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Radiation-induced Dissolution of a Recalcitrant Aluminum Oxyhydroxide in Liquid Cell TEM

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Boehmite (γ-AlOOH) is a layered aluminum oxyhydroxide mineral that is highly resistant to dissolution. It plays an important role in the biogeochemical cycling of aluminum (which is toxic to plants and animals), the extraction of aluminum from bauxite ore via the Bayer process, and in the treatment of aluminum-rich radioactive waste generated during the nuclear fuel cycle. The ability to predict and control the precipitation and dissolution of boehmite is key to these processes.

The rate of dissolution is affected by nanoparticle size, degree of crystallinity and presence of crystal defects, ratio of basal to lateral surface area, aggregation of particles, availability of reactive surfaces, and presence of surface coatings or metal dopants. Changes in nanoparticle size and morphology are particularly interesting because they affect the ratio of bulk to surface free energy and thermodynamic stability of the particles. The chemical dissolution of boehmite is traditionally performed at high pH (pH 13-15) and elevated temperature (>80 °C). Most studies of boehmite dissolution monitor only solution chemistry, not particle morphology, and it is commonly assumed that dissolution occurs from the lateral edges.

Surprisingly, boehmite nanoparticles suspended in deionized water were observed to dissolve when imaged in a liquid cell in a transmission electron microscope (TEM) operating at 200 and 300 kV in both bright field TEM and dark field scanning TEM modes. Current evidence suggests that the dissolution of boehmite induced by electron beam radiation may occur via different mechanism than caustic dissolution. Previous work by Conroy and Soltis [1] showed that the dissolution of 50-100 nm rhombohedral boehmite plates proceeded via delamination of the layered mineral structure followed by dissolution of the individual layers, and that larger, Fe-doped boehmite and the layered mineral gibbsite ($Al(OH)_3$), which is more sensitive to chemical dissolution, did not dissolve under identical conditions.

One limitation of the previous work was the difference in size between the Fe-doped and undoped boehmite nanoparticles. This work uses liquid cell TEM to examine the dissolution behavior of a broader suite of boehmite nanoparticles, including size-controlled Fe-doped and undoped particles. We found that the dissolution of 100-200 nm boehmite particles was dependent on electron flux, and that these particles required a flux of ca. 10× greater than was used in the earlier work by Conroy and Soltis in order to dissolve. The Fe-doped particles were reexamined at this higher flux and found to not dissolve even when the flux was increased to ca. 40× the original. Figure 1 shows liquid cell TEM images of undoped and Fe-doped boehmite nanoparticles before (A, undoped only) and after (B and C) prolonged exposure to a 200-keV electron beam. We compare boehmite particles ranging in size from 20-300 nm with varying degrees of post-synthesis annealing and hydrogen/deuterium isotopic substitution via liquid cell TEM, Raman

spectroscopy, and X-ray diffraction to probe the effects of crystal size, crystallinity, and preferential bond breakage during the radiation-induced dissolution of boehmite nanoparticles.[2]

References:

[1] M Conroy, JA Soltis, RS Wittman, FN Smith, S Chatterjee, X Zhang, ES Ilton and EC Buck, Scientific Reports **7**(2017), 13274.
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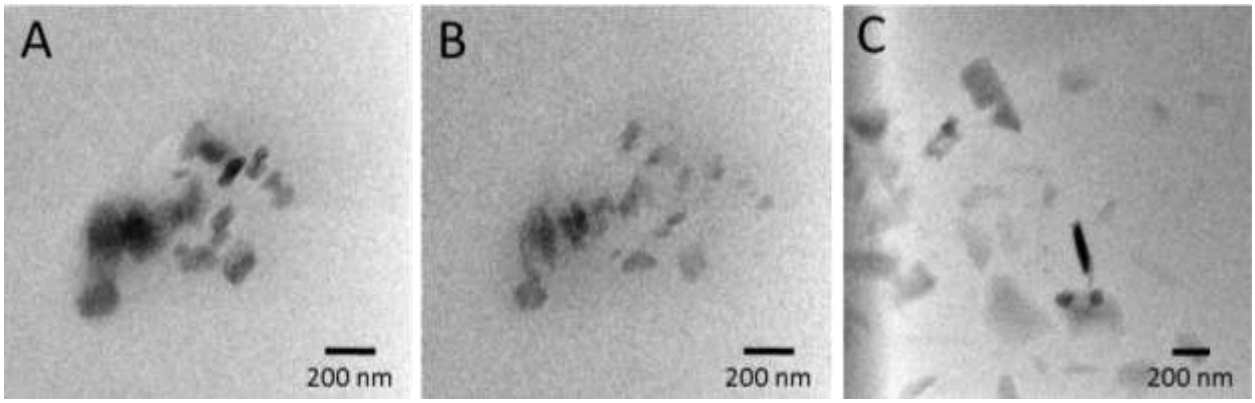

Figure 1: Liquid cell TEM images of boehmite nanoparticles in water. A) Undoped boehmite at the beginning of the imaging session, with electron beam exposure limited to the time required to focus the microscope and find a suitable area. B) After 20 additional minutes of exposure at a flux of 300 e^-/nm^2. C) Fe-doped boehmite after 20 minutes of electron beam exposure at a flux of 300 e^-/nm^2.

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