

The relation between Li ↔ Na substitution and hydrogen bonding in five-periodic single-chain silicates nambulite and marsturite: A single-crystal X-ray study

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ABSTRACT

Isomorphic nambulite, natronambulite, marsturite, and lithiomarsturite belong to the p-p (pectolite-pyroxene) series of pyroxenoid group minerals with five-periodic single chains of tetrahedra and the common simplified composition $(\text{Li,Na})(\text{Mn,Ca})_4[\text{Si}_5\text{O}_{14}(\text{OH})]$ ($Z = 2$, space group $P\bar{1}$). New crystal structure refinements including localization of H positions of four samples (two nambulite, one natronambulite, and one marsturite) with varying Li and Na concentrations and major to trace element compositional data from different localities are presented. Na occupies a strongly distorted eightfold-coordinated site (M5). Li replacing Na has a substantially smaller ionic radius and occupies a pocket of the large M5 coordination polyhedron and is only fivefold coordinated by oxygen. Thus, the Li ↔ Na substitution has a significant influence on the bond-valence sums of oxygen sites forming the large cage around M5. Two of the cage-building oxygen sites (O1 and O11) are involved in hydrogen bonding. If M5 is occupied by Na or empty as in the closely related babingtonite, $\text{Ca}_2\text{Fe}_2[\text{Si}_5\text{O}_{14}(\text{OH})]$, the OH-group is at O1 and exhibits a strong hydrogen bond to O11. If a pocket of M5 is occupied by Li, the hydrogen bond system is reversed with OH at O11 and a strong hydrogen bond to O1. This study emphasizes that short hydrogen bonds with O-H...O separations of ca. 2.46 Å may be modified by homovalent substitution, which contributes to the understanding of strong hydrogen bonds and their role in the stability of hydrous pyroxenoids with strongly curled silicate chains.

Keywords: Nambulite, marsturite, pyroxenoid, Fianel, Molinello, Gozaisho, crystal structure, hydrogen-bonding