of the main text with the reference to the corresponding figure in the manuscript.

4. Details of the models employed to extract information from the experimental design

A. Linear Model for Yield

Table S2. Model parameters for barite yield (%): t represents the Student t value, Pr > |t| is the two-tailed p-value evaluating the null hypothesis against an alternative that the mean is not equal zero, lower and upper bound are the extremes of the 95% confidence interval.

Variable	Value	Standard error	t	Pr > |t|	Lower bound (95%)	Upper bound (95%)
Intercept	-191.2	108.2	-1.77	0.108	-432.4	49.99
pH	-10.43	2.920	-3.57	**0.005**	-16.94	-3.928
T (K)	0.682	0.244	2.792	**0.019**	0.138	1.226
$[Ba^{2+}]$ (mM)	0.286	0.276	1.036	0.324	-0.329	0.902

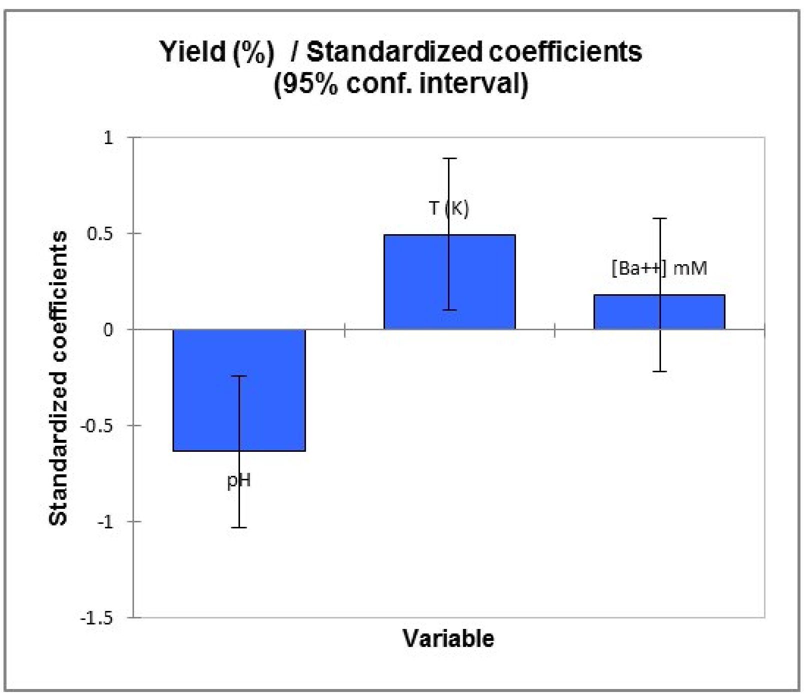

Figure S11. Graphical representation of the standardized regression coefficients for barite yield (%) and their 95% confidence intervals.

B. *Linear model for minimum size*

Model equation:

$$Minimum\ size\ (\mu m) =- 2.957 + 0.05783 * pH + 6.656 * 10^{-3} * T(K) + 9.459 * 10^{-3}[Ba^{2+}](mM)$$

Table S3. Model parameters for barite minimum size (µm): t represents the Student t value, Pr > |t| is the two-tailed p-value evaluating the null hypothesis against an alternative that the mean is not equal zero, lower and upper bound are the extremes of the 95% confidence interval.

Source	Value	Standard error	t	Pr > |t|	Lower bound (95%)	Upper bound (95%)
Intercept	-2.957	2.082	-1.420	0.205	-8.052	2.137
pH	0.058	0.086	0.672	0.526	-0.153	0.268
T (K)	0.007	0.005	1.403	0.210	-0.005	0.018
$[Ba^{2+}]$ (mM)	0.009	0.005	1.780	0.125	-0.004	0.022

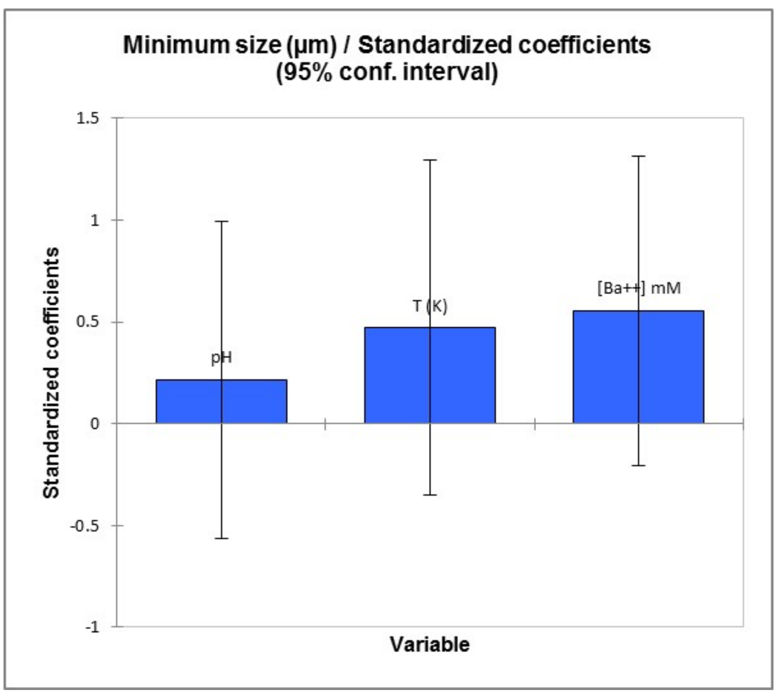

Figure S12. Graphical representation of the standardized regression coefficients for barite minimum size (µm) and their 95% confidence intervals.

C. Linear model for maximum size

Table S4. Model parameters for barite maximum size (µm): t represents the Student t value, Pr > |t| is the two-tailed p-value evaluating the null hypothesis against an alternative that the mean is not equal zero, lower and upper bound are the extremes of the 95% confidence interval.

Source	Value	Standard error	t	Pr > |t|	Lower bound (95%)	Upper bound (95%)
Intercept	-27.11	9.461	-2.865	**0.029**	-50.256	-3.956
pH	-0.699	0.391	-1.787	0.124	-1.655	0.258
T (K)	0.076	0.022	3.503	**0.013**	0.023	0.128
$[Ba^{2+}]$ mM	0.053	0.024	2.186	0.071	-0.006	0.112

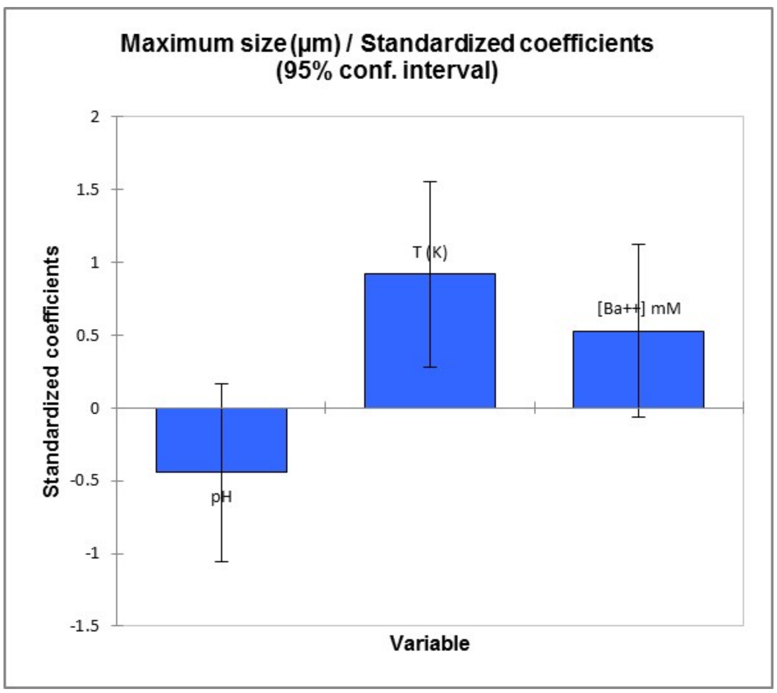

Figure S13. . Graphical representation of the standardized regression coefficients for barite maximum size (µm) and their 95% confidence intervals.

D. *Linear model for median size*

Model equation:

$$Median\ size\ (\mu m) = -11.53 - 0.4051 * pH + 3.367 * 10^{-2} * T(K) + 2.483 * 10^{-2}[Ba^{2+}](mM)$$

Table S5. Model parameters for barite median size (µm): t represents the Student t value, Pr > |t| is the two-tailed p-value evaluating the null hypothesis against an alternative that the mean is not equal zero, lower and upper bound are the extremes of the 95% confidence interval.

Source	Value	Standard error	t	Pr > |t|	Lower bound (95%)	Upper bound (95%)
Intercept	-11.53	6.085	-1.895	0.107	-26.42	3.355
pH	-0.405	0.251	-1.611	0.158	-1.020	0.210
T (K)	0.034	0.014	2.429	0.051	0.000	0.068
$[Ba^{2+}]$ mM	0.025	0.016	1.599	0.161	-0.013	0.063

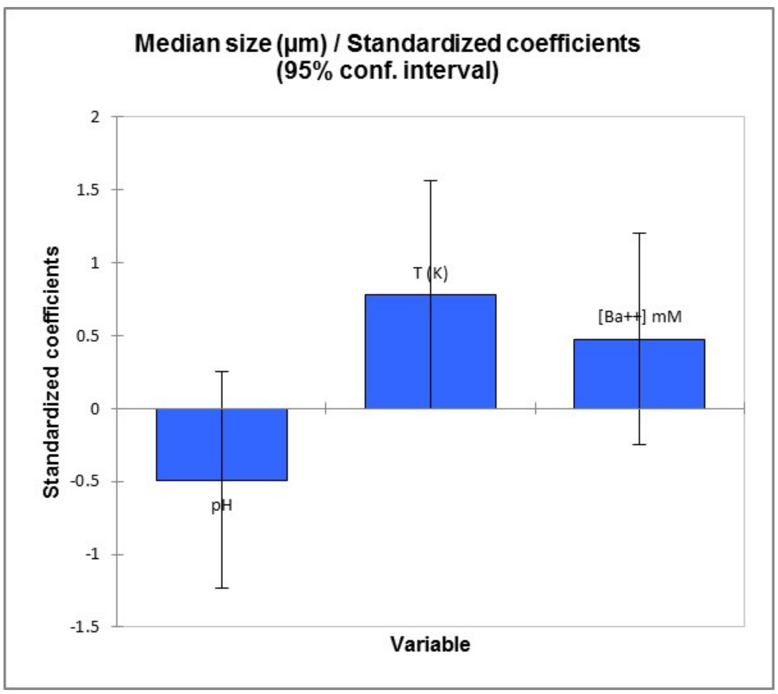

Figure S14. . Graphical representation of the standardized regression coefficients for barite median size (µm) and their 95% confidence intervals.

5. References

1. S. W. Provencher, *Comput. Phys. Commun.*, 1982, **27**, 229-242.