Crystal Structure of a New Representative of the Cancrinite Group with a 12-Layer Stacking Sequence of Tetrahedral Rings


* Faculty of Geology, Moscow State University, Vorob’evy gory, Moscow, 119992 Russia
** Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1a, Irkutsk, 664033 Russia
*** Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninski pr. 59, Moscow, 119333 Russia
**** Irkutsk State University of Transport Communications, ul. Chernyshevskogo 15, Irkutsk, 664074 Russia

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Abstract—The crystal structure of a 12-layer tounkite-like mineral of the cancrinite group was determined for the first time by single-crystal X-ray diffraction analysis (the unit-cell parameters are \( a = 12.757 \) Å, \( c = 32.211 \) Å). The structure was refined in the space group \( P3 \) to \( R = 0.035 \) using 3834 reflections with \(|F| > 2\sigma(F)\). Si and Al atoms occupy tetrahedral framework positions in an ordered fashion. The average distances in the tetrahedra are \( \bar{\alpha} = 1.611 \) Å and \( \bar{\beta} = 1.723 \) Å. The stacking sequence of the layers is described as \( \text{CACACBCBCACB} \), where \( A, B, \) and \( C \) are six-membered rings arranged around the \([2/3 1/3 z]\), \([1/3 2/3 z]\), and \([0 0 z]\) axes, respectively. In the structure of the mineral, the columns along the \([0 0 z]\) axis are composed of cancrinite cages. The columns along the \([2/3 1/3 z]\) and \([1/3 2/3 z]\) axes contain alternating cancrinite, bystrite, and liotite cages. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The mineral tounkite was discovered as bottle-green crystals in the Malo-Bystrinskoe lazurite deposit (Lake Baikal region, Russia) and described in [1]. However, we failed to obtain a reliable structural model of this mineral because of structural disorder, as evidenced by the diffusion character of the hkl reflections with \( l \neq 3n \). Later, a tounkite-like mineral, which we tentatively named ordered tounkite [2], was discovered in lazurite-bearing rocks of the Tultuisko deposit in association with calcite, diopside, afghanite, and anisotropic lazurite. This mineral forms more perfect columnar bluish crystals up to 1 cm long. The aim of this study was to establish the structure of these crystals.

EXPERIMENTAL

The chemical composition of a specimen was studied by electron-probe X-ray microanalysis on a JCXA-733 microanalyzer. The empirical formula calculated for 12 (Si + Al) and \( Z = 6 \) is \( \text{Ca}_{2.58}\text{Na}_{3.18}\text{K}_{0.18}\text{Si}_{15.99}\text{Al}_{0.01}\text{O}_{24} \left(\text{SO}_{4}\right)_{1.75}\text{Cl}_{1.33} \).

The unit-cell parameters \( a = 12.755(3) \) Å and \( c = 32.218(5) \) Å were determined by the photographic method and refined on an automated Bruker Platform diffractometer equipped with a CCD detector (Toledo, United States). X-ray diffraction data were collected on the same diffractometer. The X-ray data set corresponded to the trigo...
RESULTS AND DISCUSSION

Complete X-ray diffraction analysis of the tounkite-like mineral gave the crystal-chemical formula \( (Z = 1) \) \( \text{Si}_{36}\text{Al}_{36}\text{O}_{144} \) \( [\text{Na}_{31.1}\text{Ca}_{3.9}\text{K}_{0.6}(\text{SO}_{4})_{9.3}(\text{SO}_{3})_{0.7}][\text{Ca}_{12}\text{Cl}_{8}] \), where the compositions of the framework and cages are enclosed in brackets. Silicon and aluminum atoms occupy tetrahedral framework positions in an ordered fashion, as evidenced by the average cation–anion distances in the tetrahedra \( \langle \text{Si}–\text{O} \rangle = 1.611 \) Å, \( \langle \text{Al}–\text{O} \rangle = 1.723 \) Å.

The aluminosilicate framework of the mineral under study, like the frameworks of other cancrinite-like minerals, consists of six-membered rings of \((\text{Si},\text{Al})\) tetrahedra arranged in layers. The layers are shifted with respect to each other along the \( c \) axis. Cancrinite and related minerals \([5–10]\) differ in both the number of layers, labeled by letters \( A, B, \) and \( C \), and their stacking sequence. For uniformity and to avoid ambiguity when comparing the stacking sequences of layers in different minerals, it was suggested \([10]\) that the six-membered rings around the \([2/3 1/3 z]\), \([1/3 2/3 z]\), and \([0 0 z]\) axes \([10]\) to be denoted by \( A \), \( B \), and \( C \), respectively. Then, the stacking sequences of layers in the structures of the minerals can be described as follows: a two-layer \( AB \) sequence in cancrinite, a four-layer \( ACBC \) sequence in bystrite, a six-layer \( ACBCBC \) sequence in liottite, an eight-layer \( A\overline{C}A\overline{B}C\overline{B}C \) sequence in afghanite, and a ten-layer \( ABCABACABC \) sequence in franzinite. In these minerals, the parameter \( c \sim 5n \) \((n = 1–5)\) varies correspondingly from 5.1 to 26.5 Å. The order in which the layers alternate determines the shapes and positions of cages in the structure. The cancrinite, bystrite, and liottite structures have three types of cages—the so-called cancrinite, bystrite, and liottite cages (Fig. 1)—linked in columns. The cancrinite cage is the smallest one. This cage is formed in structures, where only one layer is sandwiched between two identical layers. In such structures, the medium layer differs from the two other layers in orientation and is present either singly or in combination with other layers. In the sodalite cage, two layers, which are shifted with respect to each other, are located between two identical layers. The bystrite cage appears in structures in which three layers are sandwiched between two identical layers. The bulky liottite cage contains five differently oriented layers. The afghanite structure consists of alternating liottite and cancrinite cages. By contrast, the columns along the \([0 0 z]\) axis in bystrite, liottite, and afghanite are of the same type and are composed of cancrinite cages. Sodalite cages are involved in the formation of columns in the franzinite structure. In this structure, sodalite and

![Fig. 1. Cages in the frameworks of the minerals of the cancrinite group: (a) a sodalite cage (cuboctahedron), (b) a cancrinite cage (hexagonal cuboctahedron), (c) a bystrite cage, and (d) a liottite cage.](image-url)