

MS15-2-5 Again for the choice of space group for the crystal structures of the scapolite group representatives
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Abstract

Scapolites are rock-forming minerals with well-pronounced crystal chemical complexity. The interest in such compounds is determined by the possibility of their use as geothermometers, as well as by their potential for greenhouse gas storage. Their crystal structure is composed of a $[(\text{Si},\text{Al})_n\text{O}_{2n}]$ framework containing eight- and four-membered rings. Calcium and sodium cations are located in the channels formed by the eight-membered rings, and carbonate, sulfate and chlorine anions are located in those formed by the four-membered rings (Fig. 1). There are three types of heterovalent isomorphism for group members, which can generally be represented as follows: $\text{Si} \Leftrightarrow \text{Al}$ (framework cations); $\text{Ca} \Leftrightarrow \text{Na}$ and $\text{CO}_3 \Leftrightarrow \text{SO}_4 \Leftrightarrow \text{Cl}$ (extra-framework species). Relations between the three schemes are not always explicit and unambiguous, but in general their joint manifestation leads to electroneutrality. The use of routine practices applicable to other aluminosilicates are often resorted to during investigations of the crystal chemical peculiarities of scapolites, especially with regard to their framework construction. These are: Lowenstein's rule referring to the aluminium and silicon order; the dependence of size of the framework tetrahedra on the type of their central cations (Si, Al). The latter indicates the preferred population in the tetrahedral positions. The highest symmetry space group used in solving crystal structures in the marialite-meyonite series $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ (Me0) – $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ (Me100), is the tetragonal $I4/m$. It is applicable to the representatives falling within the compositional range of the two end members. In the middle region, however, additional reflexes are observed in the diffraction patterns, which require the use of the primitive $P42/n$ of the tetragonal syngony. Drawing boundaries between the representatives of the two space groups, especially those with high calcium content, is still controversial.

This work presents results of single-crystal X-ray investigations of scapolites from three localities, two of which are reported for the first time. The studied samples have been identified as Me71; Me75, and Me80. Their crystal chemical characteristics relate them to the disputed area for selection of a space group. In search of an opportunity to refine the arrangement of framework cations, the structure of each phase has been solved in three space groups: $I4/m$, $P42/n$, and the monoclinic $I2/m$. The obtained results shed new light on the choice of space group for description of scapolites crystal structures, as well as on the preferred by silicon and aluminium ions positions and hence for their ordering in the framework construction.

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Schematic presentation of scapolite structure

