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Electronic Supplementary Information

Effect of ferrous iron on the nucleation and growth of $CaCO_3$ in slightly basic aqueous solutions

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Ca_T/Fe_T	REACTOR C^{IV} (pH = 8.5)	REACTOR $CaCl_2$	REACTOR $FeCl_2$	REACTANT 1 C^{IV} (pH = 9)	REACTANT 2 $[CaCl_2]$, $[FeCl_2]$	pH	$\Omega_{calcite}$
No iron	11.5 mM	0.285 mM	0	152 mM	71.285 mM	8.5	6.46
100	11.5 mM	0.285 mM	2.85 µM	152 mM	71.285 mM 0.0057 mM	8.5	6.46
50	11.5 mM	0.285 mM	5.7 µM	152 mM	71.285 mM 0.0114 mM	8.5	6.46
25	11.5 mM	0.285 mM	11.4 µM	152 mM	71.285 mM 0.0228 mM	8.5	6.46

Table S1. Solution compositions used for the growth experiments according to the constant composition method.

Ca_T/Fe_T	$NaHCO_3$	$CaCl_2$	$FeCl_2$	pH	$\Omega_{calcite}$ / $SI_{calcite}$
no iron	26 mM	0.33 mM	0	8.1	5.89 / 0.77
100	26 mM	0.33 mM	0.0033 mM	8.1	5.89 / 0.77
50	26 mM	0.33 mM	0.0066 mM	8.1	5.75 / 0.76
25	26 mM	0.33 mM	0.01319 mM	8.1	5.75 / 0.76
12.5	26 mM	0.33 mM	0.0264 mM	8.1	5.75 / 0.76

Table S2. Composition of solutions flowed over calcite surfaces during *in situ* AFM experiments.

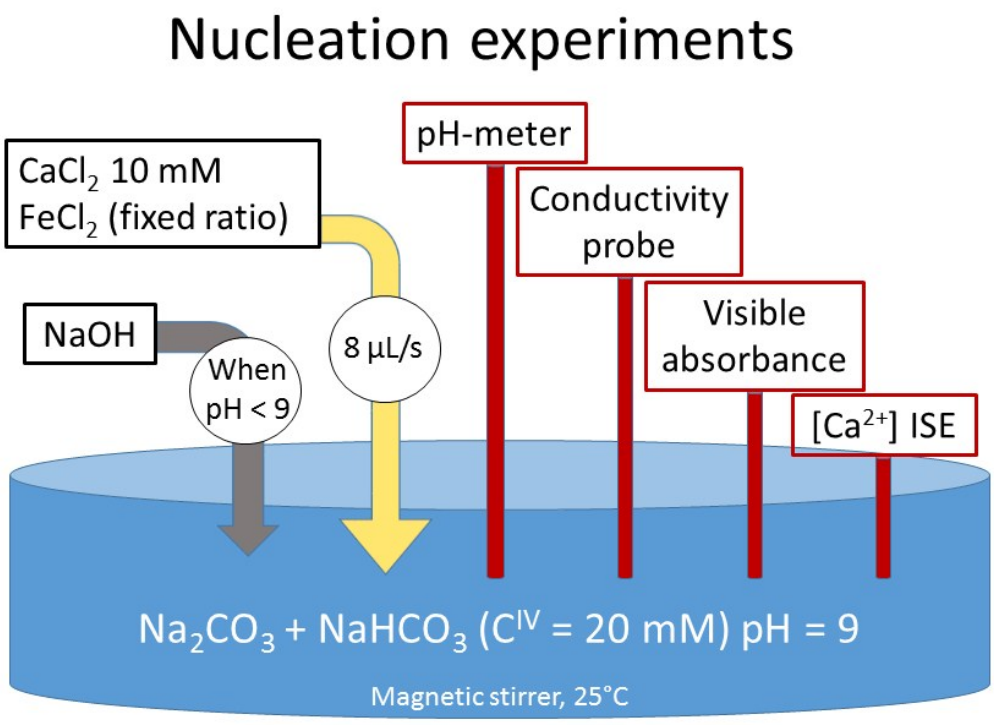


Fig. S1 Schematic representation of the experimental setup used during nucleation experiments.

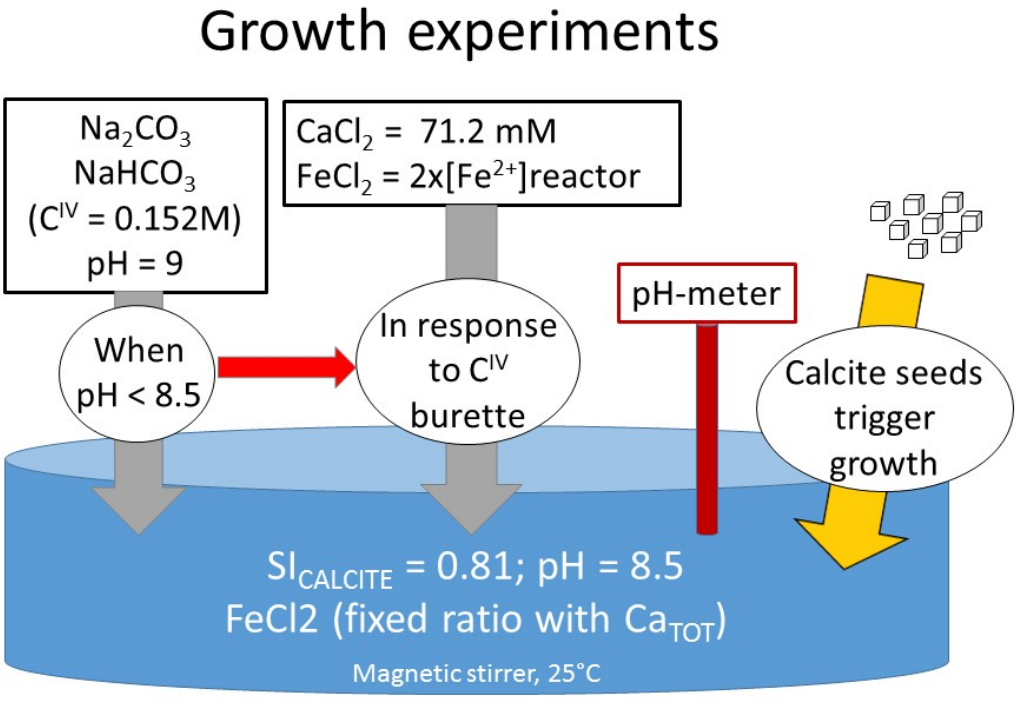


Fig. S2 Schematic representation of the experimental setup used during growth experiments.

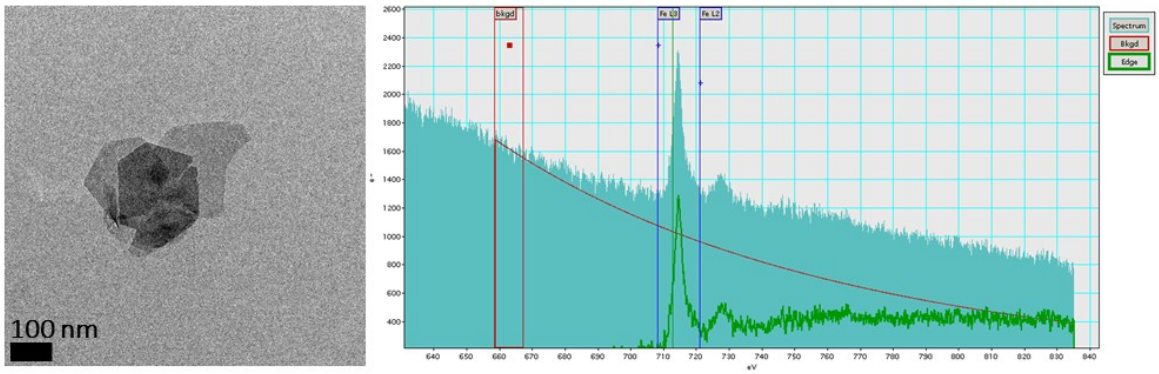
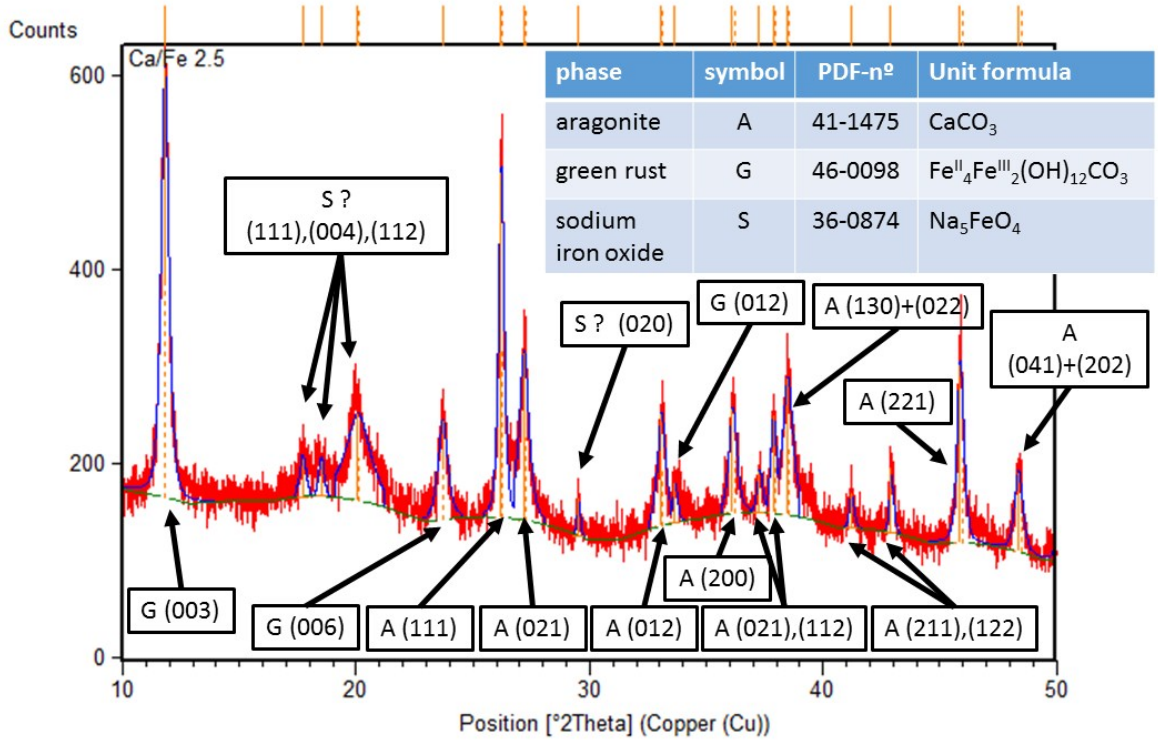


Fig. S3 Electron energy loss spectroscopy (EELS) analysis of the secondary phase founded in the sample from a nucleation experiment $Ca_T/Fe_T = 5$. The presence of secondary phase with hexagonal shape was observed in several Fe-bearing experiments by SEM, FESEM, EMPA or TEM analysis. The analysis of Fe $L_{2,3}$-edge spectra revealed a proportion of $Fe^{2+} \approx 80\%$ ($Fe^{3+} \approx 20\%$) confirming that ferrous iron remained the most abundant valence state for iron in our system.



phase	symbol	PDF-nº	Unit formula
aragonite	A	41-1475	$CaCO_3$
green rust	G	46-0098	$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3$
sodium iron oxide	S	36-0874	Na_5FeO_4

Fig. S4 XRD pattern of the solid product from a nucleation experiment ($Ca_T/Fe_T = 2.5$), reflections belonging to aragonite and to green rust are indexed. Unindexed lines have been assigned to sodium iron oxide because it was the only Fe-bearing compound (in the PDF-2 database) with intense reflections in the region 18-20 [2θ, Cu-Kα].