Palenzonaite, berzeliite, and manganberzeliite: structural control of $(\text{As}^{5+}, \text{V}^{5+}, \text{Si}^{4+})\text{O}_4$ tetrahedra in garnet structures

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Palenzonaite NaCa$_2$Mn$_2$$(\text{V}^{5+}\text{O}_4)_3$, berzeliite NaCa$_2$Mg$_2$(As$^{5+}$O$_4$)$_3$, and manganberzeliite NaCa$_2$Mn$_2$$(\text{As}^{5+}\text{O}_4)_3$ are cubic minerals with garnet structure (space group $Ia$$_3$d) and tetrahedral V$^{5+}$, As$^{5+}$ at Z charge balanced by divalent cations at the octahedral Y site and by Na and Ca at the dodecahedral X site. Using electron-microprobe analysis (EMPA) and single-crystal X-ray diffraction methods, the crystal chemistry of palenzonaite (from the Molinello and the Gambatesa mines, Italy, and the Fianel mine, Switzerland), berzeliite (from Långban, Sweden, and Montaldo, Italy), and manganberzeliite (from Varenche, Italy, and the Gozaisho mine, Japan) were studied. Structure refinements converged to $R_1$ values of 1.36-2.42%. According to results of chemical analyses, the tetrahedral site of these garnets is mainly occupied by pentavalent cations such as As$^{5+}$ and V$^{5+}$ but also Si$^{4+}$ randomly occupies the tetrahedron (max. 20%) charge-balanced by an increased Ca/Na ratio at the X site. Although the $<Z$-O$>$ and $<Y$-O$>$ distances in the garnet structure show a positive correlation against mean ionic radii of each occupant ($R^2 = 0.96$ for Y and 0.88 for Z), $<X$-O$>$ has no correlation with variable (Na, Ca) occupancy (Fig. 1). The XO$_8$ of berzeliite is smaller than that of palenzonaite and manganberzeliite. The low average charge at X makes XO$_8$-polyhedra to soft links between more rigid octahedra (Y) and tetrahedra (Z) although the Na/Ca ratio at X is important for charge balance. Thus, the volume of XO$_8$ is not governed by the cation distribution at X. Mixed valence substitution (Na, Ca) at X in vanadate and arsenate garnets is favourable to accomplish divalent cations (Mg and Mn) at Y. The size of Mg and Mn$^{2+}$ allows the shared octahedral-dodecahedral edge to be similar to the unshared octahedral edge, which is a measure of lattice distortion in garnet structures.

Keywords: palenzonaite, berzeliite, manganberzeliite, crystal structure, pentavalent cations

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