Implications for the Nomenclature of p-p Hydropyroxenoids: the Crystal Structure of Marsturite from the Molinello mine, Liguria, Italy

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The previously unstudied crystal structure of the p-p (pectolite-pyroxene) hydropyroxenoid marsturite, originally described from Franklin, New Jersey, USA (Peacor et al., 1978), has been determined using a sample from the Molinello mine, Val Graveglia, Liguria, Italy (sample in collection of Stift Melk, Melk, Austria).

Refinement of the single-crystal intensity data (Mo-Kα X-radiation, CCD area detector, RT, \(R(F) = 5.5\) %) gave triclinic space-group symmetry \(P-1\) (no. 2), with \(a = 6.771(1)\), \(b = 7.697(2)\), \(c = 11.720(2)\) Å, \(α = 106.83(3)\), \(β = 92.40(3)\), \(γ = 94.41(3)\), \(V = 581.6(2)\) Å\(^3\).

The results confirm that marsturite belongs to a group of four isotypic silicate minerals, viz. nambulite - \((\text{Li,Na})\text{Mn}_{4}\text{Si}_{5}\text{O}_{14}(\text{OH})\) (Narita et al., 1975), natronambulite - \(\text{NaMn}_{4}\text{Si}_{5}\text{O}_{14}(\text{OH})\) (Matsubara et al., 1985), lithiomarsturite - \(\text{LiCa}_{2}\text{Mn}_{2}\text{Si}_{5}\text{O}_{14}(\text{OH})\) (Peacor et al., 1990) and marsturite - \(\text{NaCaMn}_{3}\text{Si}_{5}\text{O}_{14}(\text{OH})\). Their topology is based on infinite silicate chains with a repeat unit of five \(\text{SiO}_4\) tetrahedra (\(\text{fünferketten}\)) which are connected to polyhedral bands of edge-sharing \(\text{Met}^{2+}\text{O}_6\) (\(\text{Met} = \text{Mn, Ca; minor Fe, Mg}\) octahedra and \(\text{CaO}_7\) polyhedra. Both chains and bands run along [011]. The [6]- to [8]-coordinated \(\text{Li}^+\)/\(\text{Na}^+\) cations occupy voids.

Refinement of the occupancies of the four divalent metal sites \(\text{M(1)}\)-\(\text{M(4)}\) and the \(\text{M(5)}\) site (occupied by either \(\text{Na}\) or \(\text{Li}\) in all members) resulted in the following structural formula:

\[
\text{Na}_{0.95}\text{Mn}_{1.00}\text{Mn}_{0.84}\text{Ca}_{0.16}\text{Mn}_{0.87}\text{Ca}_{0.13}\text{Ca}_{0.84}\text{Mn}_{0.24}\text{Si}_{5}\text{O}_{14}(\text{OH}).
\]

The bulk composition is very similar to the one reported for the type material (Peacor et al., 1978) and to marsturite from Molinello EMP-analysed by Palenzona (1987). The dominance of \(\text{Ca}\) on the \(\text{M(4)}\) site is in good agreement with predictions of Peacor et al. (1990) and crystal-structure data reported for the other members. The inferred preference of \(\text{Ca}\) also for the \(\text{M(2)}\) site is confirmed as well. The maximum \(\text{Ca}:\text{Mn}\) ratio in these hydropyroxenoids appears to be 1:1. Thus, at least one hypothetical end-member is awaiting its discovery in nature: \(\text{NaCa}_2\text{Mn}_{2}\text{Si}_{5}\text{O}_{14}(\text{OH})\), with \(\text{Ca}\) dominant on both \(\text{M(2)}\) and \(\text{M(4)}\).

The very strong hydrogen bond (ca. 2.5 Å) in these hydropyroxenoids will also be discussed.

References


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