Oxalate Driven Goethite Dissolution in Cold, Dark, Acidic Environments

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Mineral dissolution is a key process driving iron biogeochemistry, creating and mobilizing bioavailable iron across different compartments of Earth's critical zone¹. Acidic regions of the Cryosphere (e.g. acid soils, acid mine/rock drainage, clouds) are especially active because freezing concentrates acids and organics into minute volumes of liquid trapped between ice (micro)crystals. It is this 'liquid intergrain boundary' that continues to drive iron dissolution within the confines of polycrystalline ice^{2, 3}. In this study, we explored the well-known case of oxalate-driven goethite dissolution in ice using batch adsorption and Raman microscopy. We find that freezing enhanced dissolution rates and yields, yet the freeze concentration effect was selective, preferentially concentrating goethite into the liquid intergrain boundary but not necessarily oxalate. This was notably captured through freeze-thaw events which made oxalate trapped in ice available to liquid water in each successive freeze-thaw event, thus triggering new fluxes of released iron. These results should thus help explain emerging fluxes of iron to the environment, especially now that climate change is increasing the frequency of freeze-thaw events and the spatial distributions of ice on Earth.

[1] Kim, Choi, Hoffmann, Yoon & Park (2010), *Environmental Science & Technology 44* (11), 4142-4148.

[2] Jeong, Kim, Min & Choi (2015), *Environmental Science & Technology 49* (21), 12816-12822.

[3] Menacherry, Kim, Lee, Choi & Choi (2018), *Environmental Science & Technology 52* (23), 13766-13773.

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