Supporting Information for

Wealth from waste: Blue mussels (*Mylitus edulis)* offer up a sustainable source of natural and synthetic nacre

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This file includes:

***Table S1**: Selected ICP-MS analytes for untreated blue mussel shells and mussel shells heated at 220 °C for 48 h. Units are in ppm.*

Analyte (LOD)	Untreated (Mixer Mill)[a]	220 °C, 48 h (Mixer Mill)	Untreated (Mortar & Pestle)[b]	220 °C,48 h (Mortar & Pestle)[b]
Li (0.001)	1.588	1.242	0.873	0.994
Ca (0.182)	353442.0	386784.4	345618.0	367614.3
Cl (4.031)	4572.6	1861.50	619.25	553.31
Cr (0.004)	7.526	3.132	1.770	1.191
Fe (0.142)	3434.395	112.692	<80.2	<99.91
Mn (0.001)	37.547	1.699	1.222	2.011
Co (0.000)	<0.15	<0.16	<0.13	<0.15
Cu (0.004)	158.99	188.603	157.654	164.724
As (0.001)	0.445	0.456	0.155	<0.41
Sr (0.0003)	809.453	894.522	798.713	827.754
Ag (0.0002)	<0.15	<0.14	<0.12	<0.15
Cd (0.000)	<0.29	<0.29	<0.25	<0.31
Hg (0.000)	<0.15	<0.15	<0.13	<0.16
Pb (0.000)	0.462	0.117	0.117	<0.08
Ba (0.0001)	11.972	3.738	1.960	1.725

[a] Mussel shells were ground in a mixer mill equipped in a 65 mL stainless steel vial with two quarter inch stainless steel balls for 12 min. [b]Mussel shells were ground using a mortar and pestle.

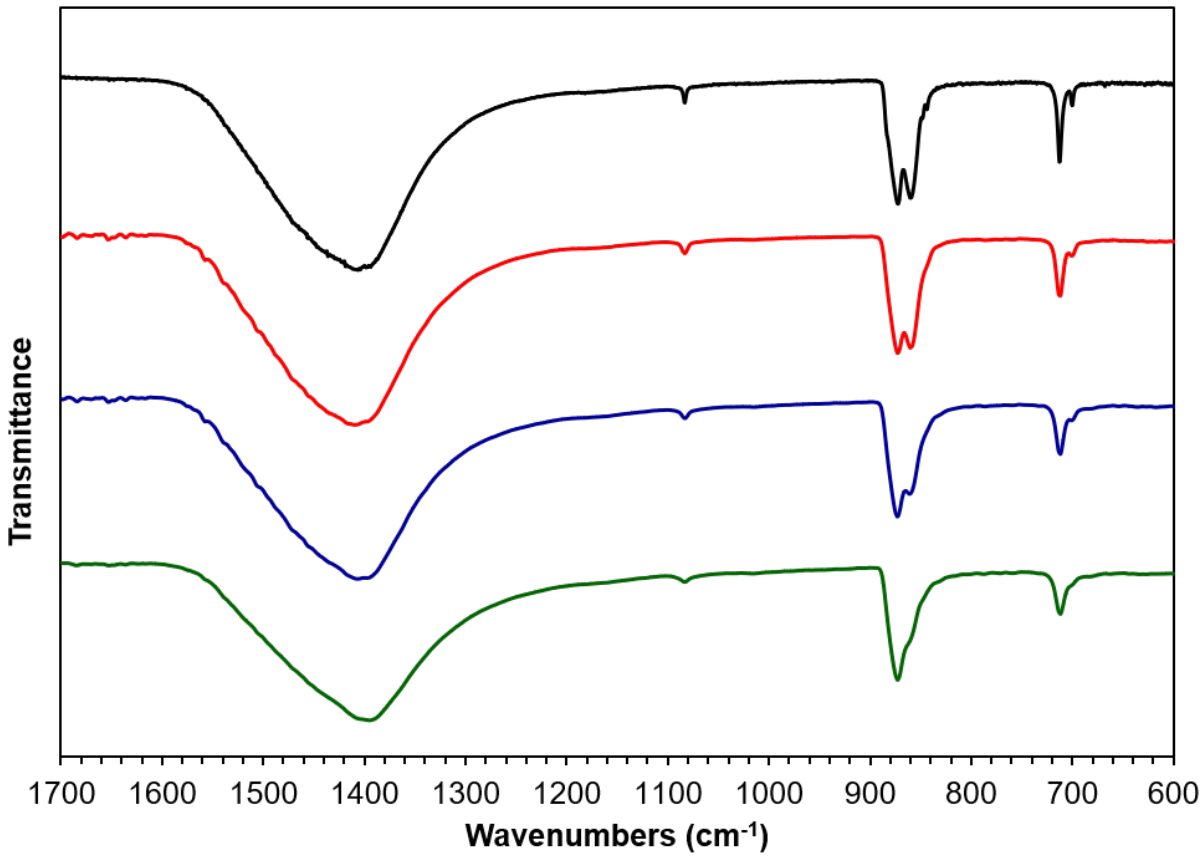


Fig. S1 *Infrared spectra of untreated mussel shells (green) and mussel shells heated to 160 °C (blue), 200 °C (red) and 225 °C (black) for 48 h.*

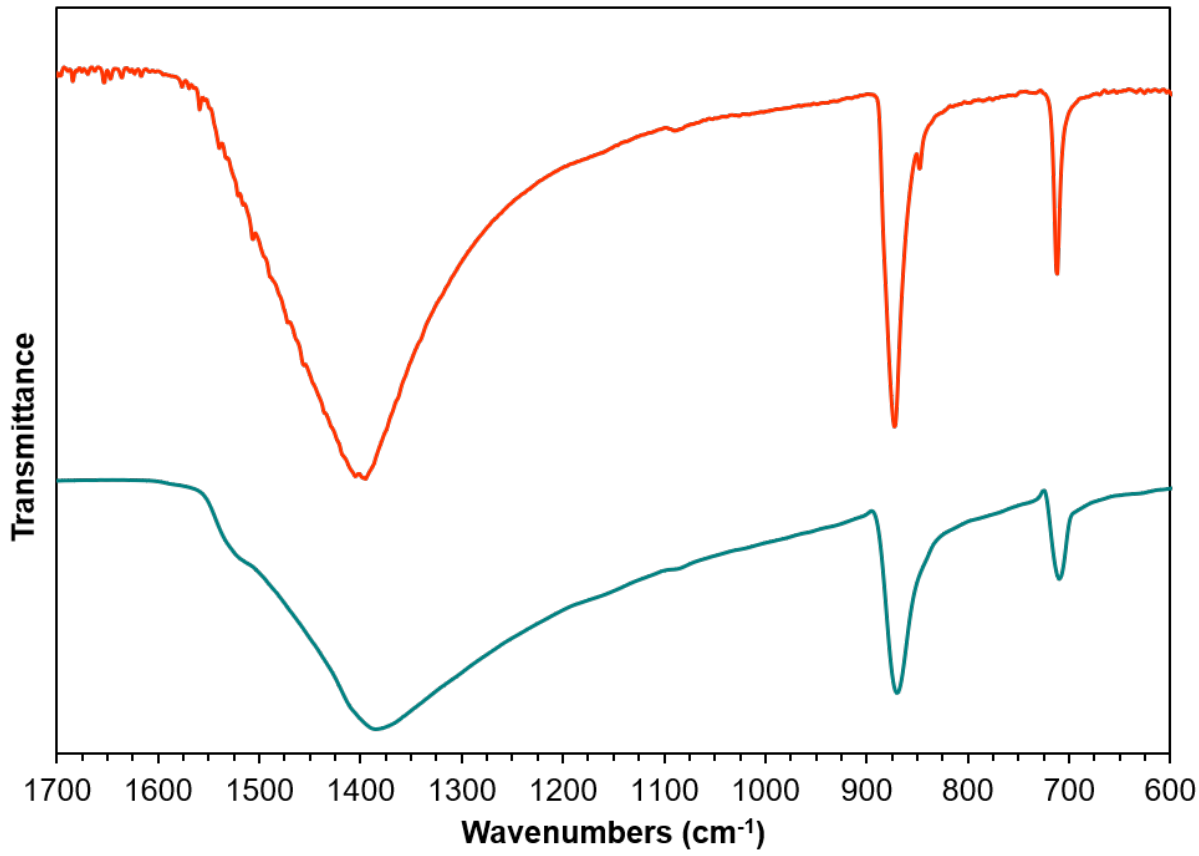


Fig. S2 *Infrared spectra of optical calcite sourced from Mexico (orange) and reagent grade calcium carbonate from Sigma Aldrich (teal). Neither samples underwent heat treatment.*

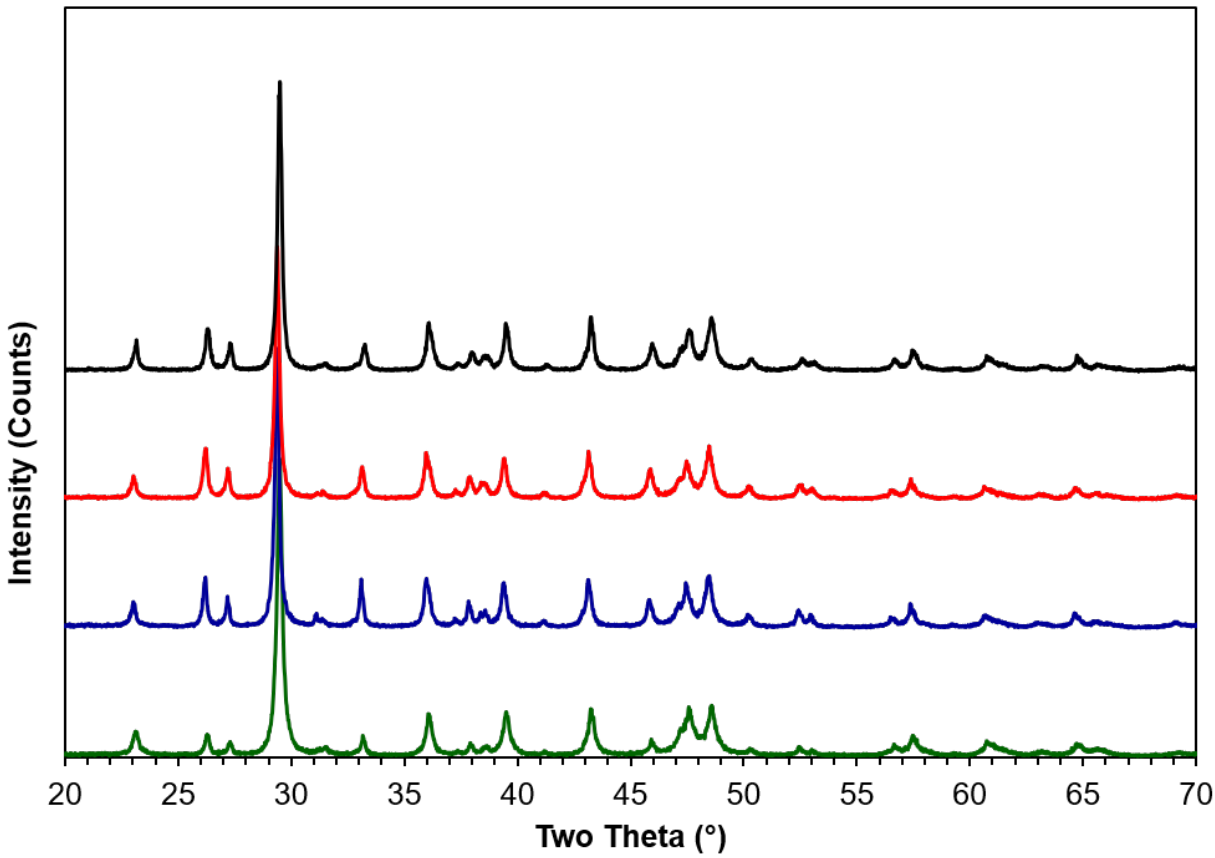


Fig. S3 *Powder XRD diffractograms for untreated mussel shells (green) and mussel shells heated to 160 °C (blue), 200 °C (red) and 225 °C (black) for 48 h.*

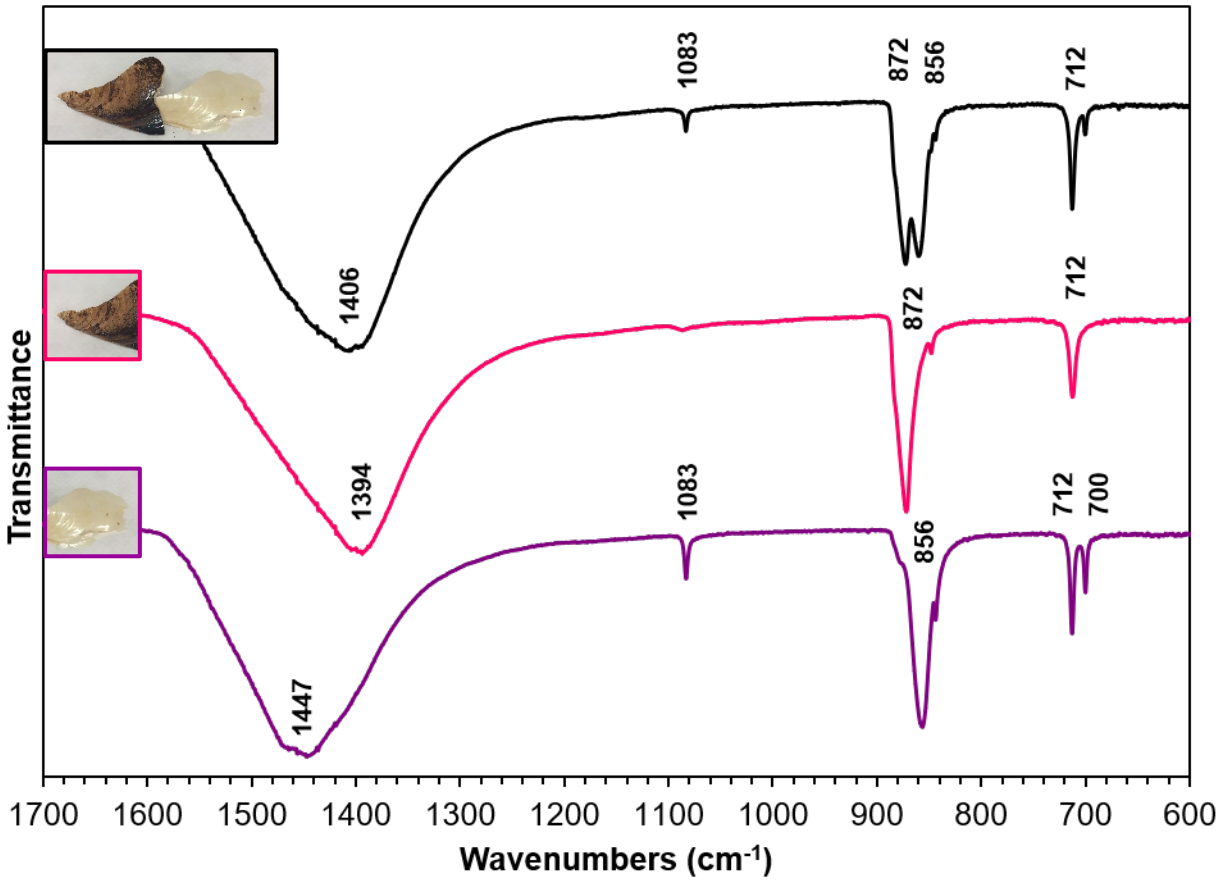


Fig. S4 *Infrared spectra for whole mussel shells heated at 220 °C for 48 h (black) and the resulting outer prismatic calcite layer (pink) and inner nacreous aragonite layer (purple) of the shell that cleanly separate as a result of heating.*

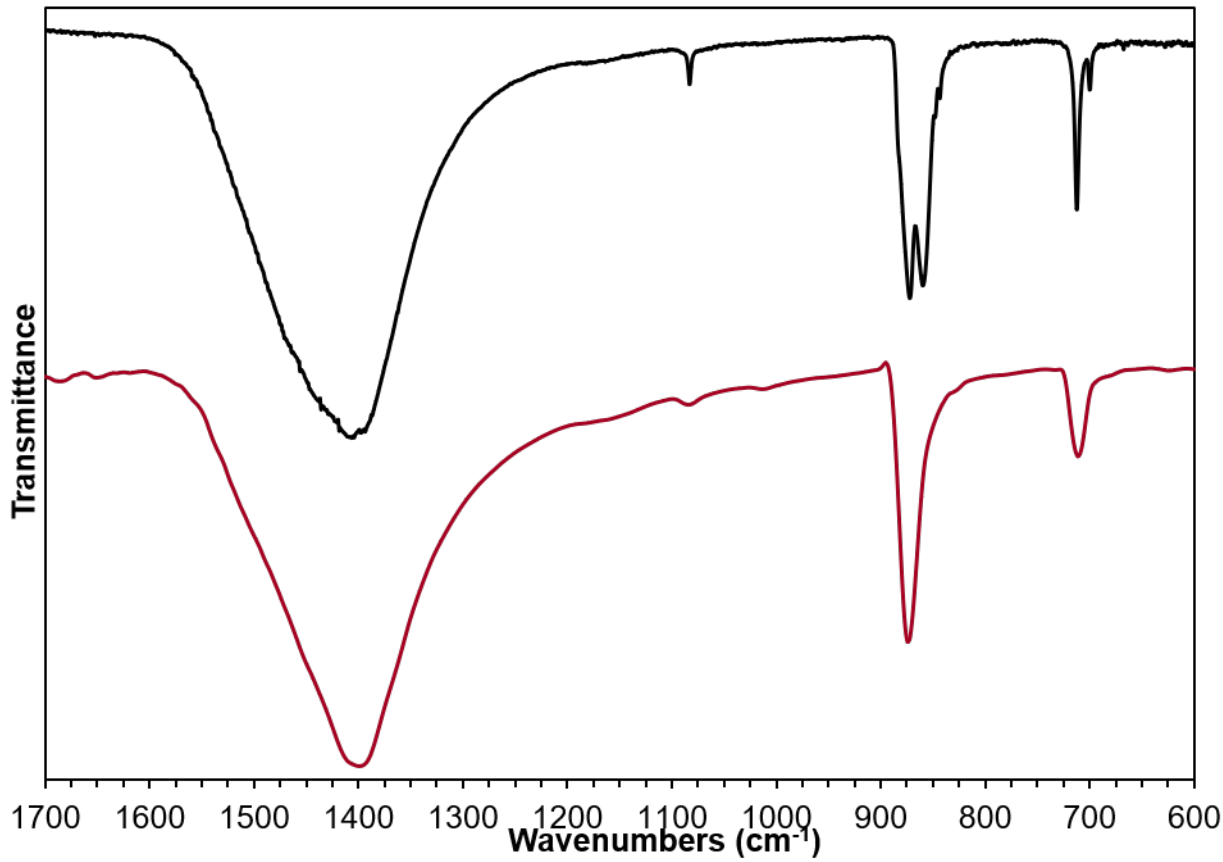


Fig. S5 *Infrared spectra of blue mussel, Mytilus edulis, (black) and eastern oyster, Crassostrea virginica, (burgundy) shells treated at 220 °C for 48 h.*

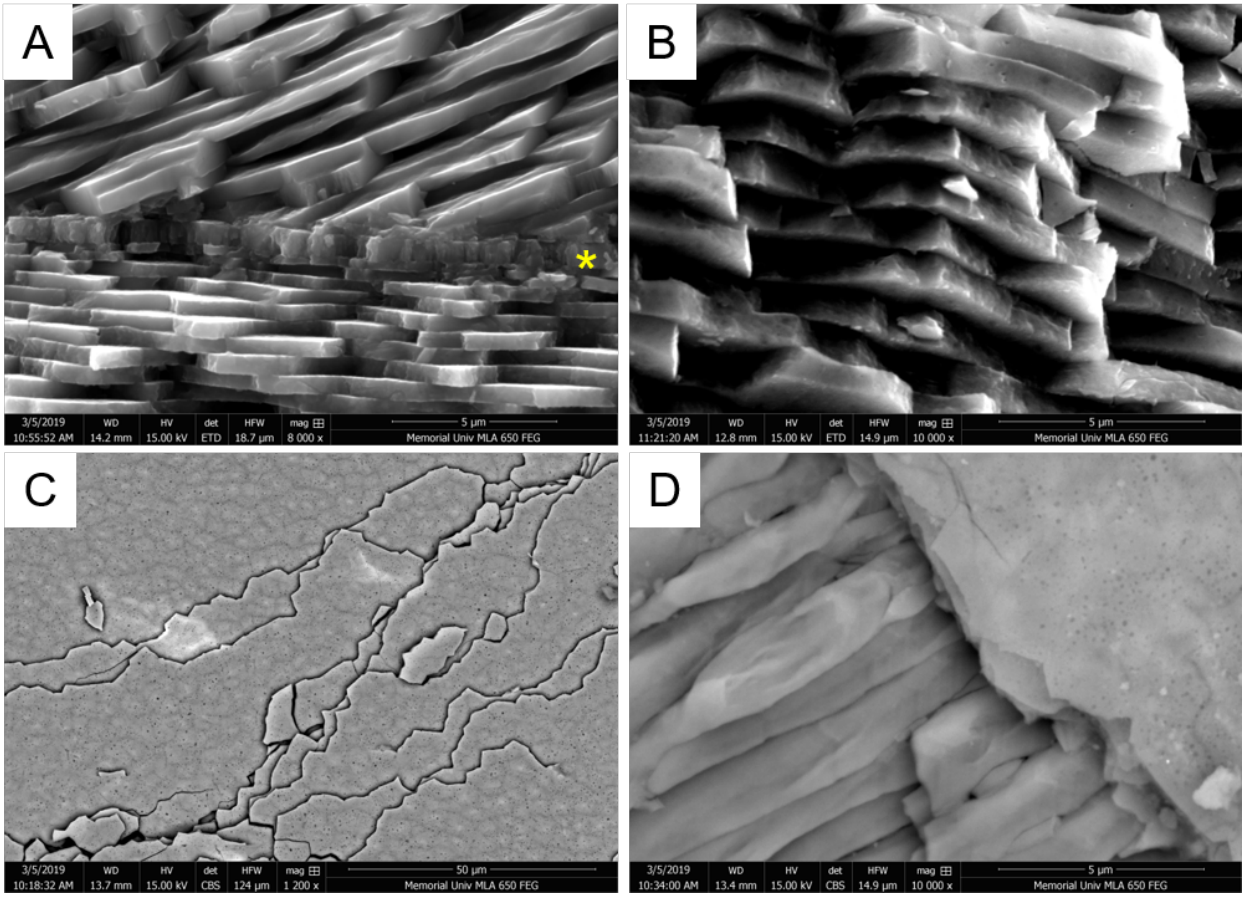


Fig. S6 *SEM micrographs of A) the cross section of untreated blue mussel shells shows the outer prismatic calcite layer separated from the inner nacreous aragonite layer by the myostracum (denoted by a star), B) cross section of the inner nacreous layer that results from heating the blue mussel shell to 220 °C for 48 h, C) the back side of the inner nacreous layer of blue mussel shell, and D) the inside of the outer layer of the blue mussel shell (where it separates from the inner nacreous layer) that clearly shows some of the myostracum attached.*

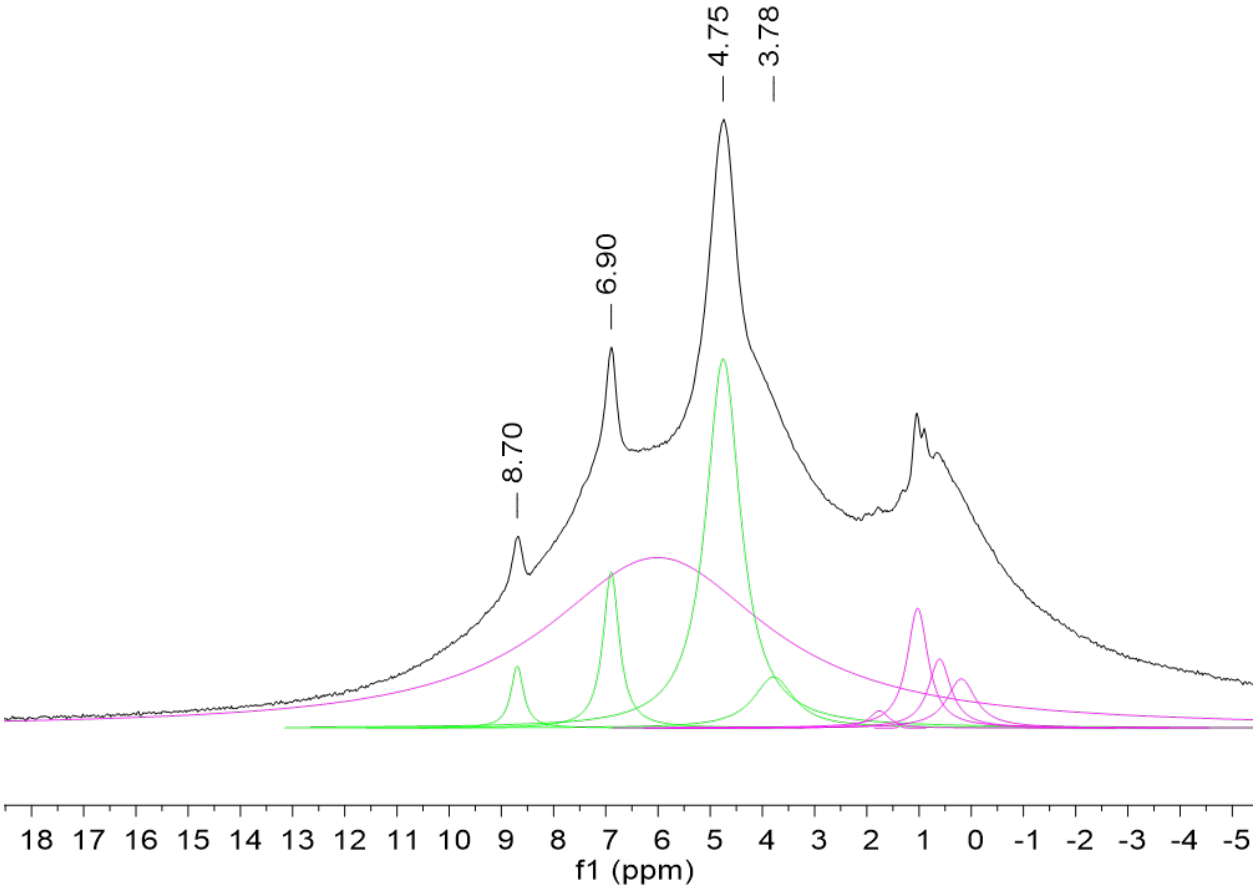


Fig. S7 *Normalized 600 MHz ^{1}H NMR spectra of untreated blue mussel shells that were ground with a mortar and pestle. 3.2 mm zirconia rotor and spinning at 20 kHz with a relaxation delay of 2 s. 16 scans. This spectrum shows the deconvolution of peaks where the pink lines (that correspond to the zirconia rotor that is shown in Figure S7) are not part of the signal from the organic matrix in the blue mussel shell.*

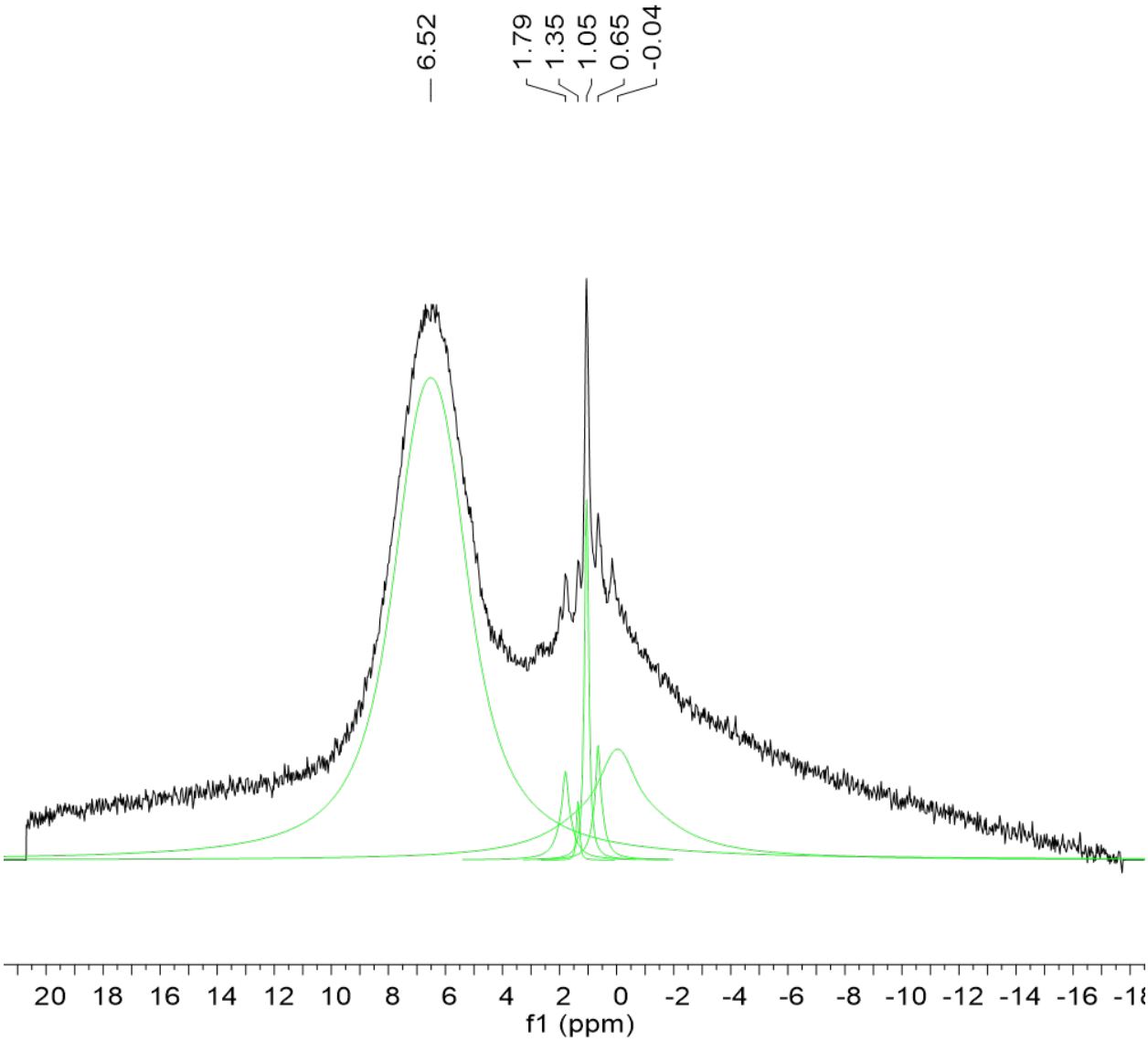


Fig. S8 *Normalized 600 MHz ^{1}H NMR spectra of empty 3.2 mm zirconia rotor. Spinning at 20 kHz with a relaxation delay of 2 s. 16 scans*

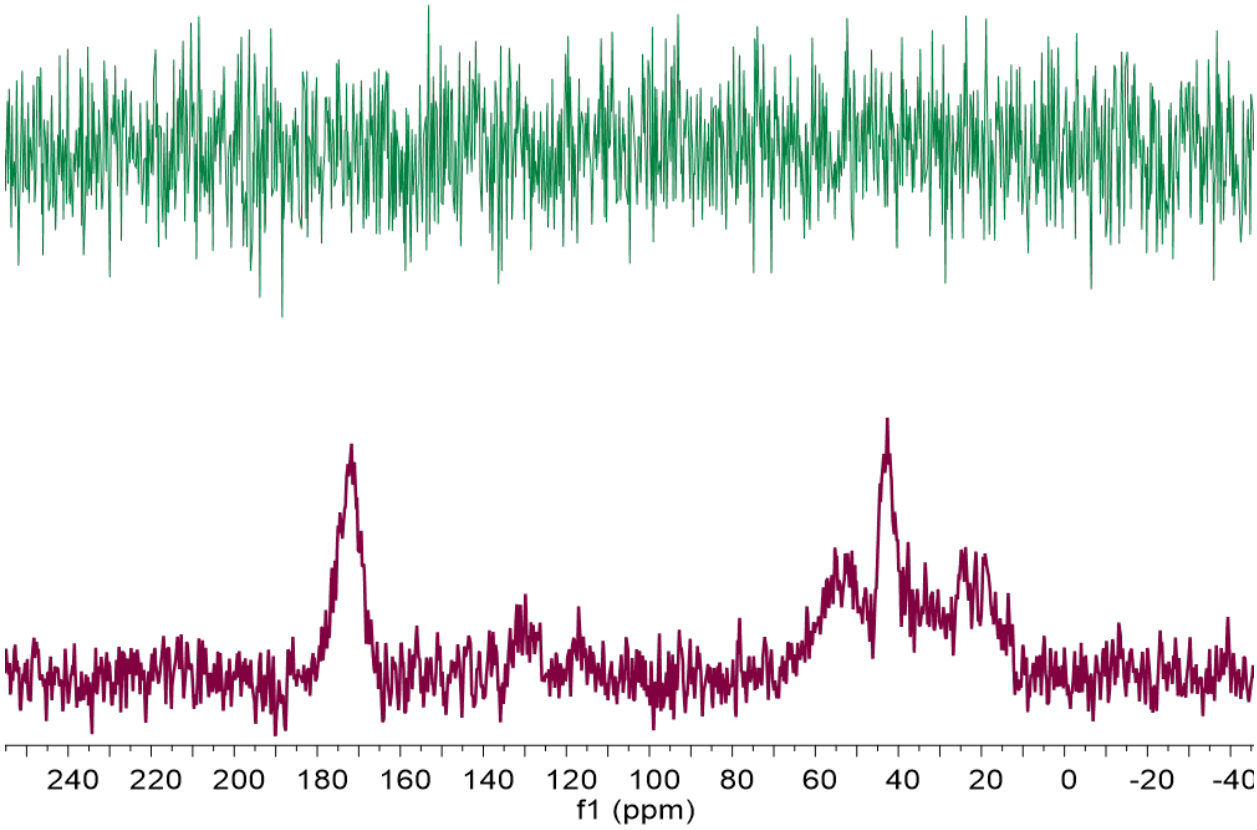


Fig. S9 *^{13}C CP MAS NMR spectra of the inner nacreous layer of blue mussel (teal) that is a result of heating the shells to 220 °C for 48 h and untreated mussel shells (purple). Acquisition of the two spectra had the same experimental conditions. 3.2 mm zirconia rotor spinning at 20 kHz with a contact time of 1 ms. Proton decoupling level of 100 kHz and a relaxation delay of 1 s. Hartmann-Hahn rf was matched to 62.5 kHz. 16k scans.*

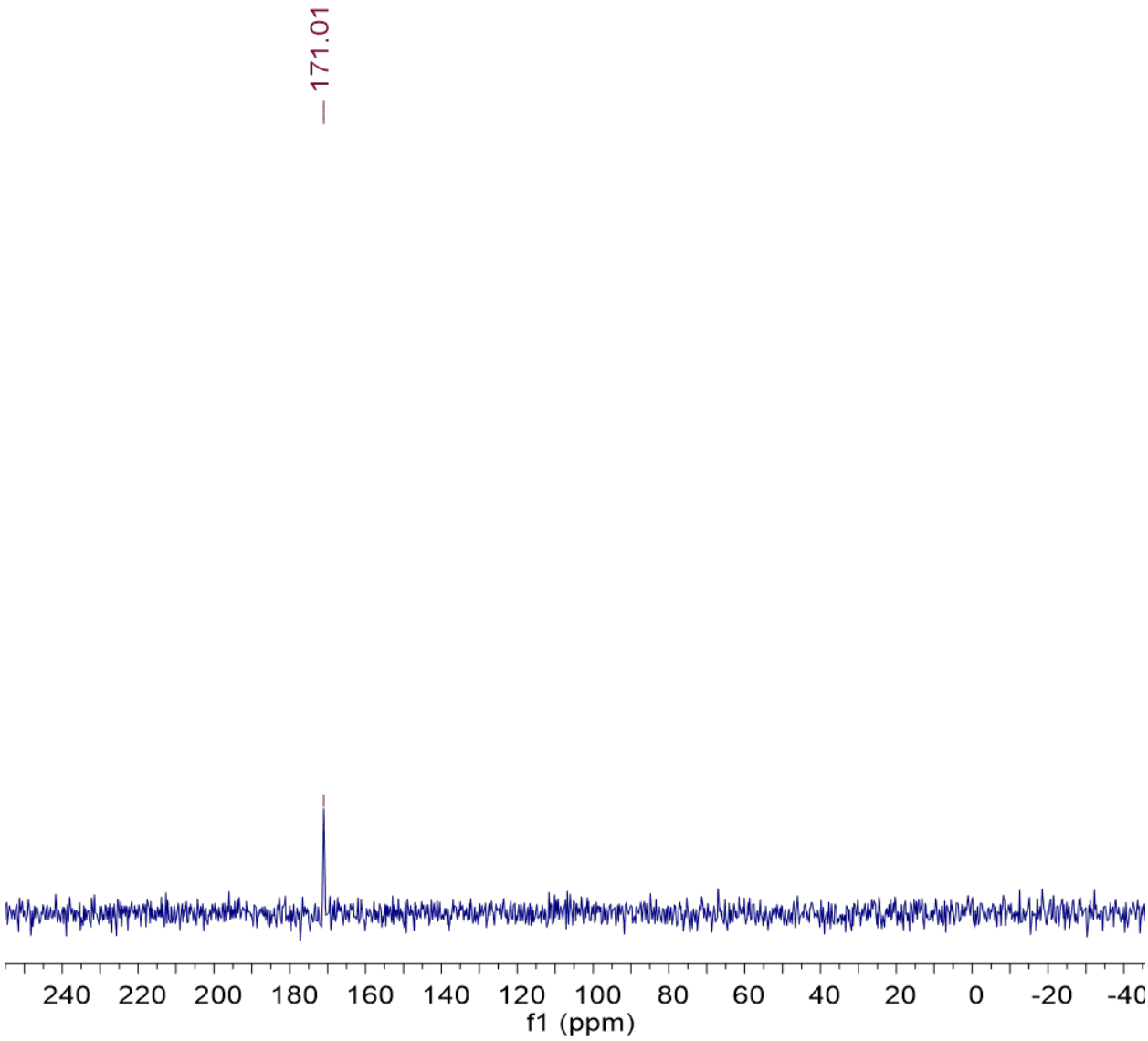


Fig. S10 *^{13}C DE MAS NMR of the inner nacreous layer of blue mussel shells ground with a mortar and pestle. 3.2 mm zirconia rotor. Spinning at 20 kHz with a proton decoupling level of 100 kHz and a relaxation delay of 320 s. 60 scans.*

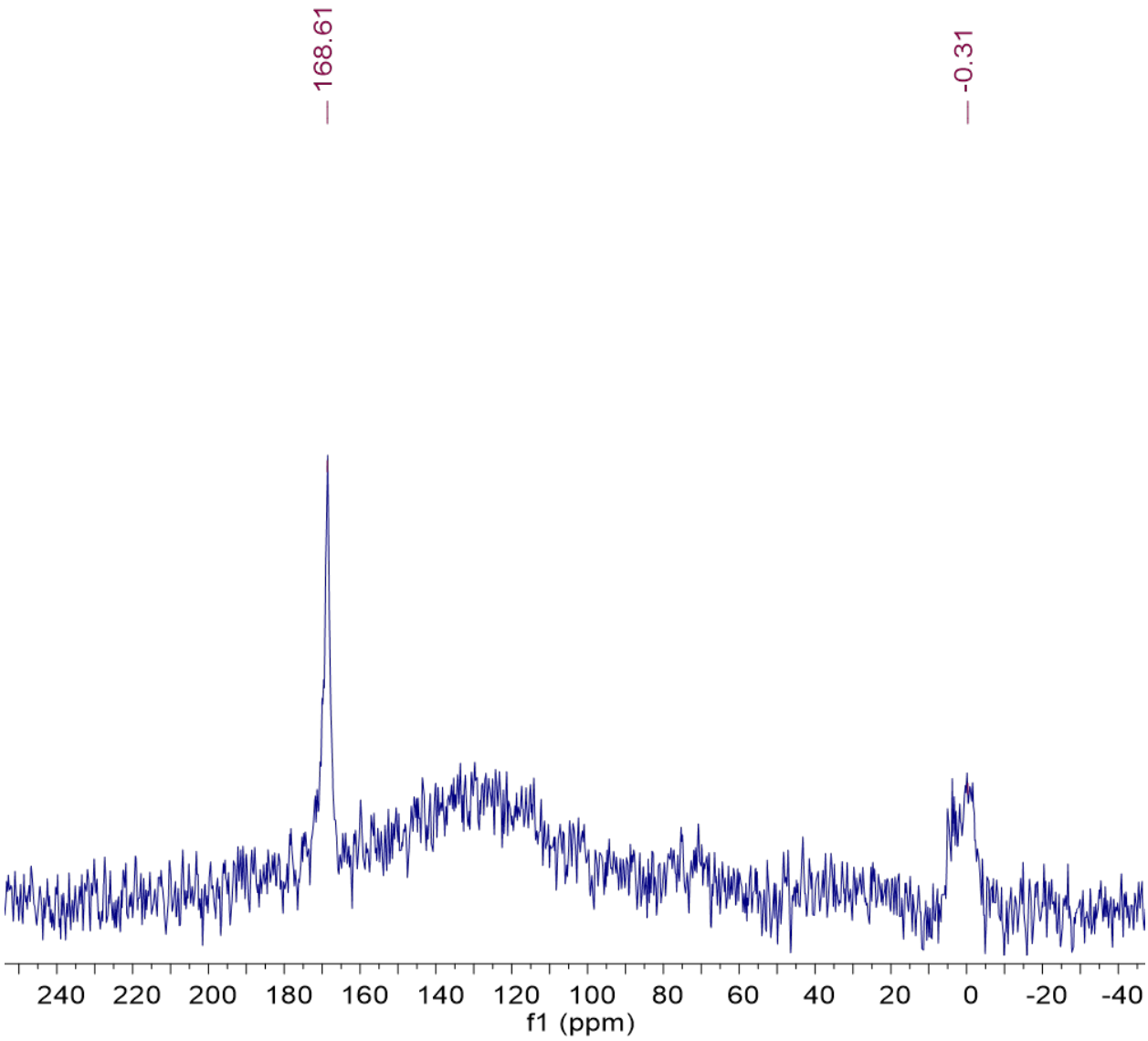


Fig. S11 *^{13}C DE MAS NMR of the outer prismatic layer of blue mussel shells ground with a mortar and pestle. 3.2 mm zirconia rotor. Spinning at 20 kHz with a proton decoupling level of 100 kHz and a relaxation delay of 10 s. 8k scans.*

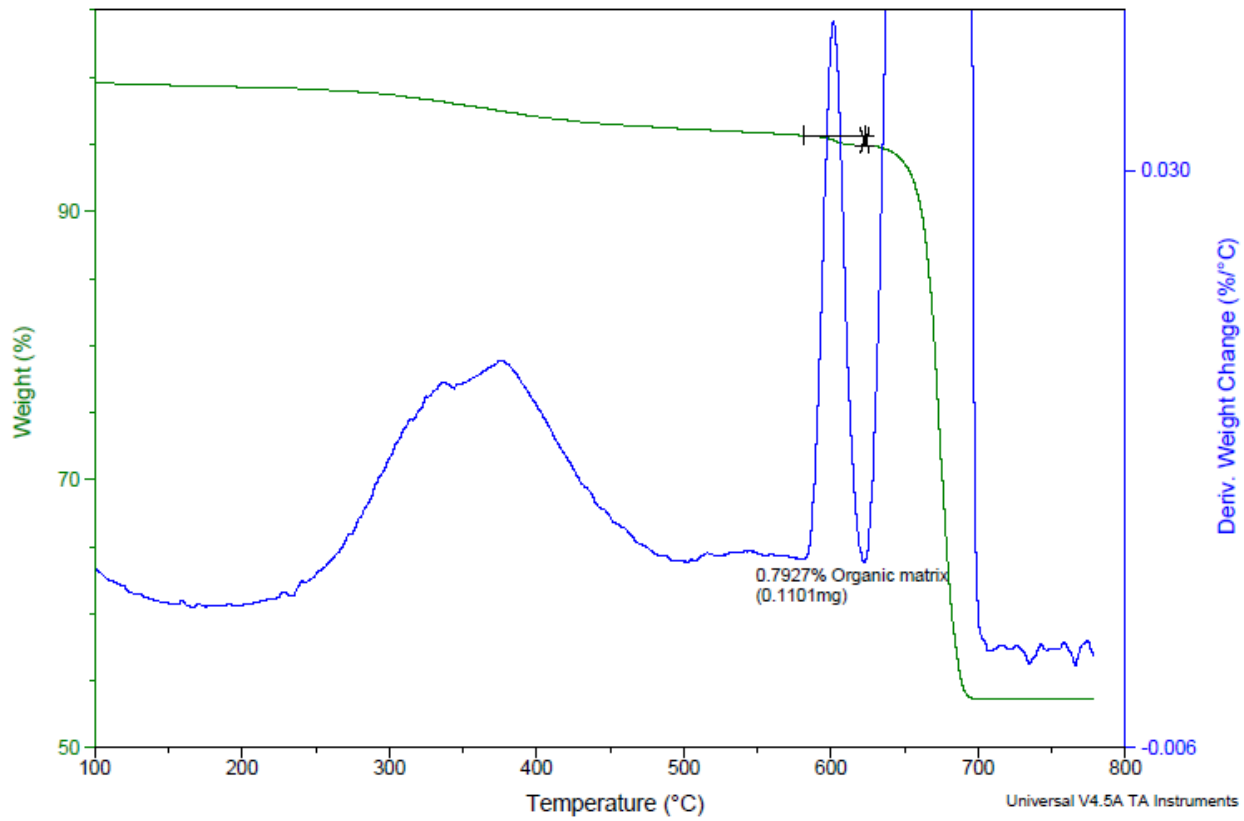


Fig. S12 *Thermogravimetric analysis of untreated blue mussel shells.*

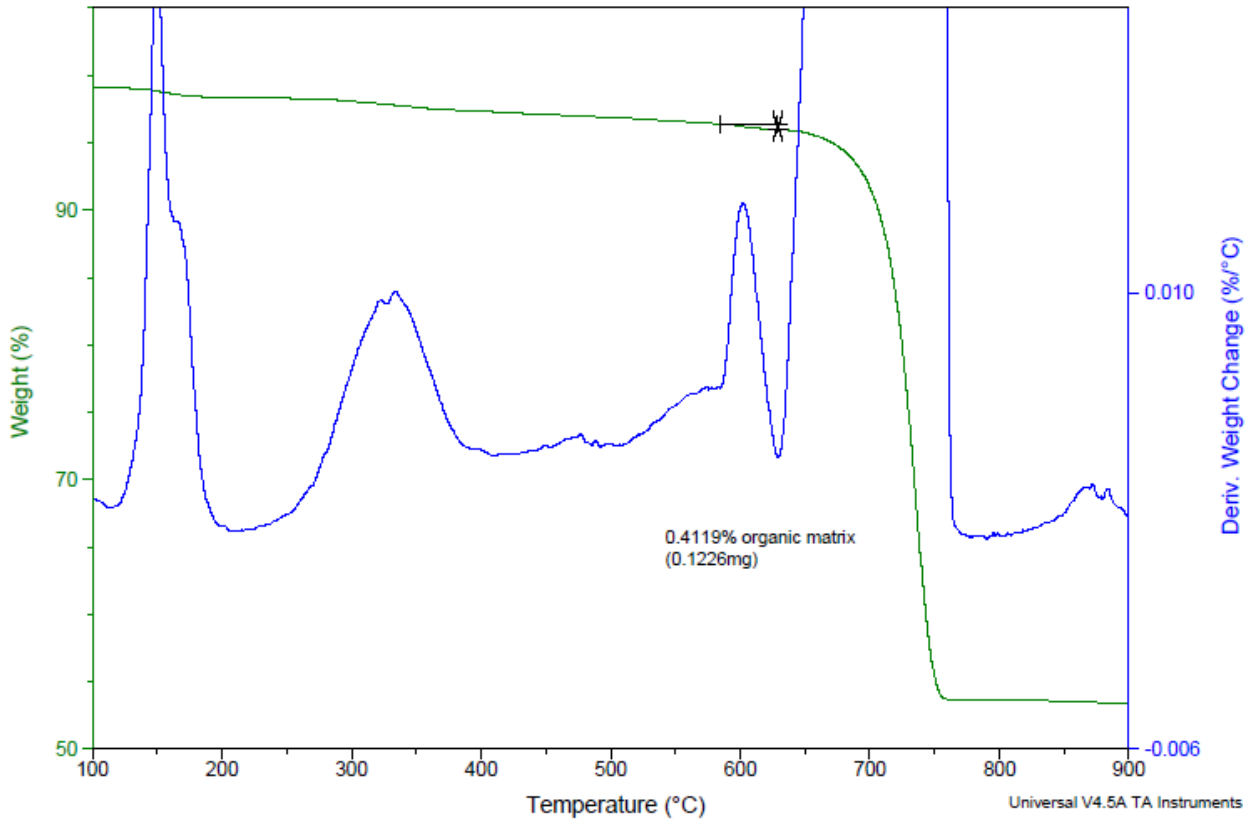


Fig. S13 *Thermogravimetric analysis of blue mussel shells that have been heated to 220 °C for 48 h.*

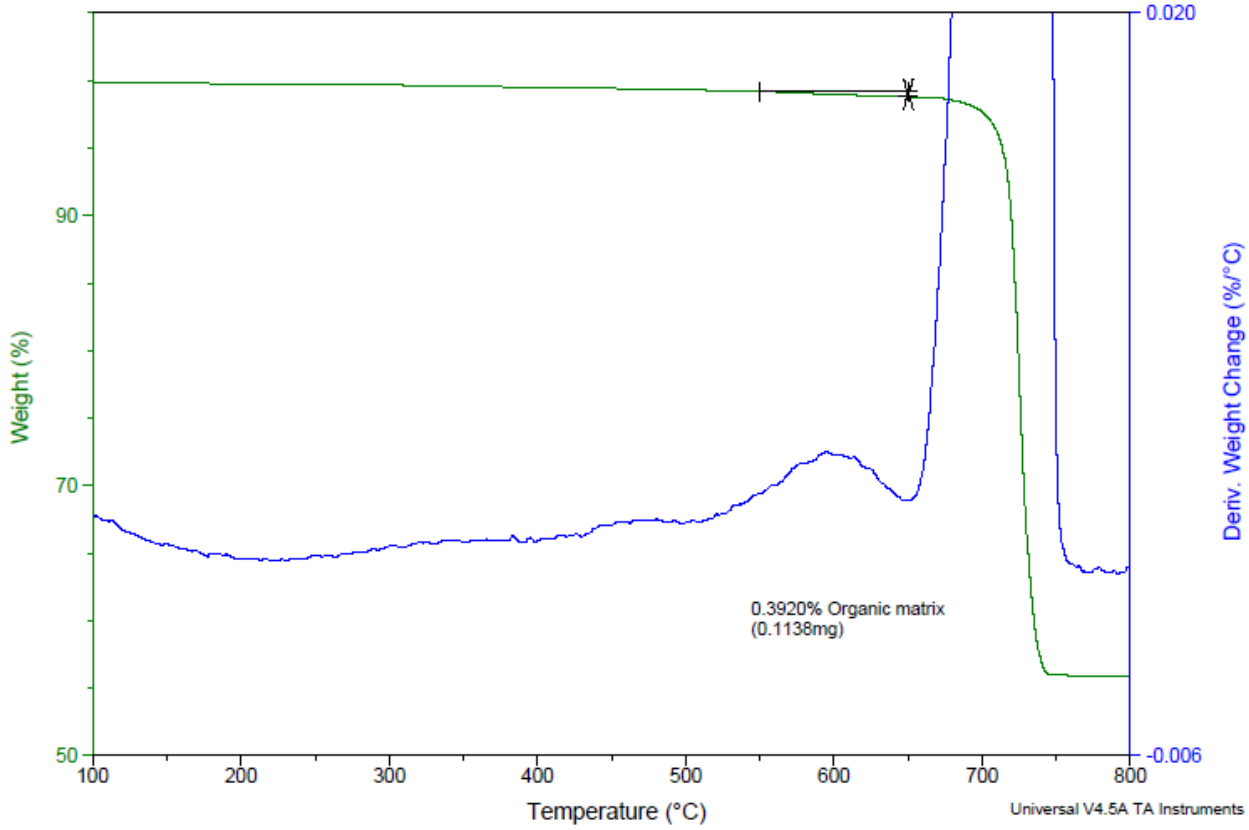


Fig. S14 *Thermogravimetric analysis of the outer layer of blue mussel shells.*

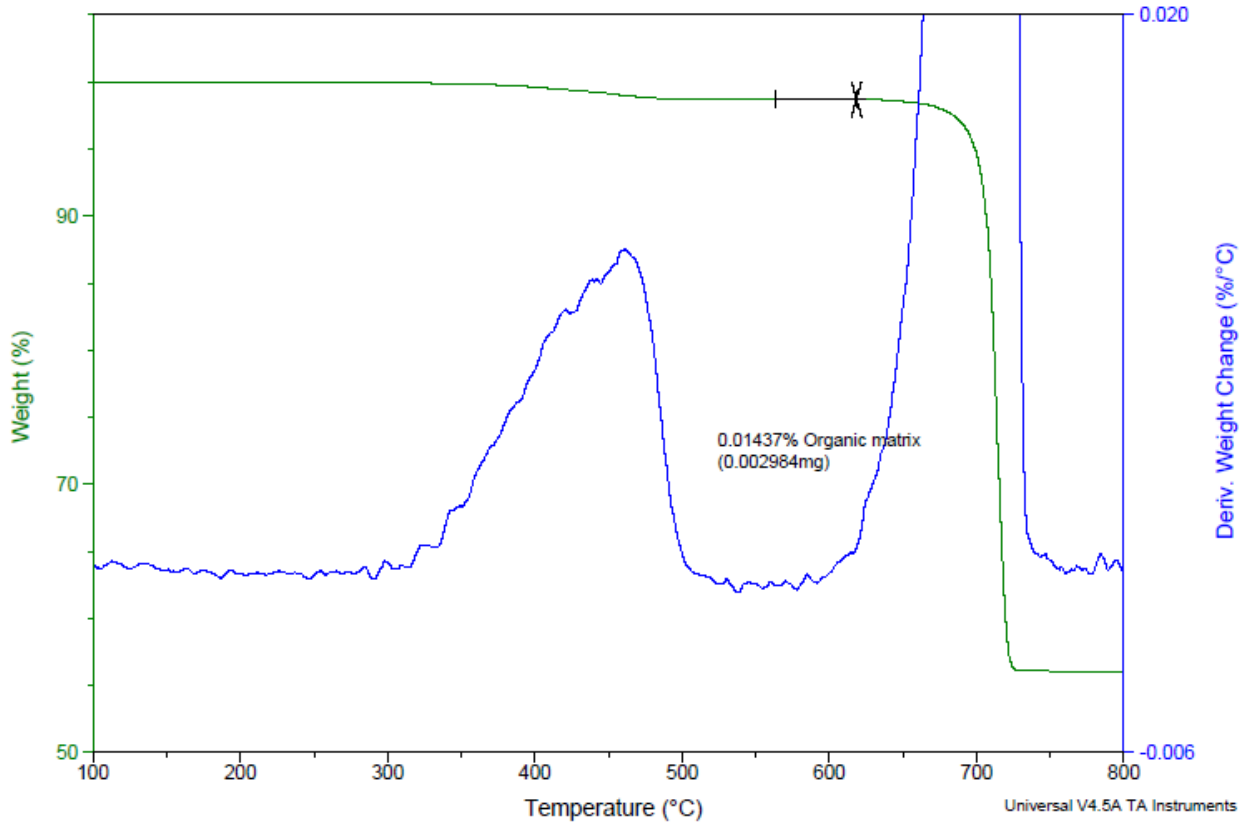


Fig. S15 *Thermogravimetric analysis of the inner layer of blue mussel shells.*

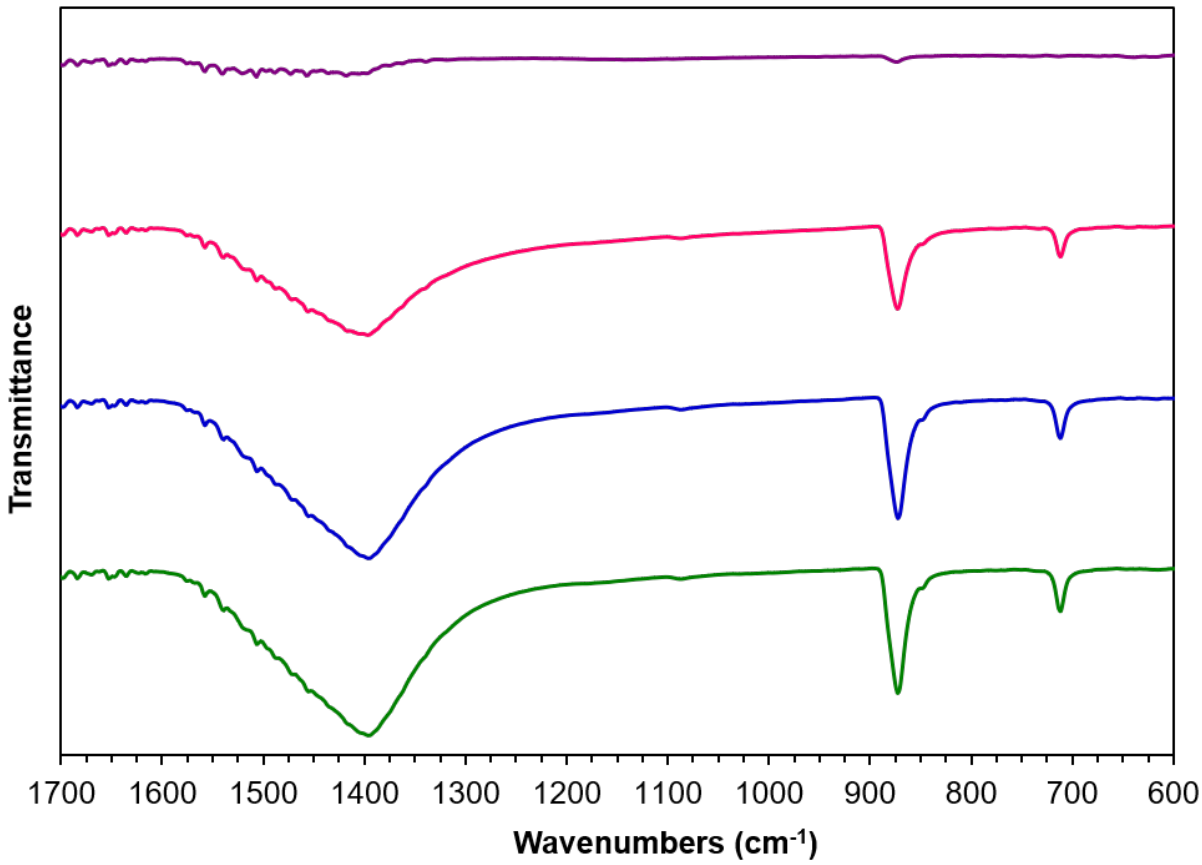


Fig. S16 *Infrared spectra of blue mussels treated from 450 °C (green), 550 °C (blue), 650 °C (pink) and 750 °C (purple) for 2 h.*

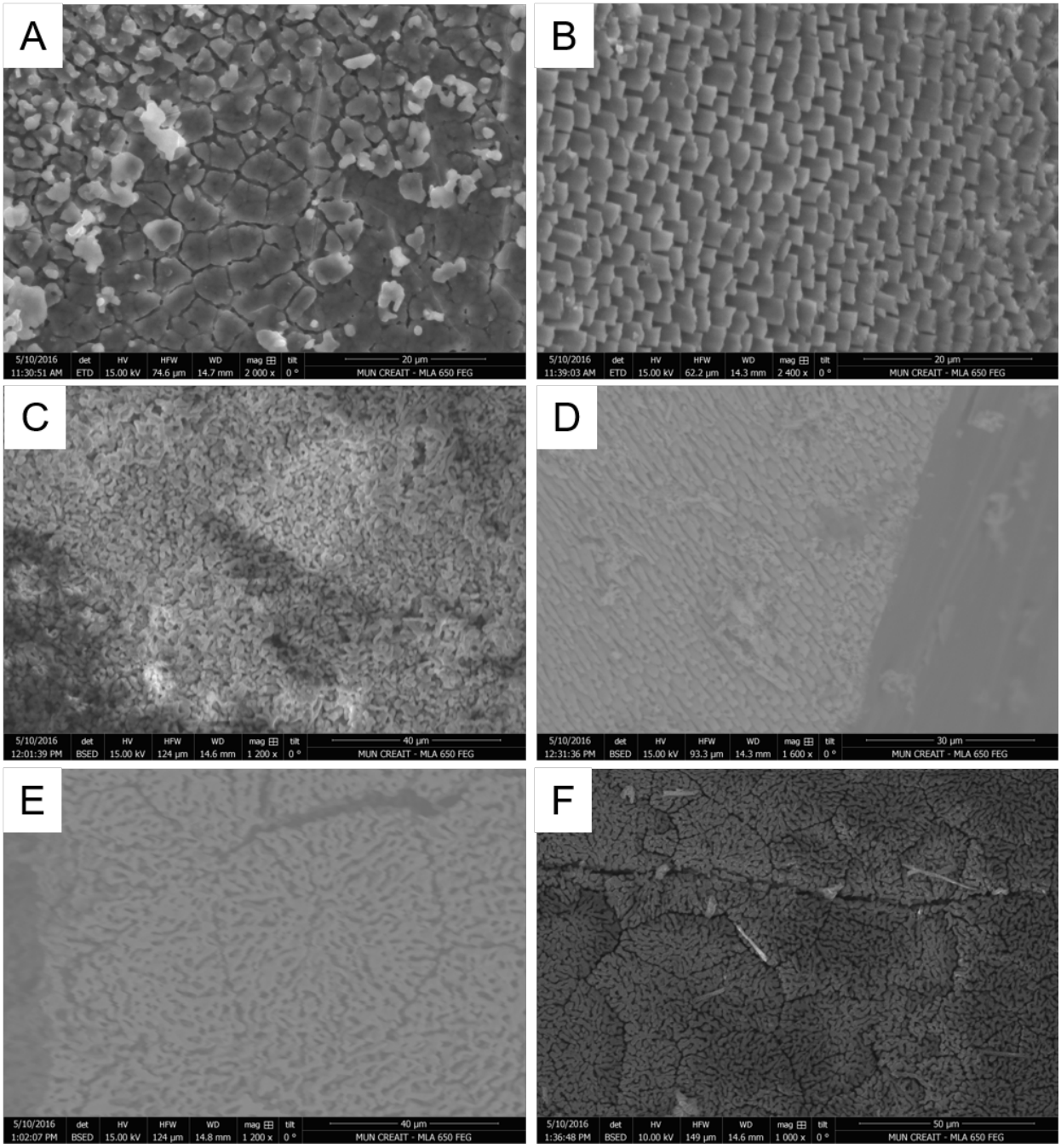


Fig. S17 *SEM micrographs of A) the inner layer of blue mussel shell after heating to 450 °C, B) the outer layer of blue mussel shell after heating to 450 °C, C) the inner layer of blue mussel shell after heating to 550 °C, D) the outer layer of blue mussel shell after heating to 550 °C, E) the inner layer of blue mussel shell after heating to 650 °C and F) the inner layer of blue mussel shell after heating to 650 °C. Shells were heated for 2 h at their respective temperatures.*

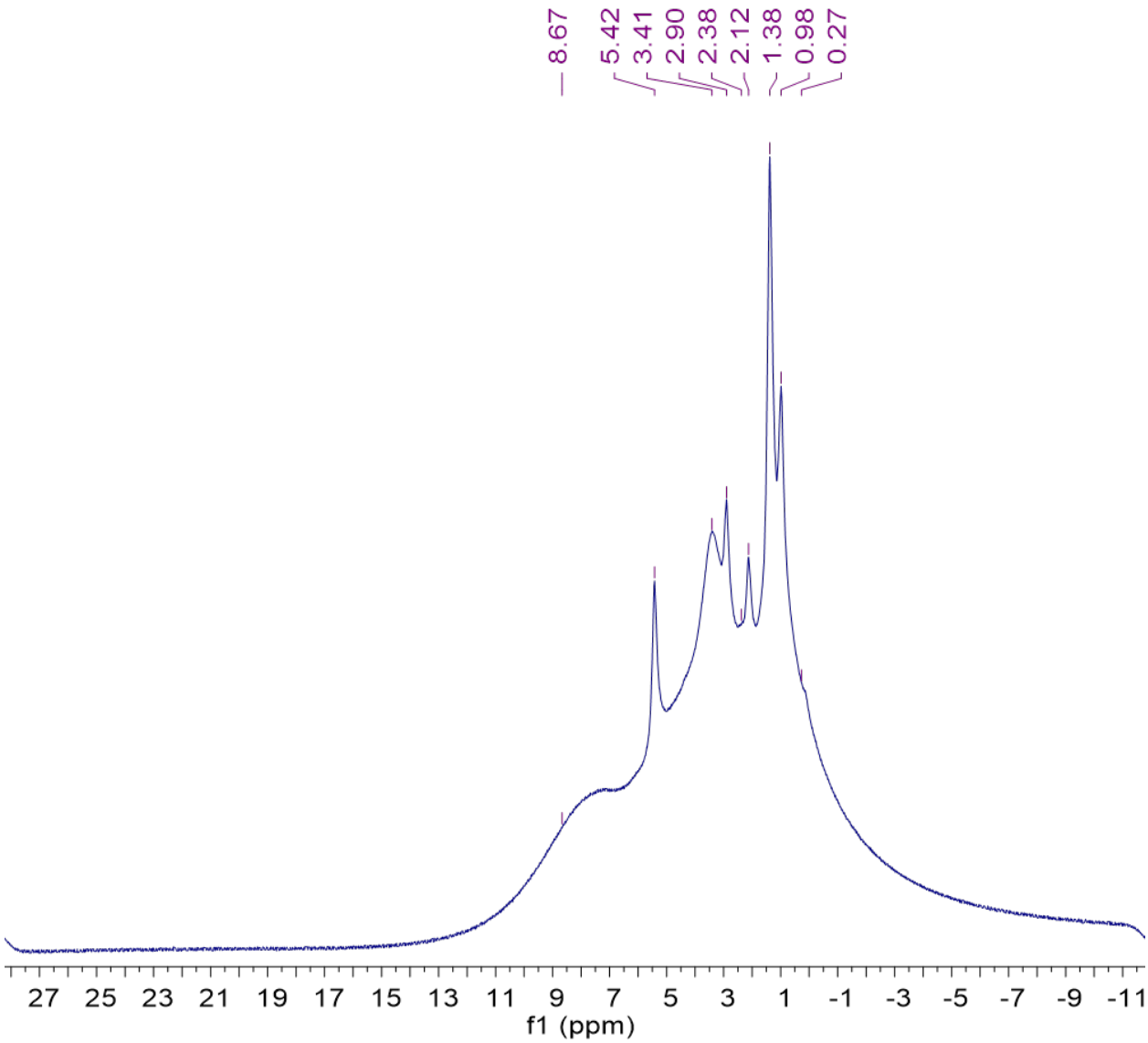


Fig. S18 *Normalized 600 MHz ^{1}H NMR spectra of freeze-dried blue mussel meat. 3.2 mm zirconia rotor and spinning at 20 kHz with a relaxation delay of 5 s. 4 scans.*

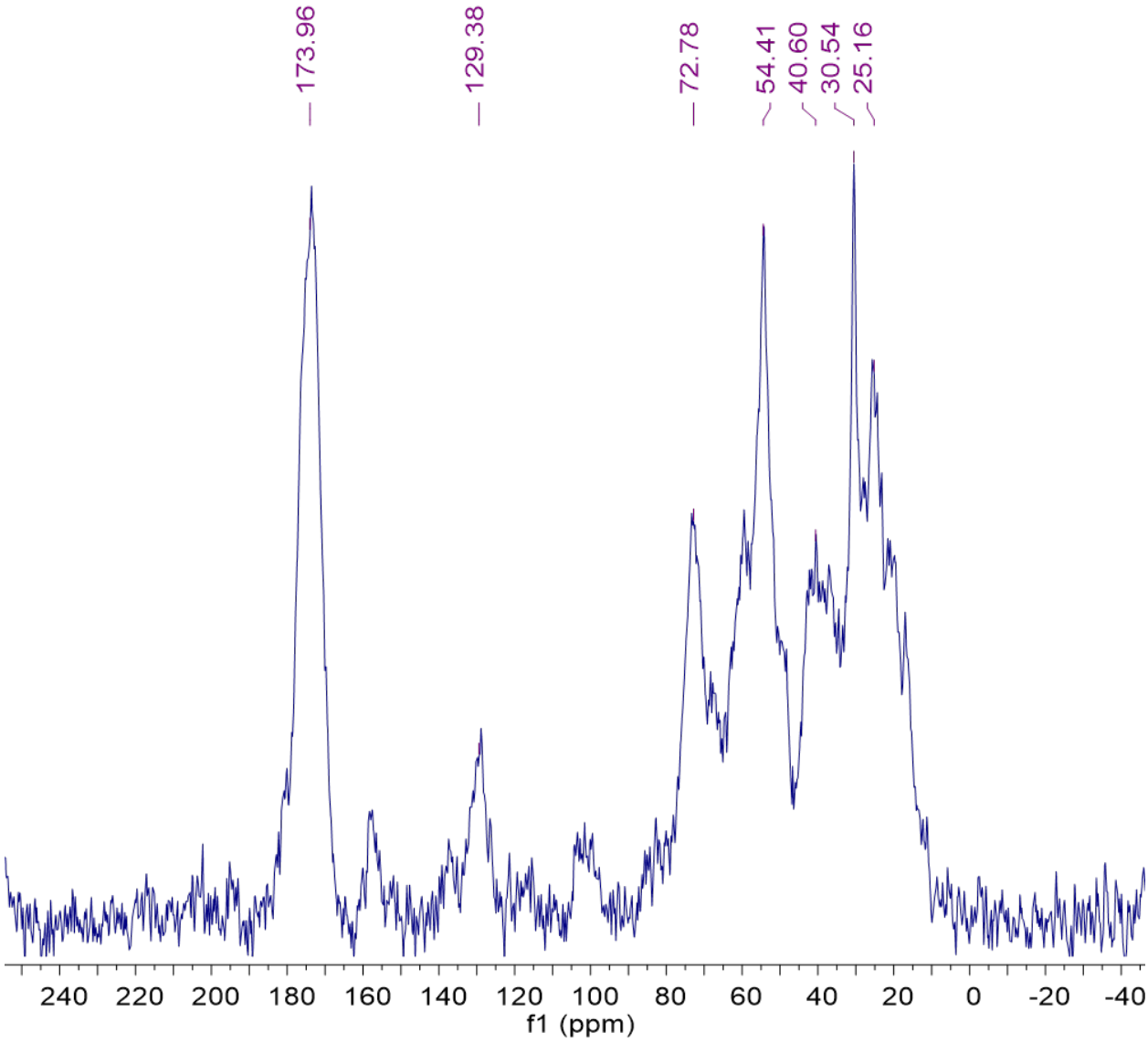


Fig. S19 *^{13}C CP MAS NMR of freeze-dried blue mussel (Mytilus edulis) meat. 3.2 mm zirconia rotor spinning at 20 kHz with a contact time of 2 ms. Proton decoupling level of 100 kHz and a relaxation delay of 3 s. Hartmann-Hahn rf was matched to 62.5 kHz. 1k scans.*

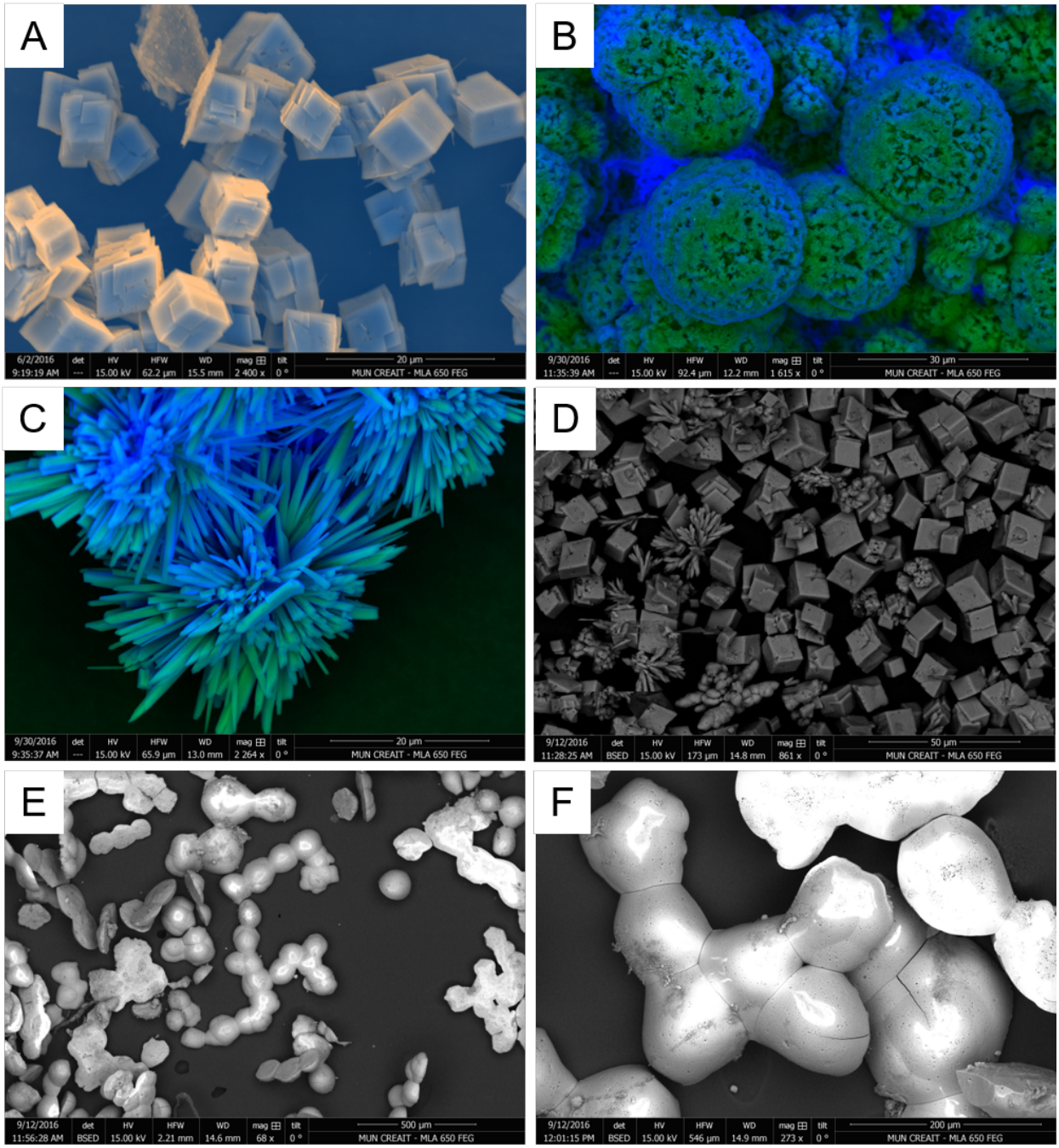


Fig. S20 *Representative SEM micrographs of synthetic $CaCO_3$ products. A) calcite, B) vaterite, C) aragonite, D) mixture of calcite, aragonite and vaterite, E) vaterite with a unique formation, similar to nacre and F) zoomed in region of vaterite.*

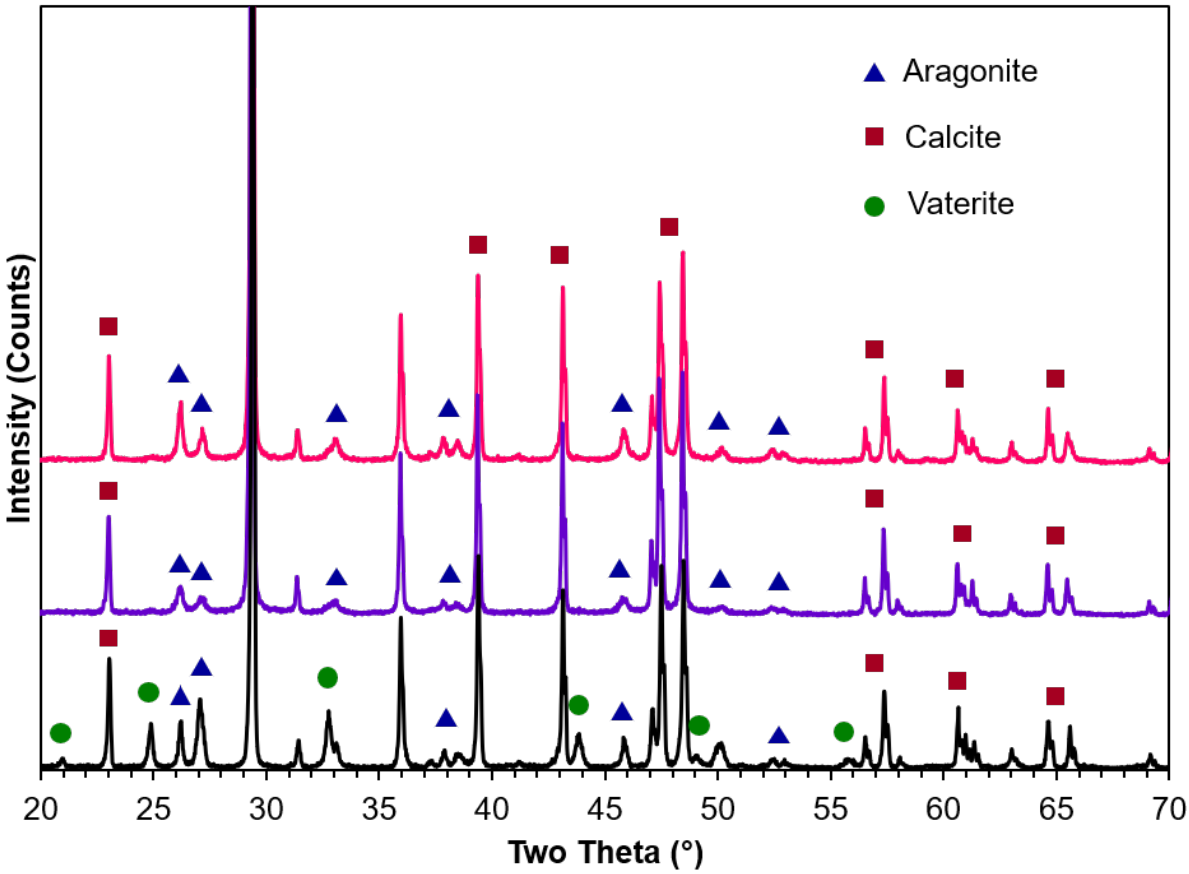
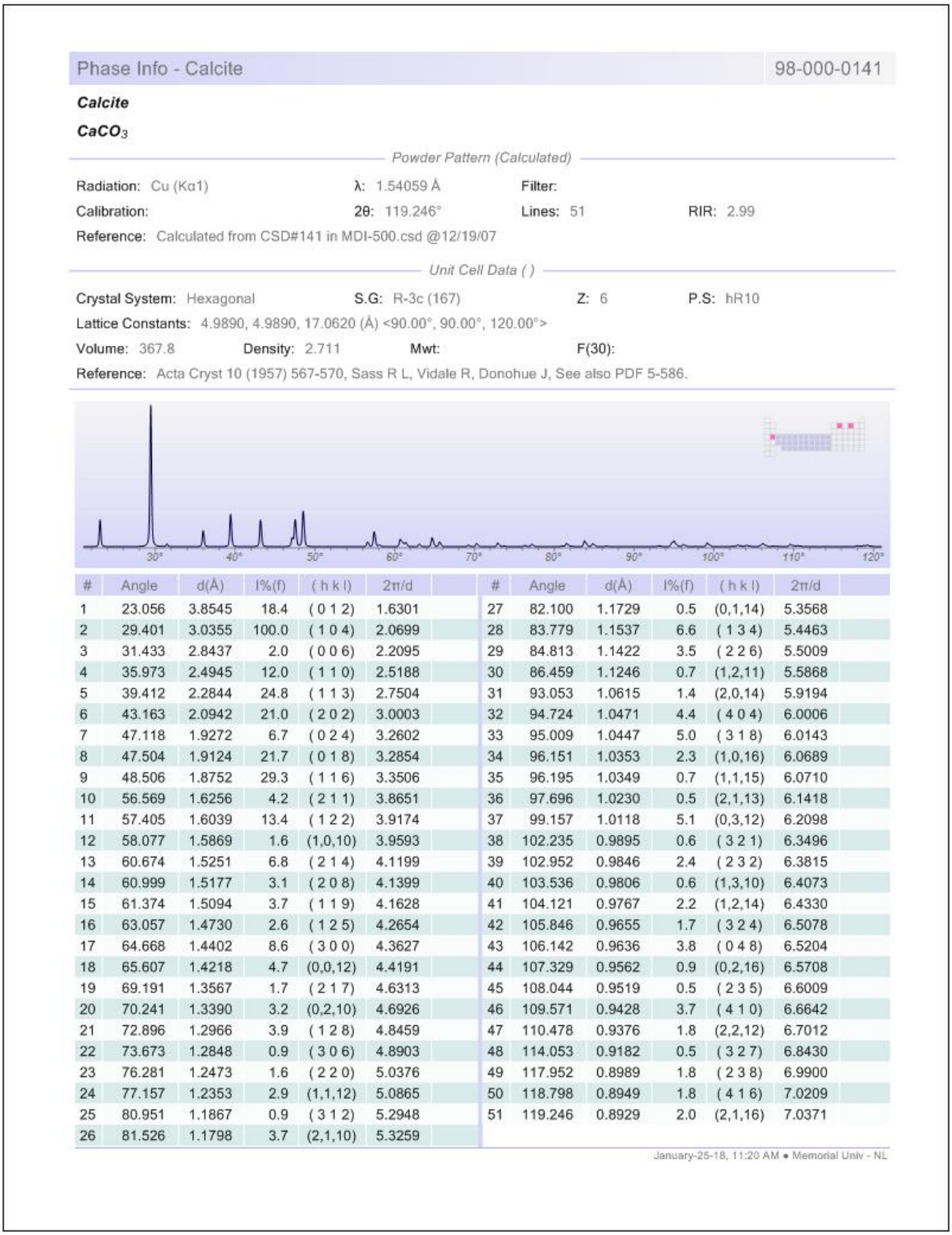


Fig. S21 Powder XRD diffractograms for synthetic $CaCO_3$ products from reaction conditions 0.8 M $CaCl_2$ and Na_2CO_3 (black), 0.8 M $CaCl_2$ and Na_2CO_3 with the addition of mussel protein hydrolysate (purple) and 0.8 M $CaCl_2$ and Na_2CO_3 with the addition of mussel protein hydrolysate and mussel shells for seeding nacre (pink). Identification of polymorphs denoted by blue triangles for aragonite, red squares for calcite and green circles for vaterite.

Fig. S22 Examples of colour and texture of dyed nacre and its use in UV cure gel nail enhancements.



Phase Info - Calcite 98-000-0141

Calcite

$CaCO_3$

Powder Pattern (Calculated)

Radiation: Cu (Kα1) λ: 1.54059 Å Filter:

Calibration: 2θ: 119.246° Lines: 51 RIR: 2.99

Reference: Calculated from CSD#141 in MDI-500.csd @12/19/07

Unit Cell Data ( )

Crystal System: Hexagonal S.G: R-3c (167) Z: 6 P.S: hR10

Lattice Constants: 4.9890, 4.9890, 17.0620 (Å) <90.00°, 90.00°, 120.00°>

Volume: 367.8 Density: 2.711 Mwt: F(30):

Reference: Acta Cryst 10 (1957) 567-570, Sass R L, Vidale R, Donohue J, See also PDF 5-586.

#	Angle	d(Å)	I%(f)	(h k l)	2π/d	#	Angle	d(Å)	I%(f)	(h k l)	2π/d
1	23.056	3.8545	18.4	(0 1 2)	1.6301	27	82.100	1.1729	0.5	(0,1,14)	5.3568
2	29.401	3.0355	100.0	(1 0 4)	2.0699	28	83.779	1.1537	6.6	(1 3 4)	5.4463
3	31.433	2.8437	2.0	(0 0 6)	2.2095	29	84.813	1.1422	3.5	(2 2 6)	5.5009
4	35.973	2.4945	12.0	(1 1 0)	2.5188	30	86.459	1.1246	0.7	(1,2,11)	5.5868
5	39.412	2.2844	24.8	(1 1 3)	2.7504	31	93.053	1.0615	1.4	(2,0,14)	5.9194
6	43.163	2.0942	21.0	(2 0 2)	3.0003	32	94.724	1.0471	4.4	(4 0 4)	6.0006
7	47.118	1.9272	6.7	(0 2 4)	3.2602	33	95.009	1.0447	5.0	(3 1 8)	6.0143
8	47.504	1.9124	21.7	(0 1 8)	3.2854	34	96.151	1.0353	2.3	(1,0,16)	6.0689
9	48.506	1.8752	29.3	(1 1 6)	3.3506	35	96.195	1.0349	0.7	(1,1,15)	6.0710
10	56.569	1.6256	4.2	(2 1 1)	3.8651	36	97.696	1.0230	0.5	(2,1,13)	6.1418
11	57.405	1.6039	13.4	(1 2 2)	3.9174	37	99.157	1.0118	5.1	(0,3,12)	6.2098
12	58.077	1.5869	1.6	(1,0,10)	3.9593	38	102.235	0.9895	0.6	(3 2 1)	6.3496
13	60.674	1.5251	6.8	(2 1 4)	4.1199	39	102.952	0.9846	2.4	(2 3 2)	6.3815
14	60.999	1.5177	3.1	(2 0 8)	4.1399	40	103.536	0.9806	0.6	(1,3,10)	6.4073
15	61.374	1.5094	3.7	(1 1 9)	4.1628	41	104.121	0.9767	2.2	(1,2,14)	6.4330
16	63.057	1.4730	2.6	(1 2 5)	4.2654	42	105.846	0.9655	1.7	(3 2 4)	6.5078
17	64.668	1.4402	8.6	(3 0 0)	4.3627	43	106.142	0.9636	3.8	(0 4 8)	6.5204
18	65.607	1.4218	4.7	(0,0,12)	4.4191	44	107.329	0.9562	0.9	(0,2,16)	6.5708
19	69.191	1.3567	1.7	(2 1 7)	4.6313	45	108.044	0.9519	0.5	(2 3 5)	6.6009
20	70.241	1.3390	3.2	(0,2,10)	4.6926	46	109.571	0.9428	3.7	(4 1 0)	6.6642
21	72.896	1.2966	3.9	(1 2 8)	4.8459	47	110.478	0.9376	1.8	(2,2,12)	6.7012
22	73.673	1.2848	0.9	(3 0 6)	4.8903	48	114.053	0.9182	0.5	(3 2 7)	6.8430
23	76.281	1.2473	1.6	(2 2 0)	5.0376	49	117.952	0.8989	1.8	(2 3 8)	6.9900
24	77.157	1.2353	2.9	(1,1,12)	5.0865	50	118.798	0.8949	1.8	(4 1 6)	7.0209
25	80.951	1.1867	0.9	(3 1 2)	5.2948	51	119.246	0.8929	2.0	(2,1,16)	7.0371
26	81.526	1.1798	3.7	(2,1,10)	5.3259						

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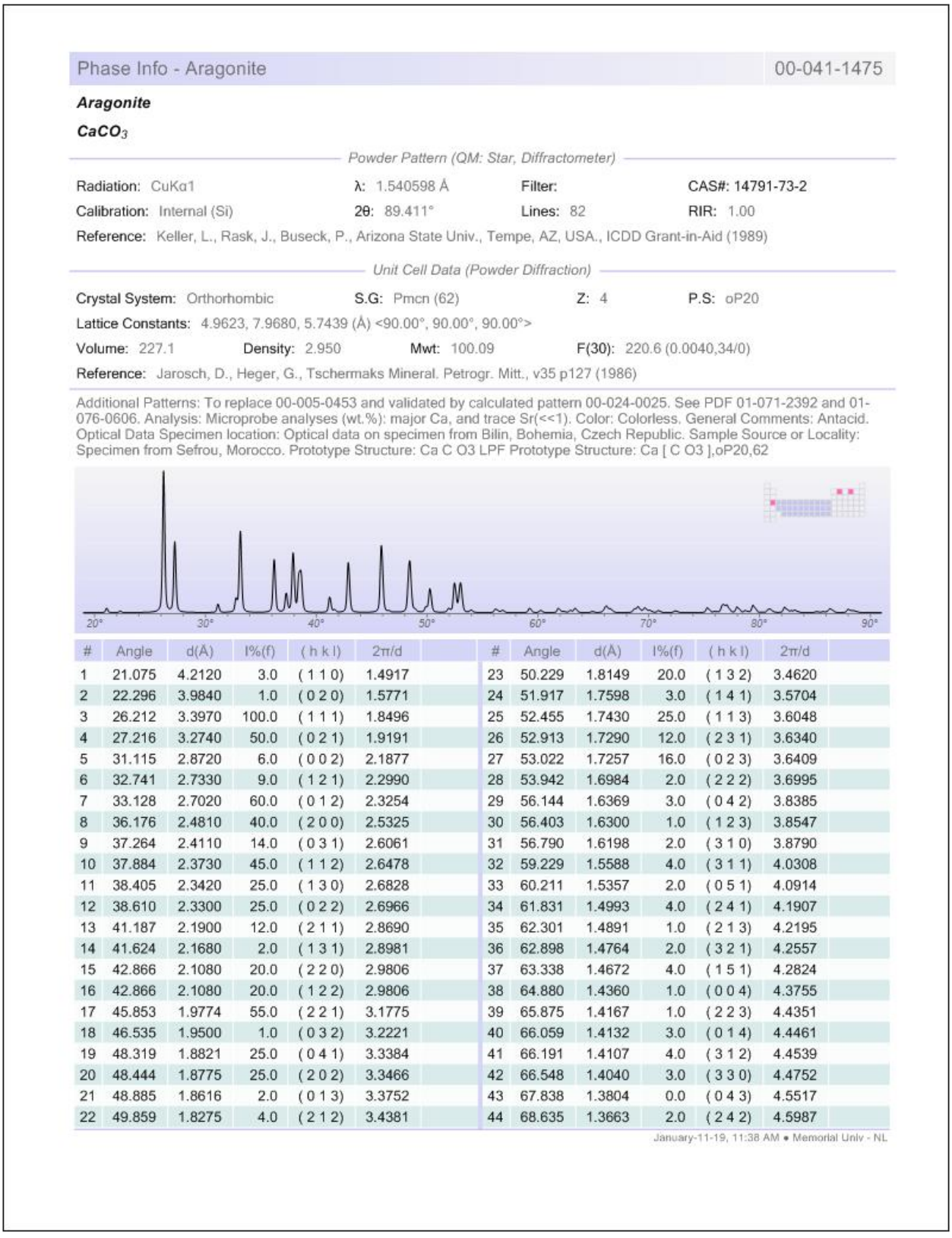
Fig. S23 *Phase information for calcite. For powder XRD comparison and identification purposes. See reference in the image.*



Phase Info - Aragonite 00-041-1475

Aragonite

$CaCO_3$

Powder Pattern (QM: Star, Diffractometer)

Radiation: CuKα1 λ: 1.540598 Å Filter: CAS#: 14791-73-2

Calibration: Internal (Si) 2θ: 89.411° Lines: 82 RIR: 1.00

Reference: Keller, L., Rask, J., Buseck, P., Arizona State Univ., Tempe, AZ, USA., ICDD Grant-in-Aid (1989)

Unit Cell Data (Powder Diffraction)

Crystal System: Orthorhombic S.G: Pmcn (62) Z: 4 P.S: oP20

Lattice Constants: 4.9623, 7.9680, 5.7439 (Å) <90.00°, 90.00°, 90.00°>

Volume: 227.1 Density: 2.950 Mwt: 100.09 F(30): 220.6 (0.0040,34/0)

Reference: Jarosch, D., Heger, G., Tschermaks Mineral. Petrogr. Mitt., v35 p127 (1986)

Additional Patterns: To replace 00-005-0453 and validated by calculated pattern 00-024-0025. See PDF 01-071-2392 and 01-076-0606. Analysis: Microprobe analyses (wt.%): major Ca, and trace Sr(<<1). Color: Colorless. General Comments: Antacid. Optical Data Specimen location: Optical data on specimen from Bilin, Bohemia, Czech Republic. Sample Source or Locality: Specimen from Sefrou, Morocco. Prototype Structure: Ca C O3 LPF Prototype Structure: Ca [C O3],oP20,62

#	Angle	d(Å)	I%(f)	(h k l)	2π/d	#	Angle	d(Å)	I%(f)	(h k l)	2π/d
1	21.075	4.2120	3.0	(1 1 0)	1.4917	23	50.229	1.8149	20.0	(1 3 2)	3.4620
2	22.296	3.9840	1.0	(0 2 0)	1.5771	24	51.917	1.7598	3.0	(1 4 1)	3.5704
3	26.212	3.3970	100.0	(1 1 1)	1.8496	25	52.455	1.7430	25.0	(1 1 3)	3.6048
4	27.216	3.2740	50.0	(0 2 1)	1.9191	26	52.913	1.7290	12.0	(2 3 1)	3.6340
5	31.115	2.8720	6.0	(0 0 2)	2.1877	27	53.022	1.7257	16.0	(0 2 3)	3.6409
6	32.741	2.7330	9.0	(1 2 1)	2.2990	28	53.942	1.6984	2.0	(2 2 2)	3.6995
7	33.128	2.7020	60.0	(0 1 2)	2.3254	29	56.144	1.6369	3.0	(0 4 2)	3.8385
8	36.176	2.4810	40.0	(2 0 0)	2.5325	30	56.403	1.6300	1.0	(1 2 3)	3.8547
9	37.264	2.4110	14.0	(0 3 1)	2.6061	31	56.790	1.6198	2.0	(3 1 0)	3.8790
10	37.884	2.3730	45.0	(1 1 2)	2.6478	32	59.229	1.5588	4.0	(3 1 1)	4.0308
11	38.405	2.3420	25.0	(1 3 0)	2.6828	33	60.211	1.5357	2.0	(0 5 1)	4.0914
12	38.610	2.3300	25.0	(0 2 2)	2.6966	34	61.831	1.4993	4.0	(2 4 1)	4.1907
13	41.187	2.1900	12.0	(2 1 1)	2.8690	35	62.301	1.4891	1.0	(2 1 3)	4.2195
14	41.624	2.1680	2.0	(1 3 1)	2.8981	36	62.898	1.4764	2.0	(3 2 1)	4.2557
15	42.866	2.1080	20.0	(2 2 0)	2.9806	37	63.338	1.4672	4.0	(1 5 1)	4.2824
16	42.866	2.1080	20.0	(1 2 2)	2.9806	38	64.880	1.4360	1.0	(0 0 4)	4.3755
17	45.853	1.9774	55.0	(2 2 1)	3.1775	39	65.875	1.4167	1.0	(2 2 3)	4.4351
18	46.535	1.9500	1.0	(0 3 2)	3.2221	40	66.059	1.4132	3.0	(0 1 4)	4.4461
19	48.319	1.8821	25.0	(0 4 1)	3.3384	41	66.191	1.4107	4.0	(3 1 2)	4.4539
20	48.444	1.8775	25.0	(2 0 2)	3.3466	42	66.548	1.4040	3.0	(3 3 0)	4.4752
21	48.885	1.8616	2.0	(0 1 3)	3.3752	43	67.838	1.3804	0.0	(0 4 3)	4.5517
22	49.859	1.8275	4.0	(2 1 2)	3.4381	44	68.635	1.3663	2.0	(2 4 2)	4.5987

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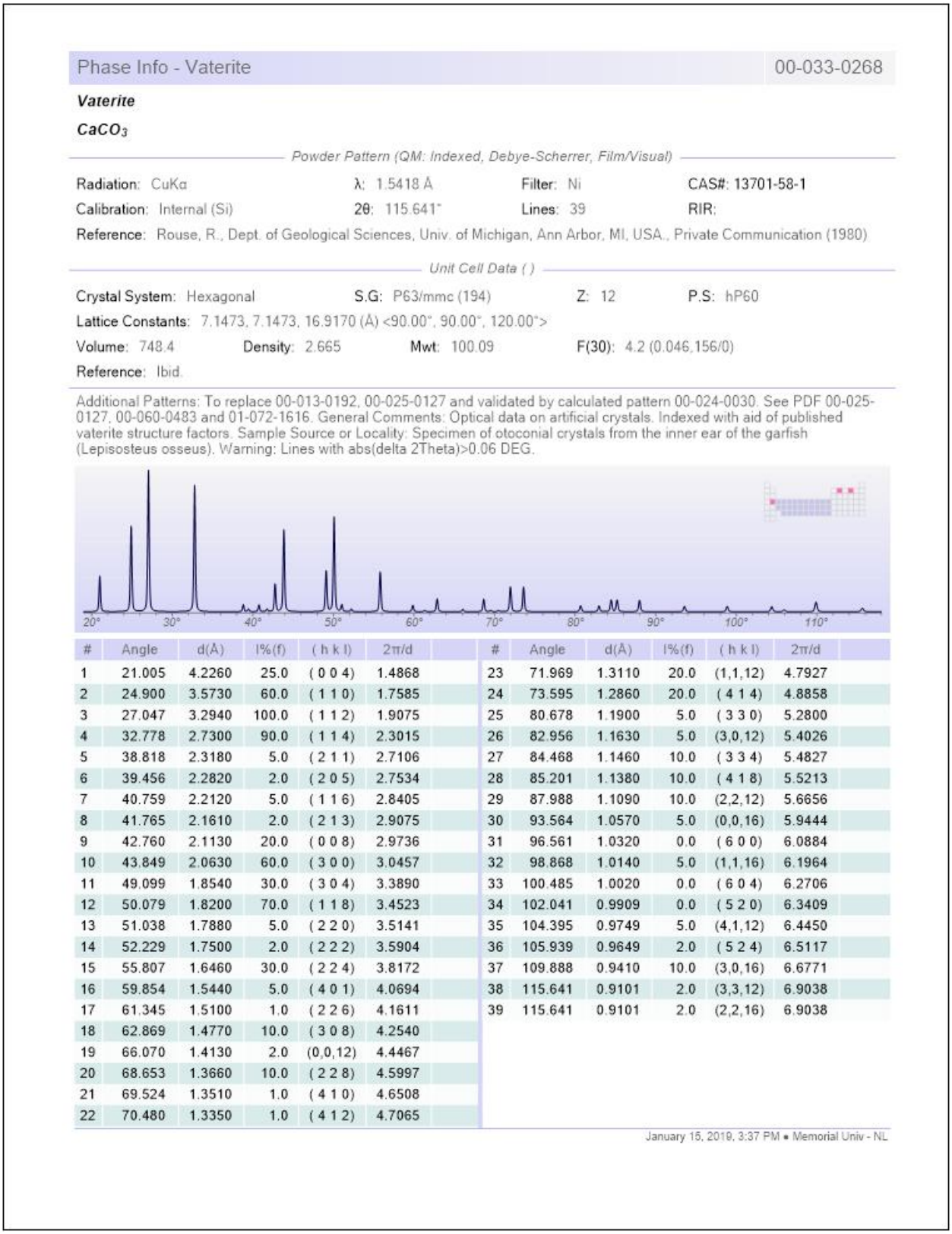
Fig. S24 *Phase information for aragonite. For powder XRD comparison and identification purposes. See reference in the image.*



Phase Info - Vaterite 00-033-0268

Vaterite

$CaCO_3$

Powder Pattern (QM: Indexed, Debye-Scherrer, Film/Visual)

Radiation: CuKα λ: 1.5418 Å Filter: Ni CAS#: 13701-58-1

Calibration: Internal (Si) 2θ: 115.641° Lines: 39 RIR:

Reference: Rouse, R., Dept. of Geological Sciences, Univ. of Michigan, Ann Arbor, MI, USA., Private Communication (1980)

Unit Cell Data ( )

Crystal System: Hexagonal S.G: P63/mmc (194) Z: 12 P.S: hP60

Lattice Constants: 7.1473, 7.1473, 16.9170 (Å) <90.00°, 90.00°, 120.00°>

Volume: 748.4 Density: 2.665 Mwt: 100.09 F(30): 4.2 (0.046,156/0)

Reference: Ibid.

Additional Patterns: To replace 00-013-0192, 00-025-0127 and validated by calculated pattern 00-024-0030. See PDF 00-025-0127, 00-060-0483 and 01-072-1616. General Comments: Optical data on artificial crystals. Indexed with aid of published vaterite structure factors. Sample Source or Locality: Specimen of otoconial crystals from the inner ear of the garfish (Lepisosteus osseus). Warning: Lines with abs(delta 2Theta)>0.06 DEG.

#	Angle	d(Å)	I%(f)	(h k l)	2π/d	#	Angle	d(Å)	I%(f)	(h k l)	2π/d
1	21.005	4.2260	25.0	(0 0 4)	1.4868	23	71.969	1.3110	20.0	(1,1,12)	4.7927
2	24.900	3.5730	60.0	(1 1 0)	1.7585	24	73.595	1.2860	20.0	(4 1 4)	4.8858
3	27.047	3.2940	100.0	(1 1 2)	1.9075	25	80.678	1.1900	5.0	(3 3 0)	5.2800
4	32.778	2.7300	90.0	(1 1 4)	2.3015	26	82.956	1.1630	5.0	(3,0,12)	5.4026
5	38.818	2.3180	5.0	(2 1 1)	2.7106	27	84.468	1.1460	10.0	(3 3 4)	5.4827
6	39.456	2.2820	2.0	(2 0 5)	2.7534	28	85.201	1.1380	10.0	(4 1 8)	5.5213
7	40.759	2.2120	5.0	(1 1 6)	2.8405	29	87.988	1.1090	10.0	(2,2,12)	5.6656
8	41.765	2.1610	2.0	(2 1 3)	2.9075	30	93.564	1.0570	5.0	(0,0,16)	5.9444
9	42.760	2.1130	20.0	(0 0 8)	2.9736	31	96.561	1.0320	0.0	(6 0 0)	6.0884
10	43.849	2.0630	60.0	(3 0 0)	3.0457	32	98.868	1.0140	5.0	(1,1,16)	6.1964
11	49.099	1.8540	30.0	(3 0 4)	3.3890	33	100.485	1.0020	0.0	(6 0 4)	6.2706
12	50.079	1.8200	70.0	(1 1 8)	3.4523	34	102.041	0.9909	0.0	(5 2 0)	6.3409
13	51.038	1.7880	5.0	(2 2 0)	3.5141	35	104.395	0.9749	5.0	(4,1,12)	6.4450
14	52.229	1.7500	2.0	(2 2 2)	3.5904	36	105.939	0.9649	2.0	(5 2 4)	6.5117
15	55.807	1.6460	30.0	(2 2 4)	3.8172	37	109.888	0.9410	10.0	(3,0,16)	6.6771
16	59.854	1.5440	5.0	(4 0 1)	4.0694	38	115.641	0.9101	2.0	(3,3,12)	6.9038
17	61.345	1.5100	1.0	(2 2 6)	4.1611	39	115.641	0.9101	2.0	(2,2,16)	6.9038
18	62.869	1.4770	10.0	(3 0 8)	4.2540						
19	66.070	1.4130	2.0	(0,0,12)	4.4467						
20	68.653	1.3660	10.0	(2 2 8)	4.5997						
21	69.524	1.3510	1.0	(4 1 0)	4.6508						
22	70.480	1.3350	1.0	(4 1 2)	4.7065						

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Fig. S25 *Phase information for vaterite. For powder XRD comparison and identification purposes. See reference in the image.*