

Bassanite, a Stable Crystalline Precursor Phase During Gypsum Precipitation at Room Temperature

/ ALEXANDER VAN-DRIESSCHE (1*), LIANE G. BENNING (2), MERCEDES OSSORIO (1), JUAN-DIEGO RODRÍGUEZ-BLANCO (2), PIETER BOTS (2), JUAN-MANUEL GARCÍA-RUIZ (1)

(1) Laboratorio de Estudios Cristalográficos, IACT, CSIC-U.Granada, Av. de las Palmeras 4, 18100, Spain.

(2) School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK.

INTRODUCTION

The precipitation of calcium sulfate phases (gypsum, bassanite, and anhydrite) from seawater lead to the formation of numerous ancient and modern evaporite deposits on Earth (Warren, 2006) and to abundant gypsum (Langevin et al., 2005) and bassanite (Wray et al., 2010) on Mars. Additionally they sometimes lead to giant gypsum crystals in caves (García-Ruiz et al., 2007; Van Driessche et al., 2011). Gypsum and bassanite ['Plaster of Paris'] are also important construction materials. But the precipitation of gypsum also poses difficulties through the formation of massive mineral-scales in pipes and other production equipment in desalination plants (Ahmed et al., 2004). The precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) from solution is generally assumed to proceed via a single step direct precipitation pathway, although a multistage process has been reported (Wang et al., 2012). But, a detailed mechanistic understanding of the stages and variations in the structural identities of the solids forming during gypsum synthesis is still missing.

MATERIALS AND METHODS

We used two fast solution sample-quenching methods [vacuum/solvent filtration (Rodríguez-Blanco et al., 2011) and cryo-quenching (Tobler et al., 2009)] and high-resolution transmission electron microscopy (HR-TEM), to investigate the early stages of the nucleation and growth process(es) leading to the precipitation of CaSO_4 phases. We performed precipitation experiments in solutions supersaturated with respect to gypsum ($\text{SI}_{\text{Gyp}} = +0.14$ to $+1.04$, Fig. 1) in order to mimic typical precipitation conditions in desalination plants and in natural evaporitic environments.

RESULTS AND DISCUSSION

Our results show that at all tested conditions the first reaction stage was dominated by the homogeneous precipitation of nanocrystalline particles (single-crystals of 10-15 nm, Fig. 2a), that we identified as the calcium sulfate hemihydrate phase bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; typical d -spacing of $6 \pm 0.3 \text{ \AA}$; $n=60$ particles). The bassanite nanocrystals form at conditions highly undersaturated with respect to bassanite ($\text{SI}_{\text{Bas}} = -0.02$ to -0.72 , Fig. 1) but supersaturated with gypsum.

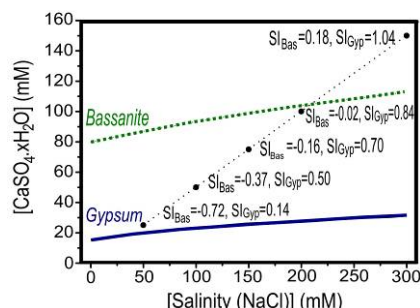


fig 1. Solubility of bassanite and gypsum calculated at 21 °C as a function of total experimental salinity (black dots) with corresponding saturation indexes (SI). The solubility curves, SI_{Bas} and SI_{Gyp} were calculated with PHREEQC (Parkhurst & Appelo, 1999).

Once nucleated, the nanocrystals grow mainly along the c -axis and evolve into nanorods, yet they maintain the same d -spacing and develop a porous aspect (Fig. 2b, c). In a second stage, these nanorods self-assemble into large aggregates, primarily co-oriented along the c -axis, (Fig. 2d), but still maintaining the bassanite nanostructure (Fig. 2e). Finally, gypsum formation dominated the 3rd and last stage of the reaction, and the bassanite aggregates transform into large, well faceted gypsum crystals (Fig. 2f). These results clearly document that the self-assembly of nanocrystalline bassanite precursors is the crucial step controlling gypsum formation from

aqueous solutions.

These time-resolved observations demonstrate that the precipitation of bassanite nanocrystals/nanorods at undersaturated conditions and their oriented self-assembly are the crucial steps controlling gypsum formation from aqueous solutions. In many other similar salt systems, precipitation from solution proceeds via an amorphous precursor and other metastable, crystalline intermediates that are however all formed above their bulk solubility [i.e., amorphous CaCO_3 (e.g. Rodríguez-Blanco et al., 2011), or amorphous $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (e.g. Dey et al., 2010)]. Recently, a similar pathway, where an amorphous calcium sulfate and hemihydrate were sequentially precipitated prior to gypsum has been suggested (Wang et al., 2012).

However, our data shows that the crystallization of gypsum does not proceed via an amorphous stage, but that it occurs via the solution-based nucleation, growth and oriented self-assembly of nanocrystalline bassanite, which precipitates within its "forbidden" undersaturated solubility region ($\text{SI}_{\text{Bas}} = -0.02$ to -0.72). Such a reaction chain suggests that at ambient conditions a different pathway for the precipitation of phases from solution and their transformation through the Ostwald rule may be important. Combined with the observation that the hemihydrate (bassanite) precipitated as a precursor to the more hydrated phase (gypsum), this contradicts the accepted bulk solubility behaviour (Freyer et al., 2003).

But, our data reveal bassanite nanoparticles and nanorods stable relative to an undersaturated solution, suggesting that the solubility of the bassanite nanocrystals must be much lower compared to bulk bassanite. Furthermore, at the lowest

palabras clave: Precursor, Basanita, Gypsum

key words: Precursor, Bassanite, Gypsum

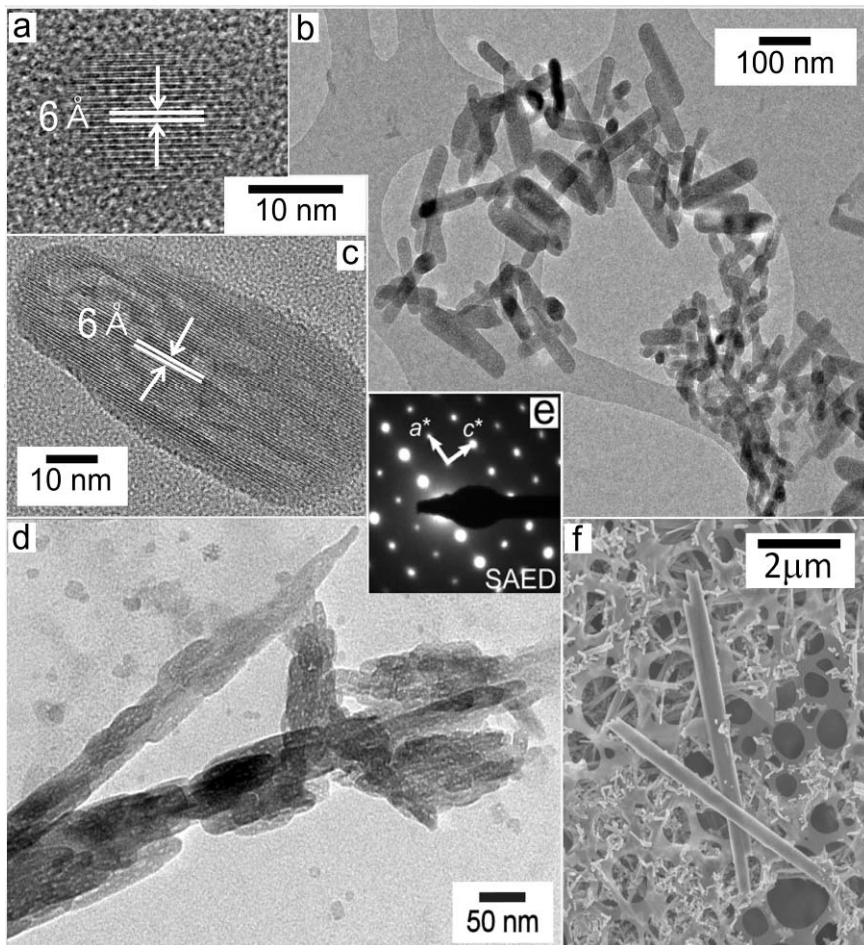


fig 2. HR-TEM and SEM microphotographs of the crystallization stages of gypsum: (a) typical nanocrystalline particle obtained in a 150 mM CaSO_4 solution, showing the 6 Å d-spacing, characteristic for bassanite; (b) bassanite nanorods obtained in the same experiment; (c) larger nanorod of bassanite; (d) large oriented aggregates formed by self-assembly of bassanite nanorods primarily along the c-axis; (e) SAED pattern of an oriented bassanite aggregate showing the reciprocal lattice structure along the a- and c-axis; (f) μm -large final gypsum crystals and bassanite nanocrystals.

supersaturation ($\text{SI}_{\text{Bas}}=-0.72$, $\text{SI}_{\text{Gyp}}=+0.14$ Fig. 1) only small and poorly formed bassanite nanorods were observed, and even after 24 hours no gypsum formed, indicating that when small particles prevail, the solubility of bassanite may actually be lower than that of gypsum.

CONCLUDING REMARKS

Our observations reveal that both the solubility of bassanite and the various inter-transformations in the calcium sulfate system need re-evaluating. On a practical level these findings show that a different reaction pathway could be responsible for the formation of the massive gypsum deposits in terrestrial evaporitic environments and that this same pathway may also be the reason for the persistence of bassanite in the low water activity environments currently postulated for Mars. Furthermore, special attention should be

paid to the bassanite precursor phase in water desalination plants as this may help reduce gypsum scaling. Finally, these results also provide a first step to a more cost-effective pathway for the production of plaster of Paris at room temperature; currently ~100 Mt/year are produced via the thermal dehydration (at 150 °C) of gypsum.

ACKNOWLEDGEMENTS

This study was supported by the Marie Curie EU-FP6 Mineral Nucleation and Growth Kinetics (MIN-GRO) Research and Training Network under contract MRTNCT-2006-035488. Funding from the School of Earth and Environment (Univ. of Leeds), the Consolider-Ingenio 2010 project "Factoría Española de Cristalización" and the project CGL2010-16882 of the Ministerio de Ciencia e Innovación is acknowledged. The authors sincerely acknowledge the help

of M. Ward, A. Brown and S. Allshorn from the Univ. of Leeds with sample characterization.

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