Manjiroite or hydrous hollandite?

JEFFREY E. POST1,*, PETER J. HEANEY2, TIMOTHY B. FISCHER3, AND EUGENE S. ILTON4

1Department of Mineral Sciences, Smithsonian Institution, P.O. Box 37012, Washington, D.C. 20013-7012, U.S.A.
2Department of Geosciences, Penn State University, University Park, Pennsylvania 16802, U.S.A.
3Chevron, 3901 Briarpark Drive, Houston, Texas 77042-5397, U.S.A.
4Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352, U.S.A.

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: \( (K_{0.19}Na_{0.17}Ca_{0.03}Ba_{0.01})_{8+}Mn_{5.82}Al_{0.14}Fe_{0.02}(O,OH)_{16} \). 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

INTRODUCTION

Manganese oxide minerals with hollandite-type structures and their synthetic analogs have long been studied for potential applications for storage of radioactive waste, ionic conductors, super capacitors, battery electrodes, and catalysts (Rossouw et al. 1992; Feng et al. 1995; Johnson et al. 1997; Kijima et al. 2005; Sauvage et al. 2007; Bruce et al. 2012; Zhang et al. 2012; Tompsett and Islam 2013; Yang et al. 2015, 2017). The Mn hollandite-group minerals occur in oxidized zones of Mn-rich deposits, in low-temperature hydrothermal veins, and as sedimentary cements and coatings, including dendrites and nodules. Some studies suggest they might also form as alteration products from biogenic Mn oxides (Grangeon 2015; Carmichael et al. 2017).

Hollandite-group Mn oxide structures consist of double chains of edge-sharing Mn\(^{4+}\)-O octahedra that corner-share with other double chains to form a framework containing large tunnels (Fig. 1). The tunnels are partially filled with large univalent or divalent cations and sometimes water molecules, and the dominant cation determines the particular mineral phase, e.g., K\(^+\) (cryptomelane), Na\(^+\) (manjiroite), Ba\(^{2+}\) (hollandite), Pb\(^{2+}\) (coronadite), and Sr\(^{2+}\) (strontiomelane). Lower-valence cations (e.g., Mn\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\), etc.) substitute for some of the Mn\(^{4+}\) to offset the positive charge of the tunnel cations. Mn hollandite minerals typically contain a variety of tunnel cations. The framework dimensions and consequent tunnel cation coordination environment apparently favor K, Ba, and Pb; smaller divalent cations such as Mg and Ca are rare in Mn hollandite-group minerals (Feng et al. 1995). Na is a common minor constituent in cryptomelane, but manjiroite is apparently rare. Hollandite phases with only divalent tunnel cations typically have half-filled tunnel sites, with cations ordered every other unit cell along the tunnels, and in those with predominantly K and Na, the tunnel sites can be as much as two-thirds to three-quarters filled. Detailed structure refinements have been reported for hollandite and cryptomelane (Post et al. 1982), coronadite (Post and Bish 1989), and strontiomelane (Meisser et al. 1999). Analogous minerals are known with Fe\(^{3+}\), e.g., akageneite (Post and Buchwald 1991; Post et al. 2003), and Tr\(^{4+}\) (Post et al. 1982; Szymański 1986) as the primary octahedral cations.

In this study, we investigated an unusual natural Mn oxide hollandite phase from the oxidized zone of a rhodochrosite-tethephroite-rhodomite bedded deposit at the Kohare Mine, Iwate Prefecture, Japan that has predominantly water molecules in the tunnels, with K, Na, Ca, and Ba. Chemical analyses, X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA) measurements combined with Rietveld refinement results using synchrotron X-ray powder diffraction data suggest the approximate chemical formula: \( (K_{0.19}Na_{0.17}Ca_{0.03}Ba_{0.01})_{8+}Mn_{5.82}Al_{0.14}Fe_{0.02}(O,OH)_{16}nH_2O \). Interestingly, the specimens studied here are labeled as type manjiroite used by Nambu and Tanida (1967) for their original mineral description, but our analyses show that Na is not the dominant...