

### 8.1.3.2 Axinite-, ioaquinite-groups and related silicates

The cyclosilicates from groups VIIIC04-VIIIC05 are listed in Table 1 [91N1]. The atomic coordinates of representative silicates are given in Table 2 and in Table 3 the lattice parameters are listed.

#### 8.1.3.2.1 Crystal structures. Lattice parameters

##### Axinite group

The axinites commonly occur as accessory phases in low- to medium- grade metamorphic environments [96G1]. The complex chemical compositions of **axinites** were studied by [79L1] and later revised by [00A1]. Their compositions may be expressed as

$^{[6]}[\text{Ca}(\text{Ca}_{1-x}\text{Mn}_x)(\text{Mn}, \text{Fe}^{2+}, \text{Mg}, \text{Zn}, \text{Al}_u, \text{Fe}^{3+}_v)(\text{Al}_{2-y}\text{Fe}^{3+}_y)]_2^{[4]}[(\text{B}_{1-z}\text{Si}_z)_2\text{Si}_{18}]\text{O}_{30}(\text{OH}_{1-w}\text{O}_w)_2$  where  $x \leq 1$ ,  $u < 1$ ,  $v < 1$ ,  $y < 1$ ,  $z \ll 1$  and  $w = (u + v + z)$ . When  $x = 0$ , i.e. calcium is close to four atoms per formula unit (apfu); the end-members are **mangan-axinite**, **ferro-axinite** and **magnesio-axinite** [68S1]. **Tinzenite** has  $\text{Ca} < 1.5$  and  $\text{Mn} > \text{Fe}$  [68S1].

The crystal structure of **axinite** is triclinic having space group  $P\bar{1}$  [69I1, 74T1]. The silicon tetrahedra in the axinite structure are joined into pairs by sharing a corner oxygen. All these pairs are further combined into larger tetrahedral groups by boron tetrahedra. This group, containing eight Si and two B tetrahedra, has the chemical composition  $\text{B}_2\text{Si}_8\text{O}_{30}$ . The *a*- and *b*-axis projections of the borosilicate group are shown in Fig. 1a,b [74T1]. The center of the group is a six-membered ring which is composed of four Si and two B tetrahedra and is almost parallel to the  $(\bar{1}21)$  plane. The cations Al, Fe, Mn and Ca are in octahedral coordination with O and (OH). The Al octahedra are fairly regular while the others are significantly distorted. A salient feature of the structure is the existence of finite chains of edge-sharing octahedra composed of four Al and two Fe (and Mn) octahedra. The latter are located at the ends of the chain. These chains are oriented approximately parallel to the [211] direction and are joined together laterally by elongated Ca octahedra to form a continuous sheet of octahedra [74T1]. The octahedral frame of the axinite structure is illustrated in Fig. 1c [74T1]. These sheets are in turn, linked together by the unique ten-membered groups of tetrahedra of Si and B. The distortion of  $\text{SiO}_4$  tetrahedra was analyzed [74T1]. The edge lengths between bridge and nonbridge oxygen atoms tend to be shorter than those between pairs of nonbridge oxygen atoms. Although the octahedra around Al are fairly regular, those around Fe are considerably distorted. Four of the twelve edges of the Fe octahedra are shared by Ca, Al or B polyhedra. This complexity of the sharing polyhedral elements was considered to be the cause of the extensive distortion of Fe octahedra [74T1]. There is an extensive elongation of the octahedron formed by oxygen atoms around Ca. According to [74T1], it would be more appropriate to call it a trigonal antiprism than a distorted octahedron. The general scheme of the hydrogen bond of axinite is illustrated in Fig. 1d. The location of the hydrogen atom is near O16.

From the above analysis, the axinite structure may be described as a sequence of layers almost parallel to the  $(\bar{1}21)$  made-up of tetrahedrally and octahedrally coordinated cations. The tetrahedral layer is built up of isolated  $\text{B}_2\text{Si}_8\text{O}_{30}$  planar clusters, whereas the octahedral layer is a continuous framework of Fe–Al–Al–Al–Al–Fe finite chains laterally connected by highly distorted Ca octahedra. The axinite structure was described in various orientations [00S1]. In [37P1] the previously chosen unit cells were revised and new axial angles were defined considering both morphological elements and structural parameters. This orientation is the one generally adopted [74T1, 79L1, 81S1, 86D1, 96G1]. With this orientation, lattice parameters for axinites are close to  $a = 7.16 \text{ \AA}$ ,  $b = 9.20 \text{ \AA}$ ,  $c = 8.96 \text{ \AA}$ ,  $\alpha = 91.9^\circ$ ,  $\beta = 98.1^\circ$ ,  $\gamma = 77.3^\circ$ . A different unit cell was proposed by [52I1] by taking  $[00\bar{1}]$  for  $[001]$ , other axes being unchanged. The unit cell had the following dimensions:  $a = 7.14 \text{ \AA}$ ,  $b = 9.15 \text{ \AA}$ ,  $c = 8.96 \text{ \AA}$ ,  $\alpha = 88^\circ 04'$ ,  $\beta = 81^\circ 36'$ ,  $\gamma = 77^\circ 42'$ . This orientation was followed by some authors [72F1] but was later found to be inconvenient. In other papers [78H1, 82P1] a third crystallographic setting was used, related to the normal setting of [37P1] by the matrix  $001/0\bar{1}0/100$ , which gave parameters close to  $a = 8.96 \text{ \AA}$ ,  $b = 9.20 \text{ \AA}$ ,  $c = 7.15 \text{ \AA}$ ,  $\alpha = 102.7^\circ$ ,  $\beta = 98.1^\circ$ ,  $\gamma = 88.1^\circ$ . See Table 3 for lattice parameters.

The lattice parameters of natural axinites were analyzed in correlation with composition [79L1]. The *a*, *b* and *c* values vary linearly with the mean radius of the cation occupying the Ca1, Ca2, Fe, Al1 and Al2 octahedral sites.

### Kainosite-(Y)

The crystal structure of kainosite is orthorhombic [50B1, 61R1, 63V1, 64P1]. The space group is Pmnb [61R1, 64P1].

### Baotite

The barium-titanium silicate baotite, was discovered and described in [59S1]. A model of baotite atomic structure based on the space group  $I4_1/a$  was published later [60S1]. In [63P1] the crystal structure was analyzed on the basis of that reported by [60S1]. However, it was asserted that the  $c$  period of the unit cell was in fact a pseudoperiod, constituting one quarter of the true translation along the tetragonal axis. The increase of the  $c$  period was attributed to ordered arrangement of the Ti(Fe) and Nb atoms in the structure. A full description of the structure was reported by [70N1]. The baotite structure may be characterized by a three-dimensional framework of infinite square stems or columns formed by the Ti octahedra and bridge metasilicate rings  $[\text{Si}_4\text{O}_{12}]$ . The channels in the framework, extending along the  $c$ -axis are filled with Ba cations [70N1]. The  $[\text{Si}_4\text{O}_{12}]$  rings are threaded on fourfold inversion axes and lie in planes perpendicular to these; the planes pass through at a level corresponding to one of the systems of inversion points of the axes. A second system of inversion points of each of the  $\bar{4}$  axes is occupied by the Cl atoms. The deviation of the Si atoms from the planes indicated is less than 0.004 Å; the O1 atoms – Table 2b – joining the tetrahedra into the rings lie not more than 0.06 Å from these planes. Practically, the  $[\text{Si}_4\text{O}_{12}]$  rings may be regarded as having maximum 4/mmm symmetry, although strictly they only obey 4. The O2–O3 edge parallel to  $c$ -axis of the Si tetrahedron is very large. The enlarged edges of the Si tetrahedra link the tips of the successive Ti and (Ti,Nb,Fe) octahedra which are connected by common horizontal edges into columns extending along the  $c$ -axis. Two projections of the baotite structure are plotted in Fig. 2 [70N1]. In the plane of the structure the end projections of the square stems, formed by the infinite columns of octahedra, are plainly distinguished – Fig. 2a. This structural detail of baotite corresponds to the principal motif of rutile. The difference lies in that, in rutile, all the octahedra are equivalent while in baotite, the  $c$ -spacing is twice that of rutile and there are two independent octahedra [70N1]. The (Nb,Fe) atoms are located into one of the two octahedra. There are two independent octahedra. These are situated in an almost equivalent manner with respect to all the structural details except the Ba atoms. It is the difference in the arrangement of the Ba atoms relative to these octahedra which is probably the cause of the isomorphic impurities location only into the Ti2 octahedron. The Cl atoms occupy the space between the translationally identical  $[\text{Si}_4\text{O}_{12}]$  rings [70N1].

### Taramellites

The general stoichiometry of taramellites is  $\text{Ba}_4(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti}^{4+}, \text{Mg})_4(\text{B}_2\text{Si}_8\text{O}_{27})\text{O}_2\text{Cl}_x$ , where  $0 \leq x \leq 1$  [80M3]. According to the prevailing octahedral cation, the names of **taramellites** (Fe), **nagashimalite** ( $\text{V}^{3+}$ ) or **titanium-taramellite** (Ti) are used in literature [84A1]. The unit cell dimensions of natural taramellite were reported by [57M1]. The first determination of the structure was given by [65M1]. The redetermination of the structure [80M3] confirmed the essential features of the [65M1] report and established the roles of Cl and B – Fig. 3.

The main structural feature of taramellite is a borosilicate radical  $(\text{B}_2\text{Si}_8\text{O}_{27})^{16-}$  which is formed by two rings of four Si tetrahedra connected by a  $\text{B}_2\text{O}_7$  group sharing two oxygen atoms with each ring – Fig. 3 [80M3]. Boron is coordinated by two O8 oxygens belonging to two different fourfold rings, by one of the “free” oxygens, O3, and by O10 which bridges the two tetrahedra of the  $\text{B}_2\text{O}_7$  groups. The anionic groups are superposed along  $a$ , with the planes of the fourfold rings roughly parallel to (100). Barium atoms lie between the fourfold rings, together with chlorine which is surrounded by three Ba atoms and by one more Ba atom at longer distance. The octahedral coordination of M atoms is formed by four oxygens (O6, O7 and two O9) of the  $\text{SiO}_4$  tetrahedra, by one O3 oxygen of a  $\text{BO}_4$  tetrahedron and by one oxygen O4. Each M octahedron shares two edges, O3–O4 or O9–O9, with two opposite adjacent octahedra; a chain of octahedra is thus formed along [100], and it connects four different anionic groups in the unit cell [80M3].

The  $\text{Fe}^{3+}$  dominates over  $\text{Fe}^{2+}$  and Ti, in iron-rich taramellite<sup>11)</sup> [57M1, 80M3] – Table 2, whereas divalent cations ( $\text{Fe}^{2+}$ , Mg) and little  $\text{Fe}^{3+}$  are present in titanium-rich taramellite<sup>13)</sup> [80M3]. For example, the refinement made on the mentioned samples give (0.75Fe+ 0.25Ti) in sample<sup>11)</sup> and (0.25Fe+ 0.75Ti) in sample<sup>13)</sup>. (For footnotes/compositions see Table 3). The site occupation of Cl is 0.89 in first case and 0.95 in the second one.

The crystal structure of iron-rich taramellites was reported by [80M3] and of Ti-rich taramellites by [84A1]. Their lattice parameters are listed in Table 3.

### Nagashimalite

The nagashimalite,  $\text{Ba}_4(\text{V,Ti})_4(\text{B}_2\text{Si}_8\text{O}_{27})\text{O}_2\text{Cl}_x$  crystallizes in an orthorhombic-type structure having space group Pmmn [80M1, 80M2, 81F1]. It is the V analogue of taramellite.

### Muirite

The simplified chemical formula of muirite is  $\text{Ba}_{10}\text{Ca}_2\text{MnTiSi}_{10}\text{O}_{30}(\text{OH,Cl,F})_{10}$  [65A1]. This was somewhat modified as compared to [65A2]. The silicate crystallizes in a tetragonal-type structure [65A2].

### Joaquinite group

The crystal structure of joaquinite was analyzed by [72C1, 72L1]. Although they based their analysis on the monoclinic space group C2/m and did not detect several atoms, the basic structure did emerge. The joaquinite structure was refined by [75D1] using the space group C2 and the positions for the remaining atoms were located. In [67S1, 72L1] such variations were found in the compositions of crystals that they proposed a number of possible end members and referred to the whole as the joaquinite group. Some other silicates were then added to this group [74C1, 82W1]. A systematic nomenclature is based on the crystal symmetry and on the composition of X position in  $(\text{Na,Fe}^{2+})_{4-x}(\text{OH})_{2-y}\text{Ba}_4\text{Ti}_4[\text{O}_{4-z}(\text{OH})_z]\text{X}_4[\text{Si}_4\text{O}_{12}]_4 \cdot 2\text{H}_2\text{O}$ , where X is a rare-earth (R), Sr or Ba. The name of **joaquinite** is to be used for a mineral that is monoclinic and R-rich and **orthojoaquinite** for the silicate that is R-rich but was shown by X-ray diffraction to be orthorhombic [72L1, 75D1]. Sr-bearing silicates are **strontio-joaquinite** (monoclinic) and **strontio-orthojoaquinite** (orthorhombic). Ba-bearing member is **bario-orthojoaquinite** (orthorhombic) [74C1, 82W1].

As mentioned above, the main feature of the joaquinite structure is essentially that given by [72C1] with the exception of the three undetected atoms [75D1]. The principal structural unit is an irregular four-membered silicate ring which is approximately parallel to (001). Symmetry equivalents of this ring are linked by  $\text{TiO}_6$  octahedra into sheets parallel to the (001) face – Fig. 4a [75D1]. The sheets are stacked in the *c*-direction with each being related to the ones above and below by the twofold axes; thus they face each other in pairs. The Ti octahedra are distinctly “below” the plane of the sheets, about one-quarter of the way to the next sheet. They share edges (the O1 and O2 atoms) with the octahedra which link the rings in the facing sheet and one set of twofold axes passes through these edges – Table 2d. The Ba atoms and water molecules lie in the plane at  $z = 0$  between the “bottoms” of the sheets, defining top and bottom on the basis of the location of the Ti atom, as above. The Ba atoms are in irregularly coordinated sites between the rings and Ti octahedra. The central holes of the rings in successive sheets overlie each other, producing cavities in which the water molecules lie [75D1]. The R, Fe and Na atoms are sandwiched between sheets which face each other top to top. The R atoms almost directly overlie the Ti atoms, being slightly below the bisecting plane at  $z = 1/2$ . Thus, they fit into holes left by the Ti octahedra in their downward displacement. The Fe and Na atoms lie exactly in the bisecting plane on a twofold axis. The coordination number of both the Ba and R atoms is high, and although their polyhedra can only be described as irregular, there seem to be no distinct anomalies in bond lengths, except that the mean bond length for R is larger than expected from ionic radii. The sheet structure can sandwich the Ba and R cations fairly neatly in a double-decker arrangement. Most of the structural misfit seems to be centered around the Fe and Na sites – Fig. 4b – which, located as they are on a twofold axis, must be considered to be highly constrained by the way in which the sheets fit together. Fe is in an unusual five-coordination with OH at the apex, and although the Na site is six-coordinated, the bond lengths are disparate [75D1]. If the structural units are considered to be a pair of sheets facing each other across a pseudo-mirror plane, then the monoclinic structure is composed of these units stacked in the *c*\*-direction with successive displacements of  $(3/8)a$ , whereas a twin has successive displacements of  $-(3/8)a$ .

According to [75D1] the orthorhombic form consists of a regular alternation of the  $+3/8$  and  $-3/8$  stacking modifications of the monoclinic form. Assuming that the structure is essentially the same as the monoclinic form, except for stacking, the space group must be Cc2m and the relationship of unit cells is shown in Fig. 4c [75D1]. The derivation of the orthorhombic structure from the monoclinic one is thus a type of unit-cell twinning. The approximate coordinates of atoms can be derived from those in the monoclinic cell and are given in Table 2 d [75D1].

### Katayamalite

Katayamalite, having ideal composition  $(\text{K},\text{Na})\text{Li}_3\text{Ca}_7(\text{Ti},\text{Fe}^{3+},\text{Mn})_2(\text{Si}_6\text{O}_{18})_2(\text{OH},\text{F})_2$  crystallizes in a triclinic lattice having space group C1 [83M1]. The corresponding lattice parameters as well as those when considering the space group P1 are given in Table 3.

### Baratovite

The baratovite mineral was described by [75D2] and the crystal structure was determined by [76S1, 79M1]. The structure consists of  $\text{Si}_6\text{O}_{18}$  rings connected by dense Ca-octahedral sheets and by Ti-octahedra, Li-tetrahedra and 12-fold K-polyhedra. As shown in the projection of the structure along [102] – Fig. 5 – pairs of rings are superimposed in this direction; the rotation angle between the two being about  $30^\circ$ . In the [102] direction the Si-O rings are connected on one side by means of a dense Ca-octahedral sheet and on the other by means of Ti-octahedra, distorted Li-tetrahedra and irregular 12-fold K-polyhedra [76S1, 79M1].

#### 8.1.3.2.2 Hyperfine parameters determined by $^{57}\text{Fe}$ NGR method

### Axinite

The  $^{57}\text{Fe}$  NGR spectra of axinite show the presence of two doublets corresponding to the two oxidation states of iron [76A1]. They determined that 5% of the iron was  $\text{Fe}^{3+}$  and assumed that it substituted for  $\text{Al}^{3+}$  in the  $\text{AlO}_5\text{OH}$  octahedra.

### Baotite

The  $^{57}\text{Fe}$  NGR spectra of baotite<sup>29)</sup> at 95 K and 298 K are shown in Fig. 6 [98S1]. Each spectrum is composed of one  $\text{Fe}^{2+}$  doublet and one  $\text{Fe}^{3+}$  doublet [92Q1, 98S1]. The  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions were supposed to substitute for  $\text{Ti}^{4+}$  in octahedral sites. The  $\text{TiO}_6$  octahedron is somewhat distorted. The hyperfine parameters are given in Table 4. The relative content of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  is dependent on sample composition.

#### 8.1.3.2.3 Optical properties

### Taramellite

The optical absorption spectra of  $\text{Ba}_4(\text{Fe},\text{Ti})_4\text{B}_2\text{Si}_8\text{O}_{29}\text{Cl}_x$  taramellite are shown in Fig. 7 [88M1]. There are several transitions which are predominantly polarized along [100]. The Fe and Ti occur in edge-sharing octahedral chains which lie along [100]. The polarization of charge transfer transitions along the vector between the interacting cations would thus predict that  $\text{Fe}^{2+}-\text{Ti}^{4+}$  charge transfer has intensity along this direction. Thus, the 460 nm band was assigned to  $\text{Fe}^{2+}-\text{Ti}^{4+}$  charge transfer [88M1]. The 460 nm band shows little increase at 83 K – Fig. 7b. The  $\text{Fe}^{2+}-\text{Fe}^{3+}$  charge transfer and intensified  $\text{Fe}^{3+}$  transitions would also contribute to the spectrum. The 700 nm band, assigned to  $\text{Fe}^{2+}-\text{Fe}^{3+}$  charge transfer, shows a large increase in intensities at 83 K. The transitions at 900 and 1150 nm have energies typical of crystal field transitions of  $\text{Fe}^{2+}$  [87M1, 88M1].

### Infrared studies

The infrared studies on **axinite** [61P1, 62M1] and optical absorption spectra [71E1] indicated that boron is in tetrahedral coordination. For IR spectrum of **kainosite** see [64P1].

The IR spectrum of **joaquinite**<sup>24)</sup> is plotted in Fig. 8 [72L1]. The sharp bands at  $\sim 3500$  and  $3560\text{ cm}^{-1}$  indicate that the structure includes significant quantities of crystallographically ordered hydroxyl groups. The band at  $\sim 610\text{ cm}^{-1}$  (corresponding to an H–O–H bending motion) and the broad absorption feature centered at  $\sim 3400\text{ cm}^{-1}$  (the O–H stretch) were attributed to water adsorbed during sample handling procedures. The lower energy region is dominated by the strong Si–O absorption near  $1000\text{ cm}^{-1}$  [72L1].

The refractive indices of some silicates are given in Table 5.