

## Crystal chemical and structural characterization of an unusual CO<sub>3</sub>-bearing sodalite-group mineral

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**Abstract:** We report the crystal chemical and structural characterization of an unusual CO<sub>3</sub>-bearing sodalite-group mineral. The sample was found in metasomatic ejecta from Mount Vesuvio, Italy. The mineral is characterised by an *a* cell parameter of 9.0352(2) Å and by a formula, recalculated from EMPA, of (Na<sub>5.28</sub>K<sub>1.40</sub>Ca<sub>1.23</sub>Fe<sub>0.01</sub>)<sub>Σ7.92</sub>[Si<sub>5.93</sub>Al<sub>6.07</sub>O<sub>24.01</sub>][(SO<sub>4</sub>)<sub>0.77</sub>Cl<sub>0.94</sub>(CO<sub>3</sub>)<sub>0.30</sub>]<sub>Σ2.01</sub>. The structure refinement, conducted in *P43n* space group, indicates that the cations are distributed among three independent sites M1, M2, and M3, each one with partial occupancy. The Cl anion is located exactly at the centre of the cages (site Cl) along with the carbon atom of the CO<sub>3</sub> group. The sulphur atom of the sulphate group is located in a site slightly displaced from the centre of the cage, similarly to some haüyne samples (site S). The sulphate group shows two different statistical orientations with probabilities of 2/3 and 1/3. Despite the very contrasted dimensions of the different anions/anionic groups involved, the framework is fully ordered with Si-O and Al-O bond distances of 1.6156(6) and 1.7341(6) Å respectively, without splitting of the framework oxygen sites (O1 and O2). This behaviour is different from that reported for nosean, lazurite and some haüyne samples.

**Key-words:** sodalite-group, feldspathoids, crystal chemistry, crystal structure.

### Introduction

The sodalite and cancrinite groups, recently grouped together (Bonaccorsi & Orlandi, 2003), consist of minerals characterized by the presence of layers of six-membered rings of TO<sub>4</sub> (T = Si, Al or Be) tetrahedra as building units. Assuming a perfect hexagonal symmetry of the layer, the stacking of the layers may be described following the Zhdanov approach (Zhdanov, 1945) for the close-packing of spheres. The occurrence of an ABC sequence gives rise to a sodalite-group mineral, whereas the other sequences are typical of the cancrinite-group. The ABC sequence framework may be described as built-up from face-shared truncated-octahedra, also called sodalite or β-cages, characterized by a topological symmetry *Im3m*. However rotation of the TO<sub>4</sub> tetrahedra and Si,Al (or Si,Be) ordering reduces the symmetry to the *P43n* space group commonly observed in natural phases. In the case of the simultaneous presence of Be, Al, and Si, a different scheme of tetrahedral cation ordering reduces the symmetry to *I4* as in the case of tugtupite (Danø, 1965; Hassan & Grundy, 1991a). Each unit cell contains two sodalite cages and, with the sole exception of bicchulite (Sahl, 1980; Dann *et al.*, 1996), each cage contains up to four extraframework M cations and up to one X anion or anionic group. Therefore, sodalite-group minerals can be described by the general

formula M<sub>7-8</sub>[T<sub>8</sub>O<sub>24</sub>] X<sub>1.5-2</sub>. Within this group, a further subdivision may be carried out based on the occurrence of Be as a tetrahedral cation (see Table 1 in Di Muro *et al.*, 2004). In this case, there are three relatively uncommon members that are characterized by having Mn, Zn, and Fe as M cations and S<sup>2-</sup> as the X anion (helvite group: Hassan & Grundy, 1985) plus tugtupite that is chemically related to sodalite *sensu stricto* apart from its uncommon tetrahedral cation distribution (see above). The remaining minerals are characterized by the presence of Na, K, and Ca as extraframework cations and Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, S<sub>3</sub><sup>-</sup>, and S<sub>2</sub><sup>-</sup> as extraframework anions or anionic groups a part from water molecules. By far the most common members of the group are sodalite 2[Na<sub>4</sub>Cl], haüyne 2[Na<sub>3</sub>CaSO<sub>4</sub>], nosean [Na<sub>4</sub>SO<sub>4</sub> • Na<sub>4</sub>H<sub>2</sub>O], and lazurite 2[(Na,Ca)<sub>4</sub>(SO<sub>4</sub><sup>=</sup>, S<sub>3</sub><sup>-</sup>, S<sub>2</sub><sup>-</sup>)]. Haüyne, nosean and lazurite show cationic variability due to Na ↔ K substitution, which leads to a linear expansion of the *a* cell parameter (Taylor, 1967; Burrigato *et al.*, 1982). On the contrary, the Na ↔ Ca substitution does not affect the *a* cell parameter. However expansion of the cell parameter is mainly controlled by the dimension of the anion/anionic group, with the two extreme compositions being represented by sodalite (Cl: *a* ~ 8.88 Å) and haüyne (SO<sub>4</sub>: *a* ~ 9.07-9.12 Å). From a linear regression of literature data, we can estimate an *a* cell parameter of 9.071 Å for a hypothetical K-free haüyne (Fig. 1), which is very close to the value of 9.065 Å reported by Taylor (1967): this

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