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Supplementary Information

Magnesium and temperature control on aragonite crystal aggregation and morphology

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Materials and Methods

Materials

Analytical grade chemicals, calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3) and magnesium chloride ($MgCl_2$) (all Sigma Aldrich) and high quality deionized water (conductivity less than 0.055 µS cm^{-1}) were used in order to prepare the stock solutions. The reactant solutions were prepared by appropriate dilution of respective stock.

Precipitation systems

Precipitation systems in which predominantly heterogeneous nucleation were investigated. The actual supersaturation, expressed with respect to aragonite, depends on applied temperature and vary in the range, $8 < S_a < 20$. The precipitation was initiated by pouring 100 cm^3 of $CaCl_2$ solution into the same volume of Na_2CO_3 solution. The initial concentrations of reactants were: $c_i(CaCl_2)$= 0.010 mol dm^{-3} and $c_i(Na_2CO_3)$= 0.005 mol dm^{-3}, while the appropriate amount of $MgCl_2$ was added into the $CaCl_2$ solution. The concentration of $MgCl_2$ varied in the range, 0.010 mol $dm^{-3} \leq c(Mg^{2+})_i \leq$ 0.100 mol dm^{-3}. After the initial mixing of the reactants, the systems were tightly closed and agitated for 2.5 h at 40 °C, 60 °C or 80 °C. The samples were gently agitated in thermostated orbital shaker in order to reduce the crystal attrition and secondary nucleation.

Characterization of precipitates

After completing the precipitation, the total volume of suspension was filtered through a 0.22 µm membrane filter, the precipitate was washed with small portions of water and dried at 105 °C. The mineralogical composition of the dried samples was determined by means of infra red spectroscopy (FT-IR Bruker, Tensor II) using KBr pellets, and by X-ray powder diffraction (PANanalytical X'PertPRO, powder diffractometer equipped with a monochromator on the diffracted beam, using Cu Kα radiation (40 mA, 40 kV)). The morphology of the crystals was examined by scanning electron microscopy (FEG SEM Hitachi 6400).

Data analyses

The known total initial concentrations of $CaCl_2$, Na_2CO_3 and $MgCl_2$ were used for calculation of molar concentrations and activities of the relevant ionic species: H^+, OH^-, CO_3^{2-}, HCO_3^-, $H_2CO_3^0$, $NaCO_3^-$, $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$, $CaCl^+$, Ca^{2+}, Na^+, Cl^-, $NaHCO_3^0$, $MgCO_3^0$, $NaCl^0$, Mg^{2+}, $MgHCO_3^+$, $MgCl^+$, $MgOH^+$, $Mg_2CO_3^{2+}$ and $NaOH^0$. Calculations were performed by using the own algorithm and the results were compared with VMINTEQ 3.0 software (available at http://vminteq.lwr.kth.se/download/). The supersaturation was defined as supersaturation ratio $S = (\Pi / K_{sp}^0)^{1/2}$ where Π is the ion activity product, $\Pi = a(Ca^{2+})\cdot a(CO_3^{2-})$, and K_{sp}^0 is the thermodynamic equilibrium constant of dissolution of the particular $CaCO_3$ phase (aragonite). The detailed calculation procedure, which takes into account the respective protolithic equilibria and equilibrium constants, as well as the charge and mass balance equations, is describe previously.[i, ii, iii] However, the equilibrium constants for species $CaCl^+$, $NaHCO_3^0$, $MgCO_3^0$, $NaCl^0$, $MgHCO_3^+$, $MgCl^+$ and $MgOH^+$, $Mg_2CO_3^{2+}$, $NaOH^0$ were taken from VMINTEQ 3.0.

Table SI1. Aragonite supersaturation (*S*a) and ionic strength (I.S/mol dm^{-3}) at the different temperatures of the starting solution at the different Mg^{2+}/Ca^{2+} molar ratios.

Mg^{2+}/Ca^{2+}	**40** (°C)		**60** (°C)		**80** (°C)	
	*S*a	I.S.	*S*a	I.S.	*S*a	I.S.
0/1	20.01	0.029	18.87	0.029	18.32	0.029
1/1	16.37	0.057	16.37	0.057	15.89	0.057
2/1	14.23	0.085	14.23	0.85	14.34	0.085
3/1	12.74	0.112	12.74	0.112	13.24	0.113
4/1	11.63	0.138	11.63	0.138	12.33	0.139
5/1	10.76	0.165	10.76	0.166	11.61	0.166
10/1	8.11	0.290	8.11	0.291	9.30	0.293

Table SI2. Unit cell parameters (Å) of aragonite (A), calcite (C), vaterite (V), Mg calcite (MgC) and monohydrocalcite (MHC) obtained in the precipitation experiments at 40, 60 or 80 °C. The unit cell parameters, *a* and *c* (*a*, *c*)for calcite, Mg calcite and vaterite are reported according a hexagonal unit cell. The aragonite unit cell for aragonite (*a*, *b*, *c*) are reported according a orthorhombic unit cell.

Mg^{2+}/Ca^{2+}	**40** (°C)	**60** (°C)	**80** (°C)
0/1	A (4.96, 7.97, 5.74) C (4.99, 17.03)	A (4.96, 7.97, 5.74) C (4.99, 17.02)	A (4.96, 7.97, 5.74) C (4.99, 17.02)
1/1	A (4.98, 8.01, 5.77) MgC (4.99, 17.02)	A (4.96, 7.97, 5.74) MgC (4.96, 16.90)	A (4.96, 7.97, 5.74) MgC (4.95, 16.87)
2/1	A (4.96, 7.96, 5.75) MgC (4.95, 16.84)	A (4.96 7.97 5.74)	A (4.96, 7.97, 5.74) MgC (4.93, 16.74)
3/1	A (4.96, 7.96, 5.75)	A (4.96, 7.97, 5.74)	A (4.96, 7.97, 5.74) MgC (4.91, 16.6)
4/1	A (4.96, 7.96, 5.75)	A (4.96, 7.97, 5.74)	A (4.96, 7.97, 5.74) MgC (4.91, 16.6)
5/1	A (4.96, 7.96, 5.75) MHC (10.56, 7.52)	A (4.96, 7.96, 5.75)	A (4.96, 7.9,7 5.74) MgC (4.93, 16.64)
10/1		A (4.96 7.96 5.75)	A (4.96, 7.96, 5.75)

Table SI3. Morphological features of calcite (C), Mg calcite (MgC) and monohydrocalcite (MCH) obtained in the precipitation experiments at 40, 60 or 80 °C.

Mg^{2+}/Ca^{2+}	**40** (°C)	**60** (°C)	**80** (°C)
0/1	(C) {10.4} rhombohedral single crystals	(C) {10.4} rhombohedral single crystals	(C) {10.4} rhombohedral single crystals
1/1	(MgC) {10.4} {11.0} prismatic single crystals	(MgC) {10.4} {11.0} prismatic single crystals	(C) {10.4} rhombohedral single crystals
2/1	(MgC) {10.4} {11.0} spherulitic aggregates	-	(MgC) {10.4} rhombohedral aggregates
3/1	-	-	(MgC) {10.4} rhombohedral aggregates
4/1	-	-	(MgC) {10.4} rhombohedral aggregates
5/1	(MHC) spherulites	-	(MgC) {10.4} rhombohedral aggregates
10/1		-	-

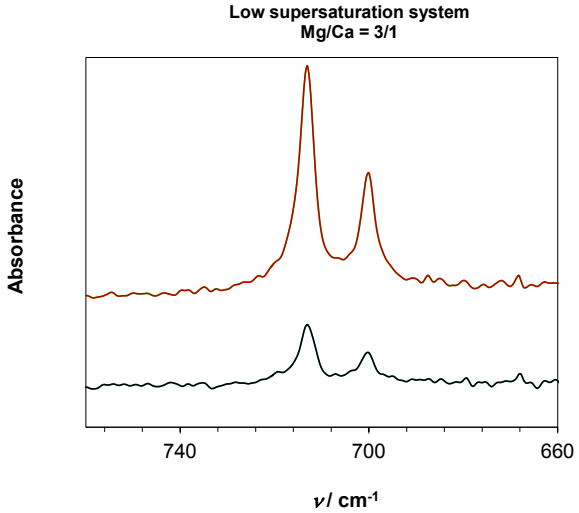

Figure SI1. FT-IR spectra of the samples obtained at *t* = 40 °C and at molar ratio, Mg^{2+}/Ca^{2+} = 3/1. Lower spectrum (blue) corresponds to the sample isolated after 30 minutes and upper spectrum (red) after 60 minutes

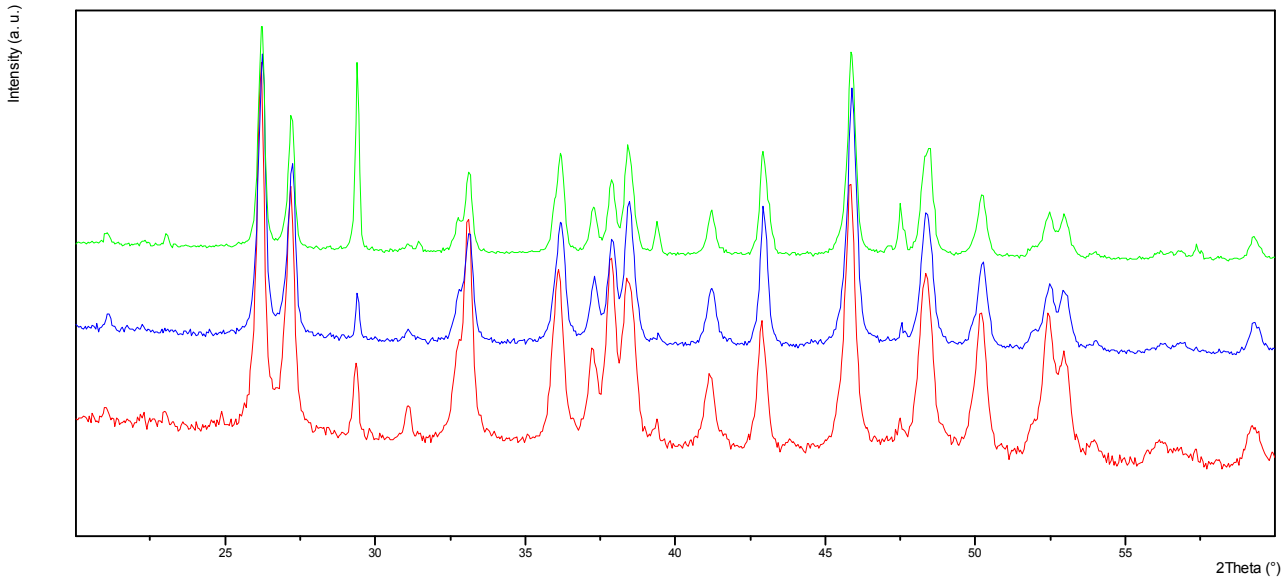

Figure SI2. X-ray diffraction patterns of calcium carbonate precipitated in the absence of Mg^{2+} at the temperature of 40 (red), 60 (blue) or 80 °C (green).

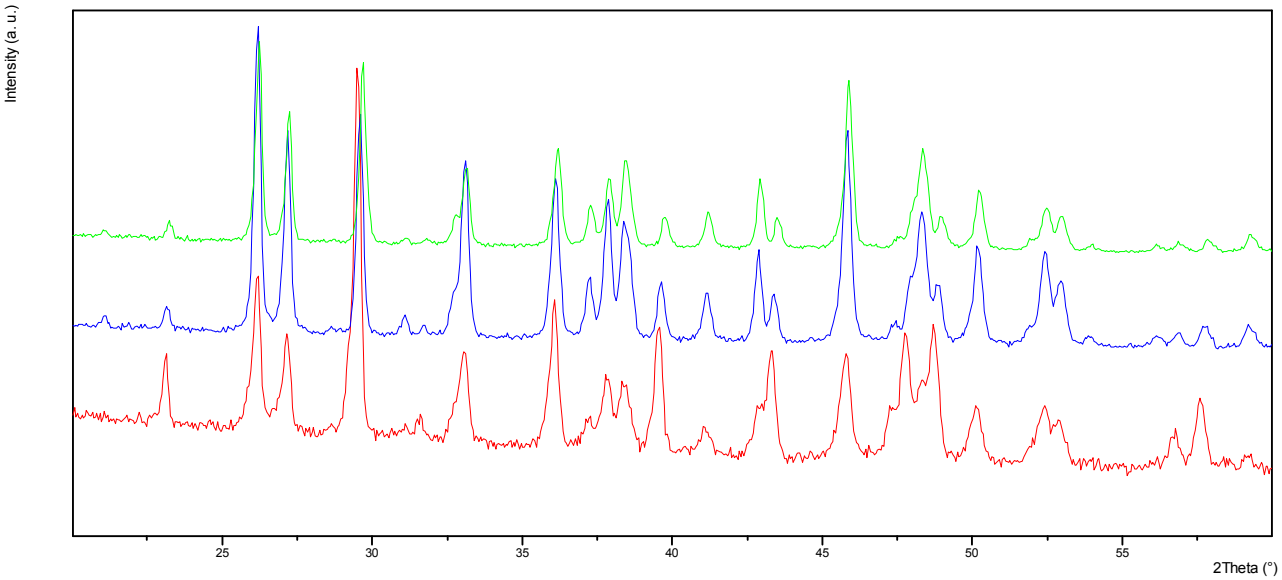

Figure SI3. X-ray diffraction patterns of calcium carbonate precipitated in the presence of Mg^{2+} with Mg^{2+}/Ca^{2+} = 1/1 at the temperature of 40 (red), 60 (blue) or 80 °C (green).

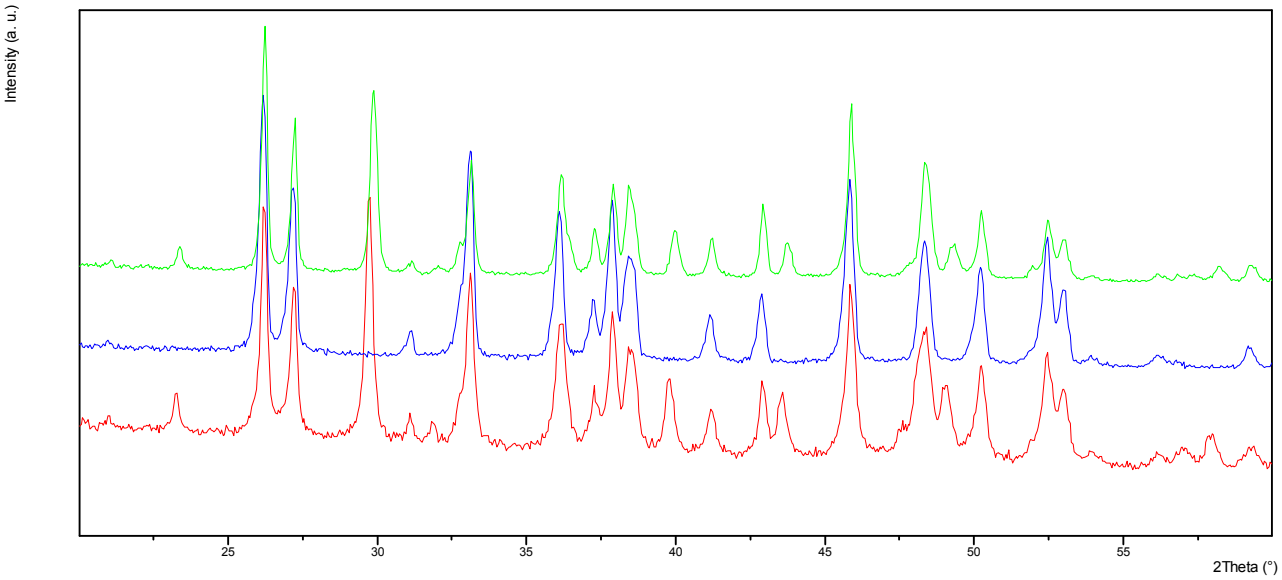

Figure SI4. X-ray diffraction patterns of calcium carbonate precipitated in the presence of Mg^{2+} with Mg^{2+}/Ca^{2+} = 2/1, at the temperature of 40 (red), 60 (blue) or 80 °C (green).

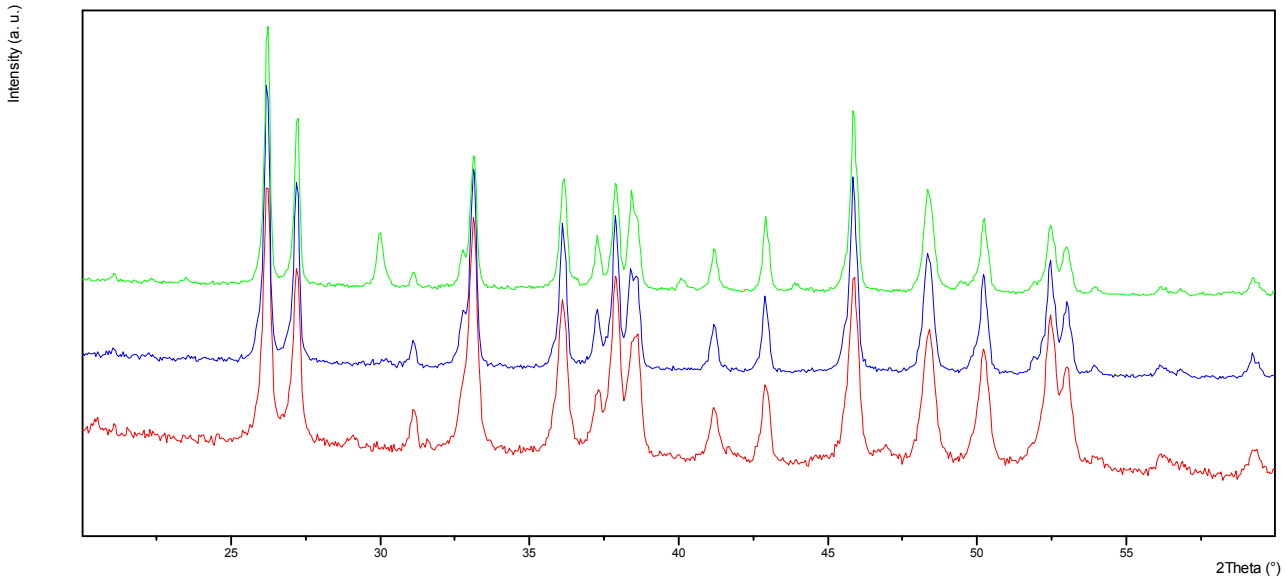

Figure SI5. X-ray diffraction patterns of calcium carbonate precipitated in the presence of Mg^{2+} with Mg^{2+}/Ca^{2+} = 3/1, at the temperature of 40 (red), 60 (blue) or 80 °C (green).

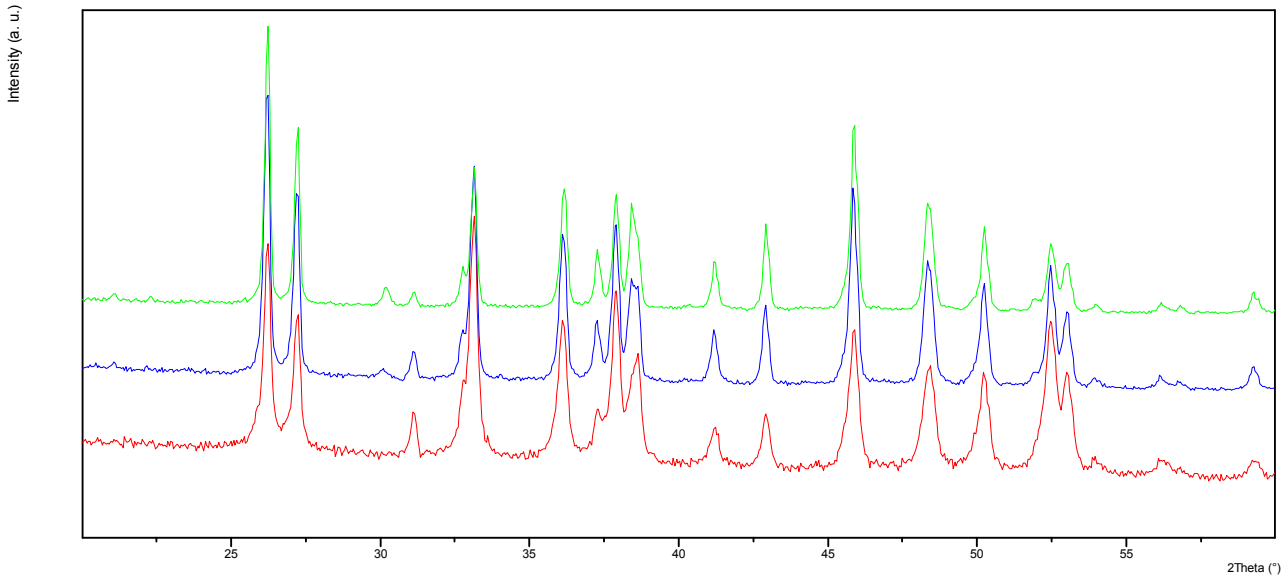

Figure SI6. X-ray diffraction patterns of calcium carbonate precipitated in the presence of Mg^{2+} with Mg^{2+}/Ca^{2+} = 4/1, at the temperature of 40 (red), 60 (blue) or 80 °C (green).

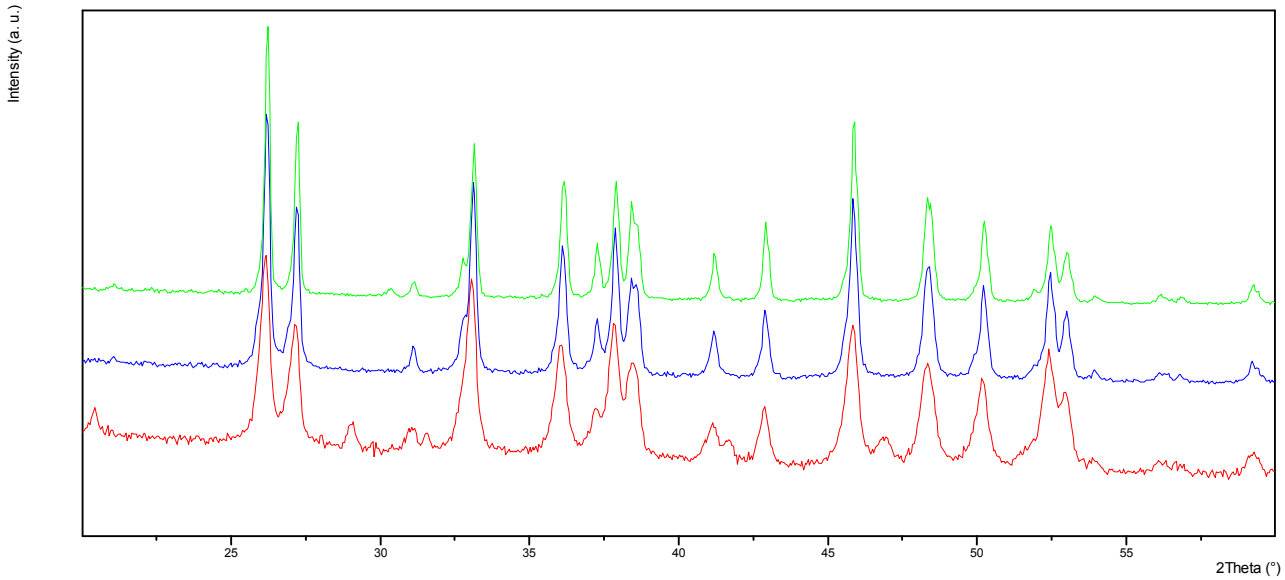

Figure SI7. X-ray diffraction patterns of calcium carbonate precipitated in the presence of Mg^{2+} with Mg^{2+}/Ca^{2+} = 5/1 at the temperature of 40 (red), 60 (blue) or 80 °C (green).

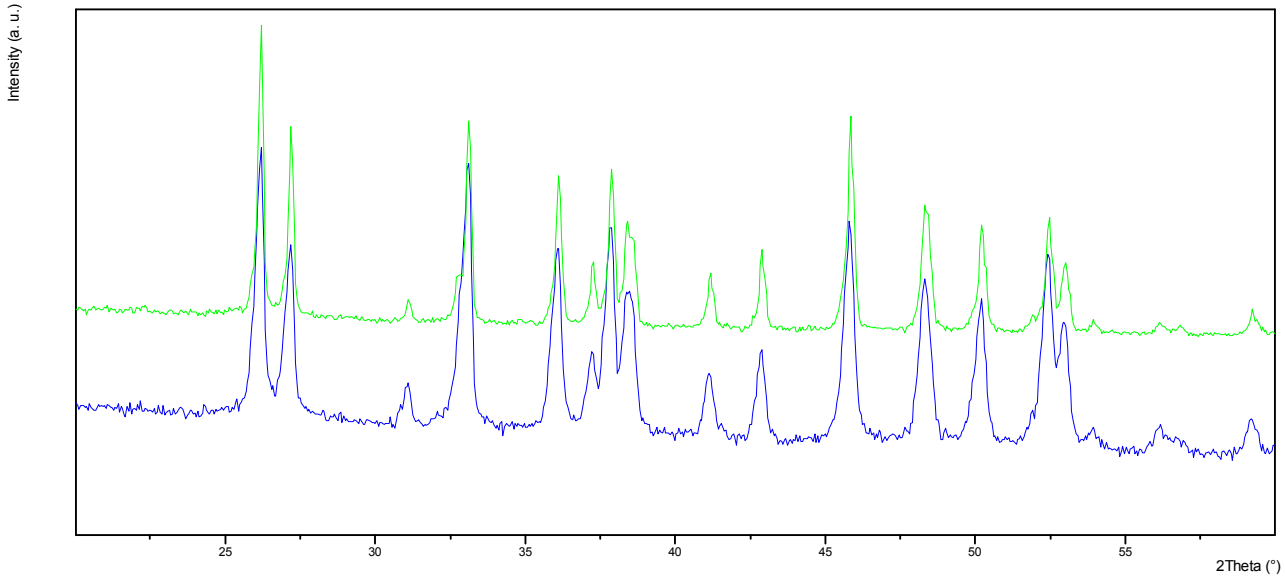

Figure SI8. X-ray diffraction patterns of calcium carbonate precipitated in the presence Mg^{2+} with Mg^{2+}/Ca^{2+} = 10/1 at the temperature of 60 (blue) or 80 °C (green).

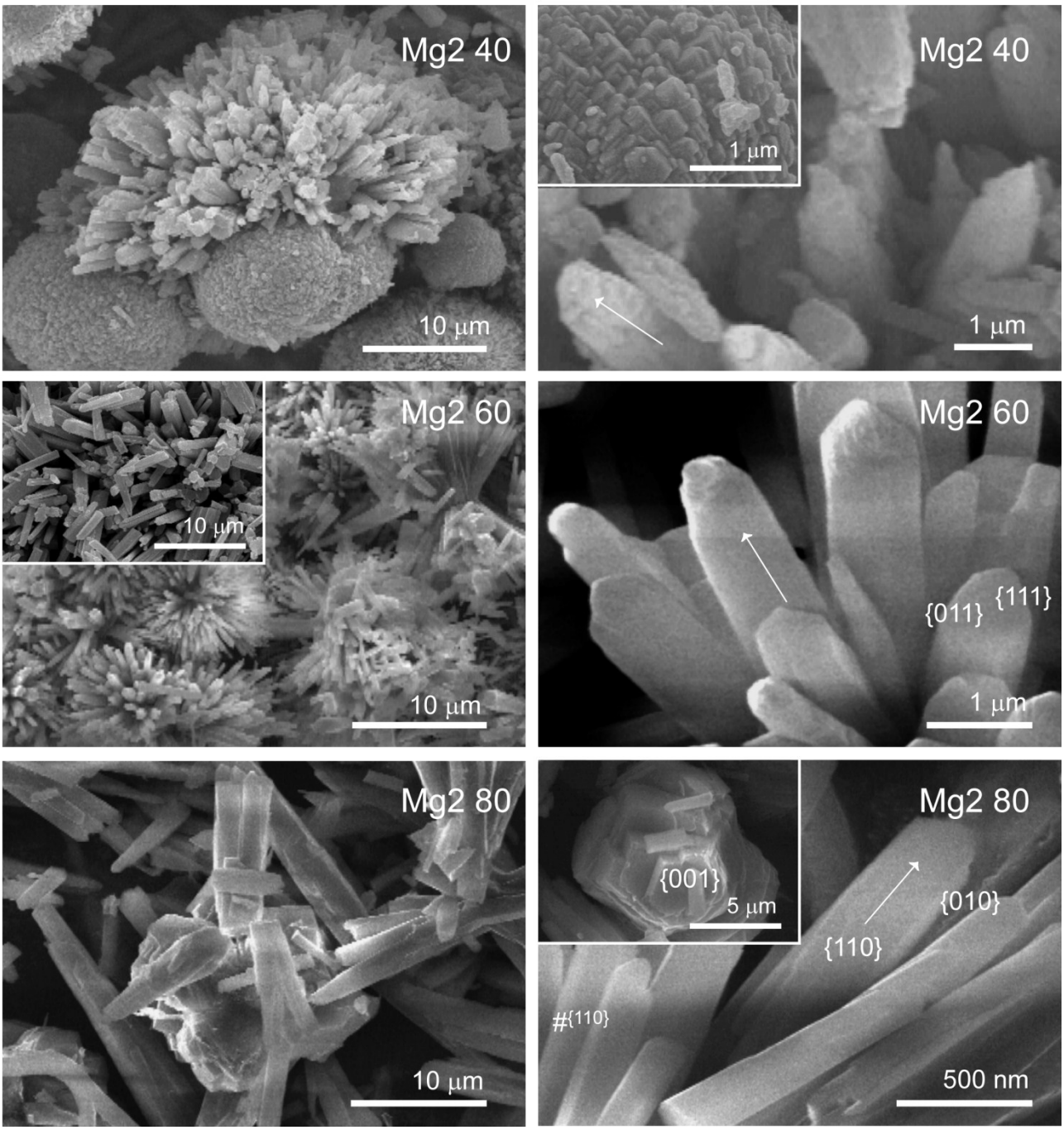

Figure SI9. Scanning electron microscopy images of the aragonite crystals (needle-like prisms or prisms) precipitated at the temperature of 40, 60 or 80 °C and Mg^{2+}/Ca^{2+} molar ratio equal to 2/1 (Mg2). Two magnifications are shown. The insets show Mg-calcite crystals co-precipitated with aragonite. The insets in Mg2 40 and Mg2 80 show Mg-calcite crystals co-precipitated with aragonite. The inset in Mg2 60 shows a low magnification view of aragonite crystals. In the images the Miller indices of the aragonite crystalline faces are indicated. The arrows indicate the crystallographic direction of the c-axis. The images are representative of the entire population of particles.

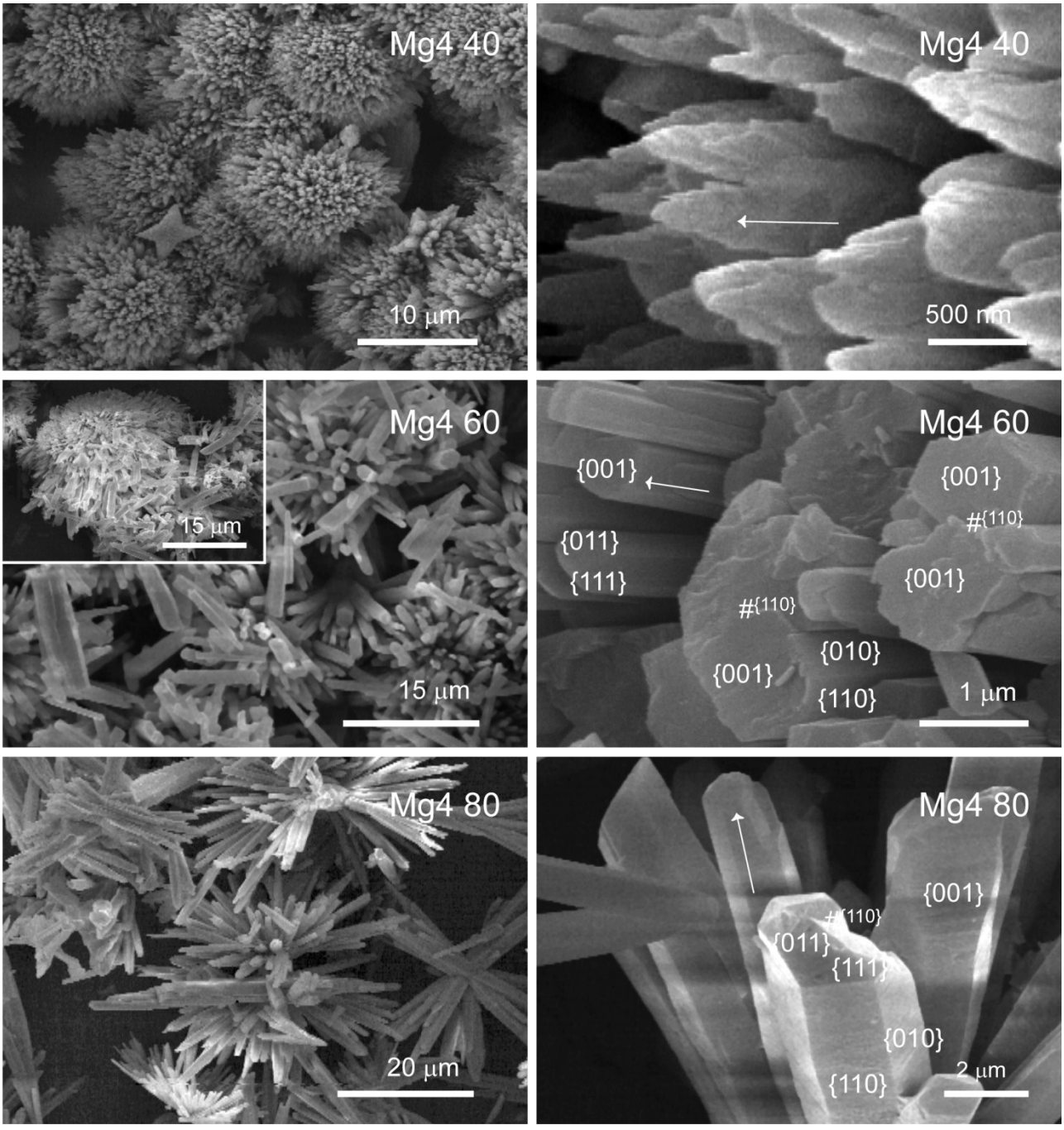

Figure SI10. Scanning electron microscopy images of the aragonite crystals (needle-like prisms or prisms) precipitated at the temperature of 40, 60 or 80 °C and Mg^{2+}/Ca^{2+} molar ratio equal to 4/1 (Mg4). Two magnifications are shown. The inset in Mg4 60 shows spherulitic aggregates of aragonite. In the images the Miller indices of the aragonite crystalline faces are indicated. Some aragonite crystals share the {110} face: the respective regions are marked with #{110}. The arrows indicate the crystallographic direction of the c-axis. The images are representative of the entire population of particles.

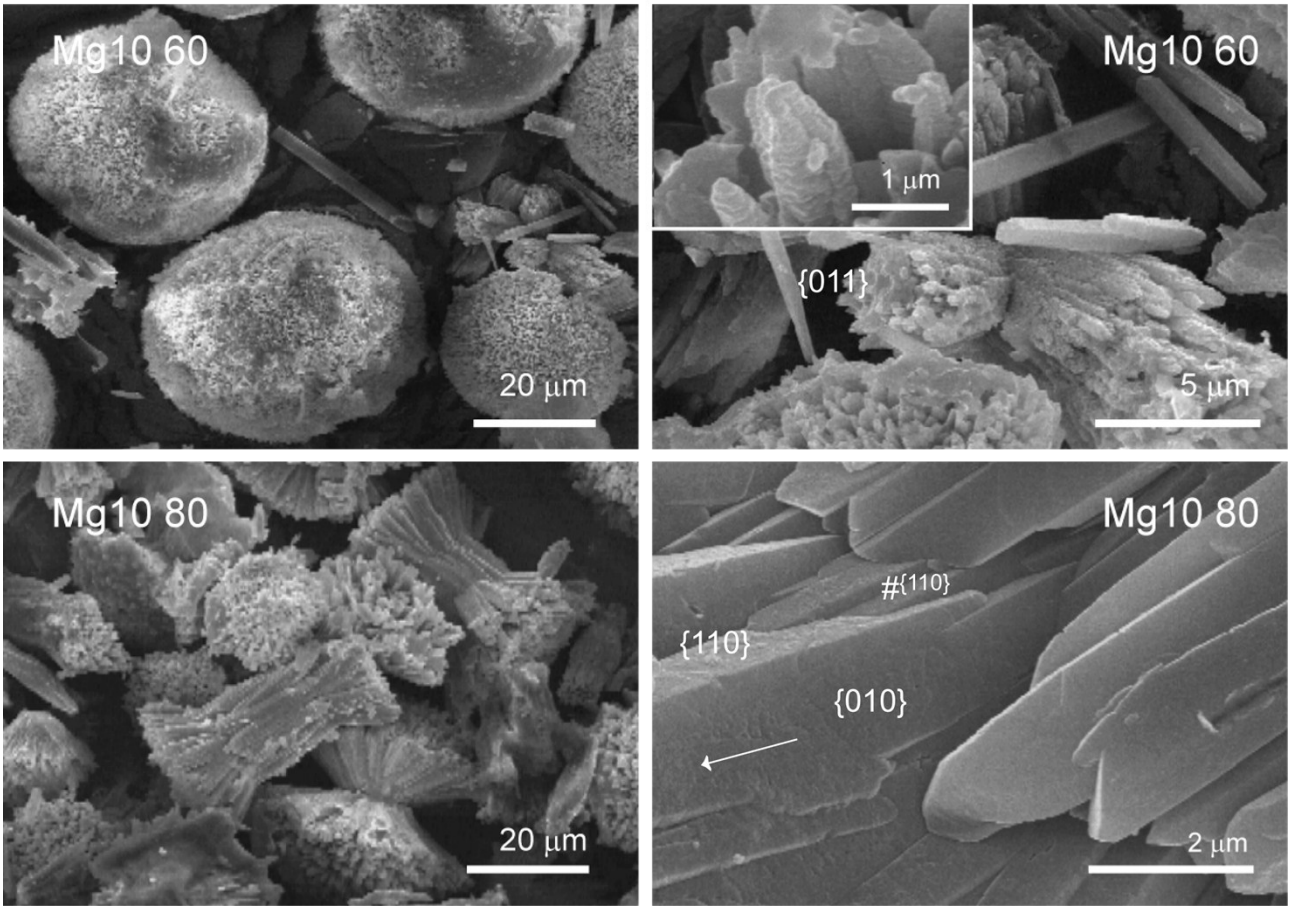

Figure SI11. Scanning electron microscopy images of the aragonite crystals (needle-like prisms or prisms) precipitated at the temperature of 40, 60 or 80 °C and Mg^{2+}/Ca^{2+} molar ratio equal to 10/1 (Mg10). Two magnifications are shown. In the images the Miller indices of the aragonite crystalline faces are indicated. Some aragonite crystals share the {110} face: respective regions are marked with #{110}. The arrows indicate the crystallographic direction of the c-axis. The inset in Mg5 60 shows spherulitic aggregates of aragonite The images are representative of the entire population of particles.

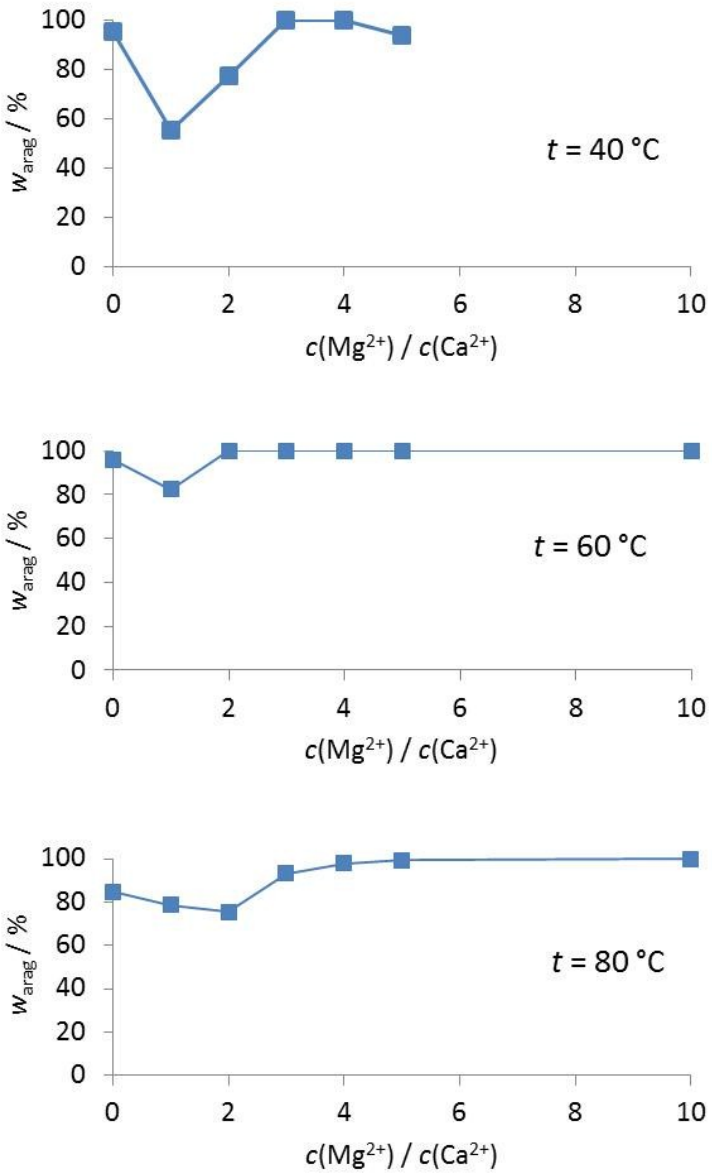

Figure SI12. Content of aragonite precipitated at different temperatures and Mg^{2+}/Ca^{2+} molar ratio.

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i D. Kralj, Lj. Brecevic and A.E. Nielsen, *J. Cryst. Growth*, 1990, **104**, 793-800.

ii L. N. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta*, 1982, **46**, 1011-1040

iii D. Kralj and Lj. Brecevic, *Colloids Surf. A Physicochem. Eng. Asp.*, 1995, **96**, 287-293