Electronic Supplementary Material (ESI) for CrystEngComm.

Project M: Investigating the effect of additives on calcium carbonate crystallisation through a school citizen science program.

Supplementary Information

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Methods

Materials

The following chemicals were purchased or donated by Sigma Aldrich and used as received; $CaCl_2.2H_2O$ and Na_2CO_3 (both ACS reagents, 99.5%), Adipic Acid (99%), L-Alanine (≥98%), L-Arginine(≥98%), L-Asparagine (≥98%), L-Aspartic Acid (≥98%), L-Cysteine (97%), L-Glutamine (≥99%), L-Glutamic Acid (≥99%), Glutaric Acid (99%), Glycine (≥99%), L-Histidine (≥99%), L-Isoleucine (≥98%), L-Leucine (≥98%), L-Lysine (≥98%), Malonic Acid (99%), L-Methionine (≥98%), L-Phenylalanine (≥98%), Pimelic Acid (99%), L-Proline (≥99%), L-Serine (≥99%), Succinic Acid (≥99%), L-Threonine (≥98%), L-Tryptophan (≥98%), L-Valine (≥98%).

Synthetic Procedure

Standard solutions of 0.1 M $CaCl_2.2H_2O$ (A) and 0.1 M Na_2CO_3 (B) were prepared using deionised water. The Control samples were made by mixing 100 mL of A and 100 mL B for two minutes in a conical flask, filtering with standardised filter paper and funnels, washing with water and subsequently quenching the reaction with isopropanol or acetone. This process was repeated eight more times with the addition of a different concentration of the additive (see Table 1) to 100 mL of A before mixing A with B. The concentrations of the additives were selected based on the maximum solubilities of the individual additives as well as the routine equipment available at the majority of schools based on conversations with multiple teachers and lab technicians e.g., balances up to 2 decimal places are the norm in school laboratories and the units conventionally used are dm^{-3}. The synthetic procedures were provided to the schools both via written procedure and video. Each school made one series with a given additive and each series was made 4 times in different schools to ensure consistency. The resulting precipitates were left to dry on the filter paper in a dry place for one week before the powdered sample was loaded into a 0.5 mm Kapton capillary. The samples were returned to Diamond and mounted in a brass pin and brass holder for the diffraction experiment. Samples were checked to ensure they were correctly filled and re-filled where necessary. Each brass holder had a barcode inset into the base that was scanned before each data collection so the sample and the scan can be correlated.

Table 1 - List of amino acids used in syntheses

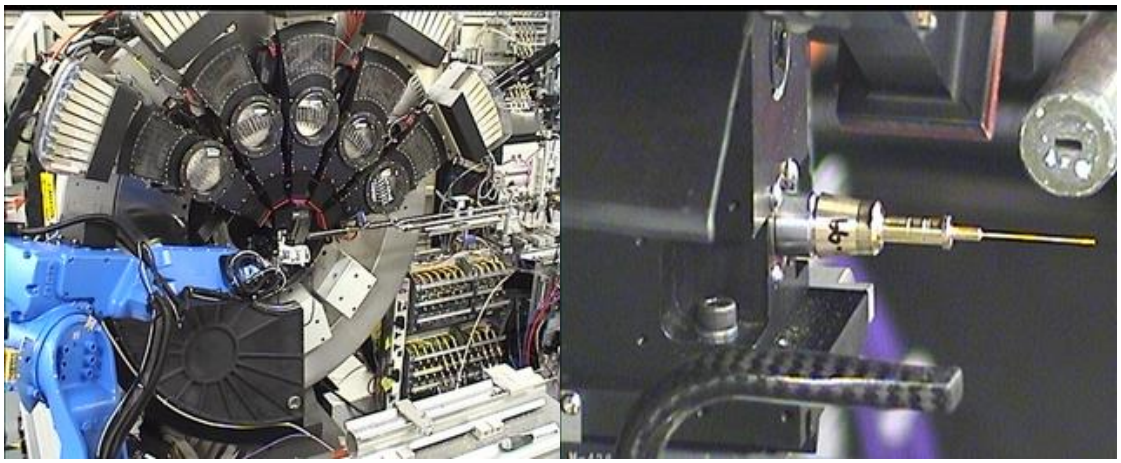
Additive Concentrations of 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2		
Ala	Arg	Asn
Cys	GluAci	Gly
His	Ile	Lys
MalAci	Met	Pro
Ser	SucAci	Thr
Val		
Additive Concentrations of 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5 and 1.75		
Leu	Phe	
Additive Concentrations of 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5		
Asp	Glu	Try
Additive Concentrations of 0.2, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.7		
Gln		
Additive Concentrations of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1		
AdiAci	PimAci	
Mixing Times (seconds)		
30, 60, 180, 240, 300, 360, , 480, 600		

Synchrotron X-ray Powder Diffraction Data Collection and Analysis

Significant software and hardware updates were implemented on I11 to upgrade the robot and carousel, to enable the scanning of the barcodes for each sample, to install cameras for sample photographs, to facilitate live tweeting of the data via @DLSProjectMLive and to create a new database to handle the data. One diffraction pattern was collected for each sample at Beamline I11 at Diamond Light Source in a 24-hour period using the Mythen II position sensitive detector.[1, 2] All data were collected at room temperature with a wavelength of 0.825786(10) Å, using the robotic arm to mount each sample (Figure 1). The Project M Scientists were provided with a modified version of the DAWN software through a web interface for phase identification of their materials and for comparison with standards and other related samples from other schools. Data were analysed using Pawley refinement via the TOPAS 4.2 software package[3] using jEdit in batch mode. An initial script was used to identify the presence of calcite or vaterite based of the intensity of the calcite 104 or the vaterite 010 reflections. Only phases indicated as present were included in the refinement. The quality of the fits was assessed and only those with clear visible peaks matching the relevant polymorph were included in further analysis.

The full dataset and associated file information are available on Zenodo.

Figure 1 - Robot (blue object to left of image) mounting the sample on the diffractometer (left) and capillary of 66-01 in position on the diffractometer (right)



Structural Information

Table 2 - Standard deviations for calcite and vaterite for the Control samples, for the samples synthesised with additives ('All Additives'), for the Mixing samples, and for Synthetic and Biogenic literature samples of Calcite. N is the number of samples in which the respective polymorph is present.

Polymorph	*a* Mean	σ_a	*c* Mean	σ_c	Volume Mean	σ_{Volume}
Calcite Control (N=84)	4. 99705	0.00186	17.06045	0.00435	368.9343	0.20184
Calcite All Additives (N=573)	4.99604	0.00193	17.07227	0.01142	369.04069	0.24107
Calcite Mixing Only (N=16)	4.99853	0.00176	17.05836	0.00294	369.10644	0.2111
Synthetic Calcite (N=13)[4-11]	4.98986	0.00204	17.06398	0.00874	367.9493	0.41268
Biogenic Calcite (N=32)[4, 11-15]	4.98168	0.01279	17.03572	0.0553	366.1441	3.0167
Vaterite Control (N= 37)	4.12802	9.05675E-4	8.47364	0.0019	125.05001	0.03634
Vaterite All Additives (N=412)	4.12814	0.00108	8.47411	0.00228	125.06424	0.04365
Vaterite Mixing Only (N=8)	4.12813	3.61E-4	8.47478	0.0012	125.07392	0.01756

Reference Cells for Vaterite Refinements

Each of the published unit cells for vaterite was used in a refinement with calcite for the set of Controls samples. Both unit cells were allowed to freely refine. The mean and standard deviations for the associated lattice parameters for the 84 calcite control samples and the 37 vaterite control samples are presented in Table 1 and 2 respectively. The Kamhi vaterite cell[16] had the lowest standard deviation for both polymorphs and had the better fit across both polymorphs, and was therefore used in this work.

Table 3 - Calcite (top) and Vaterite (bottom) units cells from refinements with the Controls samples

Calcite						
Vaterite Unit Cell Used	*a* Mean	σ_a	*c* Mean	σ_c	Volume Mean	σ_{Volume}
Demichelis C1_1[17]	4.99712	0.00335	17.05667	0.02115	368.8621	0.60168
Demichelis C121[17]	4.99696	0.00291	17.05797	0.01354	368.8665	0.52991
Demichelis P3231[17]	4.99818	0.00919	17.04344	0.10397	368.7256	1.09263
Wang P3231[18]	4.99741	0.00507	17.06042	0.00857	368.9869	0.68683
Kamhi[16]	4.99701	0.00186	17.06068	0.00441	368.9334	0.20376

Vaterite														
Vaterite Unit Cell	*a* Mean	σ_a	*b* Mean	σ_b	*c* Mean	σ_c	*Al* Mean	σ_{Al}	*Be* Mean	σ_{Be}	*Ga* Mean	σ_{Ga}	Volume Mean	σ_{Volume}
Demichelis C1_1[17]	12.74956	0.21857	7.13808	0.04587	25.66026	0.14105	89.69247	0.55628	99.60814	1.07794	90.73727	0.58051	2301.413	27.62445
Demichelis C121[17]	12.39038	0.01675	6.9528	0.03174	9.44425	0.03473	--	--	115.1022	0.06779	--	--	736.7459	0.90549
Demichelis P3231[17]	7.664	0.01314	--	--	26.0543	0.02316	--	--	--	--	--	--	1325.325	4.16663
Wang P3231[18]	7.14305	0.05582	--	--	25.48654	0.19765	--	--	--	--	--	--	1126.199	16.31555
Kamhi[16]	4.12802	9.05675E-4	--	--	8.47364	0.0019	--	--	--	--	--	--	125.05001	0.03634

Calcite refined mean lattice parameters and standard deviations

Table 4 - Calcite refined mean lattice parameters and standard deviations for the additives presented in this work

Calcite							
Additive	N total	Mean	σ_a	Mean	σ_c	Mean	σ_{Volume}
Controls	84	4.99705	0.00186	17.06045	0.00435	368.9343	0.20184
AdiAc	15	4.99322	8.48E-4	17.07069	0.00521	368.59036	0.09299
Ala	27	4.99584	0.00162	17.06989	0.00731	368.9587	0.21637
Arg	23	4.99862	0.00189	17.05815	0.00386	369.11639	0.21048
Asn	27	4.99485	0.0013	17.0818	0.00509	369.07034	0.16759
Asp	30	4.99407	0.00204	17.08525	0.00999	369.02928	0.26124
Cys	26	4.99547	0.00104	17.08063	0.00913	369.13691	0.12424
Gln	22	4.99651	5.71E-4	17.07627	0.0085	369.19653	0.14765
Glu	38	4.99458	0.00153	17.08509	0.0163	369.10079	0.23734
Gly	29	4.99605	0.00104	17.08192	0.01148	369.2499	0.27933
His	34	4.99579	0.001	17.07625	0.00713	369.08959	0.20019
Ile	23	4.99688	6.31E-4	17.0639	0.00194	368.98334	0.09935
Leu	28	4.9966	7.29E-4	17.0659	0.0052	368.98479	0.09538
Lys	31	4.9986	7.57E-4	17.05989	0.00214	369.14998	0.08843
MalAci	8	4.9931	0.00285	17.07218	0.00738	368.6043	0.38494
Met	16	4.99662	4.52E-4	17.07319	0.00794	369.14615	0.14165
Mixing	16	4.99853	0.00176	17.05836	0.00294	369.10644	0.2111
Phe	18	4.99568	9.46E-4	17.06715	0.00291	368.87668	0.15516
PimAci	14	4.99355	0.00125	17.06917	0.00331	368.60483	0.21887
Pro	26	4.99755	0.00112	17.06475	0.0032	369.10128	0.15911
Ser	26	4.99598	0.00267	17.07246	0.01009	369.03492	0.27523
SucAci	10	4.9955	0.00216	17.06813	0.00771	368.87097	0.28413
Thr	30	4.99565	0.00101	17.07927	0.00509	369.13388	0.16318
Trp	24	4.99691	0.00101	17.06915	0.01069	369.10071	0.21153
Val	32	4.99637	0.00107	17.06452	0.0028	368.92081	0.15107
All Additive Samples	573	4.99604	0.00193	17.07227	0.01142	369.04069	0.24107

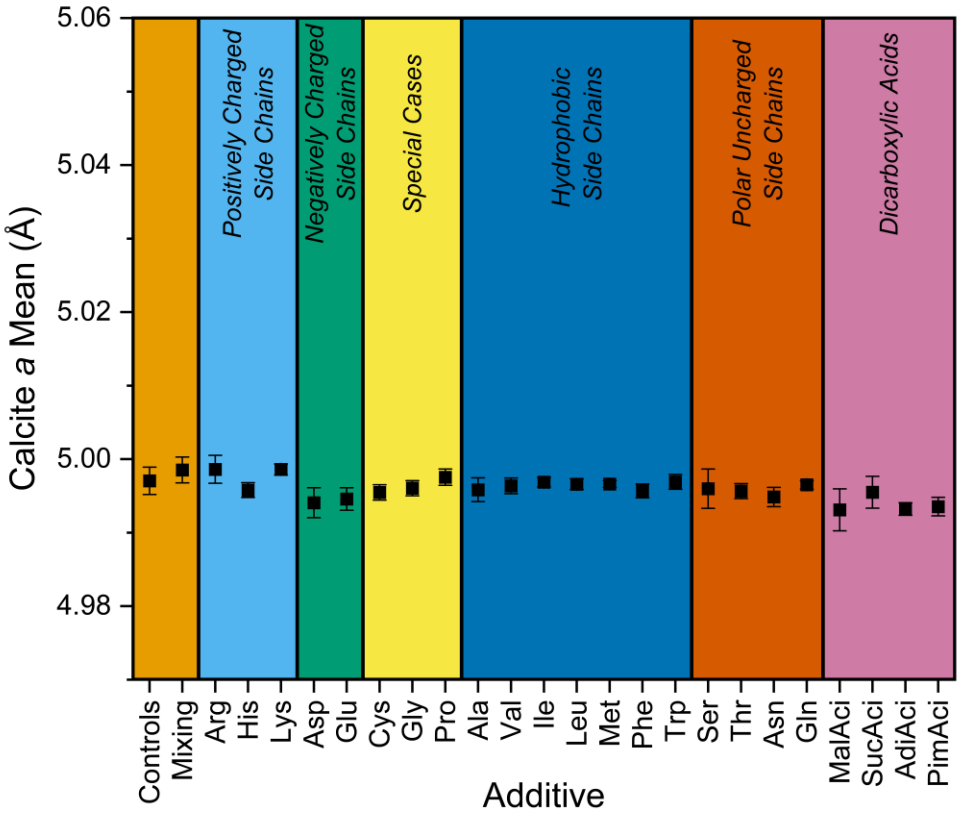
Vaterite refined mean lattice parameters and standard deviations

Table 5 - Vaterite refined mean lattice parameters and standard deviations for the additives presented in this work

Vaterite							
Additive	N total	Mean	σ_a	Mean	σ_c	Mean	σ_{Volume}
Controls	37	4.12802	9.05675E-4	8.47364	0.0019	125.05001	0.03634
AdiAc	10	4.12773	5.88E-4	8.47364	0.00183	125.03256	0.02133
Ala	23	4.12859	9.58E-4	8.47267	0.00224	125.07015	0.0357
Arg	12	4.12712	0.00138	8.47536	0.00308	125.02069	0.04983
Asn	22	4.12756	9.35E-4	8.47518	0.00143	125.04503	0.04032
Asp	23	4.12682	0.00126	8.4779	0.00178	125.04049	0.06051
Cys	17	4.12833	8.51E-4	8.47376	0.00104	125.07067	0.04344
Gln	17	4.12774	5.17E-4	8.47469	9.04E-4	125.04888	0.02607
Glu	36	4.12768	0.00134	8.47502	0.00313	125.04991	0.04325
Gly	27	4.12902	0.00117	8.47369	0.00164	125.11133	0.05636
His	24	4.12854	8.11E-4	8.47297	0.00175	125.07149	0.02886
Ile	14	4.12831	4.01E-4	8.47364	0.00169	125.0677	0.01699
Leu	14	4.12863	5.55E-4	8.47281	0.00128	125.07508	0.02421
Lys	12	4.12761	5.46E-4	8.47412	0.00149	125.03244	0.0181
MalAci	6	4.12611	0.00119	8.47756	0.00315	124.99228	0.06198
Met	9	4.12769	5.08E-4	8.47444	0.00114	125.04196	0.02483
Mixing	8	4.12813	3.61E-4	8.47478	0.0012	125.07392	0.01756
Phe	15	4.12824	9.15E-4	8.47284	0.00167	125.05175	0.03505
PimAci	5	4.12835	8.44E-4	8.47375	0.00113	125.0718	0.03776
Pro	24	4.1283	4.79E-4	8.474	0.00129	125.0721	0.02596
Ser	25	4.12907	7.93E-4	8.47293	0.00189	125.10357	0.03629
SucAci	4	4.12786	0.00129	8.47645	0.00587	125.08221	0.02426
Thr	26	4.12845	7.78E-4	8.47377	0.00106	125.07807	0.03665
Trp	23	4.12841	5.12E-4	8.47357	0.00149	125.07275	0.02654
Val	16	4.1285	5.69E-4	8.47256	0.00166	125.06319	0.02562
All Additive Samples	412	4.12814	0.00108	8.47411	0.00228	125.06424	0.04365

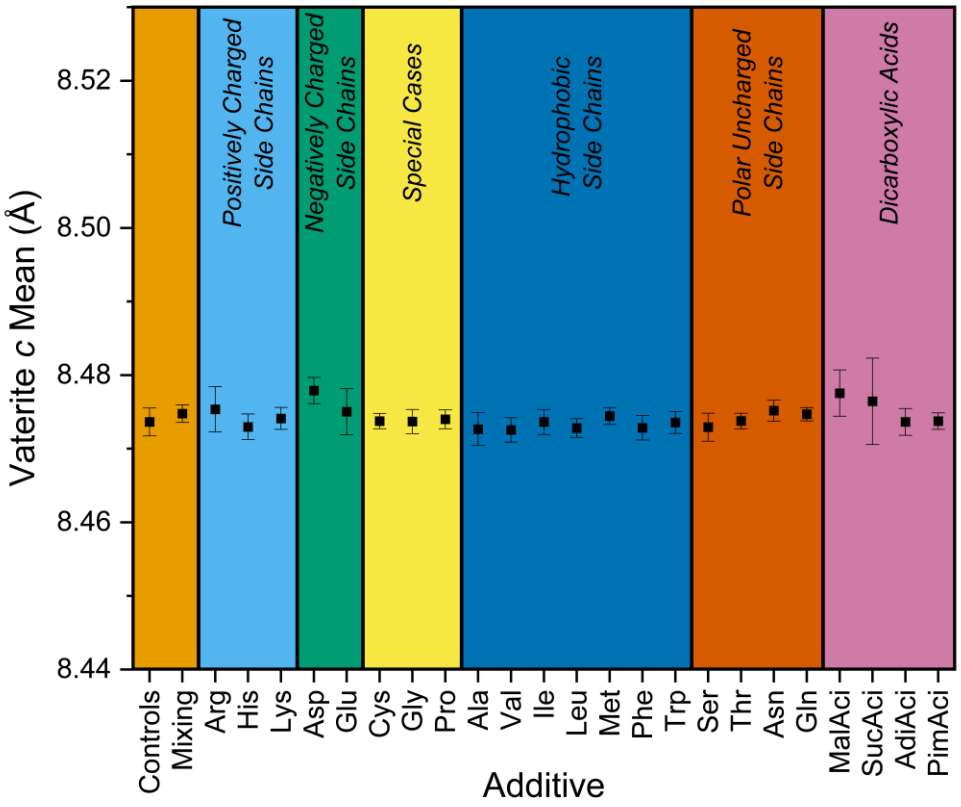
Calcite *a* for Additive Groupings

Figure 2 - The mean lattice parameter of calcite *a* with the corresponding standard deviations, presented on the same relative scale and categorised according to the additive groupings (presented in increasing size).



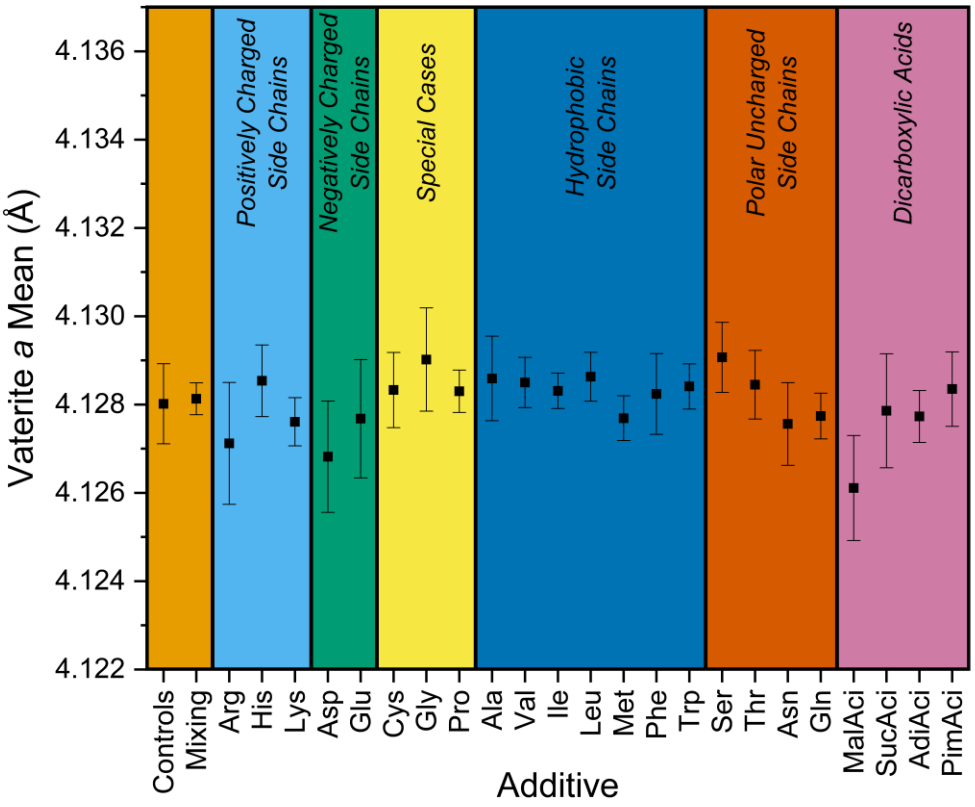
Vaterite *c* for Additive Groupings

Figure 3 - The mean lattice parameter of vaterite *c* with the corresponding standard deviations, presented on the same relative scale and categorised according to the additive groupings (presented in increasing size).



Vaterite *a* for Additive Groupings

Figure 4 - The mean lattice parameter of vaterite *a* with the corresponding standard deviations and categorised according to the additive groupings (presented in increasing size). Note that here this graph has a smaller y-axis range than Figure 10(b) in the paper.



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