

Tracking transformation processes in the Mg phosphate mineral system – A mineralogical study for environmental applications

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Phosphorous is an essential component of all living beings and is an important component in fertilizers. It is a scarce element on Earth and mining of phosphorous deposits is environmentally harmful (Manning, 2008). Therefore, recent research is focusing on P-recovery from anthropogenic sources, e.g., from wastewaters. The mineral struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is recovered from wastewater and reutilized as a slow-release nitrogen and phosphorus fertilizer (Le Corre et al. 2009). However, struvite is unstable under atmospheric conditions, leading to its decomposition and transformation into other phosphate phases (Tansel et al. 2018). This subaerial transformation has not yet been characterized and kinetic parameters for the transformation reactions are unknown.

In this study, the decomposition and transformation of struvite was investigated by altering synthetic μm - and mm -sized crystals at different temperatures (22–60 °C) in open and closed systems for up to 10 months. Phase transformations were monitored by optical microscopy and Raman spectroscopy and transformation kinetic parameters were quantified by powder X-ray diffraction (XRD) and Rietveld analysis.

Struvite transformed to different products following different mechanisms. In open systems, and at 22 °C, struvite transformed to newberyite ($\text{Mg}(\text{PO}_3\text{OH}) \cdot 3\text{H}_2\text{O}$) by losing its ammonia and three of its water molecules. However, struvite remained fairly stable and at 22 °C this transformation proceeded only by 15 % even after 10 months. In contrary, at 37 and 60 °C, struvite transformed faster and primarily to another phase - dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) which retained its ammonia but lost five out of six water molecules; newberyite occurred only as a minor product (< 5 wt.-%). In the open system, the phase formation proceeded about 35 % faster at 37 °C and 100 % faster at 60 °C compared to 22 °C. In contrast, in the closed system even after 10 months at 60 °C struvite remained stable and the transformation barely started (< 2 wt.-%). The XRD data showed that after about 8 months at 37 °C and after 2 months at 60 °C in the open system amorphization of struvite occurs through the complete loss of ammonia and water.

Microscopic imaging revealed that both newberyite and dittmarite were characterized by pseudomorphic overgrowth after struvite, while showing similar optical properties. Yet, the kinetic data indicates different formation mechanisms for the two phases. The partial pressure of water and ammonia in the reacting atmosphere, which was documented by the differences in open and closed kinetic rates, as well as differences in the crystal structures were the main drivers for the breakdown of struvite to the two other magnesium phosphate phases.

As struvite is used as a slow-release fertilizer in agriculture, our results document that its transformation to newberyite leads to the loss of ammonia, which has important implications for fertilizer storage. Even at 22 °C, after 10 months 15 % of the ammonia is lost. Although at higher temperatures (≥ 37 °C) the transformation leads to the retaining of ammonia in the

dittmarite structure, such a temperature requires a higher energy demand for storage. Therefore, our study indicates that struvite fertilizer should not be stored at ambient conditions, but at temperatures below 22 °C and in closed containers.

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