

## Crystal chemistry of macfallite: Relationships to sursassite and pumpellyite

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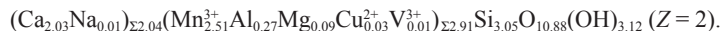
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### ABSTRACT

The crystal chemistry of macfallite from Keweenaw County, Michigan was studied using electron microprobe, thermogravimetry (TG), differential thermal analysis (DTA), powder Fourier transform infrared (FTIR) spectroscopy, and single-crystal X-ray diffraction methods. The chemical formula derived from the electron-microprobe measurements is



An analysis using the intensities of the  $\text{Mn}L\beta$  and  $\text{Mn}L\alpha$  X-ray lines shows that most Mn is trivalent. The weight loss from TG measurement is 7.7 wt% at 1000 °C, most of which is interpreted to be due to the loss of structural OH groups. The crystal structure of macfallite [ $a = 8.959(3)$ ,  $b = 6.072(2)$ ,  $c = 10.218(4)$  Å,  $\beta = 110.75(3)^\circ$ , space group  $P2_1/m$ ], which is isostructural with sursassite, was refined using 1717 unique reflections to  $R = 4.1\%$ . The site populations at the three independent octahedral sites, Mn1, Mn2, and Mn3, are  $\text{Mn}_{0.82}\text{Al}_{0.06}\text{Mg}_{0.09}\text{Cu}_{0.03}$ ,  $\text{Mn}_{0.75}\text{Al}_{0.25}$ , and  $\text{Mn}_{0.95}\text{Al}_{0.05}$ , respectively. In agreement with a bond-valence analysis, three crystal-chemically different OH groups are located at the O6, O10, and O11 positions. The site O7 is mostly occupied by oxygen, but minor amounts of hydroxyl may be located there as well. The powder FTIR spectrum in the region of the OH-stretching vibrations is characterized by three strong bands at 3413, 3376, and 3239  $\text{cm}^{-1}$  and an additional broad absorption band around 2900  $\text{cm}^{-1}$ . The latter results from a relatively strong hydrogen bond, O6-H $\cdots$ O11, with a length of  $\sim 2.63$  Å. Although there are three main hydroxyl groups occurring in macfallite, the exact number depends on the concentration of trivalent and divalent cations at the Mn1 site. If divalent cations occur at Mn1, a fourth OH group is necessary to maintain charge balance.

**Keywords:** Macfallite, pumpellyite, sursassite, Mn silicates, hydrous silicates, FTIR spectroscopy, crystal structure