Electronic Supplementary Material (ESI) for CrystEngComm
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Supporting Information

Unfastening pearl nacre nanostructures under shear

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Planetary Ball Milling

The shell nacre was milled according to the parameters in table 1. Other conditions tested but not listed in the table, include shorter durations (1, 5 and 10 minutes), lower speed (200 rpm), less balls (100x5 mm-balls and 2x20 mm-balls), and/or smaller sample size (100 mg). However, those conditions did not give optimum yield and introduced a lot of contamination as discussed in the paper.

Table S1. Ball milling conditions of each sample

Sample #	Sample Size (g)	Ball Size	No of Balls	Excipient Milli Q	Speed (rpm)	Duration
1	15	5 mm	200	15ml	400	4 hrs
2	15	5 mm	200	15ml	600	2 hrs
3	15	5 mm	200	15ml	800	30 mins
4	15	5 mm	200	15ml	1000	20 mins
5	15	5 mm	200	15ml	1000	30 mins
6	5	20 mm	4	30ml	400	2 hrs
7	10	20 mm	4	15ml	400	2 hrs
8	15	20 mm	3	15ml	400	2 hrs
9	15	20 mm	4	15ml	400	2 hrs
10	20	20 mm	4	15ml	400	2 hrs
11	5	20 mm	4	30ml	600	2 hrs
12	10	20 mm	4	15ml	600	2 hrs
13	15	20 mm	3	15ml	600	2 hrs
14	15	20 mm	4	15ml	600	2 hrs
15	20	20 mm	4	15ml	600	2 hrs

Following the milling process the samples were suspended in 100 mL of Milli Q water and the suspension was immediately decanted into a clean container leaving the partially milled nacre behind, which was dried and weighed. The suspension was filtered using filter paper with a pore size of 2.5 µm. The residue was redispersed in 100 mL Milli Q water and centrifuged at 3220 x g for 15 minutes. The supernatant was transferred and kept, while the pellet was redispersed in 100 mL Milli Q water and centrifuged as above. The residue was dried, weighed, and kept for analyses.

Conventional Ball Milling

As a comparison of the effectiveness of the planetary mill, a one-off experiment using a SPEX SamplePrep 8000D Dual Mixer/Mill® was carried out using a sample size of 15 g, 12 3/8" stainless steel ball and double distilled water as an excipient. The milling time was set to 2 hours at a speed of 875 cycles/min. Figure S1 shows TEM images of damaged aragonite tablets as a result of the milling process.

TEM Images of Damaged Tablets

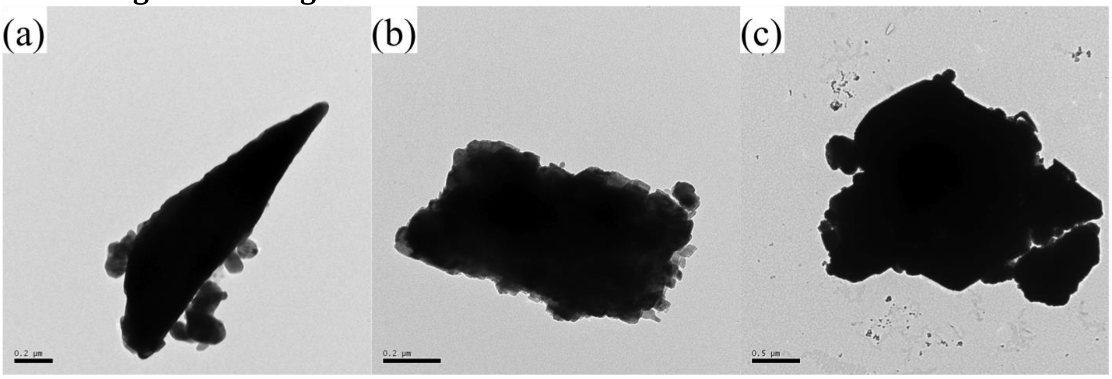

Fig. S1 Damaged aragonite tablets. (a) The tablet does not look like a polygonal aragonite tablet. (b) The rough edges of the tablet are due to the shear force of conventional milling. (c) The damaged tablet almost being cracked into two pieces. The bar sizes are 0.2 μm (a-b) and 0.5 μm (c).

Particle Size Distribution (Mastersizer Hydro 2000S)

Table S2. Particle Size Distribution.

Sample #	d (0.1)	d (0.5)	d (0.8)	d (0.9)	Max
1	0.688	3	48.164	141.798	724.436
2	0.597	1.822	22.07	102.793	316.228
3	0.747	2.284	5.611	16.336	120.226
4	0.737	2.546	17.313	41.89	91.201
5	0.003	4.522	45.022	103.635	724.436
6	0.456	14.852	327.987	450.803	831.764
7	0.012	6.667	366.765	499.038	954.993
8	0.888	2.949	6.554	9.309	22.909
9	0.928	3.279	8.744	16.381	91.201
10	0.861	2.809	6.696	10.404	26.303
11	0.777	2.634	6.958	11.704	26.303
12	0.799	2.669	9.806	51.585	138.038
13	0.883	3.172	10.347	65.436	181.97
14	0.802	2.495	5.805	12.241	91.201
15	0.84	3.185	304.735	470.047	954.993

d(0.1) value indicates 10% of the samples are below that size, d(0.5) value means 50% of the samples are below that size, d(0.8) value means 80% of the samples are below that size, d(0.9) value means 90% of the samples are below that size, Max value indicates the largest possible size of that sample. All values are in micrometer.

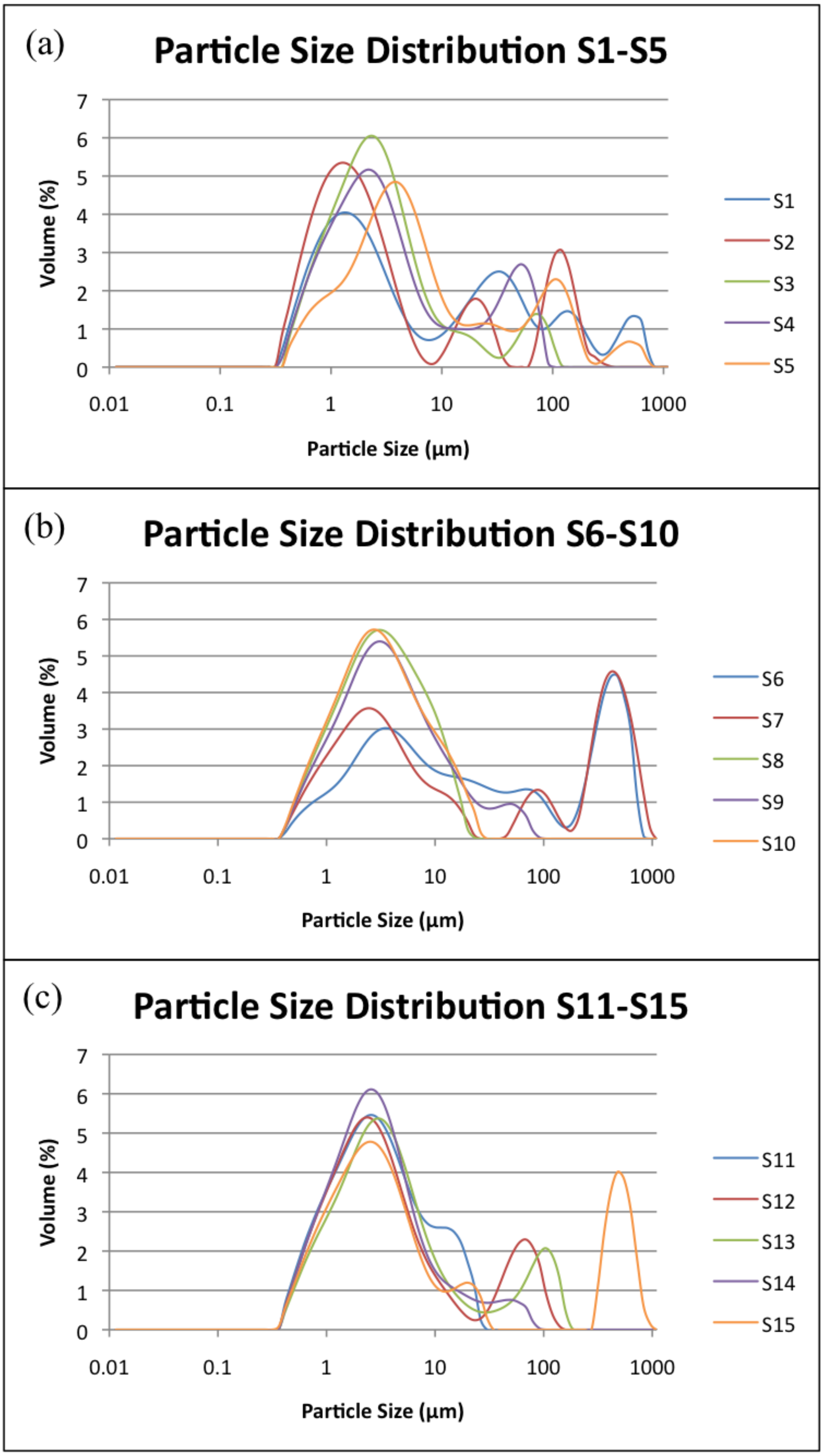

Fig. S2 Particle size distribution of samples 1-5(a), 6-10(b) and 11-15(c).

Scanning Electron Microscopy (SEM)

Samples were embedded on carbon tape and layered with 3 nm Platinum (Pt).

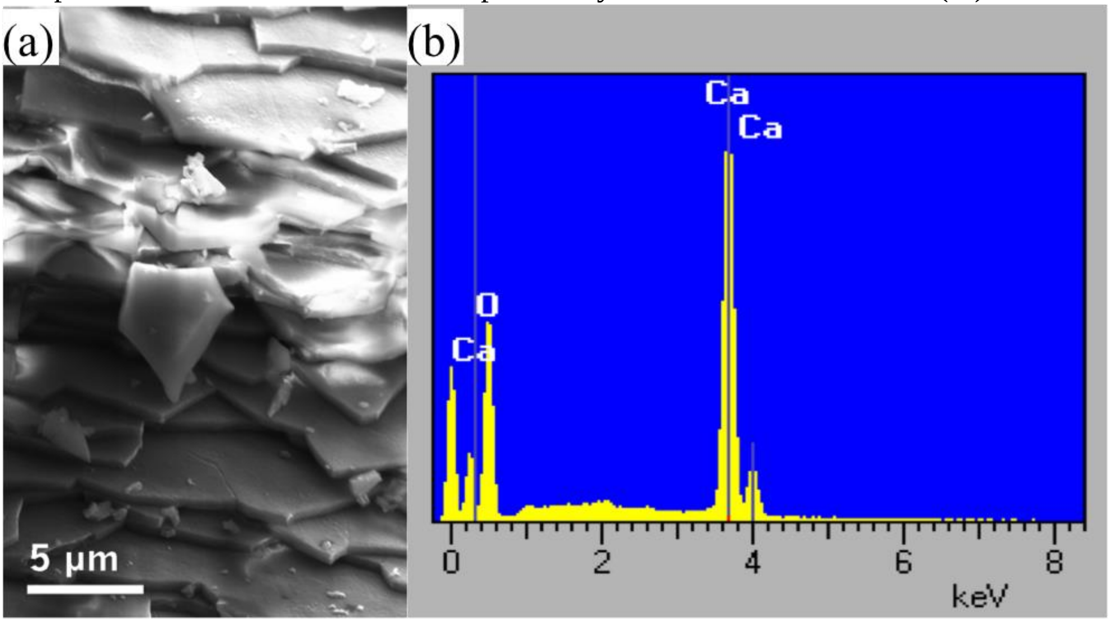

Fig. S3 Crushed nacre. (a) Multiple layers of aragonite tablets from crushed nacre, and (b) its elemental analysis.

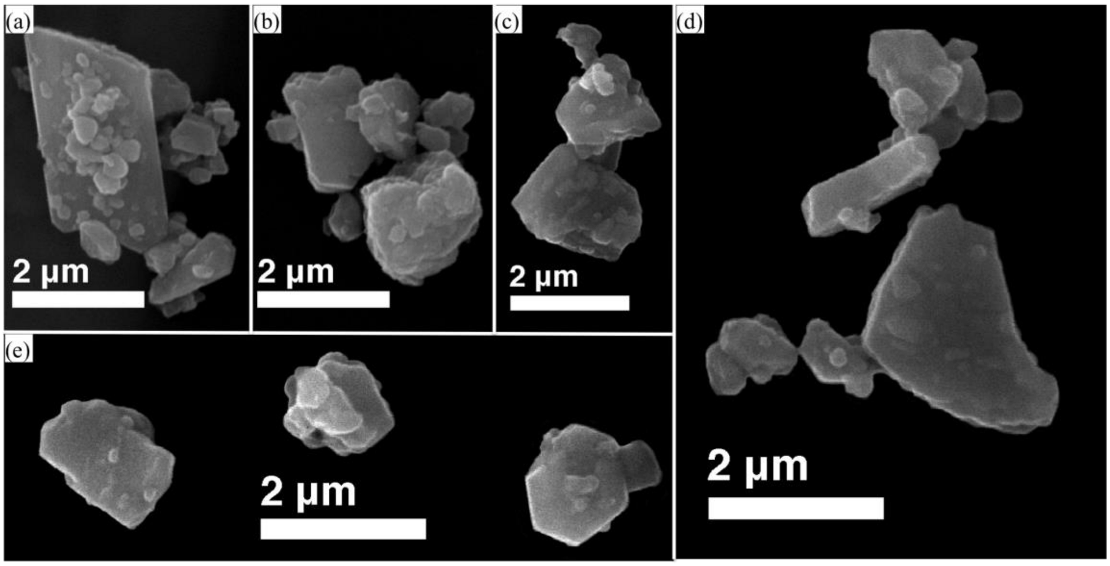

Fig. S4 Milled nacre with various sizes and shapes.

X-Ray Diffraction (XRD)

Ground and milled nacre were subjected to X-Ray powder diffraction analysis. Ground nacre was analysed as a control to determine the effect of heat and shear forces from milling processes on the phase transformation of aragonite. The percentage compositions are summarized in Table S3. It is worthy to note that this analysis was meant for qualitative instead of quantitative analysis. So, the number below is a guide only as the margin of error from the software could be as high as 20%.

Table S3. Percentage compositions analysis from XRD.

Sample	Aragonite	Calcite	Other
Ground	79%	21%	
1	100%	0%	
2	75%	25%	
3	62%	38%	
4	66%	34%	
5	84%	16%	
6	100%	0%	
7	100%	0%	
8	89%	11%	
9	91%	9%	
10	93%	7%	
11*	95%	0%	5% ZrO_2
12	100%	0%	
13	100%	0%	
14	100%	0%	
15	89%	11%	
Conventional	86%	14%	

XRD analysis of sample 9 before and after DSC treatment shows that aragonite transformed to calcite after treatment (see Figure S5 below).

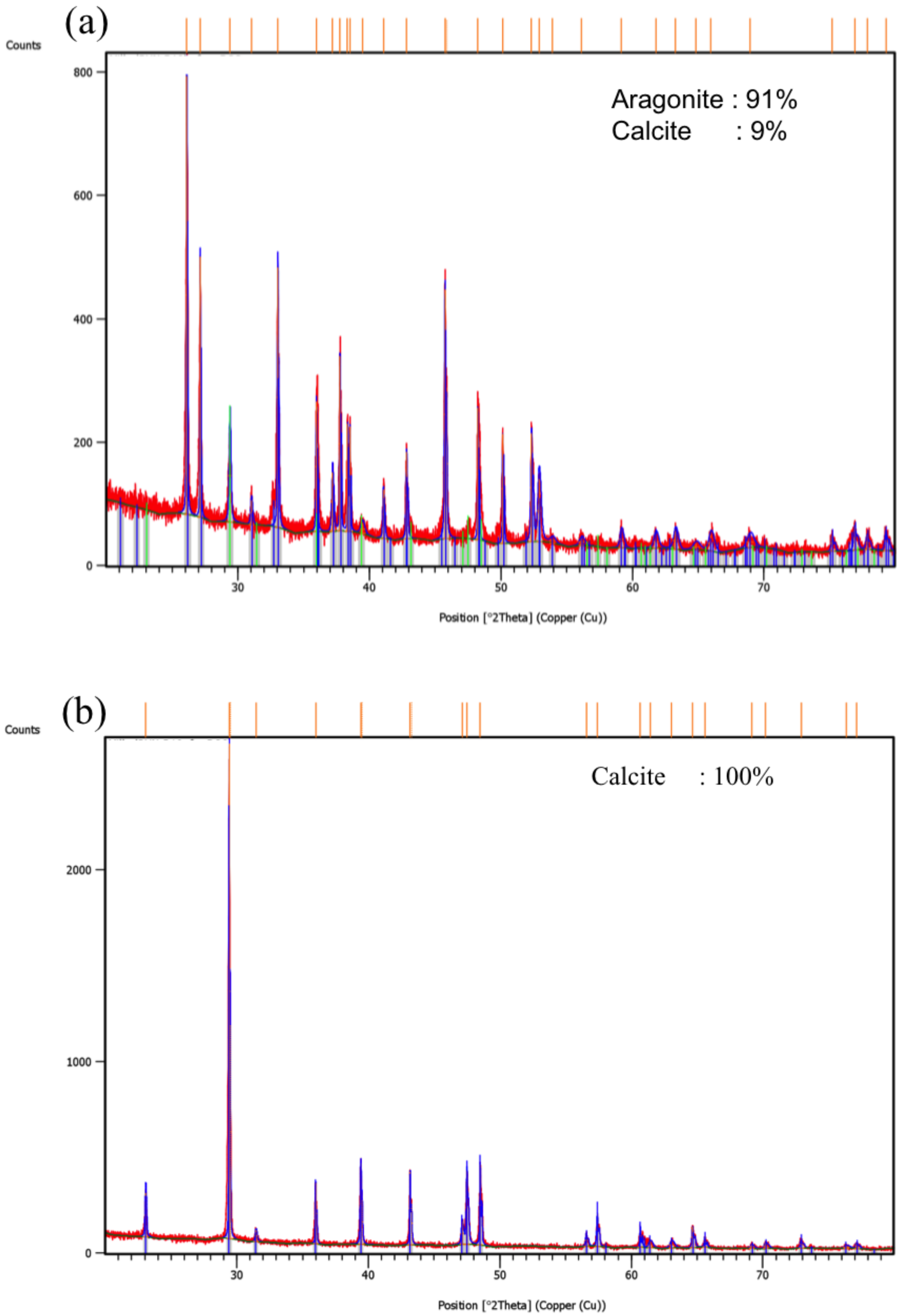

Fig. S5 XRD spectrum of sample 9 before (a) and after (b) DSC treatment showing that it only contains calcite.

Differential Scanning Calorimetry (DSC)

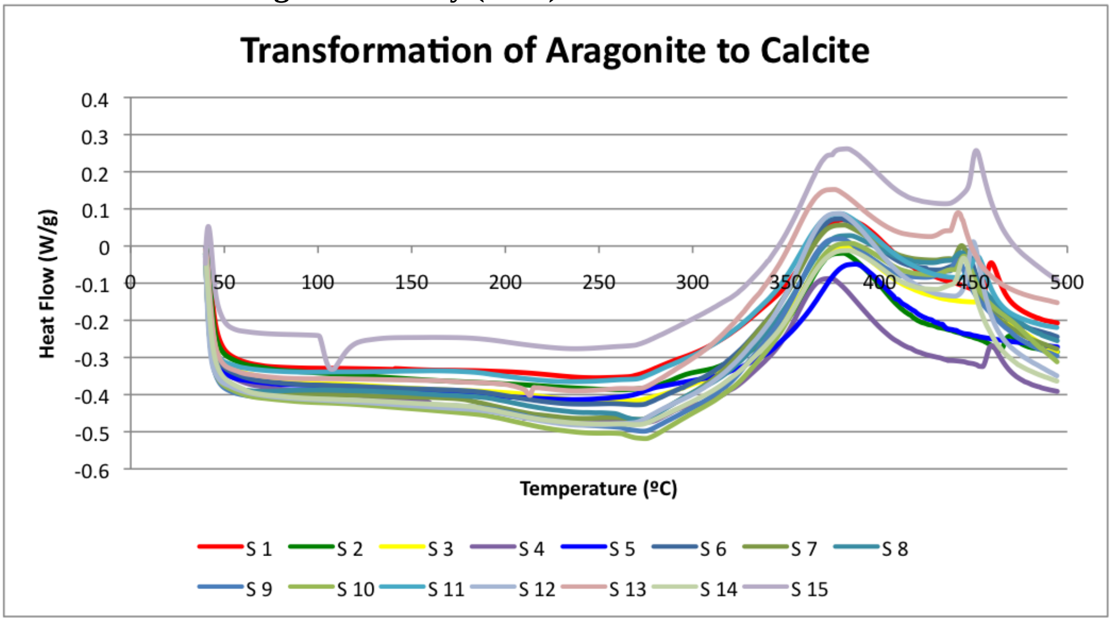

Fig. S6 DSC graph of the 15 samples.

Fourier Transform Infrared Spectroscopy (FTIR)

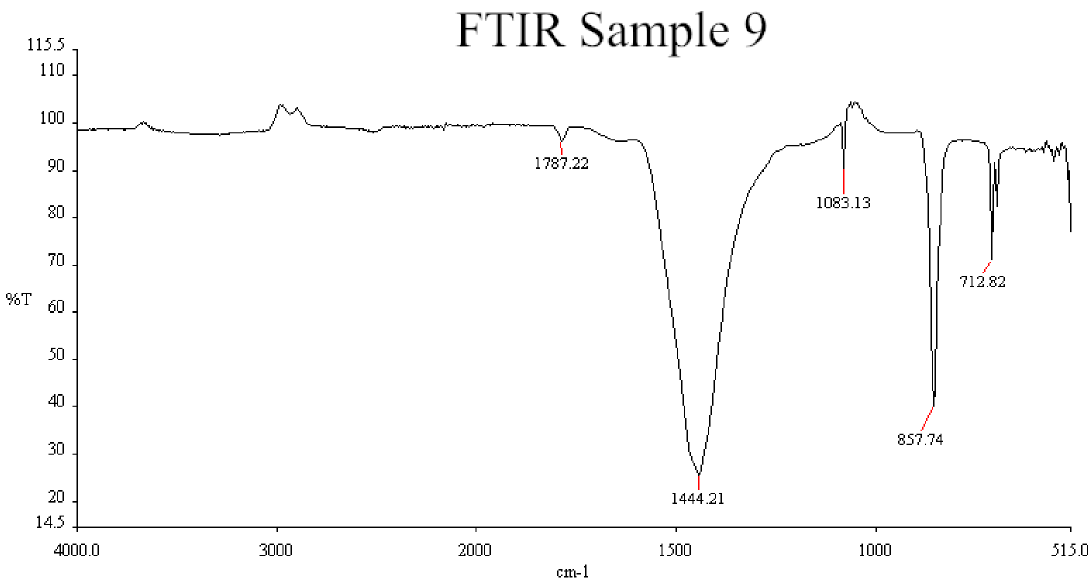

Fig. S7 FTIR of Sample 9 corresponds to aragonite.

Electronic Supplementary Material (ESI) for CrystEngComm

Inductively Coupled Plasma Mass Spectrometry and Atomic Emission Spectrometry (ICP MS – AES)

Full analysis results of the ground nacre and the planetary milled nacre were given in Table S4.

Table S4. ICP MS – AES data

Sample\Atom	Na	Mg	Al	P	S	K	Ca	Fe	Sr	Zr	Li
Ground	4810	1050	20.2	8.4	184	79.3	356000	32.2	1090	9.3	0.5
S 1	2420	1600	14.3	7.0	169	24.6	363000	6.0	1220	1100	0.4
S 2	1790	1990	30	2.7	164	15.3	364000	14.8	1180	5970	0.4
S 3	2100	4040	6.3	8.3	169	20.3	382000	10.3	1150	828	0.4
S 4	2190	1670	29.3	6.0	168	12.3	373000	7.1	1050	3140	0.5
S 5	951	1690	13.6	4.3	166	6.81	376000	9.1	1150	2730	0.6
S 6	3340	2400	47.7	1.1	161	38.3	366000	10.8	1090	10800	0.5
S 7	3500	1270	108	2.5	166	36.4	361000	5.9	1090	3520	0.5
S 8	3530	2650	0.2	5.3	178	38	370000	7.13	1210	25.1	0.6
S 9	3510	2070	4.59	7.2	174	34.4	366000	8.9	1180	1600	0.5
S 10	3430	1760	8.6	8.1	175	32	363000	6.8	1150	1640	0.6
S 11	3280	9750	416	9.7	134	28.8	315000	25	909	104000	0.3
S 12	3010	3440	94.4	8.3	169	31	361000	15.7	1070	24200	0.5
S 13	3350	1970	12.1	6.1	167	40.5	366000	3.1	1170	2110	0.5
S 14	3180	1770	21.5	4.7	168	34.2	370000	4.3	1070	5420	0.5
S 15	3160	3140	26.7	8.9	171	34.8	360000	8.7	1110	5880	0.6

Sample\Atom	As	Se	Rb	Y	Nb	Mo	Pd	Ag	Cd	In
Ground	< 0.1	< 0.1	< 0.1	0.2	0.2	0.3	< 0.1	< 0.1	< 0.1	< 0.1
S 1	< 0.1	< 0.1	< 0.1	51.1	0.4	0.2	< 0.1	0.2	1.2	< 0.1
S 2	< 0.1	< 0.1	< 0.1	408	0.6	0.6	< 0.1	0.2	6.0	< 0.1
S 3	< 0.1	< 0.1	< 0.1	61.1	0.61	0.2	< 0.1	< 0.1	0.9	< 0.1
S 4	< 0.1	< 0.1	< 0.1	179	0.6	0.4	< 0.1	< 0.1	3.2	< 0.1
S 5	< 0.1	< 0.1	< 0.1	185	3.1	0.4	< 0.1	0.1	3.2	< 0.1
S 6	< 0.1	< 0.1	< 0.1	21.9	1.3	1.1	< 0.1	0.4	10.9	< 0.1
S 7	< 0.1	< 0.1	< 0.1	5.2	1.33	0.5	< 0.1	0.2	4.0	< 0.1
S 8	< 0.1	< 0.1	< 0.1	0.2	0.2	0.2	< 0.1	< 0.1	< 0.1	< 0.1
S 9	< 0.1	< 0.1	< 0.1	1.8	0.4	0.3	< 0.1	< 0.1	1.6	< 0.1
S 10	< 0.1	< 0.1	< 0.1	2.0	0.5	0.3	< 0.1	< 0.1	1.9	< 0.1
S 11	< 0.1	< 0.1	< 0.1	119	4.7	8.6	< 0.1	4.2	111	< 0.1
S 12	< 0.1	< 0.1	< 0.1	26.4	1.0	1.9	< 0.1	0.8	21.8	< 0.1
S 13	< 0.1	< 0.1	< 0.1	2.6	0.6	0.3	< 0.1	< 0.1	2.2	< 0.1
S 14	< 0.1	< 0.1	< 0.1	7.23	0.6	0.6	< 0.1	0.2	5.8	< 0.1
S 15	< 0.1	< 0.1	< 0.1	7.5	0.7	0.6	< 0.1	0.2	6.2	< 0.1

Sample\Atom	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Hg
Ground	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 1	< 0.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1	6.3	< 0.1	< 0.1	< 0.1
S 2	< 0.1	< 0.1	< 0.1	< 0.1	0.8	< 0.1	36.2	< 0.1	< 0.1	< 0.1

S 3	< 0.1	< 0.1	< 0.1	< 0.1	0.2	< 0.1	5.9	< 0.1	< 0.1	< 0.1
S 4	< 0.1	< 0.1	< 0.1	< 0.1	0.4	< 0.1	17.1	< 0.1	< 0.1	< 0.1
S 5	< 0.1	< 0.1	< 0.1	< 0.1	0.4	< 0.1	16.8	0.2	< 0.1	< 0.1
S 6	1.61	0.8	2.1	0.8	5.3	1.5	58.7	0.1	< 0.1	< 0.1
S 7	0.5	0.3	0.7	0.3	1.7	0.5	20.2	< 0.1	< 0.1	< 0.1
S 8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1
S 9	0.2	< 0.1	0.2	< 0.1	0.6	0.2	7.8	< 0.1	< 0.1	< 0.1
S 10	0.2	< 0.1	0.3	< 0.1	0.7	0.2	9.4	< 0.1	< 0.1	< 0.1
S 11	10.9	5.3	14.5	5.7	39.1	10.8	489	0.4	0.3	< 0.1
S 12	2.7	1.3	3.5	1.4	9.4	2.6	112	< 0.1	< 0.1	< 0.1
S 13	0.3	0.1	0.4	0.1	0.9	0.3	11.3	< 0.1	< 0.1	< 0.1
S 14	0.7	0.4	0.9	0.4	2.4	0.7	29.4	< 0.1	< 0.1	< 0.1
S 15	0.8	0.4	1.0	0.4	2.6	0.7	31.7	< 0.1	< 0.1	< 0.1

Sample\Atom	Be	Sc	Ti	V	Cr	Mn	Co	Ni	Cu	Zn
Ground	< 0.1	0.2	44.3	1.2	2.5	2.7	0.2	0.9	1.6	2.5
S 1	< 0.1	0.2	6.9	2.0	1.0	8.3	0.2	0.7	2.2	2.6
S 2	< 0.1	0.8	5.1	2.2	1.0	7.3	0.2	0.4	0.7	2.6
S 3	< 0.1	0.2	58.1	1.0	0.4	7.5	0.1	0.5	0.5	8.8
S 4	< 0.1	0.5	9.1	2.2	0.8	9.7	0.2	0.4	0.4	3.4
S 5	< 0.1	0.5	7.2	2.3	0.8	8.5	0.2	0.4	0.8	1.1
S 6	< 0.1	1.5	15	1.9	0.9	11.5	0.2	0.7	1.0	2.1
S 7	< 0.1	0.7	12.1	2.5	0.8	11.8	0.2	0.5	1.0	2.1
S 8	< 0.1	0.2	7.0	1.5	0.9	8	0.2	0.5	0.8	1.6
S 9	< 0.1	0.4	9.4	1.7	1.0	8.3	0.2	0.5	1.5	0.2
S 10	< 0.1	0.4	10.9	1.9	0.9	9.4	0.2	0.4	0.6	1.6
S 11	< 0.1	10.7	61.6	1.2	1.9	10.5	0.2	2.2	0.4	0.3
S 12	< 0.1	2.5	23.5	2.2	1.3	9.8	0.2	0.9	0.9	4.4
S 13	< 0.1	0.5	11.4	1.6	0.8	8.9	0.2	0.4	0.5	1.7
S 14	< 0.1	0.9	15.2	2.2	0.8	9.0	0.2	0.6	0.9	0.5
S 15	< 0.1	0.9	16.1	2.0	0.8	10.3	0.2	0.5	0.5	0.9

Sample\Atom	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Eu
Ground	0.8	< 0.1	< 0.1	< 0.1	0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 1	1.3	< 0.1	< 0.1	< 0.1	0.8	< 0.1	0.9	< 0.1	< 0.1	< 0.1
S 2	1.9	< 0.1	< 0.1	< 0.1	0.5	< 0.1	0.8	< 0.1	< 0.1	< 0.1
S 3	1.3	< 0.1	< 0.1	< 0.1	0.5	< 0.1	0.7	< 0.1	< 0.1	< 0.1
S 4	0.5	< 0.1	< 0.1	< 0.1	0.4	< 0.1	1.6	< 0.1	< 0.1	< 0.1
S 5	1.1	< 0.1	< 0.1	< 0.1	0.8	< 0.1	1.1	< 0.1	< 0.1	< 0.1
S 6	0.9	< 0.1	< 0.1	< 0.1	1.6	0.4	1.2	< 0.1	0.4	< 0.1
S 7	0.9	< 0.1	< 0.1	< 0.1	1.0	0.2	0.7	< 0.1	0.2	< 0.1
S 8	0.7	< 0.1	< 0.1	< 0.1	0.6	< 0.1	0.3	< 0.1	< 0.1	< 0.1
S 9	0.5	< 0.1	< 0.1	< 0.1	0.6	< 0.1	0.3	< 0.1	< 0.1	< 0.1
S 10	0.1	< 0.1	< 0.1	< 0.1	0.7	< 0.1	0.4	< 0.1	< 0.1	< 0.1
S 11	1.4	< 0.1	0.3	< 0.1	7.4	2	7.8	0.6	2.8	0.2
S 12	0.4	< 0.1	< 0.1	< 0.1	2.3	0.5	2.3	< 0.1	0.7	< 0.1
S 13	0.8	< 0.1	< 0.1	< 0.1	0.8	0.2	0.7	< 0.1	< 0.1	< 0.1

S 14	0.7	< 0.1	< 0.1	< 0.1	0.9	0.2	0.7	< 0.1	0.2	< 0.1
S 15	0.3	< 0.1	< 0.1	< 0.1	1.1	0.2	0.8	< 0.1	0.2	< 0.1

Sample\Atom	Tl	Pb	Bi	Th	U	Ga	Ge	Gd	Tb	Sm
Ground	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 1	< 0.1	0.4	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 2	< 0.1	0.3	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 3	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 4	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 5	< 0.1	0.1	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 6	< 0.1	0.2	< 0.1	2.2	4.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 7	< 0.1	0.2	< 0.1	0.7	1.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 8	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 9	< 0.1	< 0.1	< 0.1	0.2	0.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 10	< 0.1	0.2	< 0.1	0.3	0.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 11	< 0.1	< 0.1	< 0.1	15.6	31.5	0.131	< 0.1	3.5	0.9	< 0.1
S 12	< 0.1	0.2	< 0.1	3.8	8.0	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 13	< 0.1	0.1	< 0.1	0.4	0.7	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 14	< 0.1	< 0.1	< 0.1	1.0	2.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S 15	< 0.1	0.1	< 0.1	1.05	2.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1