

#### 8.1.4.4 Aenigmatite, pectolite and umbite groups of silicates

The silicates from the above groups are listed in Table 1 [91N1]. From the pectolite group, the wollastonite, bustamite and ferrobustamite properties were discussed already in chapter 8.1.4.1 in relation with those of other related pyroxenes and pyroxenoids. According to [91N1] the labuntsovite minerals were classified in group VIIID9. Later on, in [02C1], the labuntsovites and nenadkevichite (group VIIIB11) were analysed together as labuntsovite-nenadkevichite group. Consequently, this group was presented in chapter 8.1.2.5 [05B1]. In this chapter 8.1.4.4 we mention only shortly the structures and lattice parameters for members of the labuntsovite group. – For atomic coordinates and temperature factors see Table 2, for crystal structure and lattice parameters see Table 3.

##### 8.1.4.4.1 Crystal structures. Lattice parameters

###### Aenigmatite group

The crystal structure of **aenigmatite**, ideally  $\text{Na}_2\text{Fe}_5\text{TiSi}_6\text{O}_{20}$  [64K1], was solved by [70M1, 71C1]. The silicate crystallizes in a triclinic-type structure having space group  $P\bar{1}$ . In Fig. 1 a clinographic projection of the atomic distribution in the triclinic cell, as well as a relation between the triclinic cell and the monoclinic pseudo-cell is shown [71C1]. The lattice sites are given in Table 2. The crystal structure consists of two sets of polyhedral layers parallel to the pseudo-monoclinic (100) plane which alternate along the  $x^*$ -direction (along the **a**-axis according to the axial glide plane along **a**). The first layer is formed by Fe-octahedra, Ti-octahedra and distorted Na-square antiprisms and the second by  $[\text{Si}_6\text{O}_{18}]_\infty$  chains connected by Fe-octahedra. The silicate chains are of the pyroxene-like type where in the repeat distance of the four tetrahedra, two consecutive tetrahedra share a common vertex with two additional tetrahedra.

The crystal structure of **serendibite** was determined [68S1, 74B1, 77H1]. According to [74B1] this is triclinic, having space group  $P\bar{1}$ .

The general formula of **rhoenite**,  $\text{X}_2\text{Y}_6\text{Z}_6\text{O}_{20}$  with  $\text{X} = \text{Na}, \text{Ca}, \text{K}$ ;  $\text{Y} = \text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+}, \text{Al}, \text{Ti}, \text{Mn}$  and  $\text{Ca}$ ;  $\text{Z} = \text{Si}, \text{Al}, \text{Fe}^{3+}$  was originally deduced by analogy with aenigmatite [64K1, 69W1, 70C1]. The silicate crystallizes in a triclinic-type structure. The crystal structures of rhoenite and aenigmatite are closely related [69W1]. In [85J1] electron microprobe analysis of some rhoenites was performed. The twelve-dimensional rhoenite composition space was defined with aenigmatite as an additive component and a set of eight linearly independent simple- and coupled-ionic exchange components.

The absence of intermediate compositions between aenigmatite and rhoenite suggests that solid solutions between the two silicates are lacking or limited by a wide range of immiscibility [74Y1].

**Dorrite** crystallizes in a triclinic-type lattice [88C1]. Dorrite is twinned, producing a pseudo-monoclinic symmetry.

**Krinovite** is isostructural with aenigmatite [68O1, 72M1, 89B1] as already shown also for serendibite. The structure of krinovite is characterized by walls formed by  $[\text{MgO}_6]$  and  $[\text{CrO}_6]$  octahedra and by distorted  $[\text{NaO}_8]$  square antiprisms. Such walls are connected through open branched vierer single chains, according to the definition of [85L1]. Additional chromium fills octahedral cavities between the walls. Chromium is located in M1, M2 and M7 sites; M1 and M2 are the “interlayer” octahedra between adjacent octahedral walls, where the term “octahedral wall” was retained for the sake of simplicity, although sodium cations within the walls (M8 and M9 sites) reach eightfold coordination [89B1]. A minor substitution of iron for magnesium was shown in natural samples; the analysis of the occupancies in the M3, M4, M5 and M6 sites revealed an average value of 95 % Mg and 5 % Fe.

The structure of **welshite** was reported by [78M1].

**Makarochkinite** crystallizes also in a triclinic-type lattice [90Y1]. The structure of makarochkinite is closely related to that of aenigmatite. In both structures the M2, M3, M5 and M6 sites are completely occupied by di- and trivalent iron, while the M7 site is almost equally filled with Fe and Ti atoms. In the M1 position there is about 10 % Ti. The M4 site is almost entirely occupied by Fe atoms but in aenigmatite only  $\frac{3}{4}$  filled. The greatest difference is displayed in the filling of the tetrahedra. The T5 and T6 sites are completely or almost completely occupied by Si atoms while T2 and T3 are filled with silicon only by 80-90 %. The T1 and T4 tetrahedra are essentially occupied by Be, whereas in aenigmatite they are occupied by Si.

Sometimes the structure of the aenigmatite-rhoenite group was given in a pseudomonoclinic centered unit cell. This fact was connected with the twinning. In [90Y1] a model of the twinning of the silicates from this group was proposed.

### Pectolite group

The main aspects of the **pectolite**,  $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ , structure were solved by [56B1] by using the film method. The structure was then refined in the space group  $P\bar{1}$  [63P1, 67P1, 76T1]. The **serandite**,  $\text{NaMn}_2\text{Si}_3\text{O}_8(\text{OH})$ , structure was analyzed by [55S1, 67P1, 76T1, 00J1]. The structure of both silicates is similar. For pectolite this is made up of double columns or bands of edge-sharing Ca octahedra which extend in the *b*-direction – Fig. 2a. Adjoining bands are linked by silicate chains and irregularly coordinated Na atoms. The silicate chains share only corners with the Ca octahedra, but five edges of the Na polyhedron are shared with the silicate tetrahedra. This is in contrast to the wollastonite structure where the Ca octahedra are found in bands which are three edge-sharing octahedra wide with the Ca1 and Ca2 octahedra each sharing one edge with the Si3 tetrahedron and the Ca3 octahedron sharing edges with only the other octahedra (see Chap. 8.1.4.1). In [63P1] was proposed that a hydrogen bond most likely exists between the very close (2.48 Å) non-bridging oxygen pair, O3 and O4 along the chain. They applied Pauling's valence sum at O3 and O4 and found that both sites are equally underbonded by about 0.5 valence units. In [67P1] the pectolite structure was further refined from X-ray diffraction data, and a small residual peak between O3 and O4 was identified in the electron density difference Fourier. Although the residual was not significantly above the background, it had a clear maximum about 0.97 Å from O3 and spread out smoothly toward O4. In [67P1] was proposed that an asymmetric hydrogen bond might form with O3-H.....O4, but that it would be highly unusual for such a short hydrogen bond distance. In [76T1] the structure of serandite was refined and they found that the O3.....O4 distance was about 2.453(4) Å, significantly shorter than in pectolite. They also observed a residual charge density between O3 and O4, but found that the peak was about 1.25 Å from both oxygen positions, resulting in a more symmetrical hydrogen bond than proposed by [67P1] for pectolite. Although the authors of [76T1] were unable to uniquely determine the hydrogen position, they postulated an alternate mode of hydrogen bonding in which H would form a hydrogen bond between O3 and O3' of an adjacent silicate chain. Subsequently [77T1] studied a manganoan pectolite crystal by X-ray diffraction, in order to solve the hydrogen position. They found that in agreement with [67P1], the difference Fourier peak in the electron density from H was closer to O3, but also very broad. On the shoulder of this broad peak and closer to O4, they defined a second position, H2. From this model they proposed a disordered mode of H bonding along the chain that would alternate between O3-H.....O4 and O3.....H-O4 configurations. In [98H1] polarized IR absorption spectra of single crystal pectolite and serandite were measured in which the authors observed a very broad absorption band parallel to *b* and centered around 1000  $\text{cm}^{-1}$  to which they assign the fundamental O-H stretching vibration – see section 8.1.4.4.2. Also observed, parallel to *c*, was a bending mode at about 1396  $\text{cm}^{-1}$  in pectolite and 1386  $\text{cm}^{-1}$  in serandite, which suggests that the hydrogen bond in pectolite is slightly stronger relative to serandite. The IR results indicate an extremely low energy of the OH-stretching vibration, consistent with a very strong hydrogen bond between O3 and O4 – Fig. 2b. It was concluded that the spectroscopic results support an asymmetric O-H.....O bond in serandite-pectolite, though structural data from neutron diffraction were not available for comparison. Short, strong hydrogen bonds with short O...O distances are likely to preferentially concentrate lighter isotopes as hydrogen as shown by [79K1]. This is also consistent with the unusually low energy of the O-H-stretching vibration and relatively long O-H distance.

In [00J1], the structure of serandite,  $\text{NaMn}_2[\text{Si}_3\text{O}_8(\text{OH})]$ , has been refined from single crystal X-ray and time-of-flight neutron diffraction data, at ambient conditions. A map of the scattering density is shown in Fig. 3 [00J1]. The proton occupies an asymmetric, double-well position between O3 and O4 confirming one of the shortest asymmetric hydrogen bonds in silicate with  $d(\text{O3}...\text{O4}) = 2.464(1)$  (X-ray) and 2.467(1) Å (neutron). The proton position closest to O3 has about 84 % occupancy and an O-H distance of 1.078(3) Å, and the position closest to O4 has an occupancy of 16 % and an O-H distance of 1.07(1) Å. The  $d(\text{H}...\text{O})$  distance of these hydrogen bonds is 1.413(3) Å and 1.41 (1), respectively. Hydrogen bond angles are 164° for H1 and 168° for H2. The  $^{47}\text{Si}$ -OH bond length (1.628(1) Å) is intermediate in length among the three other Si-O bonds in the dominantly (84 %) hydrated Si1 tetrahedron. The lattice sites for serandite are listed in Table 2b.

Although the silicate chains of three tetrahedral repeat in bustamite, wollastonite and the pectolite – serandite series are similar, the differences in cation arrangements in the octahedral layers result in three structures with distinct stacking schemes of tetrahedral and octahedral layers. According to [78O1] the alternating distribution of Mn in M3 and Ca in M4, as –Mn-Ca-Mn-Ca is essential for the structure of bustamite. When the corresponding sites are both occupied by Ca, forming the band of -Ca-Ca-Ca-Ca-, the structure must be of wollastonite type. In pectolite – serandite, the stacking of tetrahedral and octahedral layers is probably determined by the Na atoms.

The wide range of solid solutions in bustamite and pectolite – serandite was suggested [78O1] to be achieved by the stepwise substitution of Ca and Mn (or Fe, Mg) in the M1 and M2 cation sites. On the Ca-rich side of the solid solution, namely the occupancy of the M1 changes, whereas M2 is variable in its occupancy on the subcalcic side of the solid solution. In addition to the stepwise substitution, another mechanism, such as a short-range order is needed to explain the substitution limit of  $\text{Ca}_{0.5}\text{Mn}_{0.5}$  in M2 site of bustamite.

Stacking disorder at polytypism in pectolite and serandite, similar to that observed in wollastonite, were also analyzed [76M1]. - The previously reported parapectolite [76M1] was later called pectolite-M2abc [78F1].

The **cascandite**, ideally  $\text{CaScSi}_3\text{O}_8(\text{OH})$ , crystallizes in a triclinic lattice, having space group  $P\bar{1}$  or  $C\bar{1}$  [82M1, 82M2]. The crystal structure – Fig. 4 – may be described in terms of two main structural units: octahedral double chains, formed by two strands of edge-sharing octahedra and tetrahedral single chains with a repeat period of three tetrahedra. Each octahedral chain is connected with six tetrahedral chains by corner sharing, whereas each tetrahedral chain is connected with three octahedral chains. Cascandite is thus classified with the three-repeat pyroxenoids (see Chap. 8.1.4.1). The three-repeat pyroxenoids develop three distinct stacking schemes of tetrahedral and octahedral structural layers that appear in the structures of the wollastonite, bustamite and pectolite-serandite series. The general topological features of cascandite are closely related to the pectolite-serandite group. The M2 site is occupied by Sc cations and is smaller than the corresponding site in the pectolite-serandite series. The difference in size between the octahedral M1 and M2 sites results in the distortion of tetrahedral chains. The A site, which in the pectolite-serandite group is occupied by Na, appears vacant in cascandite. In this respect cascandite is unique in the entire three-repeat pyroxenoid family [82M1].

**Foshagite**,  $\text{Ca}_4(\text{Si}_3\text{O}_9)(\text{OH})_2$ , is a fibrous calcium silicate. The crystal structure was analyzed by [58G1, 58M1]. Then, it was shown that the crystal structure is triclinic [60G1]. It is built from  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions, together with infinite  $(\text{SiO}_3)_\infty^{2-}$  chains similar to those evidenced in  $\beta\text{-CaSiO}_3$  (Chap. 8.1.4.1), to which foshagite is closely related. The foshagite crystals show partial stacking disorder. In [60G1] the factors governing the relative stability of different stacking arrangements were discussed.

**Trabzonite**, ideally  $\text{Ca}_4\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ , was reported to crystallize in a monoclinic-type structure [87S1, 88J1].

### Umbite group

The **umbite**,  $\text{K}_2\text{ZrSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  structure has been studied [81I1, 93I1]. A statistically significant replacement of Zr by Ti was established [93I1]. The refinement of the structure was performed in the orthorhombic space group  $P2_12_12_1$  and monoclinic-type structure  $P2_1$  – Table 3 [93I1]. In spite of a slight deviation from the perfect orthorhombic structure ( $\gamma=90.07(2)^\circ$ ), the orthorhombic space group  $P2_12_12_1$  has been considered to be the most probable. In the structure of umbite the M-octahedra,  $(\text{Zr,Ti})\text{O}_6$  and T-tetrahedra,  $\text{SiO}_4$ , form a three-dimensional MT-condensed framework. In this framework, the ratio of the numbers of M- and T-polyhedra is equal to 3. The K atoms and the  $\text{H}_2\text{O}$  molecules are localized in the MT cavities. Each M-octahedron is connected to six T-tetrahedra. The T-tetrahedra, in addition to M-O-T bonds, form T-O-T bonds with each other. The T-radical that appears has the form of an infinite chain with a repeating period of 3T-tetrahedra. **Paraumbite**,  $\text{K}_3\text{Zr}_2\text{H}(\text{Si}_3\text{O}_9)_2\cdot n\text{H}_2\text{O}$ , crystallizes in an orthorhombic-type structure [81I1].

In [97D1, 00Z1] titanium silicate  $\text{K}_2\text{TiSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  was synthesized and the crystal structure was determined. The silicate appeared to be isostructural with the alkaline Zr-silicate umbite [81I1] and  $\text{K}_2(\text{Zr}_{0.86}\text{Ti}_{0.14})\text{Si}_3\text{O}_9\cdot\text{H}_2\text{O}$  minerals [93I1]. The crystal structure of  $\text{K}_2\text{TiSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  is built from  $\text{TiO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra in form of a three-dimensional corner-sharing mixed framework  $[\text{TiSi}_3\text{O}_9]_n^{2n-}$  – Fig. 5. Non-water oxygen atoms are systematically shared between either Si-Si or Si-Ti atoms. In the unit cell, four  $[\text{Si}_3\text{O}_9]_\infty$  chains running along the *a*-axis are connected with each other by Ti-isolated octahedra. The eight-membered ring ellipsoidal tunnels, alternating edges of octahedra and tetrahedra, running in the [100] direction, are filled with potassium cations K2 and water molecules. The potassium cations K1 are in opposite corners of six-membered rings rectangular tunnels delimited by edges of octahedra alternating with two corner-sharing tetrahedra. Both potassium coordination polyhedra have irregular shapes. The Si-tetrahedra in the wollastonite-type chains are connected with Ti octahedra forming either diortho- or triortho-groups – Fig. 5b. In this way seven-sided windows are delimited by the edge of four tetrahedra and three octahedra. These windows interconnect the octagonal and hexagonal tunnels running along the *a*-axis. Consequently the long-chain polysilicate structure of  $\text{K}_2\text{TiSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  is rather opened. The lattice sites are listed in Table 2.

**Kostylevite**,  $\text{K}_4\text{Zr}_2\text{Si}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$  crystallizes in a monoclinic structure having space group  $\text{P2}_1/\text{a}$  [81I2, 83K2]. The structure consists of a framework of  $\text{Zr}[\text{Si}_6\text{O}_{18}]^{4-}$  in which each ring of Si-tetrahedra rests on 6Zr-octahedra and each octahedron is bonded to three rings. Along the *c*-axis is a wide channel in which half the atoms of K and all the  $\text{H}_2\text{O}$  are located. The silicate is dimorphous with umbite.

**Labuntsovite**,  $(\text{K},\text{Na})_8(\text{Ti},\text{Nb})_9(\text{SiO}_3)_{16}(\text{O},\text{OH})_{10} \cdot x\text{H}_2\text{O}$ , crystallizes in space group  $\text{I2}/\text{m}$  [74G1]. The **manganese-rich analog of labuntsovite** crystallizes in a monoclinic-type lattice, space group  $\text{C2}/\text{m}$  [98G1]. The structure was reported to differ from that of labuntsovite in having vacant the position normally occupied by Na, with Mn dominant in the position typically occupied by  $(\text{Mg},\text{Fe}^{2+},\text{Mn})$ . In case of the labuntsovite Ca analog, distinguishing features are absence of Na, the high Ca content and ordering of K, Ba and Ca in the structure channels, which reduces the symmetry to  $\text{Cm}$  [01R1]. The Ca-Nb labuntsovite is characterized by  $\text{Nb} > \text{Ti}$  [00Y1].

**Kuzmenkoite** is a silicate of the labuntsovite family. In [98G1] a centrosymmetric space group typical of labuntsovite was reported. Using the analogy with other minerals of this family [94R1, 94R2] a high degree of decationization of the sample with probable lowering of symmetry was expected [00R1]. The reinvestigation in the space group  $\text{Cm}$  showed a number of additional statistically occupied and split positions [00R1]. According to [00R1], the structure of kuzmenkoite – Fig. 6 – is characterized by a mixed framework consisting of “deformable” chains of  $\text{Ti}(\text{Nb})$ -octahedra linked via four-membered rings of Si-tetrahedra characteristic of labuntsovite and nenadkevichite. The channels along the coordinate axes are filled with small and large cations and water molecules. The structure of kuzmenkoite is characterized by a high Mn-content and an almost complete absence of Na atoms (which are replaced by oxonium ions and water molecules). The structure is highly distorted. Thus, all the positions within the channels are split spaced by shortened distances from one another, and only partly occupied. Different occupancies of the positions (related by a twofold rotation pseudoaxis) indicate a lowered symmetry.

#### 8.1.4.4.2 Optical properties

##### Pectolite, serandite

Polarized IR absorption spectra of pectolite and serandite are given in Fig. 7. Generally the spectra of pectolite ( $E \parallel b$  and  $E \parallel c$ ) and serandite ( $E \parallel b$  and  $E \parallel c$ ) are very similar [98H1], as must be expected from the isotypic structures. The  $E \parallel a$  spectrum of serandite (pectolite) is generally flat in the region between 4000 and 1200  $\text{cm}^{-1}$ . Around 1200...800  $\text{cm}^{-1}$  stretching modes of silicate tetrahedra were observed and the silicate bending modes and the lattice modes of the remaining structural constituents occur at lower energies. The  $E \parallel b$  spectra of both silicates show a very broad, absorbing region, which starts from around 3500  $\text{cm}^{-1}$  and increases to a preliminary maximum around 1500...1400  $\text{cm}^{-1}$ . A typical feature of the spectra are also the shallow humps around 2800, 2300 and 1750  $\text{cm}^{-1}$ . At 1200  $\text{cm}^{-1}$  there is an asymmetric gap. Similar to the  $E \parallel a$  spectra, the silicate stretching modes appear around 1200...800  $\text{cm}^{-1}$  and the silicate bending and lattice modes below 800  $\text{cm}^{-1}$ . The  $E \parallel c$  spectra are similar to the  $E \parallel a$  spectra except that they show an additional mode at 1396  $\text{cm}^{-1}$  (pectolite) and 1386  $\text{cm}^{-1}$  (serandite). These sharp bands were assigned to a bending mode of the strongly hydrogen-bonded OH group. Another OH-bending mode might be assumed in the  $E \parallel b$  spectra between 850 and 800  $\text{cm}^{-1}$  adjacent to the silicate stretching modes. At low temperatures the spectra are similar to those at room temperature.

Analyzing the spectra in [98H1] it was concluded that the FTIR spectra in both silicate show a broad absorption region parallel to the silicate chains (*b*-direction), that is centered around 1000  $\text{cm}^{-1}$ , which is interrupted by a transmission window, and which is superimposed by sharp silicate, lattice and overtone modes. This band was assigned to the OH-stretching mode consistent with the alignment of the O-H...O hydrogen bond parallel to *b* and the short O...O distance (2.45...2.48 Å). The OH-bending modes at 1396  $\text{cm}^{-1}$  and 1386  $\text{cm}^{-1}$  for pectolite and serandite, respectively (in IR spectra parallel to *c*), at low temperatures, shift to higher frequencies (1403  $\text{cm}^{-1}$  at 83 K in pectolite), whereas the down-shift of the OH-stretching mode cannot be observed due to the extremely broad band width. The slightly higher energy of the bending mode in pectolite indicates a slightly stronger hydrogen bond with respect to serandite. However, the bond length in serandite is slightly shorter than in pectolite. An asymmetric O-H...O bond was suggested in pectolite and serandite.

For IR spectra of pectolite and serandite see also [66R1, 76T1].

Some refractive indices are listed in Table 4.