

# Quantitative Analyses of the Early Stages of Iron Oxide Formation

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## Introduction

The precipitation of minerals from aqueous solutions is usually considered to conform to the principles of classical nucleation theory (CNT) [1]. However, it has been shown recently that many systems do not follow the pathways predicted by CNT [2]. As the character of chemical interaction in iron oxides is intermediate between covalent and ionic, it represents an interesting and important system for extending our understanding of the mechanisms of mineral nucleation.

## Analyses of precursors and intermediates during the formation of iron oxides

Hydrolysis of aqueous iron(III)-solutions occurs already at very low pH-levels. To gain insight into the precipitation process it is necessary to make the different stages of the reaction accessible to analytical methods. This includes highly dynamic and very small species. A titration setup was used to guarantee controlled and homogeneous nucleation [3], enabling the systematic examination of the process by increasing the ion concentrations slowly and continuously. The development of composition and chemical and physical properties of the solution are traced *in situ* by continuous measurements of pH-values and ion concentrations, light scattering and UV-Vis spectroscopy. Additional information is obtained by taking samples and examining them with *ex situ* (cryogenic-) electron microscopy, analytical ultracentrifugation, dynamic light scattering, particle tracking microscopy etc. The application of multiple analytical methods provides complementary data, yielding global information on the system.

## Results

The results of this study suggest that the hydrolysis of iron(III) leads to a multistep process starting with a polymerization-like reaction in which polynuclear species of iron(oxo)-hydroxides are formed. Further growth into larger particles occurs through aggregation of these precursors which might be triggered by a nanoscopic phase separation event and thus, the development of interfaces.

[1] Becker, Döring (1935) *Ann. Phys.* **24**, 719–752. [2] Gebauer, Kellermeier, Gale, Bergström, Cölfen (2014) *Chem. Soc. Rev.* [3] Gebauer, Völkel, Cölfen (2008) *Science* **322**, 1819-1822