On the mechanism of iron(III) (oxyhydr)oxide nucleation

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Playing important roles in geology, biology, medicine, and industry, iron (oxyhydr)oxides are of great interest [1, 2]. In spite of a vast amount of literature on iron chemistry, however, iron oxide precipitation is still not well understood. Formation pathways via inorganic oligomeric or polymeric species have been proposed, and described by means of classical nucleation theory.

Here, we show that the pathway of iron oxide formation passes through multiple stages, during which the system distinctly changes its chemical behavior. This governs the phase separation event, upon which the complex inorganic precursors that are present at the earliest stages of the reaction change their thermodynamic solute speciation to become a new phase, which subsequently grows via aggregation.

Our results show that the formation of iron oxides is consistent with the notions of the so-called pre-nucleation cluster pathway [3]. Furthermore, we demonstrate that this mechanism can explain the occurrence of distinct forms, ferrihydrite, akageneite and hematite, based on basic chemical notions rather than the general concept of supersaturation.

[1] Flynn (1984) *Chem. Rev.* **84**, 31-41. [2] Baumgartner & Faivre (2015) *Earth-Sci. Rev.* **150**, 520-530. [3] Gebauer, Kellermeier, Gale, Bergström & Cölfen (2014) *Chem. Soc. Rev.* **43**, 2348-2371.