

Electronic Supplementary Information (ESI)

for

Revisiting the Roles of Salinity, Temperature and Water Activity in Phase Selection during Calcium Sulfate Precipitation

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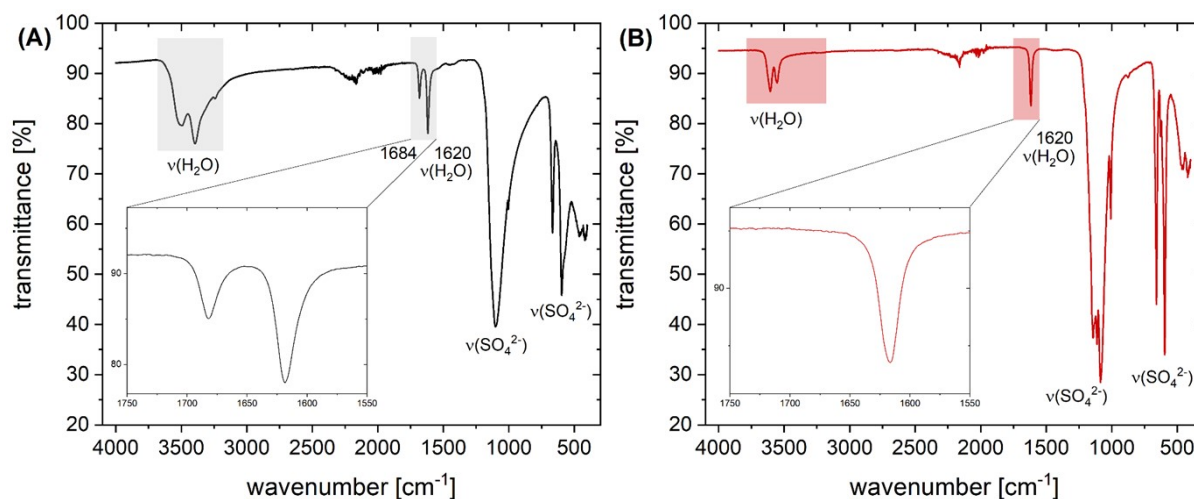


Figure S1: ATR-IR spectra of (A) pure gypsum and (B) pure bassanite. Characteristic stretching vibrations of sulfate groups and structural water are highlighted.

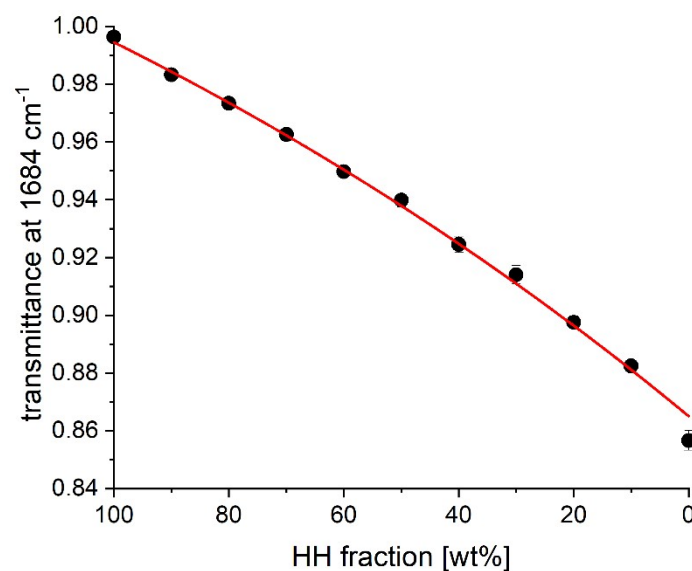


Figure S2: Plot of the IR transmittance at 1684 cm^{-1} (in units of transmission) as a function of bassanite content in defined mixtures of DH and HH. Dots represent experimental data, while the full line shows an exponential fit.

c(CaSO₄) [mol/L]	c(NaCl) [mol/L]	Temperature [°C]	Reaction time [min]	HH fraction [wt%]	Yield [g]	
0.1	0.8	90	5	8	0.063	
		80	5	42	0.042	
		70	5	0	0.064	
		60	20	0	0.023	
	2.8	90	5	83	0.035	
		80	5	82	0.023	
		70	5	0	0.050	
		60	20	0	0.018	
	4.3	90	5	93	0.063	
		80	5	91	0.051	
		70	5	9	0.041	
		60	20	1	0.013	
	0.2	0.8	90	5	86	0.199
			70	5	0	0.224
			50	5	8	0.118
		2.8	90	5	90	0.197
70			5	58	0.181	
50			5	35	0.121	
4.3		90	5	91	0.211	
		70	5	88	0.194	
		50	5	68	0.167	
0.4		0.8	90	5	2	0.504
	50		5	0	0.644	
	2.8	90	5	83	0.482	
		50	5	0	0.365	
	4.3	90	5	90	0.504	

Table S1: Summary of the different conditions at which calcium sulfate was precipitated in the present work, including values for the resulting phase composition (i.e. the fraction of hemihydrate deduced from ATR-IR spectroscopy as shown in Fig. S2) and the concomitant yield of solid material (given as average numbers determined by gravimetric analyses of the dried precipitates with a precision of ± 0.001 g). Generally, more material is obtained at higher CaSO_4 concentrations (as expected). In most cases, the yield increases with temperature at a given CaSO_4 concentration due to the inverse solubility of calcium sulfate phases, whereas no clear trend can be observed as a function of salinity (probably because the salinity influences phase selection, which in turn determines the yield). At conditions where HH is favoured, less precipitate was usually obtained as compared to DH-rich materials, likely as a consequence of the higher solubility of HH and/or kinetic factors (note that most reactions were stopped after 5 minutes, which may not be enough for precipitation to be completed in some cases).

$c(\text{CaSO}_4)$ [mol/L]	$c(\text{NaCl})$ [mol/L]	$c(\text{Na})$ [mmol per mol CaSO_4]	$c(\text{Cl})$ [mmol per mol CaSO_4]	Formed solid phase(s)
0.1	0.8	14.2	0.6	DH (92%)
	2.8	214.7	10.6	HH (83%)
	4.3	309.4	3.5	HH (93%)
0.2	0.8	183.1	0.8	HH (86%)
	2.8	296.8	3.3	HH (90%)
	4.3	334.6	2.4	HH (91%)
0.4	0.8	157.3	1.9	DH (98%)
	2.8	309.4	3.4	HH (83%)
	4.3	347.3	6.6	HH (90%)

Table S2: Results of elemental analyses on the sodium and chloride content of calcium sulfate powders precipitated at 90 °C at varying CaSO_4 concentrations and in the presence of different amounts of added NaCl with a fixed reaction time of 5 min. The obtained sodium and chloride concentrations were normalised with respect to the calculated HH/DH content in the samples. Note that the detected chloride concentration is considerably lower (by a factor of 20-200) than the sodium content, which indicates preferential sodium incorporation. Traces of chloride might originate from NaCl remainders on the surface of the CaSO_4 particles, which could not fully be removed during isolation, and/or from minor chloride incorporation into the water channels of bassanite.

$c(\text{NaCl})$	$c(\text{Na})$	$c(\text{Cl})$	$c(\text{Ca})$	Major solid
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[mol/L]	[mol/100g]	[mol/100g]	[mol/100g]	phase formed
0.8	0.072	0.002	0.636	DH
		+ 2 · 0.053	- 0.050	
2.8	0.178	0.003	0.586	HH
		+ 2 · 0.015	- 0.012	
4.3	0.207	0.003	0.574	HH

Table S3: Results of elemental analyses on the sodium, chloride and calcium content of calcium sulfate powders precipitated at 90 °C at 0.1 M CaSO₄ in the presence of different amounts of added NaCl with a fixed reaction time of 5 min. The obtained values are given in moles of Na, Cl and Ca per 100 g precipitate. Note that the increase of the amount of detected sodium corresponds to about two times the decrease of the calcium content, indicating partial replacement of Ca²⁺ by Na⁺ in the lattice with increasing salinity. Moreover, the Na:Ca molar ratio in the powder obtained at 4.3 M NaCl and 90 °C is found to be ca. 2:5, which fits well to the composition derived by DSC for this sample (1.01Na₂SO₄·4.99CaSO₄·2.90H₂O).

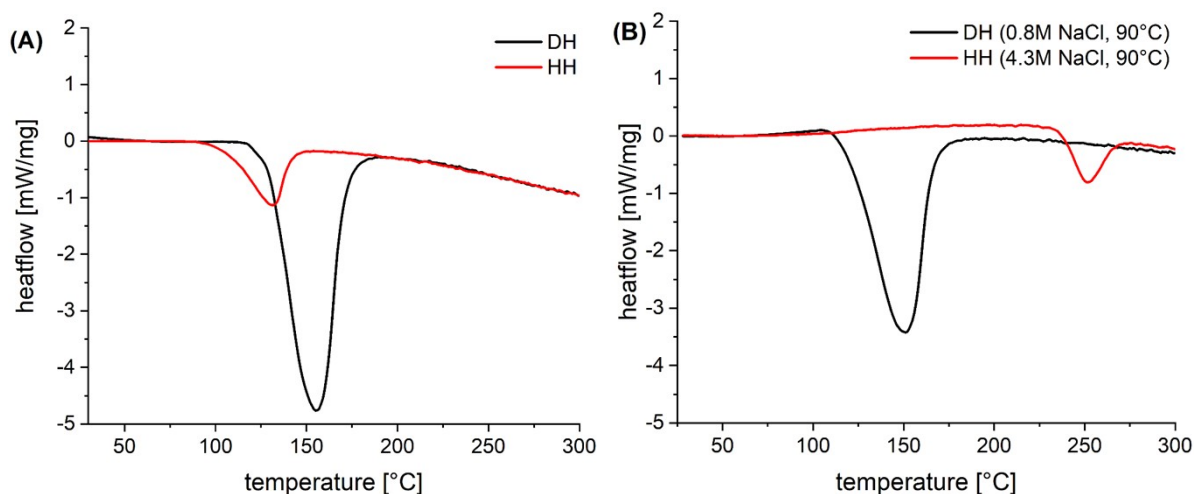


Figure S3: DSC curves of (A) pure DH and HH references and (B) DH and HH powders precipitated in the presence of NaCl at 90 °C with a reaction time of 5 min. Note the clear shift in the transition temperature of HH in (B), which indicates significant incorporation of sodium ions into the bassanite structure.

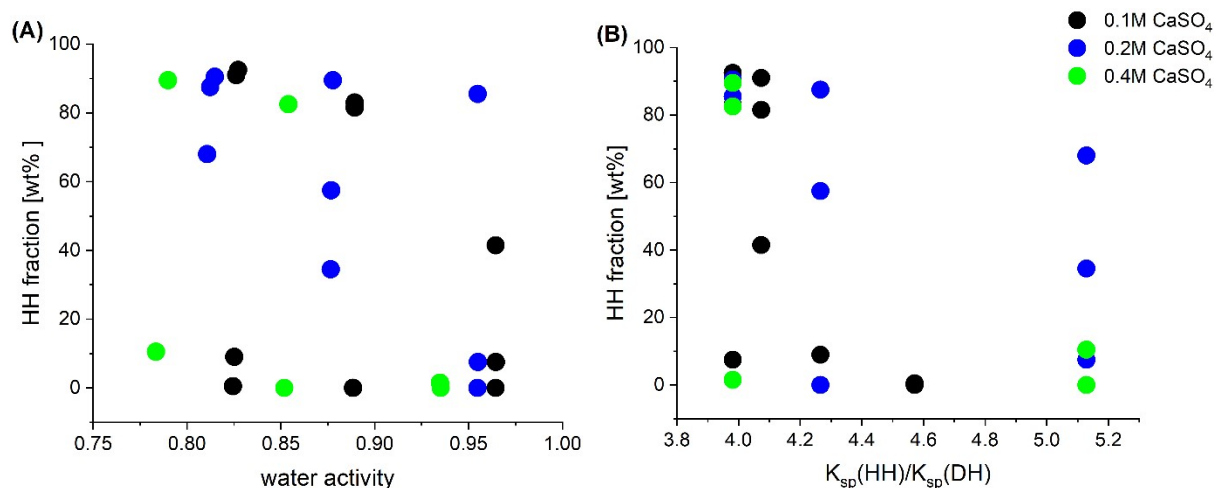


Figure S4: Plots of the fraction of hemihydrate formed in precipitation experiments under different conditions as a function of calculated values for the (A) water activity and (B) ratio of solubility products of HH and DH. Note that there is no obvious correlation between the obtained HH amount and any of the two calculated parameters.

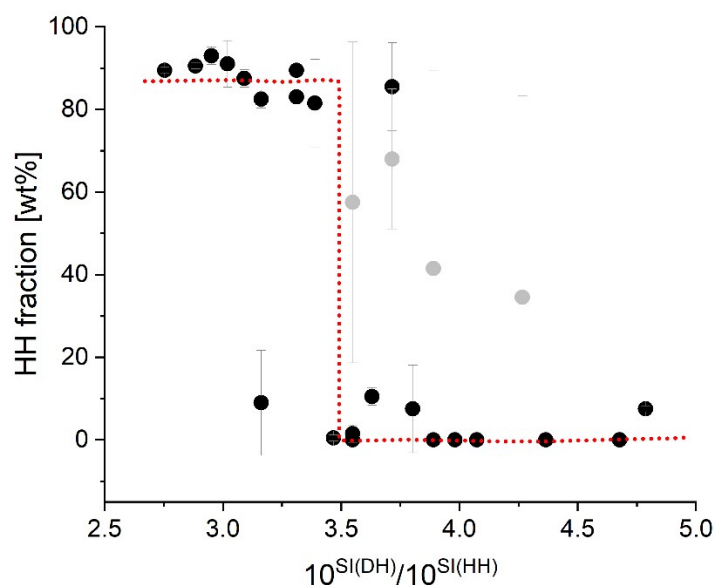


Figure S5: Correlation between the experimentally determined hemihydrate content in CaSO₄ powders precipitated under different conditions (with a fixed reaction time of 5 min) and the decadic ratio of the saturation indices calculated for DH and HH at the beginning of each reaction. The plot shows all datapoints obtained in this work, including those exhibiting standard deviations larger than 15 % (grey circles). The large error bars associated with these datapoints are a consequence of the pronounced sensitivity of the experiments at borderline conditions (i.e. near the abrupt threshold in relative supersaturation at which HH formation becomes kinetically favoured), where already minor variations in e.g. temperature during reaction or isolation can cause strong differences of the output in terms of phase composition.

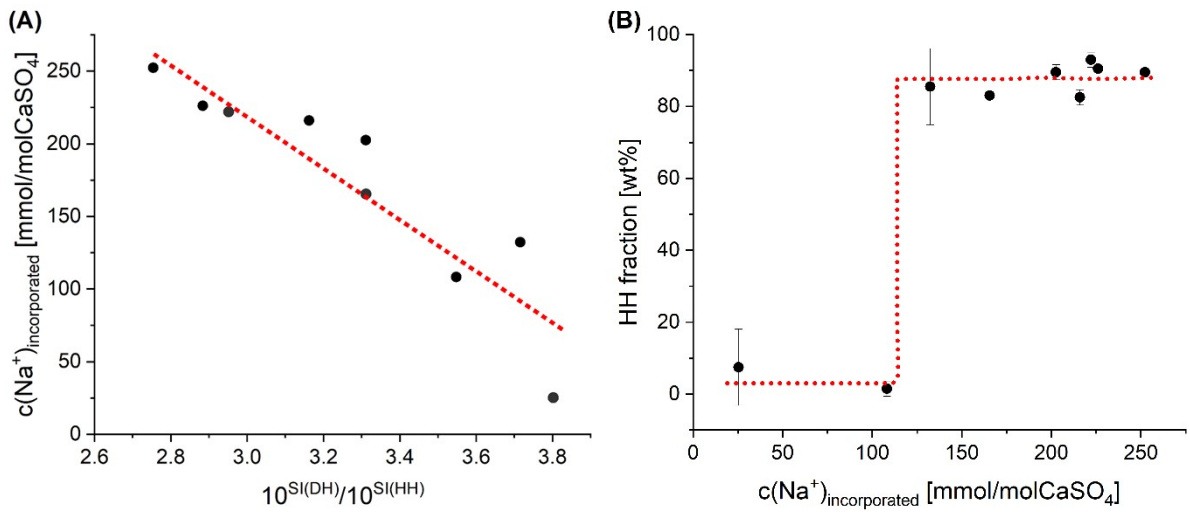


Figure S6: Correlations of the incorporated sodium concentration with the supersaturation ratio (A) and of the HH ratio with the incorporated sodium content (B). The data shown in the figure are based on precipitation experiments at 90 °C and 0.1, 0.2 and 0.4 M CaSO₄ with a reaction time of 5 min. The dashed lines are meant to visualise the observed trends.