The molecular mechanism of iron(III) oxide nucleation

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Playing important roles in geology, biology, medicine, and industry, iron oxides are of great interest [1, 2]. In spite of a vast amount of literature on iron chemistry, 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. Herein, 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 follows a pathway that is consistent with the basic literature on iron chemistry; however, the notions of a recently proposed, alternative framework —the so-called pre-nucleation cluster pathway [3]— are required to understand the event of phase separation.

[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.