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Crystal chemistry of Zn-rich rhodonite ("fowlerite")

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ABSTRACT

Rhodonite (ideally $MnSiO_3$) is a triclinic pyroxenoid that typically contains significant concentrations of Ca, Fe, and Mg. A variety called fowlerite contains concentrations of Zn up to 10 wt% and has been found only at Franklin, New Jersey. Data from electron microprobe analyses, single-crystal X-ray structure refinements, and preliminary Mössbauer spectra suggest marked differences in the crystal chemistry of rhodonite and fowlerite. Cations in Zn-poor rhodonites and in fowlerites exhibit distinct substitutional trends. Substitution of Zn in fowlerite occurs entirely at M4, and Ca displays a stronger preference for M5 in fowlerite than in Zn-poor rhodonite. Further, the distinctive compositional variations in fowlerite lead to strongly mutually correlated lattice parameter variations distinct from those in Zn-poor rhodonite. Mean M-O distances in fowlerite, with the exception of <M2-O>, are strongly correlated with all unit-cell edges. For Zn-poor rhodonites, neither <M2-O> nor <M4-O> are significantly correlated with cell edges, and the mean bond lengths for M1, M3, and M5 are correlated strongly with only *a* and *b*.

The most striking distinctions between fowlerite and typical rhodonite occur in the geometrical details of M4 and M5. Distortion in the M4 site of magnesian rhodonite, typical Mn-rich rhodonite, and fowlerite increases with both increasing electron population and mean electronegativity. The M4 site assumes increasing amounts of tetrahedral character with increasing electron density (i.e., increasing Zn concentration). As M4 becomes more Zn-rich, tetrahedral, and covalent in character, M5 becomes more Ca-rich, less distorted, and more ionic in character. This suggests that "pure" fowlerite (nominally $Ca_{0.2}Zn_{0.2}Mn_{0.6}O_3$, or $CaZnMn_3O_{15}$) may contain an unequivocally four-coordinated M4 site occupied solely by Zn, and with Ca largely restricted to M5.