

# Nucleation and crystallization of vivianite via nanoparticulate amorphous ferrous phosphate: a combined spectroscopic and microscopic study

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Nucleation and crystallization of mineral phases are universally observed processes controlling biogeochemical cycles in many natural and synthetic systems. Yet, the exact parameters controlling the transformation of ions to crystals – whether via the classical or non-classical pathway - are not well understood. In the ferrous-phosphate system particularly, the formation pathway of the thermodynamically stable mineral phase vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) – a phase often found in ancient and modern anoxic lakes, sediments and soils, remains unknown. To unravel the discrete stages of nucleation and crystallization of vivianite, we experimentally monitored the formation and transformation of solid phases in aqueous solutions by employing correlated, time-resolved *in situ* (UV-vis spectrophotometric) and *ex situ* (e.g., XRD, TEM, XAS, PDF etc.) methods. We isolated and characterized a novel amorphous ferrous phosphate precursor (AFEP), that forms nanoparticles in the size range of 50-100 nm diameters. With time, these AFEP nanoparticles crystallize to the thermodynamically stable end-product vivianite following the non-classical pathway. This requires fundamental structural changes in AFEP and the incorporation of additional water molecules and  $\text{Fe}^{2+}$  and  $\text{PO}_4^{3-}$  ions. Our results offer fundamentally new insights into a previously unknown aqueous/non-classical amorphous-to-crystalline transformations in the  $\text{Fe}^{2+}$ - $\text{PO}_4^{3-}$  system. The findings have particular relevance to processes in anoxic ferruginous, non-sulfidic and yet phosphate-rich, aqueous systems like soils and modern stratified lakes as well as in ferruginous ancient oceans, where AFEP could be an important intermediate phase prior to vivianite crystallization.