

New Insights into Struvite Formation: Relevance for Phosphorus Recovery from Wastewaters

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The mineral struvite is a magnesium ammonium phosphate hexahydrate [MAP, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$] that is a common component of kidney stones [1] and a prime scale forming mineral in sewage and wastewater treatment systems [2]. At present, struvite formation is being widely investigated as a possible way to recover phosphorus (P) from wastewater streams [3]. Such P-recovery approaches are highly attractive because struvite can be used as a slow-release fertilizer and substitute for conventional fertilizers, thus helping to reduce the environmental impact of excess P release into aquatic systems and the demand on rock phosphate, whose resources are slowly but surely running out.

Considering the relevance of struvite in such diverse and multidisciplinary fields like biomineralization, and industrial and environmental technologies, it is not surprising that numerous studies aim to elucidate its crystallization behaviour. Yet, a detailed understanding of the early crystallization stages is still lacking although such knowledge would help control and manipulate struvite precipitation reactions that are crucial in these diverse systems and applications. In an attempt to fill this knowledge gap we employed a set of in situ characterization techniques enabling us to directly follow (i) the heterogeneous and (ii) homogeneous crystallization of struvite at high spatial and temporal resolution. Firstly, by using atomic force microscopy (AFM) in connection with a fluid cell, we imaged the initial stages of heterogeneous struvite formation on a dissolving brucite ($\text{Mg}(\text{OH})_2$) substrate acting as a Mg source [4]. Our results demonstrate that brucite dissolution and struvite precipitation are closely coupled within a thin fluid boundary layer at the solid-fluid interface. We further show that the heterogeneous crystallization of struvite occurs via a continuous process involving (i) the formation of surface (inner-sphere) complexes and (ii) the subsequent nucleation and growth of primary nanoparticles, followed by (iii) their continuous aggregation, fusion and possible transformation to a crystalline phase.

Secondly, we followed the homogeneous formation of struvite through in situ and time-resolved, synchrotron-based X-ray scattering experiments. Our results from small and wide-angle X-ray scattering (SAXS, WAXS) and pair distribution function analysis (PDF) indicate that struvite formation is preceded by the fast precipitation of apparently non-crystalline nanoparticles (up to 50 nm in diameter) that later self-assemble and crystallize to struvite. Our work is the first to report that both the heterogeneous and homogeneous formation of struvite occurs through non-classical, particle-mediated crystallization pathways. This new knowledge contributes to the discussion regarding the early stages of crystal formation in general and may provide a key in designing novel struvite-based fertilizers or developing more effective struvite-scaling inhibitors.

[1] Coe et al. (1992). *New Engl. J. Med.*, 327(16), 1141-1152. [2] Ohlinger et al. (1998). *Water Res.*, 32(12), 3607-3614. [3] Kataki et al. (2016). *Waste Manage.*, 49, 437-454. [4] Hövelmann and Putnis (2016). *Environ. Sci. Technol.* 50, 13032-13041.