

Non-classical nucleation in calcium sulfates – Insights from the hyper-arid Atacama Desert

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Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) are among the dominant evaporite minerals in the Atacama Desert [1]. They are distributed ubiquitously, and play a key role in local landscape evolution.

The formation mechanism of especially anhydrite has been a matter of scientific debate for more than a century [2]. To date, there exists no model that can reliably predict anhydrite formation at earth's surface conditions. While thermodynamics favor its formation [3], it is hardly achieved on laboratory time scales at conditions fitting the Atacama Desert. Long induction times for nucleation have recently been modeled by Ossorio et al. [4]. However, anhydrite can be readily found in the Atacama Desert. Recently, the mineral was synthesized in flow-through reactors as a byproduct of K-jarosite dissolution at high water activity ($a_w=0.98$) and room temperature [5], even-though the thermodynamic stability field begins only under a value of ~ 0.8 . Additionally, recent studies investigated the nano-structure of various calcium-sulfates, which advocate for highly non-classical crystallization behavior [6]. The specific roles of particulates, ionic or organic reagents working as catalysts for the non-classical crystallization pathway remain to be determined.

Here, we present recent results from flow-through experiments as well as analyses of anhydrite samples from the Atacama Desert. Flow-through experiments were performed to systematically explore the domains of flow rate, composition, ionic-strengths and starting materials. Neither primary, nor secondary anhydrite was produced in any of these experiments. Analyses on Atacama samples reveal the existence of at least three distinct anhydrite facies, with differing mineralogy and micro- to nano-structures. The facies are (1) aeolian deposits with sub- μm grain sizes, (2) (sub-)surface nodules that formed from aeolian deposits and (3) selenites with secondary anhydrite rims. Possible mechanisms of their formation will be discussed.

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