

High resolution microscopic observation of mineral nucleation, self assembly and transformation: the calcium sulfate system.

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Used various fast and time resolved sample quenching methods combined with high-resolution electron microscopy and selective area electron diffraction we show that the thermodynamically stable phase gypsum forms at room temperature via a three stage process. In stage one the homogeneous precipitation of nanocrystals identified as bassanite, the calcium sulfate hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, occurs. Interestingly, in our experiments bassanite formed below its predicted solubility. In a second stage the bassanite nanoparticles grew into bassanite nanorods that self-assembled into elongated c-axis co-oriented aggregates prior to transforming in stage three into gypsum – the calcium sulfate dihydrate. With this work we show that in the calcium sulfate system a novel crystallization route that does not follow the often-invoked amorphous precursor path (e.g., amorphous calcium carbonate [1]) controls the crystallization. Our findings demonstrate that a stable nanocrystalline precursor phase can form below its bulk solubility, and that in the CaSO_4 system a less hydrated phase, bassanite, forms before the more hydrated one, gypsum, and that the self-assembly of nanoparticles plays the crucial role in the final crystallization. These findings are important because gypsum and bassanite both play important roles in natural [2] and industrial processes [3] but their precipitation mechanisms remain largely unexplored. Understanding why bassanite forms prior to gypsum [4] can lead to more energy efficient construction materials and also help devise better anti-scaling strategies for water desalination. Furthermore, quantifying how bassanite and gypsum form helps explain the persistence of CaSO_4 phases at low water activities on Mars [4] and potentially such a new crystallization route could be responsible for the formation of the massive gypsum deposits in terrestrial evaporitic environments [2] or giant gypsum crystals formed in caves [5,6].

[1] Rodríguez-Blanco et al (2011) *Nanoscale* 3: 265-271 [2] Warren, J. K. (2006) *Evaporites: sediments, resources and hydrocarbons*, pp. 1035. Springer-Verlag, Berlin Heidelberg. [3] Mi, B., Elimelech, M. (2010) *Environ. Sci. Technol.* 44, 2022-2028. [4] Van Driessche, A.E.S., et al. (2012) *Science* 336, 69-72 [5] Wray, J. J., et al., (2010). *Icarus* 209, 416-421. [5] García-Ruiz, J.M., et al. (2007). *Geology* 35, 327-330. [6] Van Driessche, A.E.S., et al. (2011). *Proc. Nat. Acad. Sci.* 108, 15721-15726.