Supplementary Materials: Reversed Crystal Growth of Calcite in Naturally Occurring Travertine Crust

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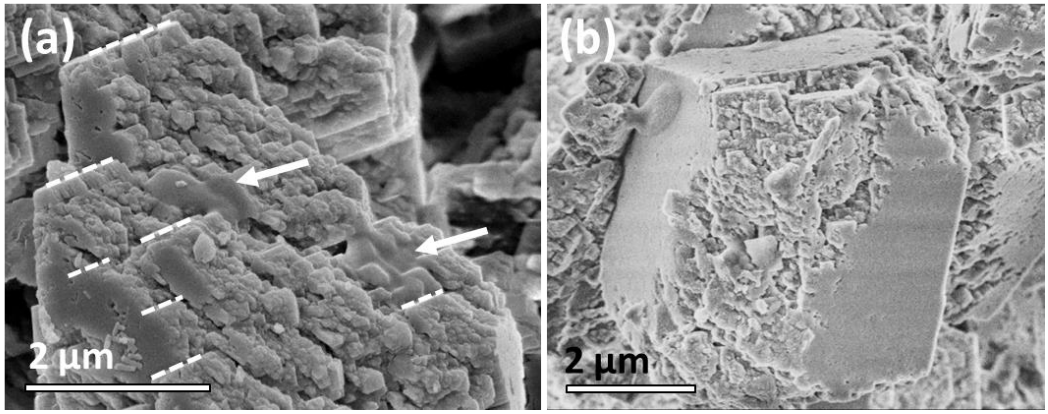

Figure S1. Additional SEM images of calcite particles found in the travertine specimen. (**a**) Calcite aggregate composed of a dense arrangement of nanosized building units. The dashed lines marking the terminal face of the building units suggest they all have a uniform orientation. The arrows mark embedded EPS molecules; (**b**) A fractured calcite particle showing that a polycrystalline core lies beneath the thin single crystalline shell.

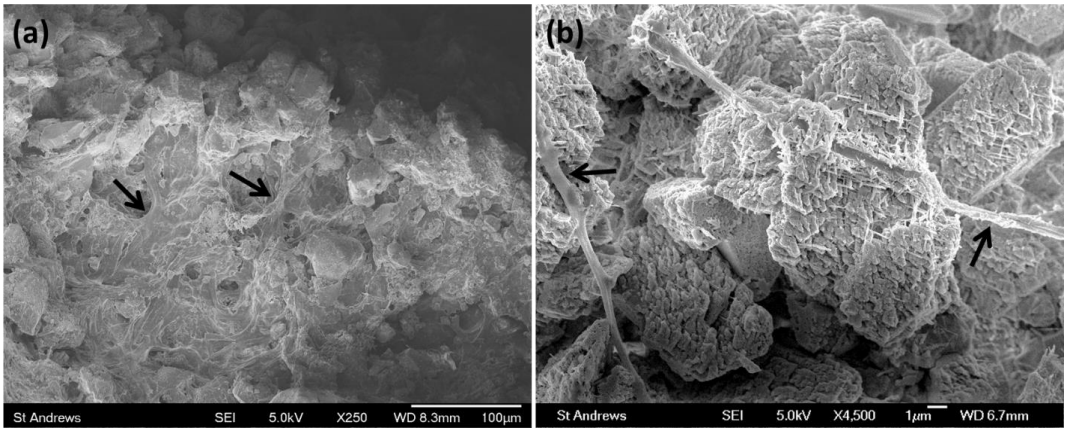

Figure S2. (**a**) Low magnification SEM image of calcite particles in the travertine specimen joined together by large filaments of EPS and obscured by a surface film of EPS; (**b**) SEM image showing calcite particles in the form of an aggregate. A higher magnification SEM image of the calcite particle in the center of the image is shown in Figure 3b. Long filaments of EPS are marked by arrows.

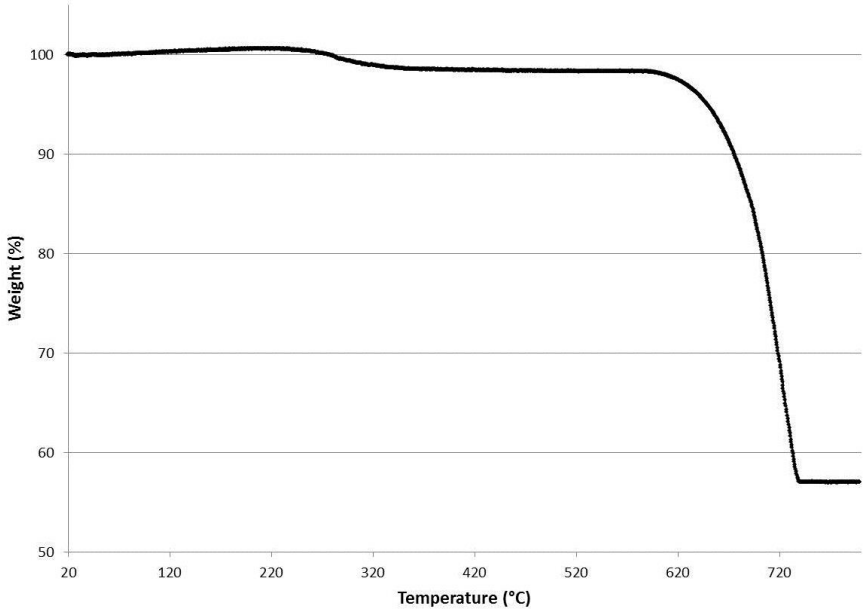

Figure S3. TGA result of the travertine specimen showing a 2.1 wt% loss between 230 °C and 380 °C and a second loss of 40.9 wt% between 590 °C and 740 °C. The first weight loss corresponds to the removal of EPS whilst the second matches to the decomposition of calcite into CaO and CO_2.

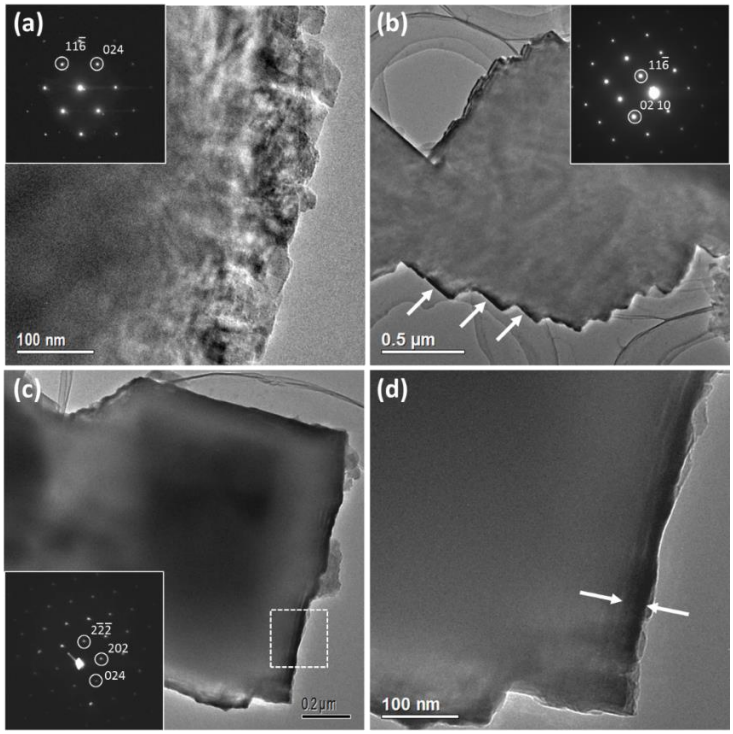

Figure S4. TEM images recorded from calcite particles found in the travertine specimen. (**a**) An aggregate of oriented nanocrystallites. The corresponding SAED pattern recorded from a large area containing many nanocrystallites is displayed in the inset; (**b**) Calcite particle displaying a non-uniform contrast and terminated by several subparallel nanocrystals (marked by arrows). The SAED pattern shown in the inset confirms the uniform orientation of building units; (**c**) Low magnification TEM image of a rhombohedral particle. The SAED pattern shown in the inset was recorded from the region marked by the square; (**d**) higher magnification image of the surface of the particle in (**c**). A dark contrasted, ~30 nm layer (marked by arrows) can be observed at the surface.

Biomimetic synthesis of calcite-chitosan: The synthetic method for calcite was the same as that used by Ritchie et al. [1] in which chitosan was used as a structure directing agent. Chitosan (1.00 g high molecular weight, from Sigma Aldrich) was added to 15 mL distilled water which was heated to 60 °C and stirred constantly until a gel formed. A mixture of 23.62 g (0.1 mol) $Ca(NO_3)_2{\cdot}4H_2O$ (99%, from Alfa Aesar) and 12.0 g (0.2 mol) urea (ACS grade, from Sigma) were added to the chitosan gel. The aqueous solution was sealed in a PTFE bottle and placed in an oven at 100 °C. A sample was removed from the oven at 2 h as well as longer incubation times of 23 h, 3 days and 9 days. The resulting solutions were centrifuged at 3400 rpm for 5 min to recover the precipitate. The $CaCO_3$ mesocrystals were washed three times with distilled water and then dried at 60 °C overnight. Electron microscopic images of the calcite-chitosan specimens are shown in Figure S5.

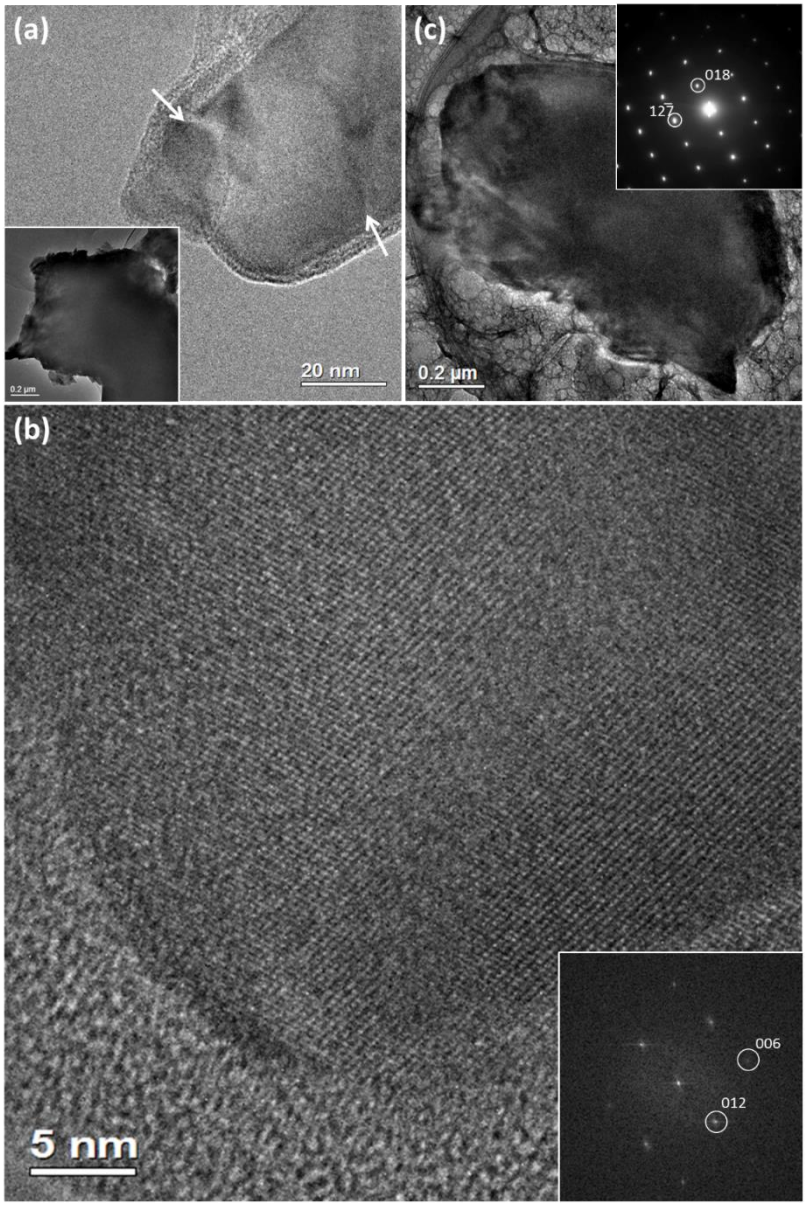

Figure S5. TEM images of a 2 h calcite particle prepared in the presence of chitosan. (**a**) TEM image showing domains with sizes of 15–50 nm. The corresponding low magnification TEM image is shown in the inset; (**b**) HRTEM image recorded from a small region in (**a**); Diffraction spots in the corresponding FFT pattern with an interplane angle of 63.1° can be indexed to the (012) and (006) crystal planes of calcite; (**c**) Low magnification TEM image. The inset is the corresponding single crystal-like SAED pattern recorded from an area covering many nanocrystallites.

Biomimetic synthesis of calcite-gelatin: The synthetic method for calcite was the same as that used by Zhan et al. [2] in which gelatin (Type B) was used as a structure directing agent. Gelatin (1.00 g, type B, 225 Bloom, from Sigma Aldrich) was added to 10 mL distilled water which was heated to 60 °C and stirred constantly until a gel formed. A mixture of 23.62 g (0.1 mol) $Ca(NO_3)_2{\cdot}4H_2O$ (99%, from Alfa Aesar) and 12.0 g (0.2 mol) urea (ACS grade, from Sigma Aldrich) were added to the gelatin gel. The aqueous solution was sealed in a PTFE bottle and placed in an oven at 100 °C for 23 h. The resulting precipitate was collected by centrifugation at 3400 rpm for 5 min and washed three times with distilled water before drying at 60 °C overnight. SEM images of the resulting calcite crystals are shown in Figure S7. A 23 h reaction was also carried out in total absence of gelatin with SEM images of the resulting crystals shown in Figure S6.

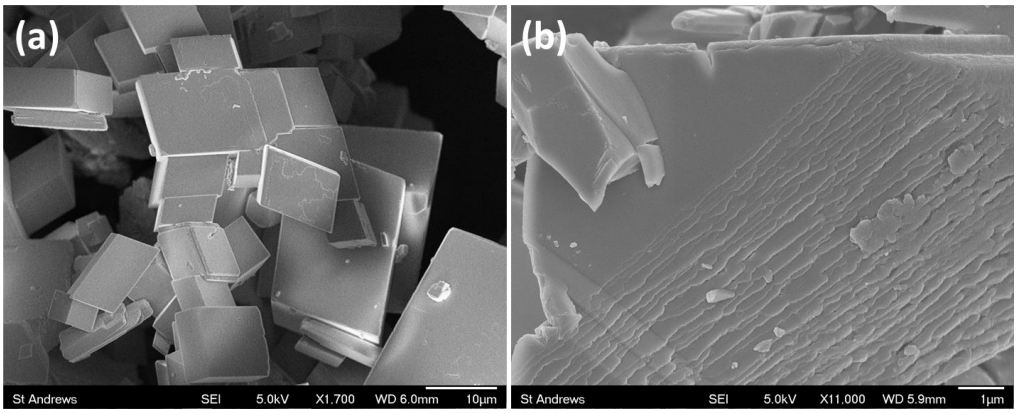

Figure S6. SEM images of 23 h calcite particles prepared in total absence of organic agents. (**a**) Low magnification image showing a uniform rhombohedral morphology; (**b**) SEM image of a fractured calcite particle. The layered structure is likely the result of crystal cleavage of the {104} surface.

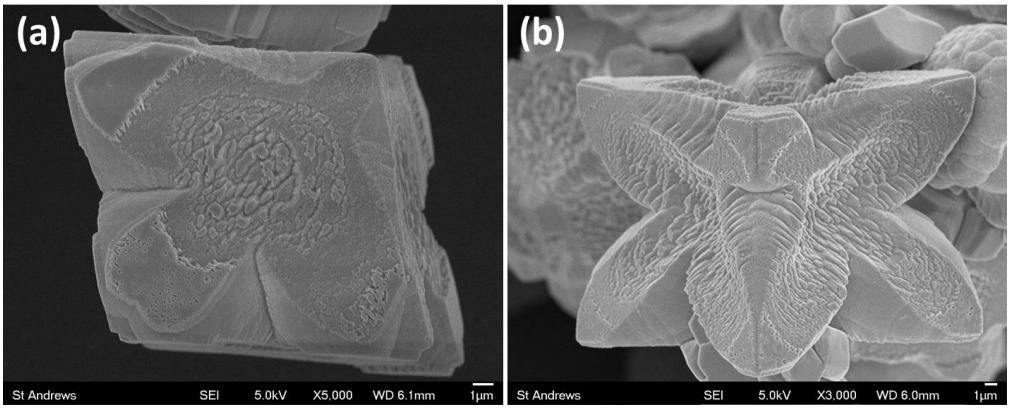

Figure S7. SEM images of 23 h calcite particles prepared in the presence of gelatin. The images show varying degrees of terraced excavations on the {104} faces.

References

1. Ritchie, A.W.; Watson, M.I.T.; Turnbull, R.; Lu, Z.Z.; Telfer, M.; Gano, J.E.; Self, K.; Greer, H.F.; Zhou, W.Z. Reversed crystal growth of rhombohedral calcite in the presence of chitosan and gum arabic. *CrystEngComm* **2013**, *15*, 10266–10271.
2. Zhan, J.; Lin, H.-P.; Mou, C.-Y. Biomimetic formation of porous single-crystalline $CaCO_3$ via nanocrystal aggregation. *Adv. Mater.* **2003**, *15*, 621–623.