American Mineralogist, Volume 110, pages 1303–1317, 2025

Nanoscale insights into weathering of Ti-bearing minerals and heterogeneous crystal growth mechanisms of nano Ti oxides in altered volcanic ash

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Abstract

A deep understanding of the formation and alteration mechanisms of titanium-bearing minerals in volcanic sedimentary sequences is crucial for a clear recognition of the Ti element cycle on Earth. Here we used micro- to nanoscale characterization techniques, including focused ion beam (FIB), high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), and nano-computed tomography (Nano-CT) to investigate nano mineralogical characteristics and formation mechanisms of authigenic Ti oxides and altered Ti-Zr-O minerals (srilankite) in altered volcanic ash across a Permian-Triassic boundary. The results indicate that the growth of anatase and brookite (TiO_2 polymorphs) nanoparticles within the volcanic ash matrix under acidic conditions is regulated by Ostwald ripening with minor semi-oriented attachment and recrystallization. Meanwhile, the growth of brookite crystals in altered srilankite particles ($ZrTi_2O_6$) is predominantly controlled by the oriented attachment mechanism. This phenomenon suggests that the growth mechanisms of TiO_2 nanoparticles are highly sensitive to the microenvironments surrounding the particles, with different growth behaviors possibly occurring even within the same layer. EELS results show that, under chemical weathering, the edges of TiO_2 crystals tend to amorphize, gradually reducing to the Ti^{3+} valence state at the edge. Following the alteration of srilankite, primary brookite crystals form in situ (particle size ~10 nm), initially growing into incomplete oriented particles through oriented attachment. Subsequently, these oriented particle fragments further grow by attaching to primary crystals in the matrix, forming large (particle size along the long axis ~300 nm) brookite crystals with consistent crystallographic orientations. This phenomenon demonstrates that during the alteration process of unstable Ti-O minerals, Ti migration does not occur across particle scales.

Keywords: Ti oxide nanoparticle, anatase, brookite, oriented attachment, chemical weathering