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Temperature-dependent Reactivity and Transformation Kinetics of Magnesium Phosphate Minerals

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Phosphorous and nitrogen are important components of fertilizers in global agriculture. The mineral struvite ($MgNH_4PO_4 \cdot 6H_2O$) occurs in vanishing guano deposits and is thus a limited resource. It is, however, recovered from wastewater and reutilized as a slow-release nitrogen and phosphorus fertilizer. However, struvite is unstable under atmospheric conditions, leading to its transformation into other phosphate phases, yet the transformation rates and mechanisms of this process are not known.

We investigated the transformation processes by reacting synthetic, µm- and mm-sized struvite crystals at different temperatures (22-60 °C) in open and closed systems. The alteration of struvite with time was monitored by X-ray diffraction (XRD), optical microscopy and Raman spectroscopy, quantifying the kinetics and phase development by Rietveld analysis.

Our data reveal different transformation products and kinetic rates depending on temperature. At 22 °C, struvite loses ammonia and part of its water transforming to newberyite ($Mg(PO_3OH) \cdot 3H_2O$), but even after 10 months only a < 15 % transformation was observed. However, at 37 and 60 °C, struvite primarily transforms to dittmarite ($MgNH_4PO_4 \cdot H_2O$), with newberyite occurring only as a minor product (< 5 wt.-%). In the open system, the formation of dittmarite proceeds about one order of magnitude faster at 60 °C compared to 37 °C, while in the closed system, this same transformation has barely started (< 2 wt.-%) after 10 months.

Microscopic imaging revealed that newberyite and dittmarite are characterized by similar textural relationships to the struvite host crystals, yet the transformation mechanisms are dependent on the partial pressure of water and ammonia in the reacting atmosphere as documented by the differences in open and closed kinetic rates. The finding that at ambient conditions (at 22 °C) struvite transforms to the ammonia-free newberyite, when ‘stored’ in dry conditions, has important implications for the use of wastewater derived struvite as a slow-release nitrogen-containing fertilizer. At higher temperatures, the ammonia is retained in the dittmarite structure and thus our data indicates that struvite fertilizer should not be stored at ambient conditions, but at temperatures below 22°C and in closed containers.