Order-Disorder in Charoite and Denisovite Structures

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Abstract. The charoite and denisovite are rare minerals. They are found as thin needle asbestos-like fibres. The structures of these minerals are composed the edge-sharing (Ca,Na)- octahedra and some types of *dreier* silicate chains. The chains are running along [001] and are located between the ribbons and walls of octahedra. In polytype charoite-90 three adjacent fragments, produced by silicate chains, are followed each other without shifts. In polytype charoite-96 the same fragments are displaced by a translation of ½*c*. In the structure of denisovite the layers parallel to (100) formed by silicate chains and the octahedra walls can be distinquished. The chains are located between neighboring octahedra walls and can be displaced either $\Delta z = + c/4$ or $-c/4$ between neighboring layers. Such an ambiguity with respect to their *z*-position along octahedra walls can lead to the formation of polytypic sequences, to twinning, to new ordered structure, or to disorder when the directions of the reverse randomly.

Keywords: Charoite · Denisovite · Crystal structure · Polytype · Order-disorder

1 Introduction

In silicate minerals such phenomenon as polytypism occurs quite often (e.g., Ferraris *et al*. 2004). In *dreier* chain silicates (nomenclature according to Liebau 1985) this phenomenon occurs most often due to stacking faults or shifts of crystal structure fragments (Jefferson and Brown 1973; Wenk et al. 1976). In these silicates, the octahedral columns of walls and separate bands and tetrahedral silicate chains are streched along the *z* axis. The parameter along the *z* axis $c \approx 7.3$ Å spans one repeat period of the tetrahedral silicate chains and two octahedra edges, respectively. So, the metrical relationships between these fragments of the structure allow the tetrahedral silicate chain to be attached to the octahedral column in two different positions, ≈ 3.65 Å apart, along the chain axis. The regular alternation of the displacements could result to a new ordered structure (polytype), or to twinning. When the directions of the displacements reverse randomly, it leads to disorder. Charoite and denisovite relates to Ca-bearing alkaline silicates with various *dreier* silicate chains and lattice parameter $c \approx 7.3$ Å (Table 1).

Table 1. The lattice parameters for charoite and denisovite structures

Parameter	Charoite-90	Charoite-96	Denisovite
a (Å)	31.96(6)	32.11(6)	31.024(1)
b (Å)	19.64(4)	19.77(4)	19.554(1)
c (Å)	7.09(1)	7.23(1)	7.1441(5)
β (°)	90.0(1)	95.85(9)	95.99(3)
V (Å^3)	4450(24)	4566(24)	4310.3(9)
Space group	$P2_1/m$	$P2_1/m$	$P2/a$

## 2 Order-Disorder in Charoite Structure

Charoite, is a beautiful semi-precious, violet stone. It was found in the alkaline intrusion of the Murun massif in Yakutiya, Siberia, Russia (Konev et al. 1996) and recently in the Patynskiy massif, Gornaya Shoriya, Southern Siberia, Russia (Kasatkin et al. 2019). The charoite was confirmed as a new mineral species in 1978 (Rogova *et al.* 1978). The chemical composition of charoite from both localities is close. Charoite from Patynskiy massif differ from the Murun charoite by the total absence of admixed Sr and F, lower Mn and substantially higher Ca content. The main difference between the charoite varieties is the color. Charoite from Murun is famous for its purple to violet coloration caused by traces of Mn^{3+}, whereas charoite from the Patynskiy massif is whitish-grey to brown. Charoite is usually found in close association with other alkaline calcium silicates such as frankamenite, canasite, miserite, tokkoite and tinaksite (Konev et al. 1996). In the structures of all of these minerals various types of *dreier* silicate chains are located between bands of edge-sharing $[(Ca,Na)O_6]$ octahedra. The silicate chains and octahedra bands are parallel to the *z*-axis with the lattice parameter $c \approx 7.3$ Å (Rozhdestvenskaya and Nikishova 2002).

The crystal chemical formula of charoite is $(K_{13.88}Sr_{1.0}Ba_{0.32}Mn_{0.36})_{\Sigma15.56}$ $(Ca_{25.64}Na_{6.36})_{\Sigma32}[(Si_6(O_{11}(O, OH)_6)_2(Si_{12}(O_{18}(O, OH)_{12})_2$ $(Si_{17}(O_{25}(O,OH)_{18})_2](OH,F)_{4.0}\cdot3.18H_2O$,   or   in   the   general case $(K,Sr,Ba,Mn)_{15-16}(Ca,Na)_{32}$ $[Si_{70}(O,OH)_{180}](OH,F)_{4.0}\cdot nH_2O$. Three different silicate chains can be distinquished in the structure: a *dreier* double chain, $[Si_6O_{17}]^{10-}$ (DC), a tubular *dreier* triple chain, $[Si_{12}O_{30}]^{12-}$ (TC) and a tubular hybrid *dreier* quadruple chain, $[Si_{17}O_{43}]^{18-}$ (QC) (Fig. 1a) (Rozhdestvenskaya et al. 2009, 2010, 2011).

The apical oxygens of *dreier* silicate chains link them to (Ca,Na)-octahedra bands.

The blocks four octahedra wide are linked by apical oxygens and form continuous zigzag walls parallel to (100) (Fig. 1a). Furthermore, a double column and two single columns bonded by common apical oxygens present isolated block four octahedra wide.

The *dreier* double chain (DC), $[Si_6O_{17}]^{10-}$ and the tubular *dreier* triple chain (TC), $[Si_{12}O_{30}]^{12-}$ were found in the xonotlite structure (Kudoh and Takeuchi 1979) and in synthetic $Li_2Mg_2[Si_4O_{11}]$ (Czank and Bissert 1993), respectively. The tubular hybrid *dreier* quadruple chain, $[Si_{17}O_{43}]^{18-}$, is more complicated. It consists of two loop-branched *dreier* single chains, a *dreier* single chain and a *dreier* double chain. The

(a)   **(b)**
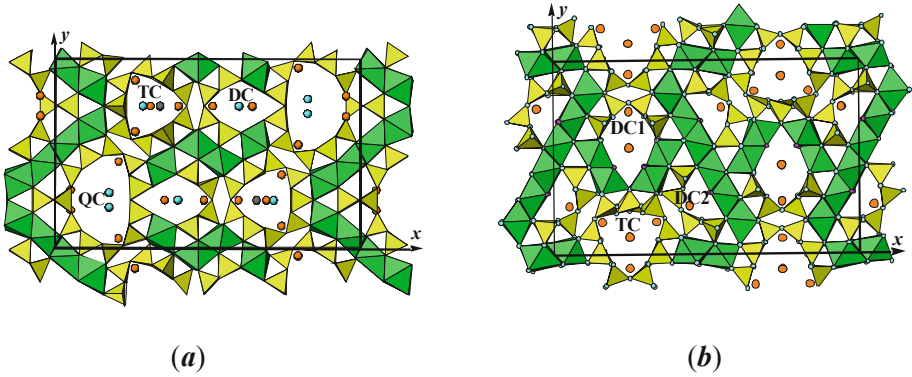
Fig. 1. Structures of charoite (a) and denisovite (b) in projected along the *z*-axis

dreier single chain is the same as found in pectolite and the *dreier* double chain is of the type found in okenite (Merlino 1983).

All *dreier* chains (DC), (TC) and (QC) have horizontal Si_2O_7 groups. The groups Si_2O_7 of neighboring chains are connected to different vertices of octahedron edge (Fig. 1a). Therefore, adjacent chains are displaced relative to each other by the length of one octahedron edge, i.e. *c*/2.

So, in charoite structure three silicate chains (DC), (TC) and (QC) are located one after another along the *x*-axis and form a fixed block (Fig. 2) (Rozhdestvenskaya et al. 2011). In the polytype charoite-90 neighboring fixed blocks follow each other without shifts. In the polytype charoite-96 neighboring fixed blocks are shifted by octahedron edge, i.e. a translation of *c*/2. The shifts take place between a hybrid *dreier* quadruple chain (QC) and a double *dreier* chain (DC). The disorder along [100] (charoite-d) have been observed actually. This is due to the random distributions + or - shifts.
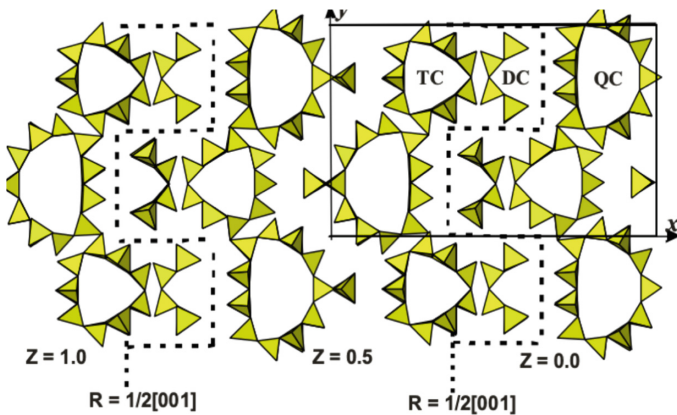
Fig. 2. The dashed line indicates the shift or "stacking fault" plane in charoite structure (Rozhdestvenskaya et al. 2011)

The monoclinic lattice parameters of charoite from the Patynskiy massif were calculated from the XRPD pattern. They were very close to the parameters of charoite-90 polytype from Murun (Kasatkin et al. 2019). However, the polytypes of charoite are very difficult to determine from the XRPD because these patterns of various polytypes are very close because of the specific features of the charoite structure (Rozhdestvenskaya, Drits 2013).
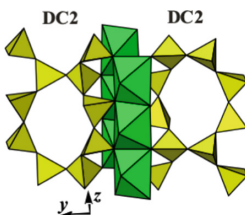
Fig. 3. Denisovite, two (DC2) on opposite sides of an horizontal octahedral wall show their relative displacement by $c/4$

3   Order-Disorder in Denisovite Structure

Rare mineral denisovite occurring as aggregates of fibres typically 200–500 nm diameter. It was discovered uniquely in the Eveslogchorr and Yukspor Mountain in Khibini massif, Kola Peninsula and in the Murun massif, Yakutia, Russia (Konev et al. 1987). It was confirmed as new mineral in 1984 year by CNMNM of IMA (Menshikov 1984). Denisovite occurs in close association with nepheline, potassic feldspar, aegirine, fluorite, apatite, biotite and yuksporite in Khibini massif (Menshikov 1984) and with aegirine, kalsilite, feldspar in Murun massif (Konev et al. 1987, 1996). The crystal chemical formula of denisovite is $K_{14.44}(Ca_{41.96}Na_{6.04})_{\Sigma=48}[(Si_6O_{17})_6(Si_{12}O_{30})_2]F_{16}(O_{0.4}OH_{3.6}) \bullet 2H_2O$, Z = 1 or in general $K_{14}Ca_{42}Na_6[Si_{60}(O,OH)_{162}]F_{16}(O,OH)_8 \bullet 2H_2O$. The denisovite structure is formed by building modules the same as those found in charoite (Rozhdestvenskaya et al. 2010, 2011) and other Ca-bearing alkaline silicates (Rozhdestvenskaya, Nikishova 2002).

In the structure the edge-sharing octahedra are arranged in columns along the z-axis with a repeat unit cell of two octahedra, corresponding to the c-lattice parameter. The individual columns are linked in wall with either one or two neighboring columns. Neighboring columns are mutually displaced along [001] by $c/4$ with respect to each other or half of the length of a vertical octahedron edge. Because of symmetry, it makes no difference if the displacement is $+ c/4$ or $–c/4$.

In the denisovite structure the octahedra walls form a rigid framework with channels along [001] direction. Channels are situated between zig-zag sequences of walls and form strips along [010] (Fig. 1b).

The structure of the mineral contains topologically distinct *dreier* silicate chains: two symmetry-related tubular *dreier* triple chain, $[Si_{12}O_{30}]^{12-}$ (TC) and six *dreier* double chain, $[Si_6O_{17}]^{10-}$ (DC) (Fig. 1b). The chains (DC) can be subdivided into two distinct

classes. Four of the xonotlite-like chains (DC2) are related by the twofold axis and the glide plane. The remaining two xonotlite-like chains (DC1) are mapped onto themselves by the twofold axis. The chains (DC1) and (DC2) are differently surrounded by octahedra walls. Thus they are symmetrically and topologically distinct.

The silicate chains are located within tubes, tunnels or half-tubes formed by octahedra walls. Thereby both, their conformation and their relative positions with respect to the octahedra framework are affected.

To vertical octahedron edges of walls the horizontal Si_2O_7 groups of a given chain (TC) and of three adjacent chains (DC1) and (DC2) are bonded. Therefore they are displaced with respect to each other by the length of one octahedron edge, i.e. $c/2$. The position of chain (TC) and of the neighbouring (DC1) and (DC2) is thus invariant with respect to the z-direction. Furthermore, since chains (DC1) and (DC2) on opposite sides of a v-shaped octahedra walls are bonded to octahedra which have only equatorial corners available for bonds with Si, the vertical Si_2O_7 groups of both (DC1) and (DC2) are at the same height. Thus, all silicate chains are fixed with respect to the z- and to the y-direction within one strip along [010]. Furthermore, because the relative shifts of all chains (DC1) and (DC2) with respect to chain (TC) are $c/2$, they are highly correlated and the whole strip is invariant with respect to the y- and z-direction. This explains why these directions are not affected by disorder.

The situation changes significantly in the x-direction. Two neighbouring strips in the x-direction are symmetrically equivalent. Each one is invariant according to what has been considered above. However, the silicate chains in both strips are displaced with respect to each other along the z-direction. Two chains (DC2) on opposite sides of the horizontal octahedra wall belong to two neighbouring strips. The horizontal octahedra wall has inversion centre. The neighbouring columns of horizontal octahedra wall are displaced by $c/4$ with respect to each other (Fig. 3). Each vertical Si_2O_7 group of chain (DC2) on opposite sides of the horizontal octahedra wall is connected with a vertical edge of one of the symmetrically equivalent octahedra. Consequently, two chains (DC2) on opposite sides of the horizontal octahedra wall are displaced by $c/4$ with respect to each other too, and thus the displacement is for the whole strip. In contrast to the octahedra columns, a silicate chain (DC2) does not have inversion symmetry and, hence, displacements by $+ c/4$ or $-c/4$ are not equivalent. In the real structure shifts in the opposite direction could result in twinning, in a new ordered structure, where shifts $+ c/4$ and $-c/4$ alternate regularly, or to disorder when the directions of the shifts reverse randomly. The stacking faults ½[001] could also lead to lost correlation. Indeed, HRTEM images (Fig. 4) show that twinning and stacking faults occur already on the length scale of a few nm. The reversal of $c/4$ displacements of silicate chains with respect to octahedra walls in combination ½[001] stacking faults explain the observed strongly diffuse l odd diffractions.
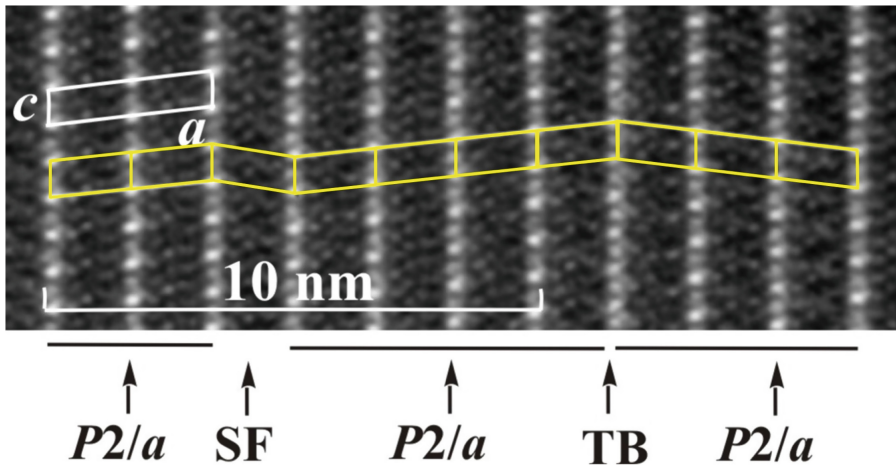
Fig. 4. HRTEM of denisovite, showing ordered $P2/a$ areas, a stacking fault (SF), and a twin boundary TB. A unit cell is indicated in white, yellow rhomboids are a guide to the eyes (Rozhdestvenskaya et al. 2017)

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