American Mineralogist, Volume 110, pages 430–445, 2025

Coexisting hematite induces and accelerates the transformation of ferrihydrite: Pathway and underlying mechanisms

Hongyan Wei[1,2,3], Jing Liu[4,*], Qingze Chen[1,2,3], Yixuan Yang[1,2,3], Haiyang Xian[1,2,3], Xiaoliang Liang[1,2,3,†], Yiping Yang[1,2,3], Jianxi Zhu[1,2,3,‡], and Runliang Zhu[1,2,3,*]

[1]CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou, 510640 China
[2]CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China
[3]University of Chinese Academy of Science, Beijing, 100049 China
[4]State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology, Taipa 999078, Macau, China

Abstract

Crystallization induced by heterogeneous surfaces is an important process in geochemistry, biomineralization, and material synthesis, but the effects of heterogeneous surfaces on the transformation of metastable phases into new crystals remain poorly understood. In this work, we studied the transformation behaviors of ferrihydrite (Fhy) in the presence of hematite (Hem) nanoplates with specific exposed facets ({001} and {113}) at different pH (4, 7, and 12). Our results reveal that the Hem nanoplates can induce the transformation of Fhy to Hem/Gth (goethite) and accelerate the transformation rate. This effect is primarily achieved by modulating the dissolution-recrystallization process, i.e., accelerating the dissolution of Fhy and promoting the heterogeneous crystallization (to form new Hem/Gth) at the surface of added Hem nanoplates, and solution pH plays a crucial role in these processes. Specifically, a relatively low supply of dissolved Fe^{3+} from Fhy at pH 4 favors island growth of new Hem at the {001} facets of Hem nanoplates and layer-by-layer growth at the {113} facets, which eventually results in the formation of thermodynamically stable pseudo-cubic morphology (exposing {012} facets). Because of the very low solubility of Fhy at pH 7, the induced transformation of Fhy by Hem nanoplates is relatively weak. While at pH 12, a high supply of dissolved Fe^{3+} from Fhy benefits the layer-by-layer growth at {001} facets of Hem and the significant heteroepitaxial growth of Gth at the {113} facets. Besides the induced transformation, the direct solid-state transformation of Fhy into Hem and the homogeneous crystallization of dissolved Fe^{3+} also contribute to the transformation of Fhy. This study reveals the mechanisms of induced transformation of Fhy in the presence of Hem nanoparticles, which will advance our understanding of the significant effects of heterogeneous surfaces in modulating metastable phases and supplement the transformation mechanisms of Fhy.

Keywords: Iron oxides, crystallization, phase transformation, heterogeneous surfaces, facet-specific