Polycrystallinity of green rust minerals and their synthetic analogs: Implications for particle formation and reactivity in complex systems†

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ABSTRACT

We demonstrate in this study that natural green rust nanoparticles and their synthetic analogs can be complex polycrystalline phases composed of crystallites only a few nanometers in size, and they often include nanometer-sized regions of amorphous material. The natural green rusts are Zn-bearing pseudo-hexagonal platelets previously identified by us in the contaminated mine drainage of the former Ronneburg uranium mine in Germany (Johnson et al. 2014). We also identified Ni- and Cu-bearing green rust platelets in the sediment underlying the drainage outflow 20 m downstream, and, using dark-field transmission electron microscopy (DF-TEM), found that these natural green rusts are not usually structurally coherent single crystals. Synthetic sulfate green rusts are also polycrystalline and composed of crystallites of only a few nanometers in size, though different synthesis conditions produced different patterns of polycrystallinity. While pseudo-hexagonal platelets are the typical morphology of green rust, we also synthesized green rust nanorods, which have not previously been reported. In addition to the known characteristics of green rusts (including a very large aspect ratio and high-energy surface topography), these natural green rusts exhibit a high abundance of defect sites and likely a rough surface topography. The combination of these characteristics has important implications for the reactivity of green rust with biogeochemical interfaces in natural and anthropogenic systems.

Keywords: Nanorod, nanoparticle, layered-double-hydroxide, iron oxide, transmission electron microscopy, texture, oriented aggregation, mine drainage

INTRODUCTION

There are many factors that influence mineral interactions with the surrounding components of Earth systems. Composition, surface atomic structure, crystal morphology, size, surface charge, and surface topography are all just a few mineral properties that affect their behavior in these complex natural settings (Hochella et al. 2012 and references therein). Nanoparticles have especially high reactivity compared to larger particles due to their small size (high surface area to volume ratio) and comparatively high-energy surface topography and atomic structure. Nanoparticles of the extensive family of iron oxides and their roles in the overall biogeochemical cycling of iron on Earth have been comprehensively studied, as well as the intimate link with the fate and transport of environmental pollutants (e.g., Banfield and Zhang 2001; Waychunas et al. 2005; Raiswell 2011; Taylor and Konhauser 2011; Dong and Lu 2012; and many references therein). However, geochemists continue to discover nanoscale nuances about iron oxide mineral structure and composition that change the way we think about their interactions with environmental systems. For example, schwertmannite is an iron oxyhydroxysulfate phase that is considered to be a mineral, but upon careful examination by high-resolution transmission electron microscopy (HR-TEM), natural samples were found to consist of both nanocrystalline and amorphous domains (French et al. 2012). The long-range order that is fundamental to the definition of a mineral does not exist in these natural samples. Studies like these that use analytical TEM techniques are useful for determining heterogeneities in nanoscale composition and structure, which highly influence a mineral’s reactivity with its surroundings. Minerals with shorter range order, abundant structural defects, and variable/gradational compositions are likely quite common in nature (Caraballo et al. 2015, and references therein).

In the complex system of anoxic underground mine drainage, another example of an iron oxide mineral, green rust, was found that appears to contain both areas of crystalline and amorphous material (Johnson et al. 2014), which warranted further investigation. Green rusts are a family of minerals that contain both reduced and oxidized iron species (Fe2+ and Fe3+) within iron hydroxide layers (aka a layered double hydroxide, or LDH), separated by an interlayer containing a wide array of anions and cations somewhat analogous to clays (Trolard and Bourrié