

Direct Observation of Dissimilar Dissolution Behaviours in a Radiation Field: An In-situ Study of Layered Aluminum Based Minerals

Conroy, M.^{1,2}, Soltis, J.³, Wittman, R.³, Smith, F.³, Chatterjee, S.³, Zhang, X.³, Ilton, E.³ and Buck, E.³

¹ Pacific Northwest National Laboratory, Ireland, ² TEMUL, Department of Physics, School of Natural Sciences & Bernal Institute, University of Limerick, Ireland, ³ Pacific Northwest National Laboratory, United States

The exact atomic structures of layered minerals have been difficult to characterize because the layers often possess out-of-plane hydrogen atoms that cannot be detected by many analytical techniques. However, the ordering of these bonds are thought to play a fundamental role in the structural stability and solubility of layered minerals. Two of the most common aluminum (oxy)hydroxide (AOH) mineral phases in nature, boehmite (γ -AlOOH) and gibbsite (γ -Al(OH)₃), are classified as layered materials. The geochemical cycling and relative stability of these two phases has attracted considerable interest, as aluminum toxicity affects plants, humans, and other animals.¹⁻² These minerals are also key components in the Bayer process, which uses dissolution/reprecipitation to purify and extract Al from bauxite ore deposits,³⁻⁴ and in the treatment of Al-rich radioactive waste generated during the nuclear fuel cycle.⁵ The structural units, or layers, are composed of aluminum hydroxide and oxy(hydroxide) chains (gibbsite and boehmite respectively) which extend along the a-axis. In contrast to micas, clays, and double hydroxides, both boehmite and gibbsite do not (normally) have layer charges arising from isomorphous substitutions; consequently the interlayer region is devoid of charge balancing ions and layer cohesion is not due to electrostatic forces. Rather, within the interlayer region a network of out-of-plane hydrogen bonds ensure the integrity of the layered structure.⁶⁻⁷ The precise positions of hydrogen atoms between the interlayers, which determines the space group, is still actively debated in literature.⁸⁻⁹

We report a new strategy of using the intense radiation field of a focused electron beam to probe the effect of differences in hydrogen bonding networks on mineral solubility while simultaneously imaging the dissolution behaviour in real time via liquid cell electron microscopy(LCEM).¹⁰ We show the loss in hydrogens from interlayers of boehmite (γ -AlOOH) resulted in 2D nanosheets exfoliating from the bulk that subsequently and rapidly dissolved. However gibbsite (γ -Al(OH)₃), with its higher concentration of OH terminating groups, was more accommodating to the deprotonation and stable under the beam.

Through a series of LCEM experiments controlling the energy of irradiation, concentration of radiolysis products, and using Fe(III)-doped boehmite we suggest that dissolution was caused by disruption of the hydrogen bonding network of boehmite which destabilized the layered structure, resulting in delamination followed by rapid dissolution. The stability of gibbsite and specifically the fact that it did not delaminate during irradiation suggests that its hydrogen bonding network is more robust under these conditions compared to boehmite. The fact that gibbsite expresses two distinct hydroxyl groups on its basal surface compared to only one for boehmite, might give the hydrogen bonding network of gibbsite a greater capacity to accommodate radiation induced defects. The surprising stability of Fe-doped boehmite relative to un-doped boehmite draws attention to the role of electron/hole pairs in the dissolution process. These results lend new insight into the importance of interlayer hydrogen ordering with regard to the structural stability of layered minerals.

1. Poschenrieder, C.; Gunsé, B.; Corrales, I.; Barcelò, J., A glance into aluminum toxicity and resistance in plants. *Science of The Total Environment* **2008**, *400* (1 - 3), 356-368.
2. Rengel, Z., Aluminium cycling in the soil-plant-animal-human continuum. *Biometals* **2004**, *17*(6), 669-689.
3. Panias, D.; Asimidis, P.; Paspaliaris, I., Solubility of boehmite in concentrated sodium hydroxide solutions: model development and assessment. *Hydrometallurgy* **2001**, *59*(1), 15-29.
4. Alex, T. C.; Kumar, R.; Roy, S. K.; Mehrotra, S. P., Leaching behaviour of high surface area synthetic boehmite in NaOH solution. *Hydrometallurgy* **2013**, *137*, 23-32.
5. Russell, R. L.; Peterson, R. A., Boehmite Dissolution Model Based on Simulant Data. *Industrial & Engineering Chemistry Research* **2010**, *49*(10), 4542-4545.

6. Digne, M.; Sautet, P.; Raybaud, P.; Toulhoat, H.; Artacho, E., Structure and Stability of Aluminum Hydroxides: A Theoretical Study. *The Journal of Physical Chemistry B* **2002**, *106* (20), 5155-5162.
7. Zuo, Z.; Huang, W.; Han, P.; Gao, Z.; Li, Z., Theoretical studies on the reaction mechanisms of AlOOH- and γ -Al₂O₃-catalysed methanol dehydration in the gas and liquid phases. *Applied Catalysis A: General* **2011**, *408* (1 - 2), 130-136.
8. Veilly, E.; Roques, J.; Jodin-Caumon, M.-C.; Humbert, B.; Drot, R.; Simoni, E., Uranyl interaction with the hydrated (001) basal face of gibbsite: A combined theoretical and spectroscopic study. *The Journal of Chemical Physics* **2008**, *129* (24), 244704.
9. Vyalikh, A.; Zesewitz, K.; Scheler, U., Hydrogen bonds and local symmetry in the crystal structure of gibbsite. *Magnetic Resonance in Chemistry* **2010**, *48* (11), 877-881.
10. Conroy, M.; Soltis, J. A.; Wittman, R. S.; Smith, F. N.; Chatterjee, S.; Zhang, X.; Ilton, E. S.; Buck, E. C., Importance of interlayer H bonding structure to the stability of layered minerals. *Scientific Reports* **2017**, *7*(1), 13274.