"Bricks-in-a-wall": the structure of Ca-SO_4 nanorods, the basic building units of gypsum crystals

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The formation pathway of gypsum ($CaSO_4 \cdot 2H_2O$) from aqueous solutions has recently been the subject of intensive research [e.g., 1-3]. However, most of the findings in these studies were based on transmission electron microscopy images and analyses of dried samples. Furthermore, the derived proposed mechanisms are conflicting. We have recently used solution-based and *in situ* and time resolved small- and wide- angle X-ray scattering experiments and showed that gypsum formation proceeds through the assembly of elongated primary precursor species (units) [4]. We argued that that these species contained anhydrous Ca-SO_4 cores that self-assemble into larger units through aggregation. However, we were unable to determine their atomic structure exactly, and to relate these structures to the emerging structure of gypsum.

To understand these structural characteristics and transition of these elongated primary species to the stable gypsum structure we employed in this current study *in situ* liquid total X-ray scattering measurements. The derived pair distribution functions (PDFs) revealed the formation of elongated clusters within 40 s of mixing of the $CaCl_2$ and Na_2SO_4 stock solutions. The thermal tensors of these "nanorods" were on average 3-5 higher as compared to the final gypsum crystals, indicating higher degrees of structural disorder in these clusters. Importantly, during the crystallization to gypsum the intensity of the nanorod contributions to the diffraction patterns decreased only by ~ 20% over the entire reaction period (3 h). Thus, gypsum crystals that formed upon aggregation and coalescence of these precursor rods actually still contained the imprints of the imperfect alignments of the "bricks-in-a-wall" nanorod structures.

Our findings demonstrate the connection between the textured, mosaic-like orientation of gypsum single crystals [5] and its apparent crystallization pathway through assembly of nanocrystalline building blocks.

[1] Wang *et al*. (2012) *J. Mater Chem*. **22**, 22055-22062, [2] Saha *et al*. (2012) *Langmuir*, **28**, 11182-11187 [3] Van Driessche *et al*. (2012) *Science* **336**, 69-72 [4] Stawski *et al*. (2015) *arXiv* **1505.04605v1,** accepted for publication at *Nat. Commun*. (2016). [5] Hildyard *et al*. (2009) *J Microsc*. **236**, 159-164