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, natronnambulite, 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 \((\text{Li,Na})(\text{Mn,Ca})_2[\text{Si}_2\text{O}_5](\text{OH})]\) \((Z = 2, \text{space group } \text{PT})\). New crystal structure refinements including localization of \(H\) positions of four samples (two nambulite, one natronnambulite, 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, Ca(\text{Fe})_2[Si_2\text{O}_5](\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

INTRODUCTION

Nambulite, \((\text{Li,Na})\text{Mn}_2[\text{Si}_2\text{O}_5](\text{OH})]\), natronnambulite, \((\text{Na, Li})\text{Mn}_2[\text{Si}_2\text{O}_5](\text{OH})]\), lithiomarsturite, \((\text{Li,Na})\text{Ca}_2\text{Mn}_2[\text{Si}_2\text{O}_5](\text{OH})]\), and marsturite, \((\text{Na, Li})\text{CaMn}_2[\text{Si}_2\text{O}_5](\text{OH})]\), belong to the p-p (pectolite-pyroxene) series of pyroxenoid-group minerals with five-periodic single chains. Their triclinic crystal structures \((Z = 2)\) are isomorphic.

Nambulite from the Funakozawa mine, Iwate, Japan, was first defined as a new species by Yoshii et al. (1972) although a corresponding mineral had already been described as a Li-containing hydrous manganese metasilicate from a high-grade regional metamorphic rock in India (Ito 1972). Narita et al. (1975) solved the crystal structure of nambulite from the Funakozawa mine and emphasized its close relation to that of babingtonite. Li-hydropyroxenoids were synthesized by Ito (1972). The end-member LiMn\(_2\)Si\(_2\)O\(_5\)(OH) (referred to as Li-hydrorhodonite in his paper) formed over a wide P-T field ranging from 500 °C at 300 MPa up to 750 °C at 200 MPa. He concluded that the maximum sodium substitution on the join LiMn\(_2\)Si\(_2\)O\(_5\)(OH)-NaMn\(_2\)Si\(_2\)O\(_5\)(OH) does not exceed Li\(_{0.3}\)Na\(_{0.7}\) under his experimental conditions (most of the runs were within the range of 500 °C/300 MPa and 850 °C/150 MPa).

The Na-analog of nambulite, natronnambulite, was discovered as an independent mineral from the Tanohata mine, Iwate, Japan (Matsubara et al. 1985), Mukhopadhyay et al. (2005) suggest that low-pressure conditions stabilize Na-rich nambulite rather than Li-rich compositions. However, they also mention that the local bulk chemistry is crucial.

The occurrence of nambulite is uncommon. In addition to the localities mentioned above, it has been reported from the Kombat mine, Namibia (von Knorringer et al. 1978; Dunn 1991), from the Cerchiara mine, Italy (Balestra et al. 2009), and from manganiferous metaptuffs of the Ossa-Morena Central Belt in SW Spain (Velilla and Jiménez-Millán 2012). Recently, nambulite was discovered from the Fianel Fe-Mn mine, Val Ferrera, Graubünden, Switzerland (Nagashima and Armbruster 2012).

Marsturite was first described by Peacor et al. (1978) from Franklin, New Jersey, U.S.A. At this locality, marsturite is associated with rhodonite, willemite, and abundant axinite-(Mn). Lithiomarsturite from the Foote pegmatite mine (North Carolina, U.S.A.) was later defined by Peacor et al. (1990) as the Li-dominant analog of marsturite. Interestingly, the Mn/Ca ratio of lithiomarsturite is approximately 1, whereas marsturite