GSA Data Repository item 2015041.

7 additional figures, 1 additional methods section, and 2 additional tables.

Supplementary Figure DR1. Example of $CaCO_3$ polymorph morphology after 6 hours at 30°C and a Mg:Ca ratio of 0.5. ara. = aragonite; cal. = calcite; vat. = vaterite. Note that among the first precipitates that were analysed vaterite was only found at Mg:Ca = 0.5 at 20°C.

Supplementary Figure DR2. Examples of SEM images from the 30° C and 25° C experiments that were used for quantification. Grayscale SEM images (upper panel) were manually marked for aragonite and calcite crystals and thus transformed into separate black and white images of aragonite (middle panel) and calcite (lowest panel).

Supplementary Figure DR3. Examples of SEM images from the 20° C and 15° C experiments that were used for quantification. Grayscale SEM images (upper panel) were manually marked for aragonite and calcite crystals and thus transformed into separate black and white images of aragonite (middle panel) and calcite (lowest panel).

Supplementary Figure DR4. Reconstruction of 3D crystal volumes from 2D SEM images. Each data point represents an individual crystal of aragonite or calcite from a subset of the experiments. Volume data were computed from a pair of stereoscopic SEM images using Alicona Mex 5.0. The aragonite- and calcite-specific regression equations were used to calculate volume from area for all other crystals that were quantified.

Supplementary Figure DR5. Quantification of experimental data. A-D: volumetric proportions of aragonite against Mg:Ca ratio at a given temperature. Each data point represents the average aragonite : calcite proportion of 10 quantified images from the same glass disc; error bars represent 1 standard deviation; data were transformed as y = log(x/100 + 1.1) prior to logistic regression which was calculated using the PAST statistical software (available at: http://folk.uio.no/ohammer/past/); red line = logistic regression line; blues lines = 95% confidence envelope. **E:** Calculation of temperature for 1%, 50% and 99% aragonite precipitation at a given Mg:Ca ratio; Mg:Ca ratios for 1% aragonite (green triangles), 50% aragonite (red squares), and 99% aragonite (blue diamonds) was based on the logistic regressions shown in A-D; the power regressions from this figure (E) were used to draw Figure 2.

Supplementary Figure DR6. Influence of experimental parameters on $CaCO_3$ polymorph proportions. (A) pCO_2 (in µatm), (B) aragonite saturation state, (C) total alkalinity (in mM/L). The different coloured symbols represent different temperatures: red diamonds=30° C, orange squares=25° C, blue triangles=20° C, turquoise circles=15° C.

Supplementary Figure DR7. Comparison between the data by Morse et al. (1997) and this study. The dashed line indicates the position of the boundary between the precipitation fields of pure aragonite and calcite as proposed by Morse et al. (1997). The green, gray and yellow fields are based on the current study.

Supplementary tables:

Supplementary Table DR1. Composition of solutions used in precipitation experiments.

Supplementary Table DR2. Conditions of pH, total alkalinity (TA), *p* CO_2, salinity (S), and saturation state (Ω) of aragonite and calcite at the start of the experiment and for the time at which the sample was collected for quantification. Saturation state (Ω) was calculated using the software CO2SYS_macro_MAC_PC_2011.xls (Pierrot et al. 2006: MS Excel Program Developed for CO_2 System Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee).

Supplementary Methods DR1.

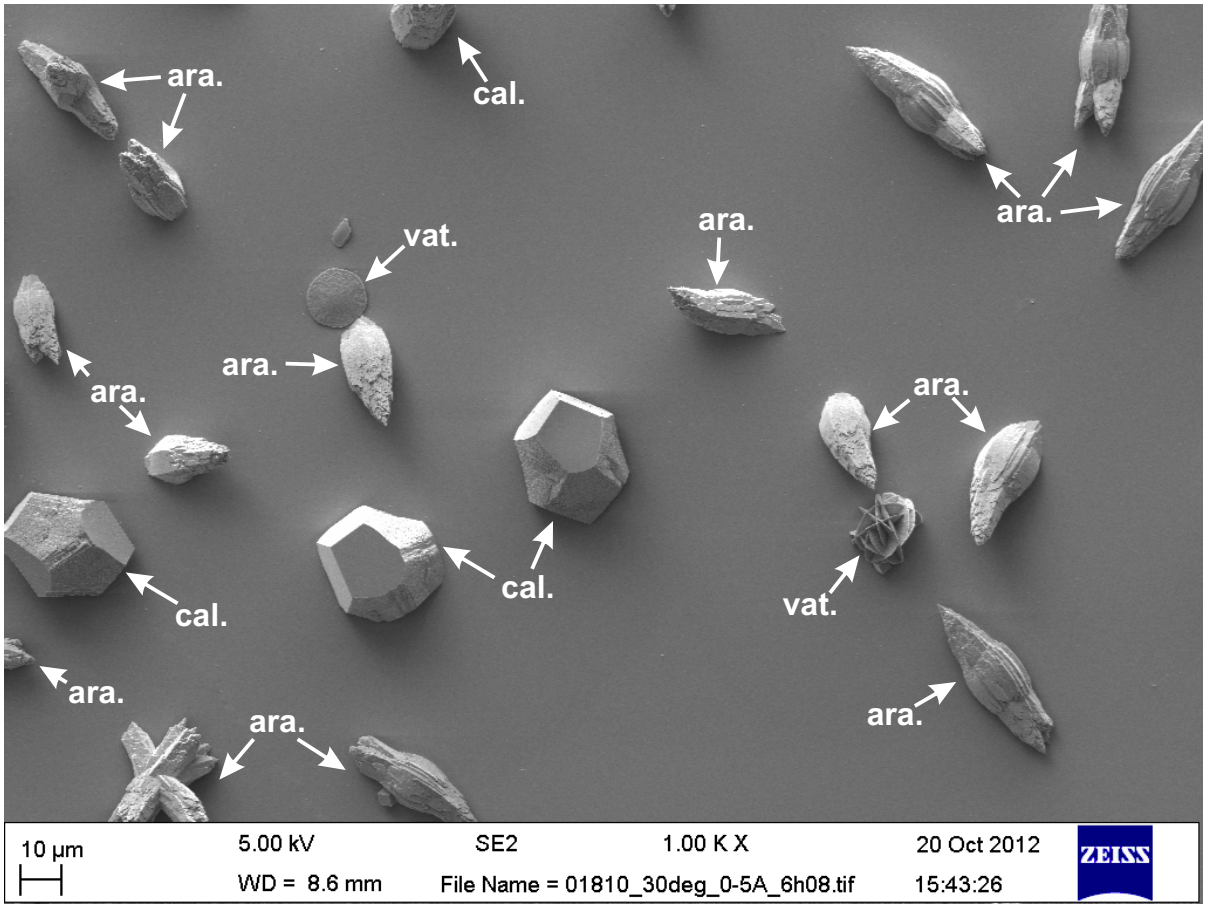
Reagents used in the experiment were:
$CaCl_2$ $2H_2O$ (Fisher; analytical reagent grade)
$MgCl_2$ $6H_2O$ (Fisher; BioReagents)
NaCl (Fisher; analytical reagent grade)
Na_2CO_3 $10H_2O$ (AnalaR).

Cleaning of glass discs:
Prior to the start of the experiment, the glass discs were cleaned by soaking for 24 hours in 5% Decon90, followed by soaking 24 hours in 10% HCl.

Temperature control during the experiments. Solutions were acclimatized overnight in incubators and only taken out to briefly to bubble CO_2 through the solution at the start of the experiment (this took less than 5 minutes) or to remove glass slides at hourly intervals (the removal of a subsample took less than a minute). Incubators were set at 15°, 20°, 25°, or 30°C and, while the incubator doors remained closed, the temperature was maintained at +/- 0.1° C.

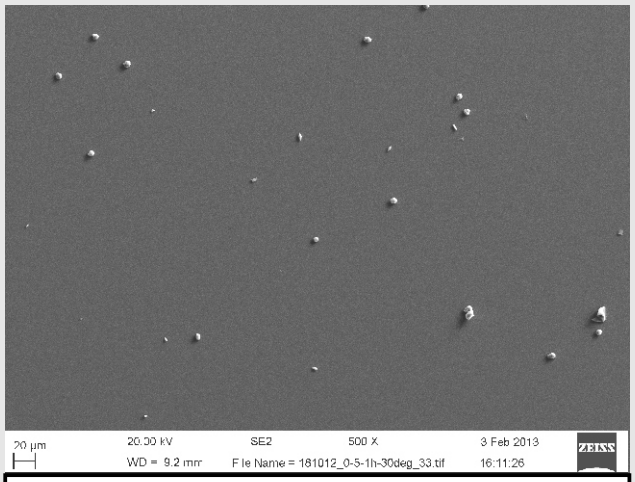
Calculation of the temperatures for Figure 2:
As a first step the Mg:Ca ratios at which 1%, 50% and 99% of aragonite would precipitate at 15°, 20°, 25°, and 30°C were estimated using logistic regression (Figure DR5 A-D). These data were then plotted as a function of Mg:Ca and temperature and a power regression was used to estimate the temperature at a given Mg:Ca ratio for 1%, 50%, and 99% aragonite precipitation (Figure DR5 E).

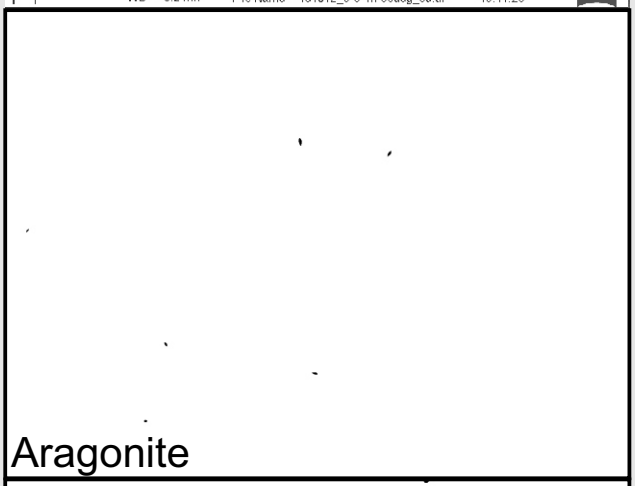
Calculation of crystal volume:
Using the SEM, individual crystals were centered on a landmark (usually the tip of a crystal) and imaged without tilt and with a tilt of 5-7^{o}. Both images were loaded into Alicona MeX 5.0 and manually aligned along the chosen feature. The software then employs algorithms that automatically identify other landmarks and calculates the topographic relief of the image surface. Crystal volumes and the associated surface area were then calculated in the software by manually marking individual crystals in the 3D model. Regressions of crystal volume and area measurements of 21 calcite and 25 aragonite crystals was used to calculate volume from area for all aragonite and calcite crystals (Fig. DR 4).

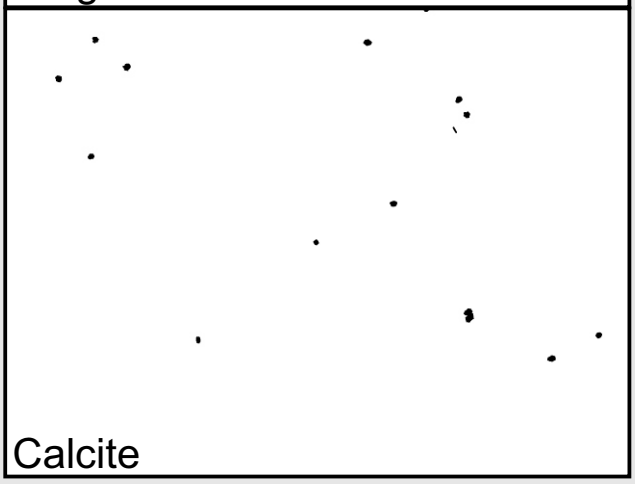


Supplementary Figure DR1

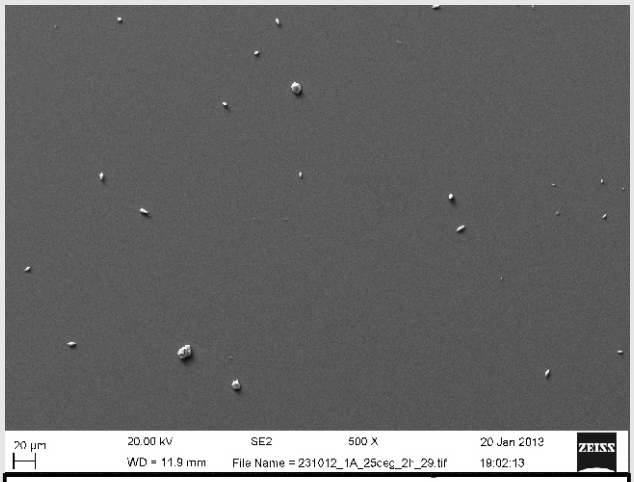
30° C; Mg:Ca = 0.5; 1st subsample
this image: 5.4% Aragonite
average of 10 images: 8.2% Aragonite

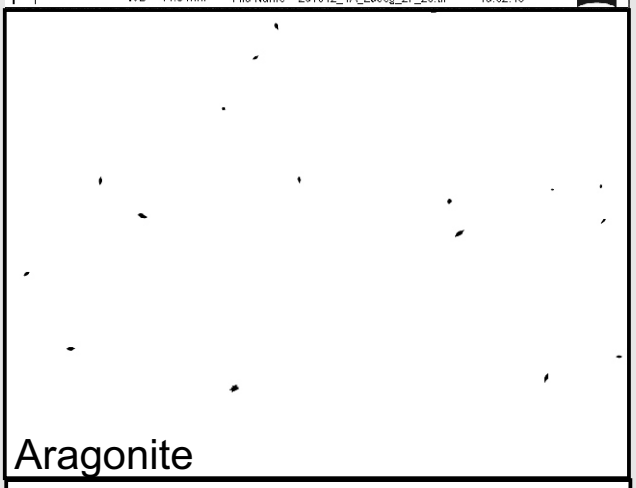


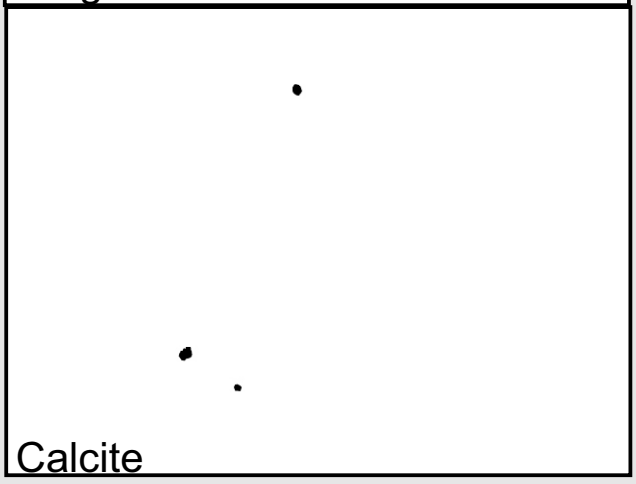




25° C; Mg:Ca = 1; 2nd subsample
this image: 22.5% Aragonite
average of 10 images: 39.3% Aragonite

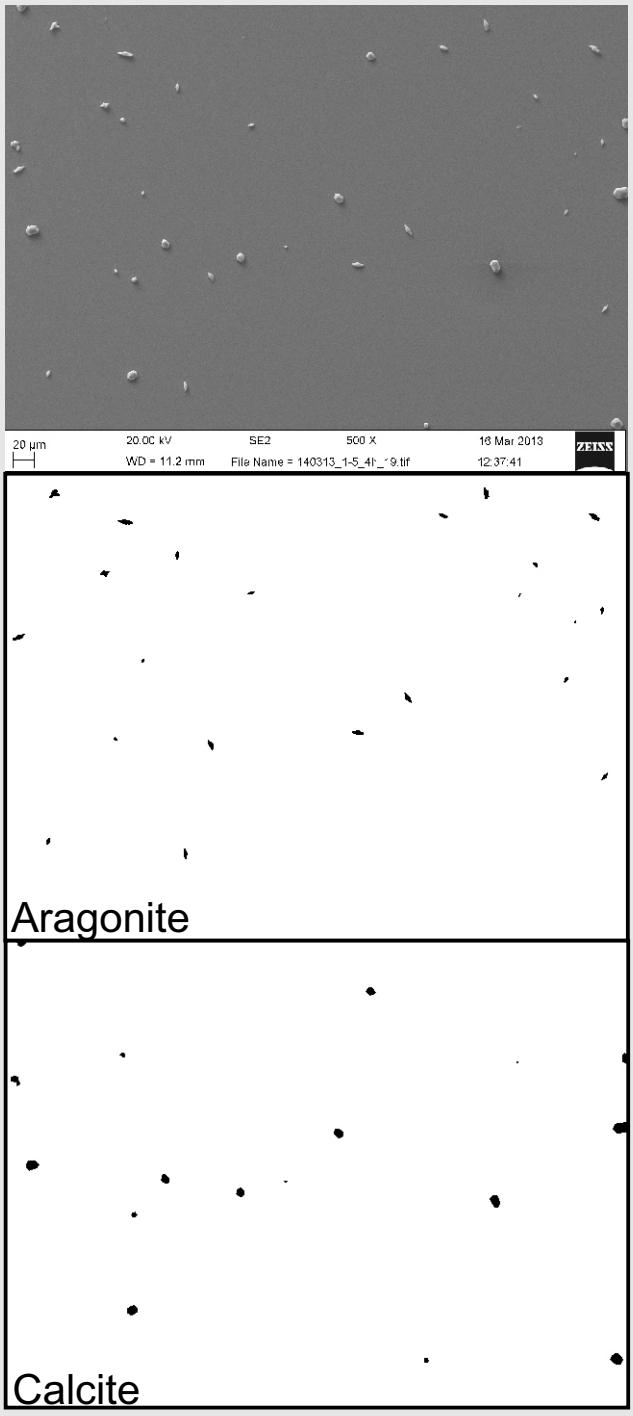




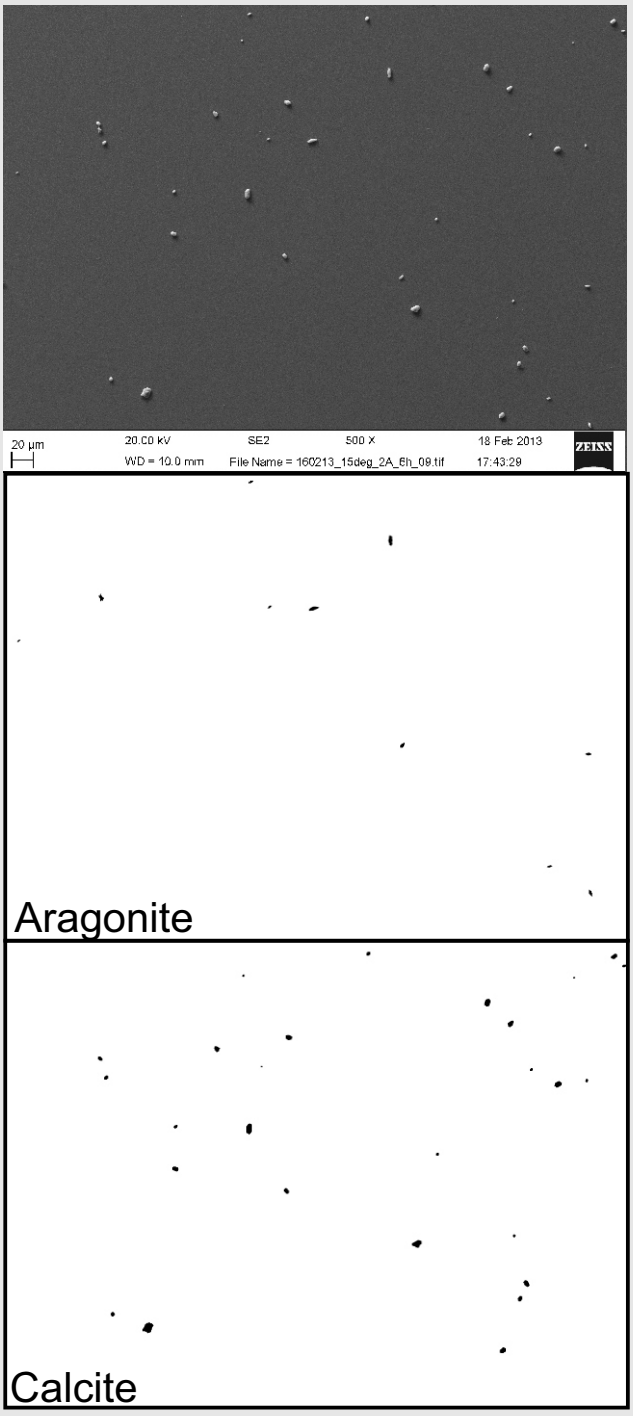


Supplementary figure DR2

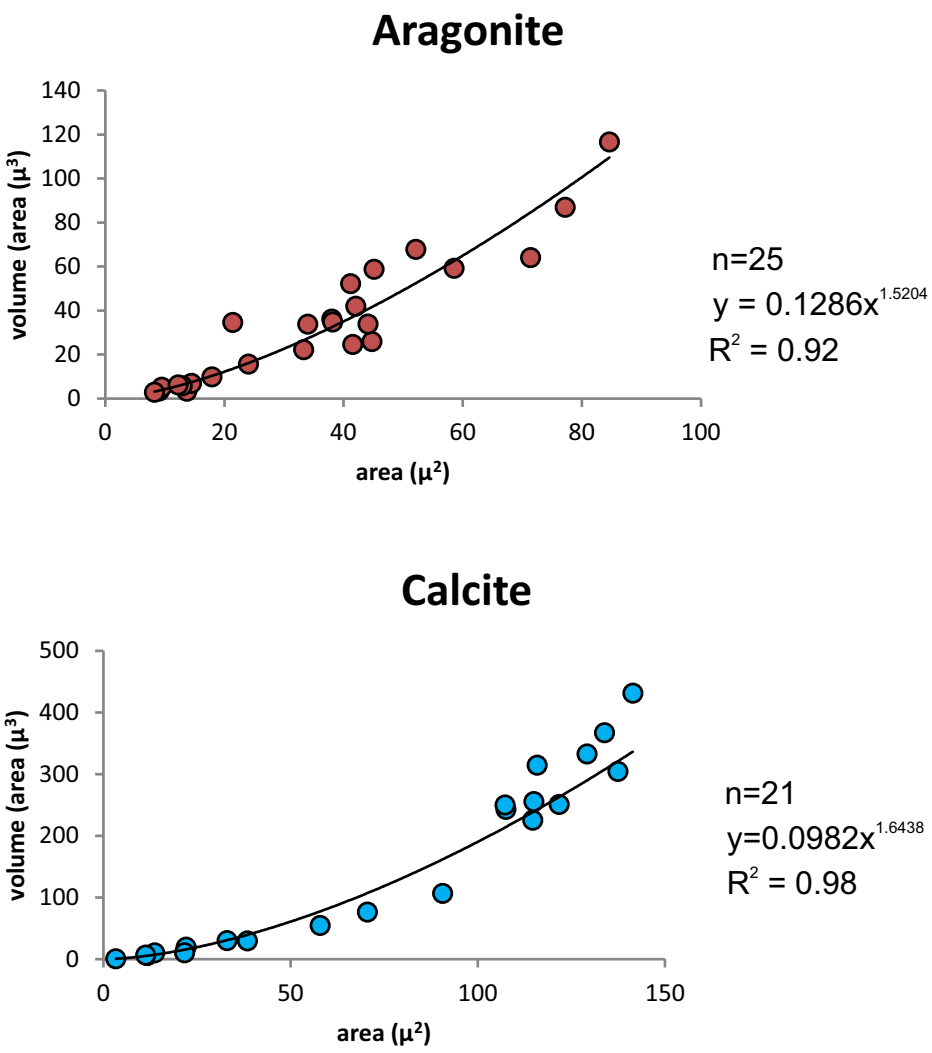
20° C; Mg:Ca = 1.5; 4th subsample
this image: 23.5% Aragonite
average of 10 images: 27.9% Aragonite



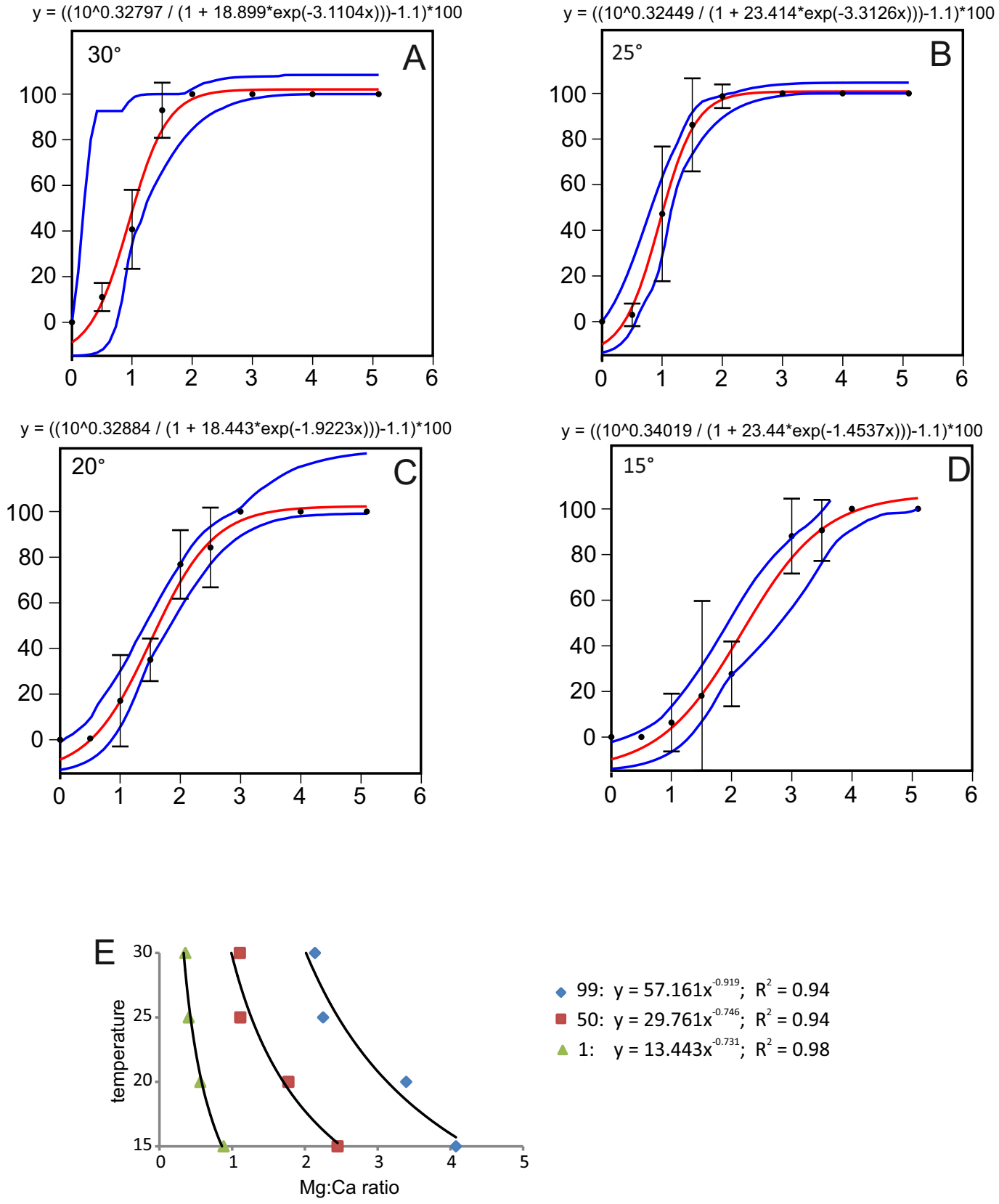
15° C; Mg:Ca = 2; 6th subsample
this image: 13.9% Aragonite
average of 10 images: 21.5% Aragonite



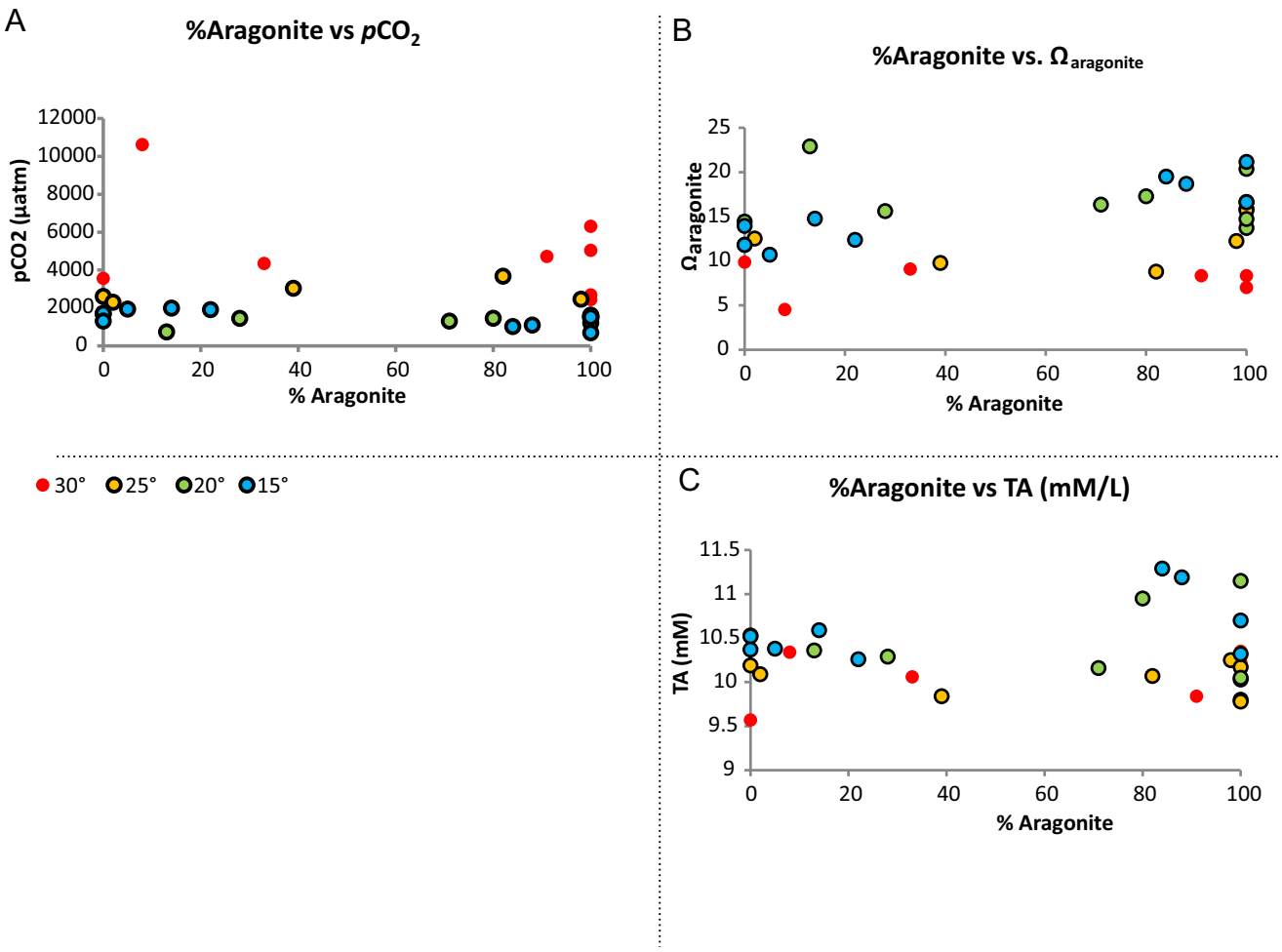
Supplementary figure DR3



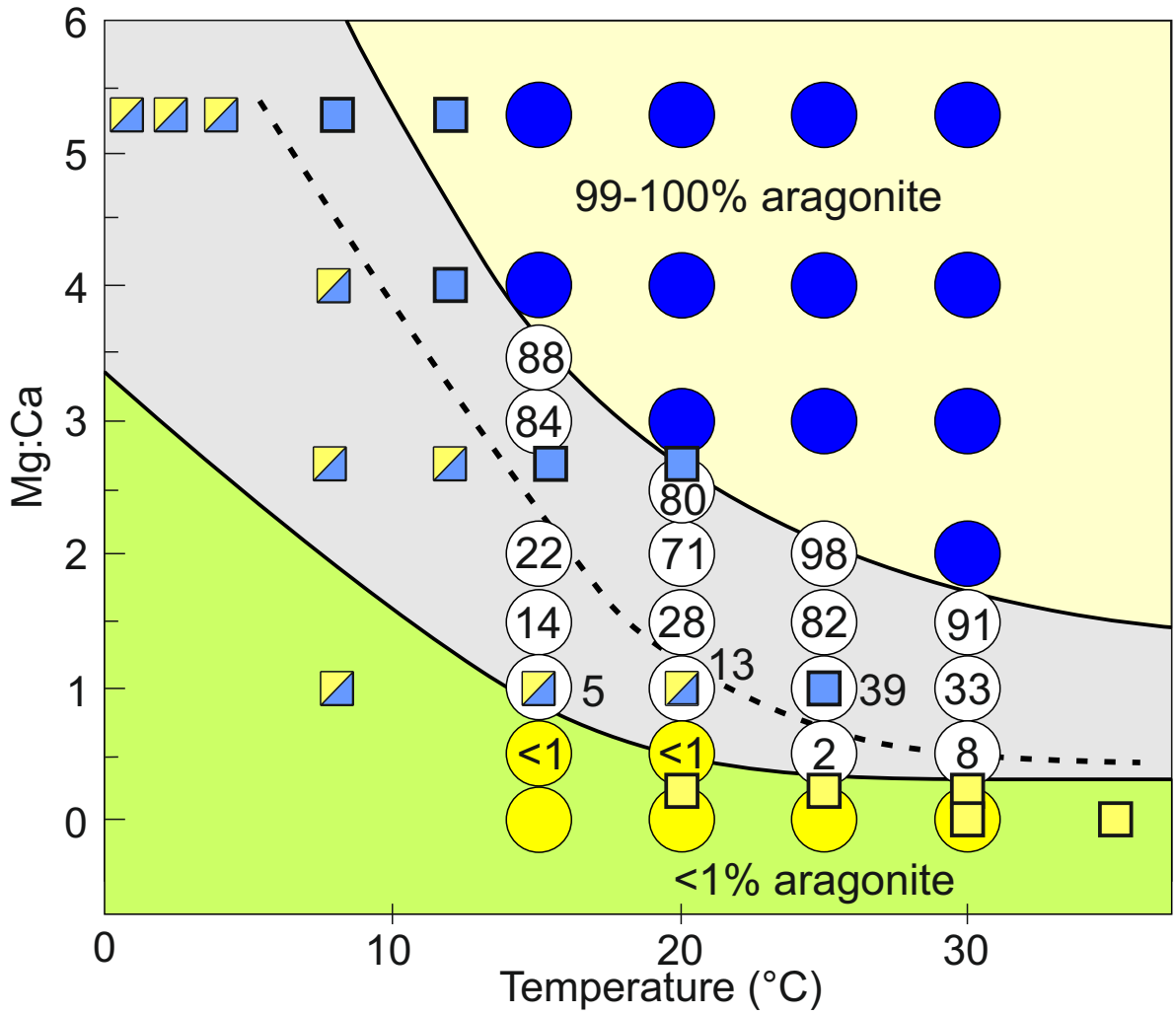
Supplementary figure DR4



Supplementary figure DR5



Supplementary figure DR6



>99% aragonite

<1% aragonite

XY XY% aragonite

this study

100% aragonite

0% aragonite (100% calcite)

calcite with aragonite overgrowth*

Morse et al. 1997

*interpreted by Morse et al. (1997) as initial calcite precipitation that was overgrown at a late stage in the experiment when Mg:Ca had significantly increased due to $CaCO_3$ precipitation

Supplementary figure DR7

		solution composition			
experiment	T (°C)	Mg:Ca	[Mg] mM (mM)	[Ca] mM (mM)	Na_2CO_3 (mM)
271212_0	**30**	**0**	0.00	5.19	5.01
181012_0.5		**0.5**	2.51	5.21	5.02
230213_1		**1**	5.13	5.17	5.02
230213_1-5		**1.5**	7.71	5.13	5.01
301012_2		**2**	10.30	5.15	5.02
301012_3		**3**	15.40	5.14	5.02
301012_4		**4**	20.58	5.15	5.00
301012_5.1		**5.1**	26.17	5.13	5.01
271212_0	**25**	**0**	0.00	5.13	5.01
231012_0.5		**0.5**	2.57	5.18	5.00
231012_1		**1**	5.04	5.22	5.03
231012_1-5		**1.5**	7.72	5.23	5.03
101112_2		**2**	10.32	5.13	5.00
101112_3		**3**	15.43	5.13	5.01
101112_4		**4**	20.56	5.17	5.00
101112_5.1		**5.1**	26.18	5.14	5.02
031212_0	**20**	**0**	0.00	5.14	5.01
140313_0-5		**0.5**	2.57	5.15	5.01
031212_1		**1**	5.16	5.12	5.01
140313_1-5		**1.5**	7.72	5.12	5.01
151112_2		**2**	10.30	5.16	5.01
140313_2.5		**2.5**	12.87	5.16	5.00
151112_3		**3**	15.42	5.12	5.00
151112_4		**4**	20.57	5.14	5.00
091012_5.1		**5.1**	26.43	5.18	5.00
281012_0	**15**	**0**	0.00	5.14	5.02
281012_0.5		**0.5**	2.58	5.12	5.00
281012_1		**1**	5.15	5.14	5.03
281012_1.5		**1.5**	7.66	5.17	5.03
160213_2		**2**	10.26	5.13	5.03
090313_3		**3**	15.44	5.16	5.01
090313_3.5		**3.5**	17.99	5.13	5.02
271112_4		**4**	20.59	5.14	5.02
160213_5.1		**5.1**	26.22	5.16	5.01

Supplementary table 1. Composition of solutions used in the precipitation experiments

			conditions at start of experiment						quantified subsample									
experiment	T (°C)	Mg:Ca	pH (NBS)	TA (mM/l)	$p\,CO_2$ (µatm)	S	Ω ara	Ω cal	minutes after start (NBS)	pH (mM/l)	TA (µatm)	$p\,CO_2$	S	Ω ara	Ω cal	%Ara.	%Cal.	%Vat.
271212_0	**30**	**0**	7.54	9.77	11690	35	3.73	5.41	64	8.02	9.57	3564	36	9.87	14.31	0	100	0
181012_0.5	**30**	**0.5**	7.09	10.26	33500	35	1.54	2.23	60	7.61	10.34	10620	35	4.53	6.57	8.15	91.85	0
230213_1	**30**	**1**	6.76	10.4	76052	35	0.71	1.03	137	7.98	10.06	4349	35	9.09	13.18	33.13	66.87	0
230213_1-5	**30**	**1.5**	6.93	10.33	50853	35	1.04	1.51	129	7.95	9.84	4720	36	8.34	12.1	90.59	9.41	0
301012_2	**30**	**2**	6.78	9.81	66379	34	0.71	1.03	82	7.92	10.23	5042	35	8.34	12.09	100	0	0
301012_3	**30**	**3**	7.01	10.09	39772	35	1.26	1.83	76	7.83	10.29	6310	35	7.02	10.18	100	0	0
301012_4	**30**	**4**	6.9	9.97	52577	34	0.94	1.36	160	8.2	10.21	2447	35	14.2	20.59	100	0	0
301012_5.1	**30**	**5.1**	6.97	10.11	44399	35	1.14	1.65	155	8.17	10.35	2688	35	13.62	19.76	100	0	0
271212_0	**25**	**0**	7.52	10.33	11057	35	3.61	5.24	62	8.12	10.19	2610	36	11.83	17.15	0	100	0
231012_0.5	**25**	**0.5**	7.32	11.83	16484	35	2.7	3.91	126	8.14	10.09	2303	35	12.53	18.17	2.11	97.89	0
231012_1	**25**	**1**	7.4	9.71	13641	35	2.64	3.83	121	8.02	9.84	3041	35	9.78	14.18	39.25	60.75	0
231012_1-5	**25**	**1.5**	7.07	10.19	31286	35	1.32	1.92	115	7.96	10.07	3678	35	8.8	12.76	82.09	17.91	0
101112_2	**25**	**2**	7.12	10.42	29986	35	1.44	2.09	137	8.17	10.25	2465	35	12.25	17.77	98.31	1.69	0
101112_3	**25**	**3**	7.11	10.3	30126	35	1.4	2.03	199	8.31	9.8	1503	35	15.88	23.02	100	0	0
101112_4	**25**	**4**	7.22	10.42	23806	35	1.79	2.6	195	8.32	9.78	1521	35	15.71	22.78	100	0	0
101112_5.1	**25**	**5.1**	7.12	9.95	28260	37	1.45	2.11	189	8.3	10.17	1612	37	16.65	24.14	100	0	0
031212_0	**20**	**0**	7.08	9.89	27117	35	1.14	1.66	126	8.15	-	-	35	-	-	0	100	0
140313_0-5	**20**	**0.5**	7.1	10.55	30315	35	1.17	1.69	176	8.21	10.53	1688	36	14.44	20.94	0.4	99.53	0.07
031212_1	**20**	**1**	6.95	9.44	35508	35	0.8	1.16	268	8.53	10.36	738	35	22.91	33.22	12.85	87.15	0
140313_1-5	**20**	**1.5**	7.16	10.35	24674	36	1.4	2.03	235	8.24	10.29	1453	37	15.62	22.65	27.97	72.03	0
151112_2	**20**	**2**	6.95	9.85	36162	35	0.86	1.24	246	8.29	10.16	1309	37	16.35	23.71	70.8	29.2	0
140313_2.5	**20**	**2.5**	7.07	10.54	30520	35	1.16	1.68	227	8.26	10.95	1457	37	17.29	25.07	79.69	20.31	0
151112_3	**20**	**3**	6.93	9.65	33517	35	0.81	1.17	181	8.21	10.03	1613	36	13.72	19.89	100	0	0
151112_4	**20**	**4**	6.98	9.79	31485	35	0.91	1.32	234	8.25	10.05	1459	36	14.73	21.36	100	0	0
091012_5.1	**20**	**5.1**	6.52	9.97	98248	35	0.33	0.48	370	8.38	11.15	1211	38	20.37	29.54	100	0	0
281012_0	**15**	**0**	6.88	11.11	42372	35	0.74	1.07	265	8.16	10.52	1717	35	11.81	17.12	0	100	0
281012_0.5	**15**	**0.5**	6.79	10.76	50821	35	0.58	0.84	264	8.25	10.37	1312	35	13.95	20.22	0	100	0
281012_1	**15**	**1**	6.83	11.21	48237	35	0.66	0.96	315	8.1	10.38	1942	36	10.71	15.53	4.6	95.4	0
281012_1.5	**15**	**1.5**	6.81	11.12	50006	35	0.63	0.91	313	8.25	10.59	1994	37	14.77	21.41	13.64	86.36	0
160213_2	**15**	**2**	6.76	10.39	43605	35	0.45	0.65	383	8.12	10.26	1914	37	12.38	17.95	21.54	78.46	0
090313_3	**15**	**3**	7.14	10.52	21980	35	1.25	1.82	350	8.38	11.29	1022	37	19.51	28.29	84.38	15.62	0
090313_3.5	**15**	**3.5**	7.17	10.47	20499	35	1.33	1.93	357	8.34	11.19	1100	38	18.69	27.11	87.56	12.44	0
271112_4	**15**	**4**	7.14	9.59	20046	35	1.14	1.66	387	8.46	10.32	695	37	21.16	30.68	100	0	0
160213_5.1	**15**	**5.1**	6.78	10.26	40714	35	0.48	0.69	535	8.24	10.7	1522	38	16.62	24.1	100	0	0

Supplementary table 2. Conditions of pH, total alkalinity (TA), salinity (S), and saturation state (Ω) of aragonite and calcite at the start of the experiment and for the time at which the sample was collected for quantification.