STRUCTURE, POLYTYPISM AND DISORDER OF DENISOVITE, $K_{14}CA_{42}NA_6SI_{60}O_{162}F_{16}(OH)_4*2H_2O$, OBTAINED BY A COMBINATION OF (S)TEM IMAGING, ELECTRON DIFFRACTION TOMOGRAPHY AND X-RAY POWDER DIFFRACTION

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Denisovite, ideally $K_{14}Ca_{42}Na_6Si_{60}O_{162}F_{16}(OH)_4*2H_2O$, is a rare mineral uniquely found in the Khibini and in the Murun massifs, Russia. A comprehensive structural characterization of denisovite was obtained by a combination of aberration-corrected high-angular annular dark-field scanning-transmission electron microscopy (AC-HAADF-STEM), high-resolution transmission electron microscopy (HR-TEM), electron diffraction tomography (EDT) and X-ray powder diffraction (XRPD).

Denisovite crystallizes in asbestos-like fibers of typical diameter of 200-500 nm. Structure investigation is complicated by the fact that all investigated fibers show pronounced diffuseness of diffraction spots along **a*** for *hkl* reflection lines with $l=2n+1$.

The structure model of denisovite (a = 31.0964 (8), b = 19.5701 (5), c = 7.21526 (12) Å, β = 96.6669 (6) °, space group $P2/a$) was first deduced on the basis of AC-HAADF-STEM images and later on obtained *ab-initio* by direct methods on the basis of EDT reflection intensities and refined by XRPD Rietveld method. The structure can be visualized as being composed by two types of dreier silicate chains: a xonotlite-like dreier double chain $[Si_6O_{17}]^{10-}$ and a tubular loop-branched dreier triple chain $[Si_{12}O_{30}]^{12-}$, both extending parallel to **c**. The silicate chains are connected by ribbons of edge-sharing (Ca,Na)-octahedra.

Similarly to the related mineral charoite (Rozhdestvenskaya et al., 2010; Rozhdestvenskaya et al., 2011), the denisovite structure can be described as an order-disorder (OD) sequence consisting of layers with translation vectors **b** and **c**, and a third basic vector **a**/2 along the missing periodicity. Layers have symmetry $P(m)2m$ and are stacked according to screw axes $2_{1/2}$ or $2_{-1/2}$ || **c**. Even if two sequences with a maximum degree of order (MDO) are possible ("$2_{-1/2}$, $2_{-1/2}$ …" and "$2_{-1/2}$, $2_{1/2}$ …"), only the first one was experimentally observed by HR-TEM imaging. In analogy with charoite, this MDO sequence corresponds to the polytype "denisovite-96". Unlike charoite, an ordered "zig-zag" MDO sequence corresponding to the hypothetical polytype "denisovite-90" was never observed.

The denisovite structure is pervasively disordered along **a** and it was never possible to collect an EDT data set without significant diffuse scattering along **a***, even for areas as small as 50 nm in diameter (about 15 cell repetitions along **a**). The pervasive disorder is confirmed by HR-TEM imaging along [010], which typically shows multiple stacking faults and reversals of the stacking angle β in a range of few unit cell repetitions.

At the structural level, the dreier silicate chains constitute a rigid module that can be connected to different sides of the octahedral bands. Neighboring modules can be shifted by +¼**[001]** or -¼**[001]**. Due to the geometrical relation

$$| a \cos(\beta) | = c/2 \quad ,$$

the β reversal can be described both by a (100) nano-lamellae twinning, or by keeping the cell setting constant and changing the space group description to *P*2/*n*.

Rozhdestvenskaya, I., Mugnaioli, E., Czank, M., Depmeier, W., Kolb, U., Reinholdt, A., Weirich, T. (2010): The structure of charoite, $(K,Sr,Ba,Mn)_{15\text{-}16}(Ca,Na)_{32}[(Si_{70}(O,OH)_{180})](OH,F)_{4.0} * nH_2O$, solved by conventional and automated electron diffraction. Mineral. Mag., 74, 159-177.

Rozhdestvenskaya, I., Mugnaioli, E., Czank, M., Depmeier, W., Kolb, U., Merlino, S. (2011): Essential features of the polytypic charoite-96 structure compared to charoite-90. Mineral. Mag., 75, 2833-2846.