Crystal chemistry of macfallite: Relationships to sursassite and pumpellyite

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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

(Ca2.03Na0.01)32.04(Mn3.51Al0.23Mg0.09Cu0.03V1.01)32.91Si3.03O10.88(OH)1.2 (Z = 2).

An analysis using the intensities of the Mn1β and Mn1α 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 = 9.859(3), b = 6.072(2), c = 10.218(4) Å, β = 110.75(3)°, space group P21/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 Mn3.62Al0.38Mg0.09Cu0.03, Mn0.75Al0.25, and Mn0.95Al0.05, 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 cm⁻¹ and an additional broad absorption band around 2900 cm⁻¹. The latter results from a relatively strong hydrogen bond, O6-H···O11, with a length of ~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

INTRODUCTION

Low-temperature silicates, many of which are hydrous, are often complex both structurally and compositionally. They often occur as fine-grained aggregates, and it is difficult to obtain good single crystals and/or sufficient amounts of material for experimental investigation. Macfallite is such a relatively low-temperature hydrous silicate with the ideal formula Ca3Mn3Si2O10(OH)2. It has been reported from three localities: (1) fissures and lenses in Keweenaw basalt near Manganese Lake, Copper Harbor, Keweenaw County, Michigan (Moore et al. 1979); (2) metamorphosed and metasomatized manganese deposits in metacherts from the Cerchiara mine, eastern Liguria, Italy (Basso et al. 1989); and (3) low-grade metamorphic rocks from the Wakasa manganese mine, Hokkaido, Japan (Miyajima et al. 1998).

The crystal structure of macfallite was first determined by Moore et al. (1985) who proposed the general structural formula Ca1Ca2Mn1Mn2Mn3Z3O11(OH)2, where Ca1 and Ca2 represent seven coordinated sites, Mn1, Mn2, and Mn3, octahedral sites, and Z, tetrahedral sites. However, the original structure determination (R = 18.4%) allowed only a description of the average crystal structure and not an examination of detailed crystal-chemical properties. Although little is known about the compositional variations in natural crystals, macfallite is compositionally similar to okokotkite (Mn4⁺-analog of pumpellyite) of composition Ca6(Mn3⁺;Mg)2(Mn3⁺;Al,Fe3⁺)Si2O6.s(OH)8 (Togari and Akasaka 1987). A polysomatic description for isostructural macfallite and sursassite, as well as pumpellyite, ardenite and lawsonite, the so-called 6 × 9 Å structures with corresponding axial translations, was presented by Moore et al. (1985) and Ferraris et al. (1986).

In this study, we investigated, further and in detail, the crystal structure and crystal-chemical properties of macfallite. The following experimental methods were used: electron microprobe analysis, thermogravimetry (TG), differential thermal analysis (DTA), powder Fourier transform infrared spectroscopy (FTIR), and single-crystal X-ray diffraction. A bond-valence analysis was also carried out. Finally, we examined the structural and compositional relationships between macfallite, pumpellyite, and sursassite including the nature of their H-bonding systems.