Electronic Supplementary Information

New Insights into the Early Stages of Silica-Controlled Barium Carbonate Crystallisation

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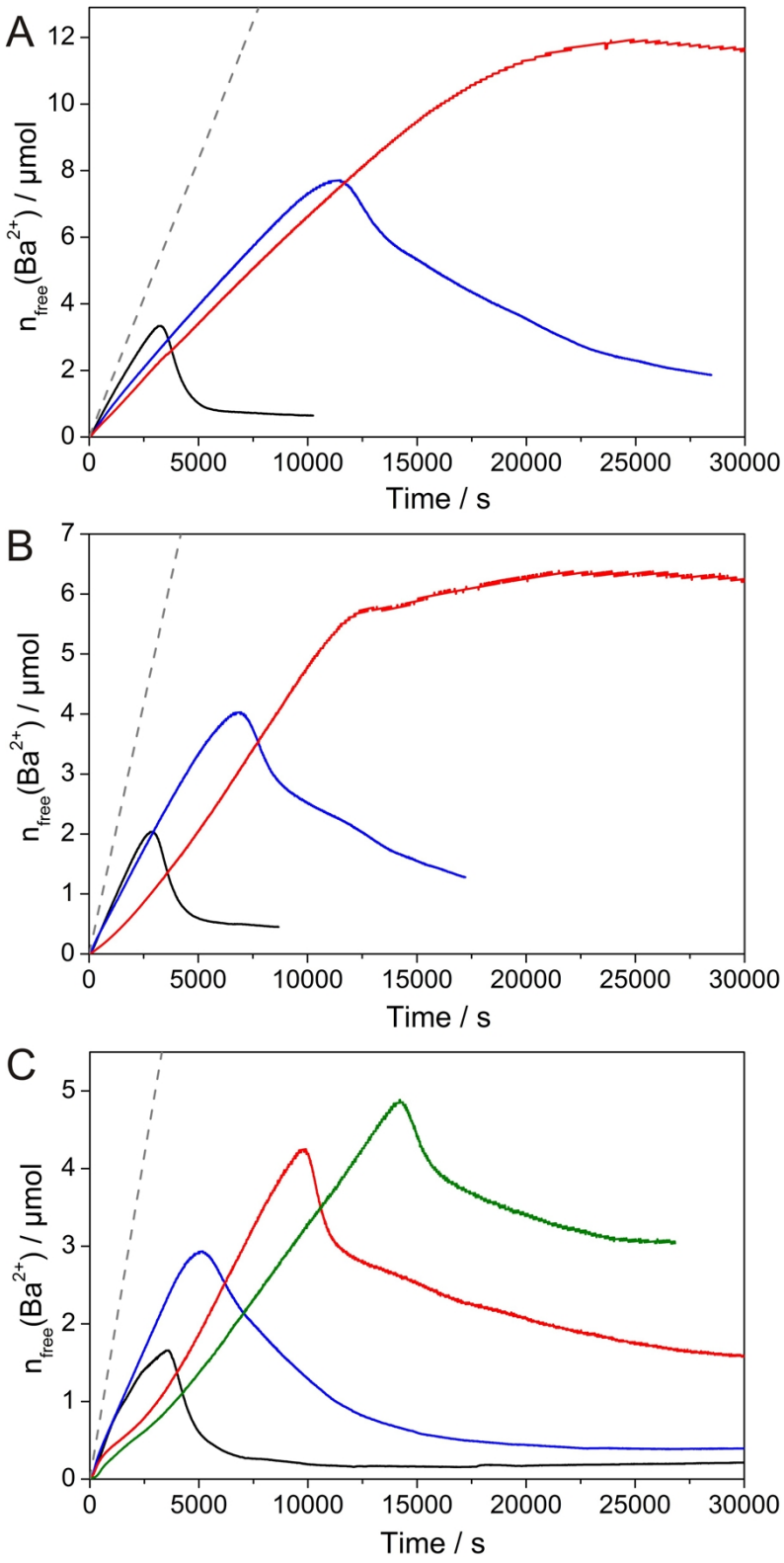

Figure S1. Time-dependent progressions of the amount of free Ba^{2+} detected upon titration of 10 mM $BaCl_2$ into 5 mM carbonate buffer at pH (A) 10.0, (B) 10.5, and (C) 11.0 in the absence of silica (black curves) and in the presence of 300 (blue curves), 600 (red curves) and 1200 ppm SiO_2 (green curve, only for pH 11). The dashed grey lines represent the dosed amount of Ba^{2+}.

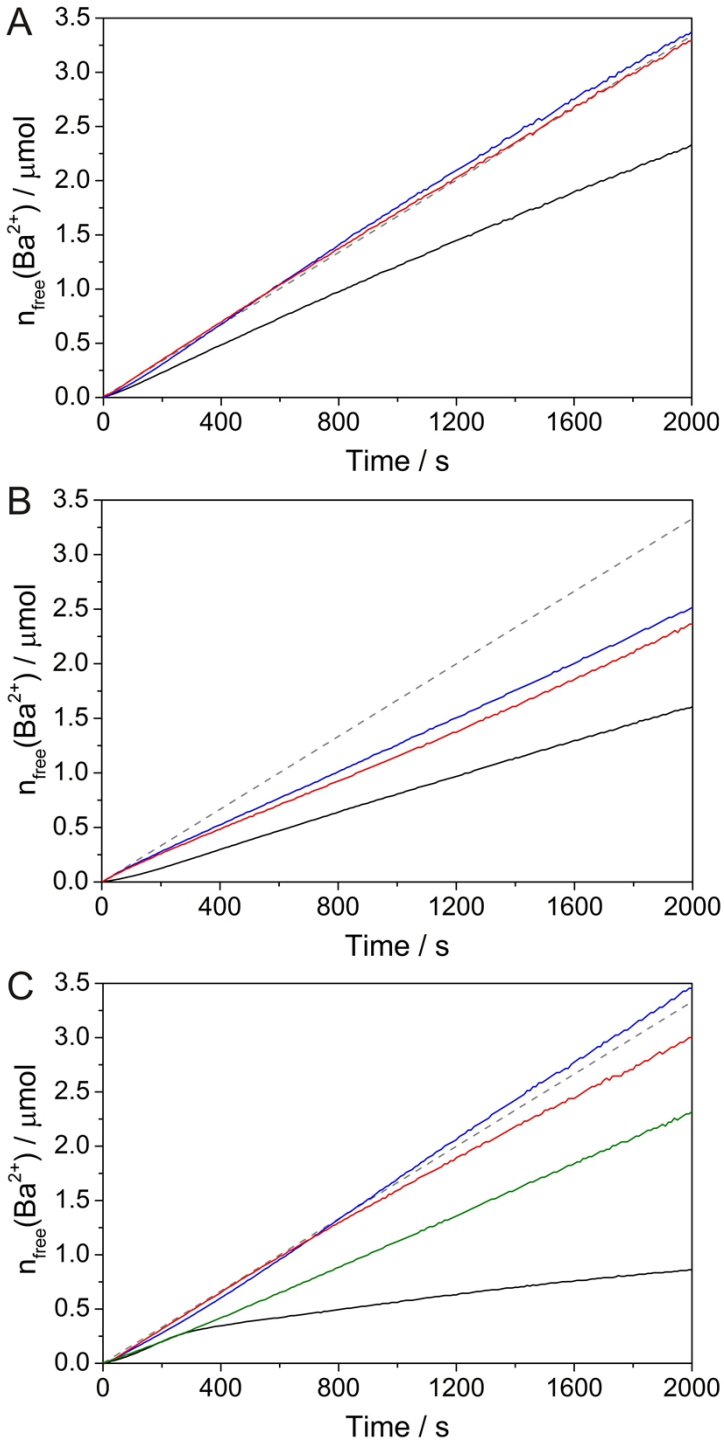

Figure S2. Amount of free Ba^{2+} traced during addition of 10 mM $BaCl_2$ to neat sodium silicate solutions at pH (A) 10.0, (B) 10.5, and (C) 11.0, as compared to corresponding data obtained upon titration into carbonate buffers with no added silica at the same pH (black curves). The silica content in the solutions was 300 (blue curves), 600 (red curves) and 1200 ppm SiO_2 (green curve, only for pH 11). The dashed grey lines represent the dosed amount of Ba^{2+}. Note that significant binding of barium ions by silicate species is only observed at pH 10.5 and at the highest silica concentration at pH 11, while in all other cases the detected free amount of Ba^{2+} more or less closely follows the dosed line.

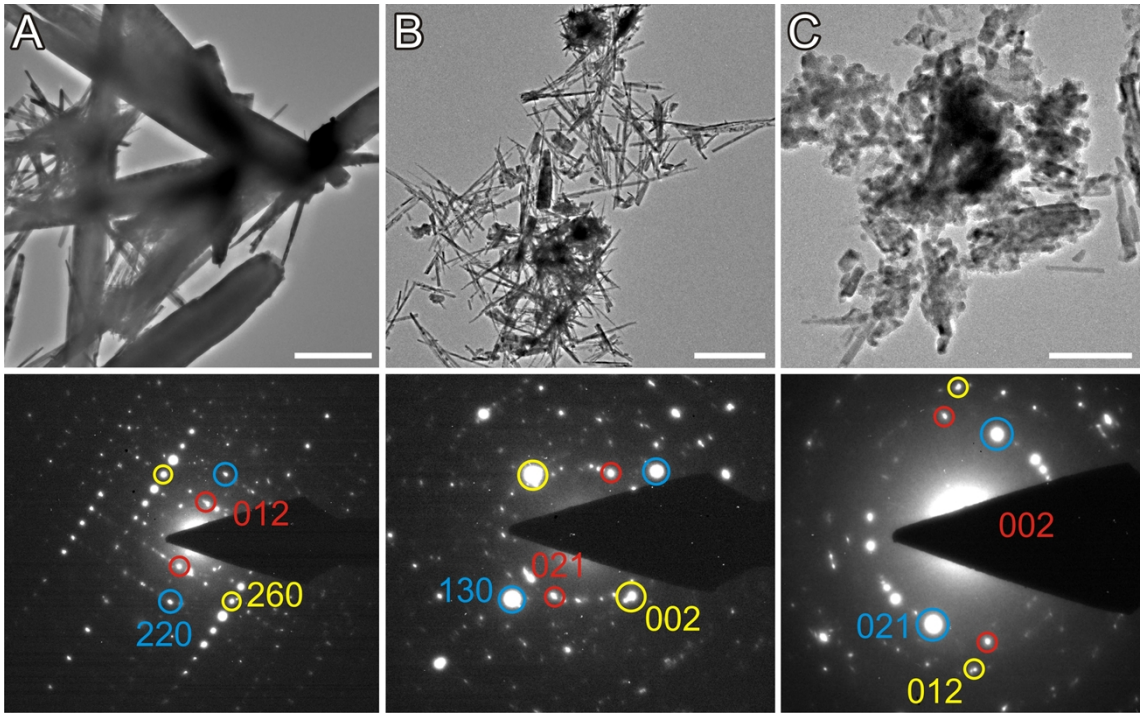

Figure S3. Additional TEM micrographs of crystals isolated from titration experiments performed at pH 10.0 in buffers containing (A) 0, (B) 300, and (C) 600 ppm SiO_2. Reflections in the corresponding electron diffraction patterns shown below can be indexed to distinct crystallographic planes of the witherite structure, as indicated. Indexing was achieved by comparing measured d-spacings with database values.[S1] Scale bars are (A-B) 1 μm and (C) 200 nm.

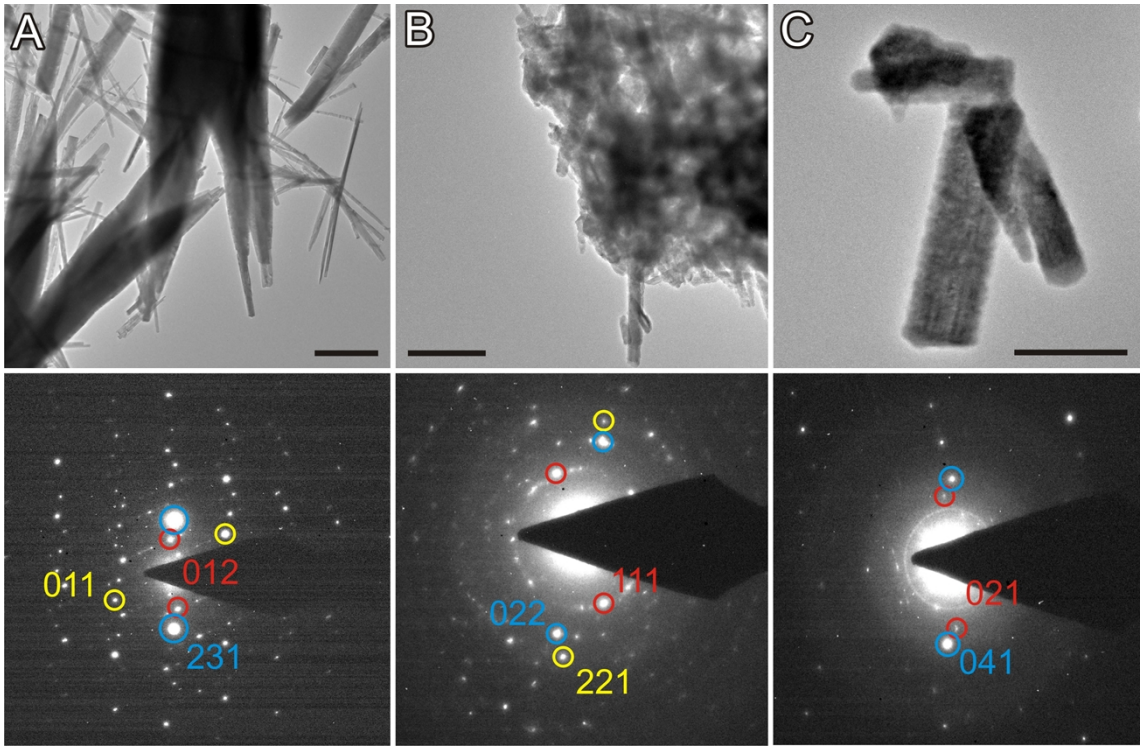

Figure S4. TEM images and ED patterns of crystalline products resulting from titration assays at pH 10.5 in the presence (A) 0, (B) 300, and (C) 600 ppm silicate. The highlighted reflections could be indexed to witherite planes as indicated. Scale bars are (A) 1 µm, (B) 200 nm, and (C) 100 nm.

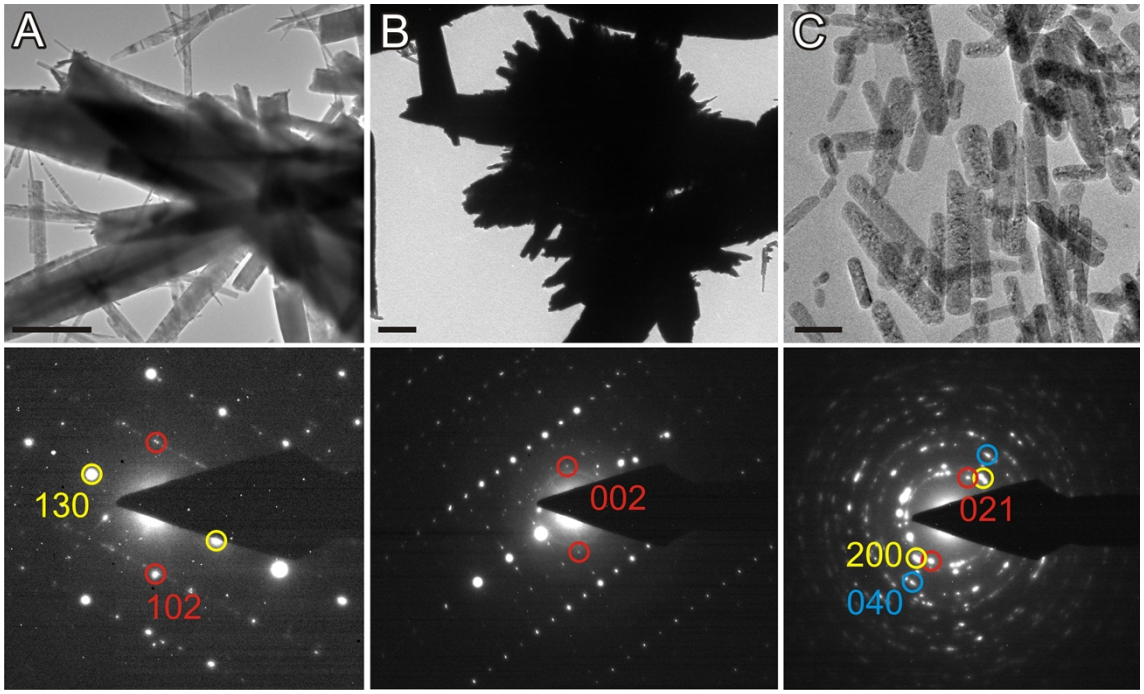

Figure S5. Supplementary TEM and electron diffraction data for particles generated in titration measurements at pH 11.0 in the absence of silicate (A) and under the influence of 300 (B) and 600 ppm SiO_2 (C). ED patterns can all be indexed assuming crystalline witherite. Scale bars are (A-B) 1 µm, and (C) 100 nm.

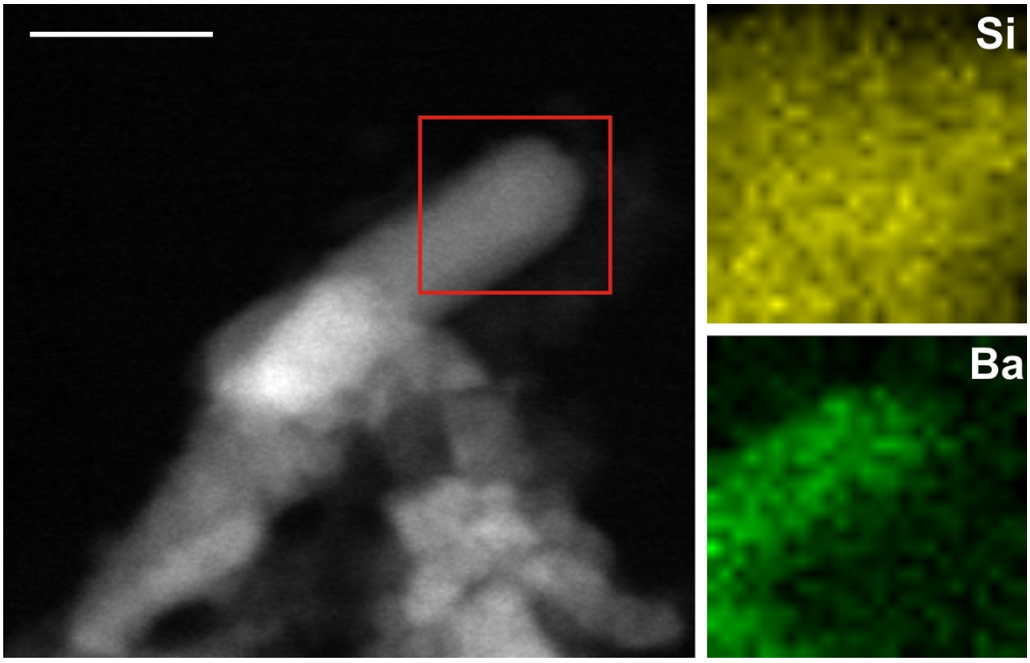

Figure S6. EDX mapping analysis of a crystal formed at pH 10.5 from a solution containing 300 ppm SiO_2. The investigated area is highlighted by the red rectangle in the corresponding STEM image (left). The resulting local distributions of Si (yellow) and Ba (green) suggest the presence of a continuous silica skin around the barium carbonate core. Scale bar: 50 nm.

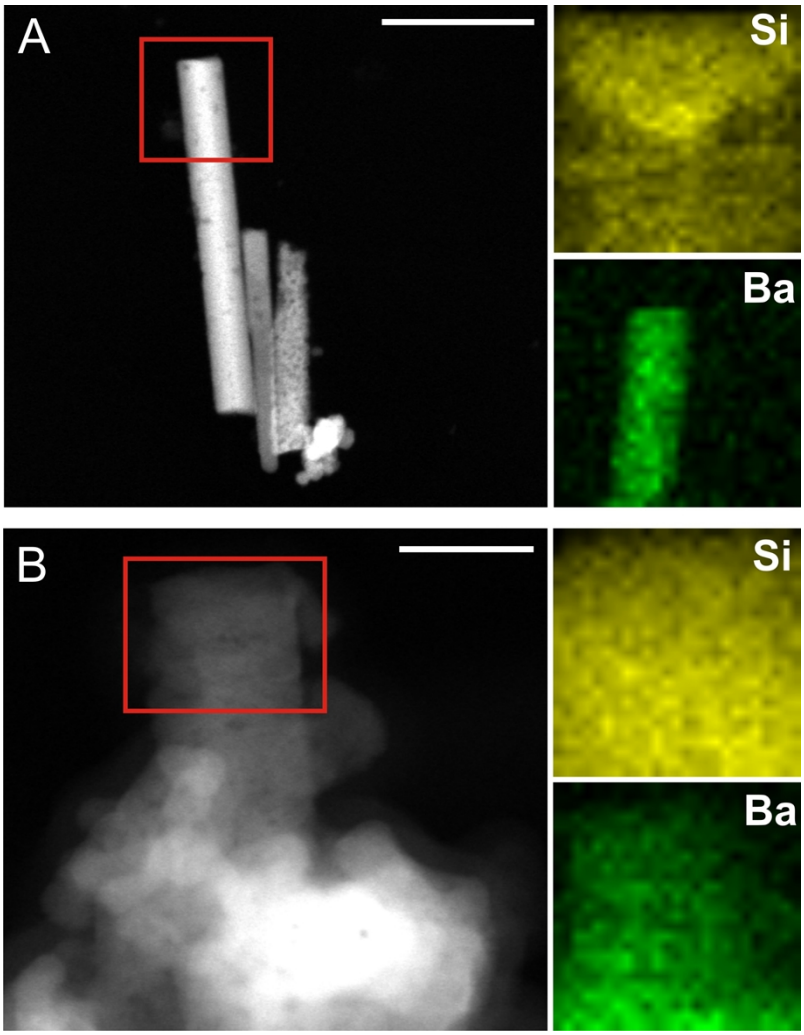

Figure S7. STEM images and corresponding EDX maps for relevant elements (Si and Ba), acquired from particles generated in titration experiments at pH 11.0 under the influence of (A) 600 and (B) 1200 ppm SiO_2. Also at this pH level, a continuous matrix of silica can clearly be discerned around the crystalline $BaCO_3$ rods. Scale bars (A) 200 nm and (B) 50 nm.

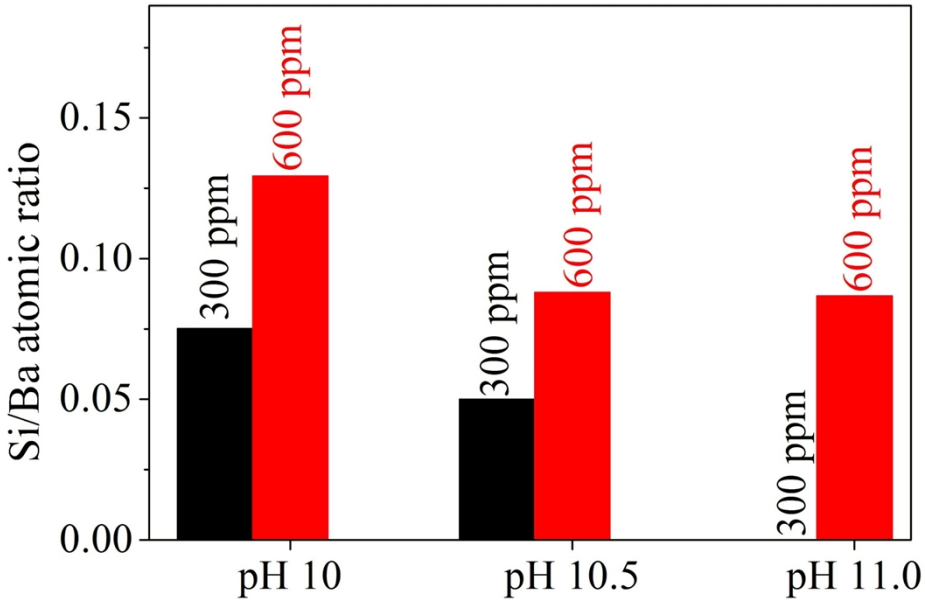

Figure S8. Si/Ba atomic ratios obtained by EDX spectroscopy from powder samples of particles formed in titration assays under different conditions (as indicated). Generally, the relative Si content in the precipitates increases with the silica concentration in solution, whereas it decreases with growing pH (both correlating inversely with the bulk solubility of silica). Note that at pH 11.0 and 300 ppm SiO_2, there is no silica associated to the $BaCO_3$ crystals. In all other cases, the determined silica content is in the same range as reported for the building units of silica-witherite biomorphs.[S2]

References

[S1] J. P. R. de Villiers, *Am. Mineral.*, 1971, **56**, 758-766.

[S2] M. Kellermeier, E. Melero-Garcia, F. Glaab, J. Eiblmeier, L. Kienle, R. Rachel, W. Kunz and J. M. Garcia-Ruiz, *Chem. Eur. J.*, 2012, **18**, 2272-2282.