General model for the aqueous precipitation of rough-surface nanocrystals and application to ferrihydrite genesis

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ABSTRACT

Ferrihydrite is a key reactive nanoparticle in the Earth surface environment that regulates nutrient and metal cycling in marine, lacustine, and groundwater settings; yet its genesis is unknown and there is no mechanistic explanation of its nanostructural nature. We develop a model, based on established aqueous precipitation theory, for rough-surface phases growing by accretion of monomers under fast diffusion conditions. The model is entirely defined in terms of a minimal set of necessary microscopic (molecular-scale) characteristic parameters. It is applied to ferrihydrite where the needed microscopic parameters are constrained by some of the mineral’s known physico-chemical properties. Our model qualitatively reproduces the main nanostructural properties and known precipitation kinetics of ferrihydrite, predicting that ferrihydrite will be nanometric in size, will have a narrow particle size distribution (standard deviation width equal to a fraction of the average particle size), and will typically precipitate from supersaturated conditions within times ranging from a fraction of a second to several days, under normal environmental-proxy conditions. The model also suggests that different metastable structures of ferrihydrite having similar rough surfaces would kinetically compete during nucleation and growth to coexist in the final product, as observed by Janney et al. (2000a, 2001).

Keywords: Ferrihydrite, precipitation, nucleation, oxyhydroxide, nanoparticle

INTRODUCTION

Ferrihydrite (Fh) is a biospheric reactive nanoparticulate authigenic mineral having approximate formula Fe₃O₄·4H₂O (Jambor and Dutrizac 1998). That Fh is ubiquitous in soils and early sediments has recently been questioned (Thompson et al. 2006; van der Zee et al. 2003), however its key role in nutrient and metal mobility in aqueous environments is well established (Buffle et al. 1989; Leppard et al. 1988; Mayer and Jarrell 1995; Rancourt et al. 2001, 2005; Rose et al. 1996; Thibault et al. 2009).

Materials science and mineralogy researchers often stress the importance of structure (crystal structure, surface structure, micro-structure) because of its relations to both genesis (synthesis route) and function (reaction and interaction pathways, mechanisms, and rates); however, these relations are rarely made explicit using predictive quantitative models.

The case of Fh has been hotly debated. The many different proposed mechanisms for the mineral genesis of Fh have been critically examined by Rancourt et al. (2005). The dominant paradigm of a formation mechanism involving a heterogeneous biotic template effect in natural aqueous environments has been challenged (Rancourt et al. 2005). Rancourt et al. (2005) proposed that the nanometric sizes (1–6 nm) of all observed natural and synthetic Fh samples were due to a common mineral genesis base on rapid aqueous precipitation and provided an estimate of predicted particles sizes from an estimate of critical nucleus sizes from classical nucleation theory.

There are competing models for the structure of Fh (e.g., Towe and Bradley 1967; Eggleton and Fitzpatrick 1988; Drits et al. 1993; Janney et al. 2000a, 2000b, 2001; Jansen et al. 2002). Recently, Michel et al. (2007a, 2007b) proposed a unique structure for all forms of synthetic Fh, whereas the high-resolution transmission electron microscopy and electron diffraction work of Janney et al. (2000a, 2000b, 2001) shows a nanoparticulate system with several different intra-particle structures. Rancourt and Meunier (2008) have shown that the single structure proposed by Michel et al. (2007b) is incorrect.

We present a new numerical model of aqueous precipitation, having no undetermined phenomenological parameters and based on a combination of the expected microscopic mechanisms (where clusters grow by accretion of monomers), classical nucleation theory, and transition state theory, that reproduces the qualitative features of the precipitation kinetics and particle size distributions (PSDs) of Fh when known or constrained values of physical properties of Fh are used. To our knowledge, this study constitutes the first modeling attempt to establish a quantitative relationship between the mineral genesis conditions and structural properties of Fh. Our work suggests that Fh is a product of fast homogeneous precipitation (or co-precipitation if co-solutes are present) and that the non-equilibrium product need not consist of a single-structure material.

Whereas our numerical model involves solving the coupled time-dependent ordinary differential equations for post-critical cluster populations from statistical physics, other recent numerical studies have used molecular dynamics simulations...