

The Crystal Chemistry of Manitobaite, $(\text{Na}_{16}\square)\text{Mn}^{2+}_{25}\text{Al}_8(\text{PO}_4)_{30}$, A New Phosphate Mineral of the Alluaudite-Group (sensu lato) from Cross Lake, Manitoba, Canada

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Manitobaite, ideally $(\text{Na}_{16}\square)\text{Mn}^{2+}_{25}\text{Al}_8(\text{PO}_4)_{30}$, is a phosphate mineral from Cross Lake, Manitoba, Canada. It occurs as large (up to 2 cm across) crystals or cleavage masses intergrown with other phosphate minerals in a phosphate pod in the intermediate and core zones of a pegmatite on the southeastern shoreline of a small unnamed island in Cross Lake, Manitoba, about 5 km north-northwest of the Cross Lake settlement, longitude $54^\circ 41' \text{N}$, latitude $97^\circ 49' \text{W}$. Manitobaite occurs as a primary mineral in a large phosphate nodule in the intermediate and core zones of the (granitic) pegmatite. The associated minerals are apatite-(CaF), apatite-(CaCl), bobfergusonite, eosphorite, dickinsonite, fillowite, triplodite, goyazite, perloffite, beusite, triplite; plus quartz, K-feldspar, muscovite, schorl, beryl, spessartine, gahnite and (Nb,Ta, Sn)-oxides. Manitobaite is opaque in large (up to 4 cm) crystals, and transparent to translucent in small (< 1 mm) grains. Colour varies from green to brown, with a colourless to very very pale green or very very pale greenish-brown streak, a vitreous to resinous luster, and manitobaite does not fluoresce under ultraviolet light. Cleavage is perfect on {010}, there is no parting, the tenacity is brittle, and the fracture is hackly. The following properties were measured on the green variety of manitobaite. The measured and calculated densities are 3.621(6) and 3.628 gcm^{-3} , respectively. Manitobaite is biaxial negative with α 1.682, β 1.691, γ 1.697, (all ± 0.001), with $X \wedge a = 31.7^\circ$ (in β obtuse), $Y \parallel b$, $Z \wedge c = 20.2$ (in β acute); $2V(\text{obs}) = 78.1(6)$, $2V(\text{calc}) = 77.9^\circ$. It is pleochroic $X = \text{orange brown}$, $Y = \text{green}$, $Z = \text{greenish brown}$, with absorption $Y \geq Z > X$ and dispersion $r > v$, medium.

The crystal structures of the green and brown variants of manitobaite, ideally $(\text{Na}_{16}\square)\text{Mn}^{2+}_{25}\text{Al}_8(\text{PO}_4)_{30}$, monoclinic, Pc , $Z = 2$: green: a 13.4517(7), b 12.5266(7), c 26.6765(13) Å, β 101.582(1) $^\circ$, V 4403.6(7) Å³, D_{calc} 3.642 g/cm^3 ; brown: 13.4499(6), b 12.5046(5), c 26.6148(11) Å, β 101.221(1) $^\circ$, V 4390.7(5)(3) Å³, D_{calc} 3.621 g/cm^3 , were solved by direct methods and refined to $R_1 = 5.0$ (6.0)% for 22,580 (25,613) unique ($F_o > 4\sigma F$) reflections collected on a Bruker single-crystal $P4$ diffractometer equipped with a 4K CCD detector and $\text{MoK}\alpha$ X-radiation. Chemical analysis by electron microprobe plus Fe^{3+} determination by Mössbauer spectroscopy gave: green: P_2O_5 44.19, Al_2O_3 6.91, Fe_2O_3 1.73, FeO 6.23, MnO 27.57, ZnO 0.54, MgO 0.73, CaO 1.71, Na_2O 9.97, sum 99.58 wt%. brown: P_2O_5 44.42, Al_2O_3 6.96, Fe_2O_3 3.54, FeO 4.66, MnO 27.86, ZnO 0.53, MgO 0.81, CaO 1.59, Na_2O 8.94, sum 99.32 wt%. The resulting empirical formulae are as follows: green: $\text{Na}_{15.55}\text{Ca}_{1.47}\text{Mg}_{0.88}\text{Fe}^{2+}_{4.19}\text{Mn}^{2+}_{18.78}\text{Zn}_{0.32}\text{Al}_{6.54}\text{Fe}^{3+}_{1.05}\text{P}_{30.08}\text{O}_{60}$; brown: $\text{Na}_{13.90}\text{Ca}_{1.37}\text{Mg}_{0.97}\text{Fe}^{2+}_{3.12}\text{Mn}^{2+}_{18.92}\text{Zn}_{0.31}\text{Al}_{6.58}\text{Fe}^{3+}_{2.09}\text{P}_{30.15}\text{O}_{60}$. The general formula of manitobaite is $(\text{Na}_{16}\square)(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Zn}, \text{Ca})_{25}(\text{Al}, \text{Fe}^{3+})_8(\text{PO}_4)_{30}$ and the end-member formula is $(\text{Na}_{16}\square)\text{Mn}^{2+}_{25}\text{Al}_8(\text{PO}_4)_{30}$. The crystal structure of manitobaite is an ordered superstructure of the alluaudite arrangement with a cell volume five times that of alluaudite. The compositional controls on alluaudite superstructures will be discussed.