Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information

Biocatalyzed mineralization in an aqueous two-phase system: Effect of background polymers and enzyme partitioning

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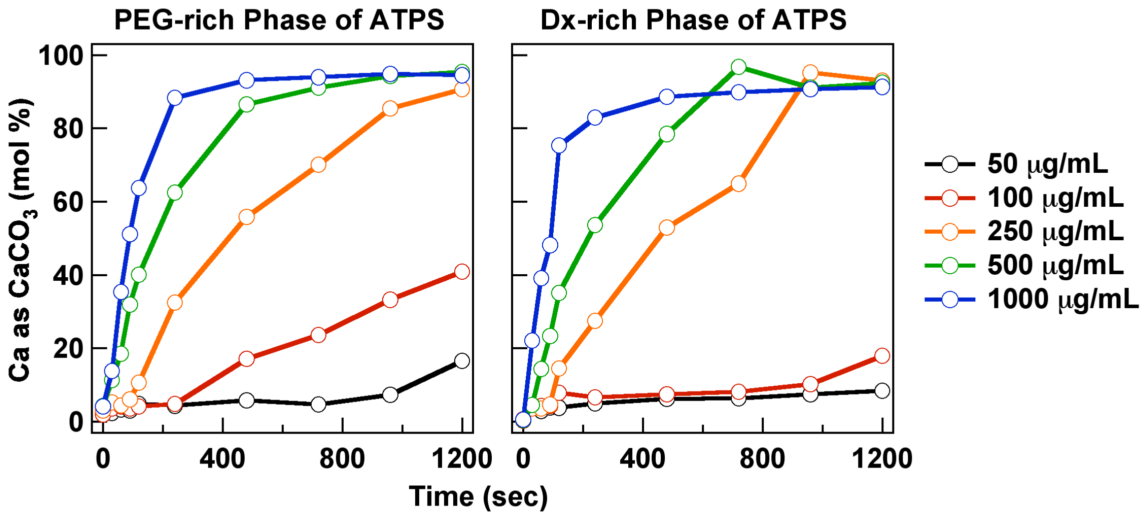
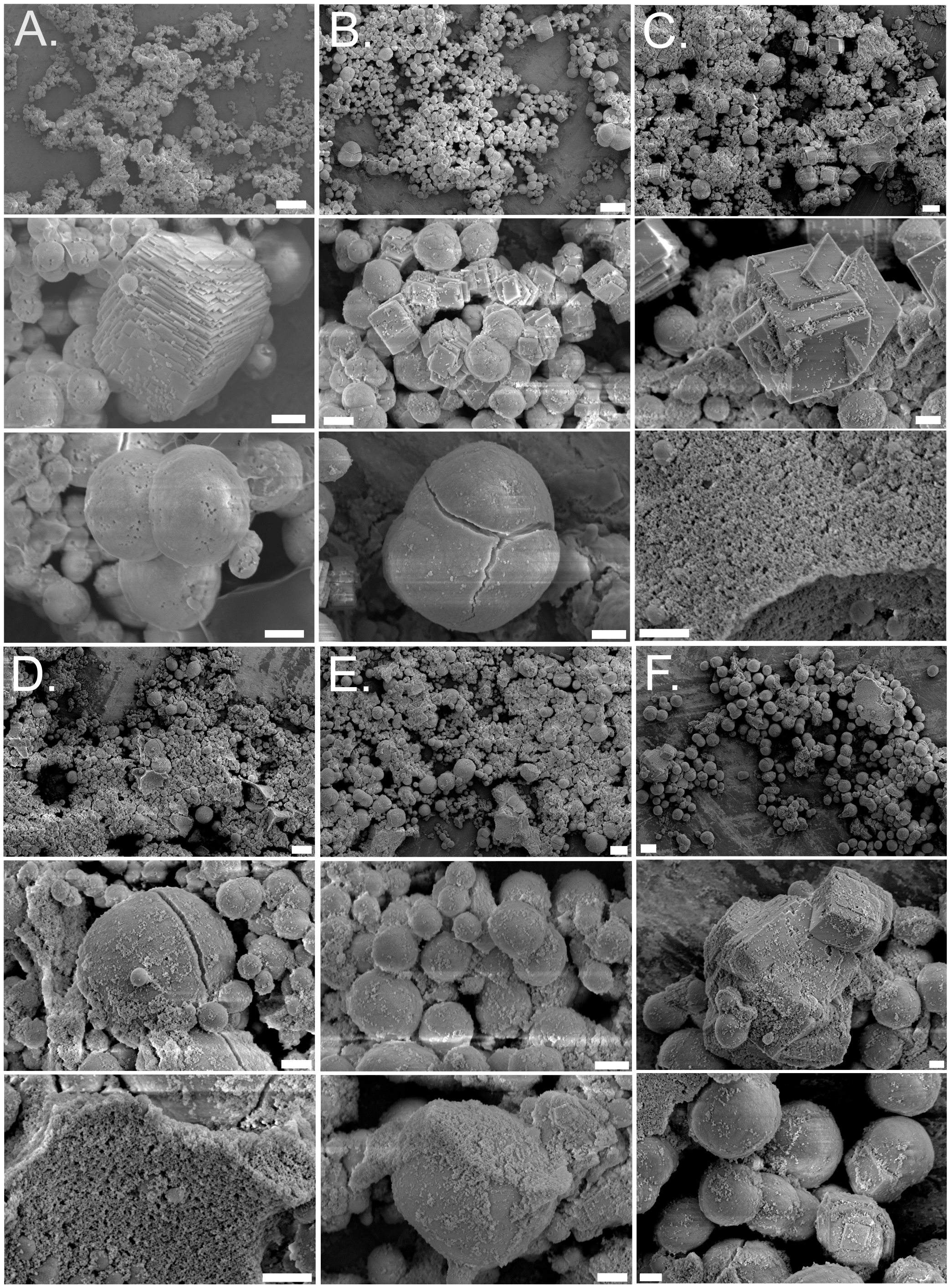
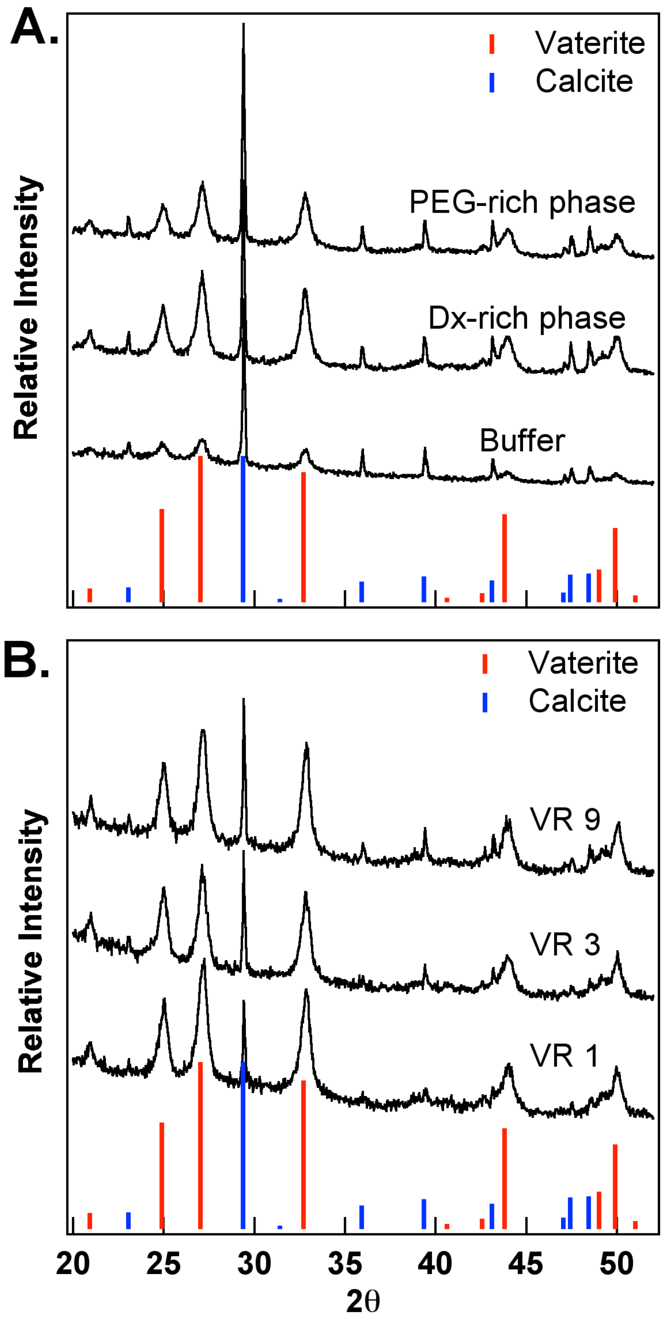


Supporting Figure 1. Calcium found as $CaCO_3$ (in mol %) in solutions containing varying urease after being exposed to 15 mM Ca^{2+} and 30 mM urea over 15 minutes while continuously stirring in PEG-rich and Dx-rich phases extracted from ATPS.



Supporting Figure 2. Comparison of SEM images for $CaCO_3$ precipitates formed in various media: 10 mM pH 7.4 Tris buffer (**A**), PEG-rich phase from an ATPS (**B**), Dx-rich phase from an ATPS (**C**), and from ATPS of V_{Dx}:V_{PEG} volume ratios 1:1 (**D**), 1:3 (**E**), and 1:9 (**F**). Upper panels show a representative wide-view (scale bars = 20 μm) and the two lower panels show close-up images (scale bars = 2 μm) of characteristic calcite, vaterite, and amorphous particles. ATPS formulations and reaction conditions are identical to that of Figure 5 of the main text.



Supporting Figure 3. XRD spectra for precipitated and dried calcium carbonate obtained from identical solutions in Figures 5 and S3; in general, precipitates were created by reaction of with 150 μg/mL urease reacting with 20 mM Ca^{2+} and 30 mM urea for 20 minutes. Figure A and B are separated to indicate solutions in and out of ATPS.

Supporting Table 1. Experimentally-determined PEG and Dx concentrations in the PEG-rich and Dx-rich phases of ATPS used in this work.

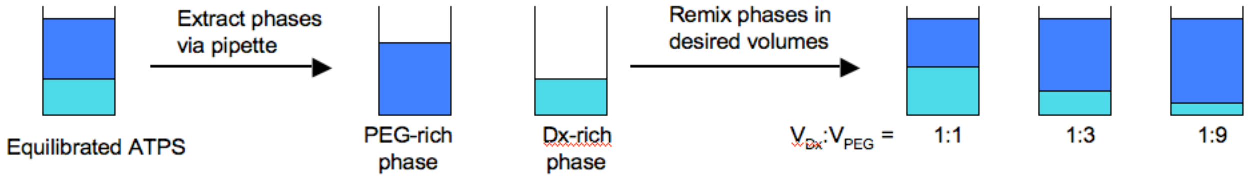
V_{Dx}: V_{PEG}	PEG-rich phase composition		Dx-rich phase composition	
	[PEG] (w/w %)	[Dx] (w/w %)	[PEG] (w/w %)	[Dx] (w/w %)
1:1	12.94 ± 0.01	4.12 ± 0.01	2.68 ± 0.02	28.67 ± 0.02
1:3	13.34 ± 0.004	4.00 ± 0.01	2.65 ± 0.006	29.37 ± 0.01
1:9	13.56 ± 0.01	3.95 ± 0.01	2.71 ± 0.04	29.84 ± 0.03

Supporting Table 2. Vaterite and calcite abundances of $CaCO_3$ precipitates in various media, determined via Reitveld refinement of XRD patterns.[a]

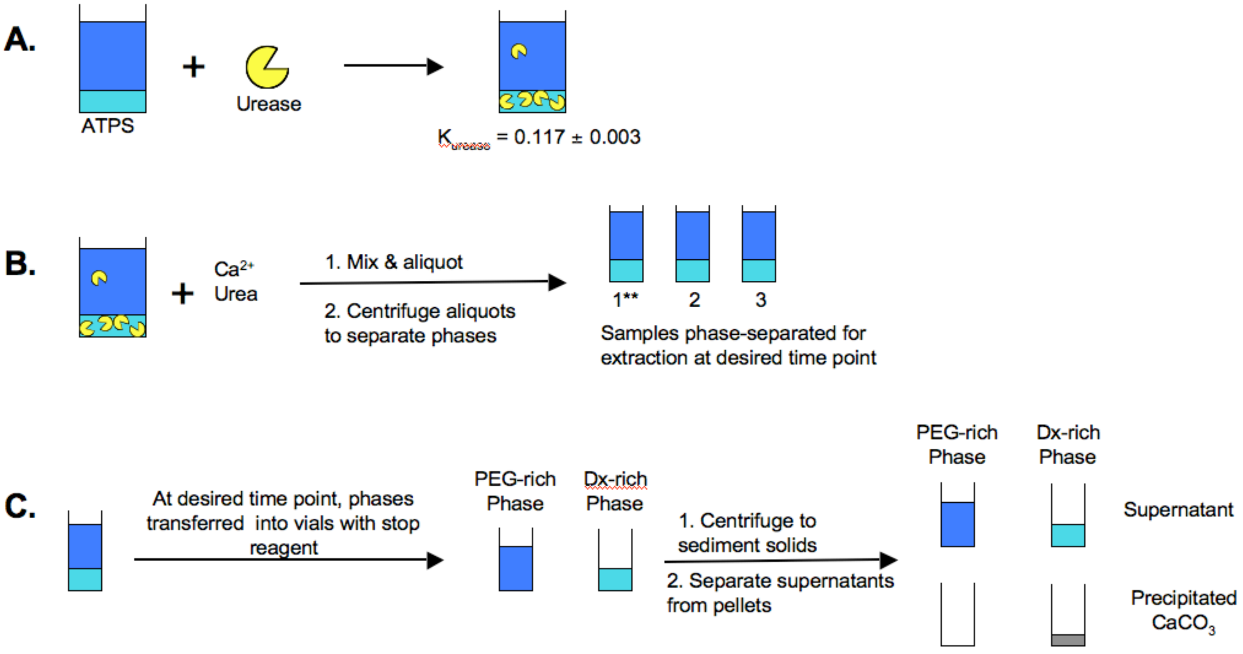
Sample	Vaterite wgt. %	Calcite wgt. %
Buffer	54.9 ± 1.7	45.1 ± 2.6
PEG-rich	77.0 ± 1.4	23.0 ± 1.3
Dx-rich	66.6 ± 1.5	33.4 ± 1.9
ATPS, 1 V_{Dx}: 1 V_{PEG}	92.6 ± 1.5	7.4 ± 0.5
ATPS, 1 V_{Dx}: 3 V_{PEG}	89.1 ± 1.4	10.9 ± 0.7
ATPS, 1 V_{Dx}: 9 V_{PEG}	85.9 ± 1.4	14.1 ± 0.8

[a] All R-value percentages for these refinements were below at least 11%, indicating a well-defined fit between the refinement parameters and the XRD pattern.

Supporting Scheme 1. Preparation of ATPS with different volume ratios



Supporting Scheme 2. ATPS sample preparation, reaction and sample retrieval via **(A)** urease partitioning, **(B)**, initiation of reaction and removal of aliquots, and **(C)** sampling timepoints, with separation of supernatant from precipitated $CaCO_3$.



1** = The first sample container always contains stop reagent to halt the reaction prior to centrifugation
Note: Repeated in triplicate

Supporting Scheme 3. Sample analysis for supernatants **(A)** and pellets **(B)** after stopping the reaction, separating the phases, and centrifuging each phase of the ATPS.