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Manjiroite or hydrous hollandite?

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Abstract

In this study, we investigated an unusual natural Mn oxide hollandite-group mineral from the Kohare Mine, Iwate Prefecture, Japan, that has predominantly water molecules in the tunnels, with K, Na, Ca, and Ba. The specimens are labeled as type manjiroite, but our analyses show that Na is not the dominant tunnel species, nor is it even the primary tunnel cation, suggesting either an error in the original analyses or significant compositional variation within samples from the type locality. Chemical analyses, X-ray photoelectron spectroscopy, and thermal gravimetric analysis measurements combined with Rietveld refinement results using synchrotron X-ray powder diffraction data suggest the chemical formula: $(K_{0.19}Na_{0.17}Ca_{0.03}Ba_{0.01}H_2O_{1.60})(Mn^{4+}_{5.02}Mn^{3+}_{2.82}Al_{0.14}Fe_{0.02})O_{13.47}(OH)_{2.53}$. Our analyses indicate that water is the primary tunnel species, and although water has been reported as a component in natural hollandites, this is the first detailed study of the crystal structure and dehydration behavior of a natural hydrous hollandite with water as the predominant tunnel species. This work underscores the rarity of natural Na-rich hollandite phases and focuses new attention on the role of hydrous components of hollandite-like phases in determining their capacities to exchange or accommodate various cations, such as Li^+, Na^+, Ba^{2+}, Pb^{2+}, and K^+ in natural systems.

Keywords: Hollandite, dehydration, Rietveld, manjiroite