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SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

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 surface area to volume ratio, and the redox properties allowed by the structural mixture of Fe^{2+} and Fe^{3+}), these polycrystalline platelets 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