

## **Characterization of Mn oxides in cemented streambed crusts from Pinal Creek, Arizona, U.S.A., and in hot-spring deposits from Yunō-Taki Falls, Hokkaido, Japan**

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### **ABSTRACT**

We report studies of recently precipitated terrestrial Mn oxides from Pinal Creek (Arizona, U.S.A.) and from Yunō-Taki Falls (Hokkaido, Japan). In addition to chemical analysis [by energy dispersive X-ray spectroscopy (EDS) and proton induced X-ray emission spectroscopy (PIXE)], the following methods were used: X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), contraction and expansion tests, thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), infrared spectroscopy (IR), and Mössbauer spectroscopy. Selected area electron diffraction (SAED) was applied in a few cases, but only on synthetic samples. The most useful methods for characterizing the 10 Å Mn minerals were XRD, contraction test, and DSC. Mössbauer spectroscopy was a very useful complementary method to XRD for differentiation of the poorly crystalline Fe compounds. IR spectroscopy was found not to be very useful in distinguishing busserite and birnessite, but a distinct pattern was observed for todorokite. For heterogeneous deposits composed of many minerals, IR was not useful without separation of phases.

Three types of samples were identified from Yunō-Taki. One of them, representing a relatively fresh deposit exposed to water, was found to be a nearly ideal busserite with an XRD pattern similar to synthetic samples. An older, non-ideal busserite could be dehydrated but not expanded, suggesting that it had been slightly transformed. The third sample was from a deposit that was dry at the time of sampling. It is a 7 Å mineral (birnessite or takanelite/rancieite). The sample also contains amorphous Fe hydroxide, confirmed by Mössbauer spectroscopy.

A test of the possibility of busserite transformation showed that autoclaving a sample of the synthetic 10 Å phyllomanganate, Mg-busserite, resulted in a compound with the XRD pattern and IR spectrum of todorokite. We suggest that this pure synthetic product be used as a model compound for the high-temperature hydrothermal 10 Å manganate with tunnel structure, todorokite. Experiments at other conditions demonstrated that synthetic busserite collapses to birnessite during dehydration.

Pinal Creek crusts are composed of quartz, feldspar, Fe minerals (magnetite, maghemite, ilmenite, hematite), and Mn minerals. Resistance to dehydration and expansion tests, and the initial endotherm shown in DSC analysis, suggest that the 10 Å manganate is todorokite. A 7 Å mineral (birnessite or takanelite/rancieite) is also present. Based on comparison of XRD and electron microscopy data for the natural samples with tests done on the synthetic samples, we postulate that the birnessite or takanelite/rancieite and todorokite found in the Pinal Creek crusts may be a transformation products of a busserite precursor.