American Mineralogist, Volume 95, pages 556–562, 2010

HRTEM investigation of trilling todorokite and nano-phase Mn-oxides in manganese dendrites

Huifang Xu,[1,*] Tianhu Chen,[1,2] and Hiromi Konishi[1]

[1]Department of Geoscience, and Materials Science Program, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.
[2]College of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, P.R. China

Abstract

We characterized manganese dendrites on three different substrate rocks (rhyolite, clayey siltstone, and limestone) using high-resolution transmission electron microscopy. Manganese dendrites are mainly composed of nanometer scale Mn-(hydr)oxides, Fe-(oxy)hydroxide, sulfate, and clay minerals including hollandite, todorokite, birnessite, goethite, amorphous Fe-hydroxide, smectite, illite, and gypsum. Each sample has a different main manganese phase. Two dendrite samples have more than one manganese phase. Todorokite crystals on a limestone sample from Altmühl Valley, Germany, showed trilling intergrowths. Chain-width disorder and chain termination occur in todorokite. The sum of the numbers of octahedral wall layers and octahedral chains were equal at both sides beyond the termination. The chain termination rule was explained by the geometry of octahedral chains and the octahedral wall layer. The trilling intergrowths of todorokite might be formed by transforming the structure from birnessite to todorokite, or by multiple, epitaxial todorokite nucleations on octahedral wall layer of todorokite or birnessite. Based on chain-width disorder in the todorokite, we suggest that the todorokite might have been transformed from birnessite.

Keywords: Manganese dendrites, origin of the dendrites, microstructure, hollandite, todorokite, birnessite, Fe-hydroxide, transmission electron microscopy