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The atomic arrangement of the ganophyllite-group modulated layer silicates as determined from the orthorhombic dimorph of tamaite, with the elusive 16.8 Å ganophyllite-group superstructure revealed

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ABSTRACT

The ganophyllite-group minerals, with general formula (K, Na, Ca)$_x$Mn$_6$(Si$_9$Al)O$_{24}$(OH)$_4$·nH$_2$O (ganophyllite = K, eggletonite = Na, tamaite = Ca), are complex modulated layer silicates that contain 2:1 trioctahedral layers with Mn^{2+}-O_6 octahedra. Pervasive superstructures have frustrated the numerous attempts at solution of the atomic arrangement of these modulated layer silicates. An orthorhombic dimorph of tamaite has been discovered and its atomic arrangement solved, elucidating the elusive structure of the ganophyllite-group minerals. The dimorph was discovered in the Val Graveglia mining district in the northern Apennines, approximately 35 km east of Genoa, Italy. The phase crystallizes in space group *Pnma*, $a = 16.8146(6)$, $b = 25.2036(9)$, $c = 13.3866(5)$ Å. The weak reflections from the 3× "superstructure" along **a**, long observed but never successfully measured in ganophyllite-group minerals, were obtained using a CCD detector and subsequently the atomic arrangement was solved and refined ($R = 0.079$). The structural modulation in ganophyllite-group minerals results from the misfit between the sheets of $Mn^{2+}O_6$ octahedra and silicate tetrahedra. The atomic arrangement consists of corrugated *T*-O-*T* layers, with inverted tetrahedra in the tetrahedral sheets connecting adjacent layers along **b**. The inverted tetrahedra exist as four-member rings, and incorporate Al, with a maximum Al occupancy of $Si_{2.00}Al_{2.00}$. Charge balance for the substituent Al is maintained by adding cations (Ca, K, Na) or $^{[6]}$Al sufficient to balance the charge lost by the Al ↔ Si substitution in the interlayer tetrahedra. Zeolitic H_2O molecules also exist in the interlayer channels. Contrary to earlier speculation, the 5.6 Å "subcell" (along **a** in the orthorhombic dimorph) observed in ganophyllite-group phases is not a true subcell, in that it does not have approximately equivalent atoms at (x, y, z), $[\sim(x + 1/3), \sim y, \sim z]$, and $[\sim(x + 2/3), \sim y, \sim z)$ for all atoms. Although the majority of the cation scattering (all Mn + 2/3 of the Si atoms) exist in a supercell-subcell relationship, as manifested in very strong $h = 3n$ and very weak (heretofore immeasurable) $h \neq 3n$ reflections, the lack of such a relationship for all atoms prohibited a successful solution based on previous assumptions of a subcell-supercell relationship.

INTRODUCTION

Ganophyllite, ideally $(K,Na,Ca)_6(Mg,Fe,Mn)_{24}(Si_{32.5}Al_{7.5})O_{96}(OH)_{16}\cdot 21H_2O$, is a complex modulated layer silicate that contains 2:1 trioctahedral layers of Mn^{2+} dominant octahedra and silicate tetrahedra; the structural modulation arises from the misfit between the large manganese octahedra and the silicate tetrahedra in the *T*-O-*T* layers (Eggleton and Guggenheim 1986). Peacor et al. (1984) have described eggletonite, the Na-dominant end-member of ganophyllite, and tamaite, described by Matsubara et al. (2000), is the calcium-dominant end-member of the ganophyllite-group.

The atomic arrangement of the ganophyllite-group minerals has been extensively studied but the structure solution has remained elusive, perhaps due to the atomic perturbations that cause the pervasive superstructures. Noe and Veblen (1999) recently recounted the attempts at unraveling the atomic arrangement of ganophyllite and reported a refinement of the ganophyllite subcell and a proposed model of the supercell. We refer the reader to that study for an excellent detailed summary of previous work and conjecture on the atomic arrangement of ganophyllite-group phases.

One of the authors (R.B.) recently collected specimens of a Ca-dominant member of the ganophyllite group from the Val Graveglia mining district in the northern Apennines, approximately 35 km east of Genoa, Italy. Examination of our Ca-dominant phase showed, unlike monoclinic ganophyllite, eggletonite, and tamaite, that the Val Graveglia material was orthorhombic, and thus is the orthorhombic dimorph of tamaite. A review of the literature revealed that the natural Ca-dominant orthorhombic phase had also been recognized by Mottana et al. (1990) but was not described as a new mineral. The orthorhombic material was suitable for structure analysis, and a CCD-based diffractometer allowed measurement of the pervasive

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