

8.1.4.3 Amphibole group of silicates

8.1.4.3.1 Crystal structures. Lattice parameters

The amphiboles are a complex group of minerals, exhibiting wide chemical variations as resulting from the general geometry of their structures [78L1, 78L2, 79L1, 81H2, 83H1]. The amphibole group is described by the general formula $A_{1-x}B_2C_5T_8O_{22}(OH,F,Cl)_2$ where A contains Na, K and $0 \leq x \leq 1$, $B = Na^+, Li^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$; $C = Mn^{2+}, Fe^{2+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ti^{4+}, Li^+$ at the octahedrally-coordinated sites and T contains Si and Al at the tetrahedral sites [60W1]. These silicates were intensively studied, their properties, particularly the crystal structures, being reviewed by [76P1, 78L1, 78L2, 78T1, 79C1, 81V1, 82V1, 83H1, 88P1, 97L1]. There are some models in describing the structure of amphiboles. The essential feature of these models is that they recognize modules based on perfectly regular-coordination polyhedra. We mention: the extended chain model [79H1], rotated chain model [70T1], close packing approach [80L1], polysomatic structures [78T1], crystallographic shear structures [73C1, 75C2]. A review of these models was given by [83H1].

Amphiboles are members of the biopyribole group. Biopyriboles form a polysomatic series of chain, ribbon and sheet silicates which includes the pyroxenes, micas and amphiboles [78T1, 81V1] – Fig. 1. The term of *polysome* was introduced to designate a crystal that can be regarded as made of chemically distinct layer-modules and *polysomatic series* to designate a series of silicates that can be regarded as being made up from the basic set of modules [78T1, 83H1]. The series is defined by pyroxene and mica end-member structures. Intermediate structures (e.g. amphiboles) can be expressed in terms of pyroxene-like (P) and mica-like (M) slabs or “modules” stacking along a direction corresponding to the [010] direction in biopyriboles [78T1, 92W1] – see also Chap. 8.1.4.1. Amphiboles have stacking sequence MP, in which there is a regular alternation of M and P modules in the [010] direction. In addition to the amphiboles, other naturally occurring intermediate structures have been recognized, including triple-chain silicates MMP (e.g. jimthompsonite) and chesterite MMPMP [78V1, 78V2] – see Chap. 8.1.4.7. The polysome was defined in terms of its chain multiplicity m and chain periodicity, p [83M1, 88M1] rather than by its module sequence [92W1]. This has advantages when considering the statistical significance of polysome sequences in polysomatically disordered biopyriboles [79V1]. The chain multiplicity is the number of tetrahedral chains which are cross-linked to form a polysome. We have for pyroxenes $m = 1$, amphiboles $m = 2$, triple-chain silicate $m = 3$, micas $m = \infty$ and chesterite $m = 2, 3$ (...232323) [92W1]. The chain periodicity is the number of distinct tetrahedra in the repeat distance along the chain length. All biopyriboles have $p = 2$. The basic structures of amphiboles and triple chain silicates (Chap. 8.1.4.7) are shown schematically in Fig. 1 [92W1].

The classification of amphiboles is based on the chemical contents of the standard amphibole formula $AB_2^{[6]}C_5^{[4]}T_8O_{22}(OH)_2$ [97L2, 04L1]. It is to be noted that possession of this formula does not define an amphibole. An amphibole must have a structure based on a double silicate chain. A biopyribole consisting of equal number of pyroxene chains and triple chains would have this formula but would not be an amphibole. The components of the formula, conventionally described above, correspond to the following crystallographic sites: A (1 site pfu), B (2 M4 sites pfu), C (a composite of 5 sites made up of 2M1, 2M2 and 1M3 pfu), T (8 sites in two sets of 4 which cannot be distinguished), “OH” (2 sites pfu). The order of allocation of the cations was given in [04L1]. The extensive solid solutions shown by amphiboles together with their widespread occurrence has presented difficulties in elaborating the nomenclature of this group. First systematic amphibole nomenclature was approved in 1978 [78L3]. This scheme was developed, refined, simplified and adjusted for newly discovered species [97L2, 04L1, 05B1]. This scheme consists of 34 root names with a range of compulsorily used prefixes to indicate particular richness in certain elements and several optionally usable modifiers for less important substitutions. Prefixes are an essential part of the mineral name [98G1]. The scheme divides amphiboles in five groups [04L1]. The end members are given in Table 1a.

1. **The Mg-Fe-Mn-Li amphiboles group** is defined as $^B(Mg,Fe^{2+},Mn^{2+},Li) \geq 1.50$ apfu – Fig. 2a [97L2, 04L1]. The **orthorhombic** structures is found in: (1) the anthophyllite series $Na_xLi_z(Mg,Fe^{2+},Mn)_{7-y-z}Al_y(Si_{8-x-y+z}Al_{x+y-z})O_{22}(OH,F,Cl)_2$ where $Si > 7.00$ and $Li < 1.00$. Most anthophyllites have the Pnma structure. Those with Pnmn structure may be prefixed proto without a hyphen; (2) the gedrite series, $Na_xLi_z(Mg,Fe^{2+},Mn)_{7-y-z}Al_y(Si_{8-x-y+z}Al_{x+y-z})O_{22}(OH,F,Cl)_2$, where $x+y-z \geq 1.00$ so that $Si < 7.00$, $Li < 1.00$; (3) the holmquistite series, $\square Li_2(Mg,Fe^{2+})_3(Fe^{3+},Al)_2Si_8O_{22}(OH,F,Cl)_2$, with $Li \geq 1.00$. The **monoclinic** structure is for the: (1) Cumingtonite – grunerite series, $\square(Mg,Fe^{2+},Mn,Li)_7Si_8O_{22}(OH)_2$, $Li < 1.00$ (most have C2/m type structure);

(2) clinoholmquistite – clinoferroholmquistite, $\square\text{Li}_2(\text{Mg}, \text{Fe}^{2+}, \text{Mn})_3(\text{Fe}^{3+}, \text{Al})_2\text{Si}_8\text{O}_{22}(\text{OH}, \text{F}, \text{Cl})_2$ with ${}^{\text{B}}\text{Li} \geq 1.00$ apfu and ${}^{\text{C}}\text{Li} < 0.5$ and (3) sodic pedrizite and sodic ferropedrizite having ${}^{\text{C}}\text{Li} > 0.5$.

2. Calcic amphiboles. The group is defined as monoclinic amphiboles in which ${}^{\text{B}}(\text{Ca}+\text{Na}) \geq 1.00$ apfu and ${}^{\text{B}}\text{Na}$ is smaller than 0.50 apfu, usually ${}^{\text{B}}\text{Ca} \geq 1.50$ apfu. The detailed classification is given in Fig. 2b. The prefixes ferri and alumino are only used when $\text{Fe}^{3+} > 1.00$ apfu and ${}^{[6]}\text{Al} > 1.00$ apfu – Table 1b. For kaersutite and ferrokaersutite, $\text{Ti} \geq 0.50$ apfu and lower Ti content may optionally be indicated as in Fig. 2b. Cannilloite requires ${}^{\text{A}}\text{Ca} \geq 0.50$ apfu.

3. Sodic-calcic amphiboles. The group is defined as monoclinic amphiboles in which ${}^{\text{B}}(\text{Ca}+\text{Na}) \geq 1.00$ apfu and $0.50 < {}^{\text{B}}\text{Na} < 1.50$ apfu. The limits for the use of end members are given in Fig. 2c with respect to Si, ${}^{\text{A}}(\text{Na}+\text{K})$ and $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$. Alumino and ferri are restricted to ${}^{[6]}\text{Al} > 1.00$ apfu and $\text{Fe}^{3+} > 1.00$ apfu.

4. Sodic amphiboles. The group is defined as monoclinic amphiboles in which ${}^{\text{B}}\text{Na} \geq 1.50$ apfu. The detailed classification is shown in Fig. 2d. Kozulite requires $\text{Mn} > (\text{Fe}^{2+}+\text{Fe}^{3+}+\text{Mg}^{2+}+{}^{[6]}\text{Al})$ with ${}^{[6]}\text{Al}$ or $\text{Fe}^{3+} > \text{Mn}^{3+}$, $\text{Li} < 0.5$ apfu. Ungarettiite has both Mn^{2+} and $\text{Mn}^{3+} > (\text{Fe}^{2+}+\text{Mg}+\text{Fe}^{3+}+{}^{[6]}\text{Al})$ with $\text{Li} < 0.50$ and $(\text{OH}+\text{F}+\text{Cl}) < 1.00$ apfu. Leakeite and kornite require $\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) \geq 0.50$, $\text{Li} \geq 0.50$ apfu with $\text{Fe}^{3+} > \text{Mn}^{3+}$ in leakeite and $\text{Fe}^{3+} < \text{Mn}^{3+}$ in kornite. Ferric-nyböite means $\text{Fe}^{3+} \geq {}^{[6]}\text{Al}$ and should be distinguished from ferri ($\text{Fe}^{3+} > 1.00$ apfu). The obertiite is characterized by $\text{Ti} \geq 0.50$ and $(\text{OH}+\text{F}+\text{Cl}) < 1.00$ apfu.

5. Na-Ca-Mg-Fe-Mn-Li amphiboles are characterized by ${}^{\text{B}}\text{Li} > 0.50$ apfu (ottoliniite, ferro-ottoliniite, whittakerite, ferrowhittakerite) and ${}^{\text{B}}\text{Li} \leq 0.50$ apfu with the added prefix parvo – Fig. 2e.

The prefixes additional to Figs. 2a-e are listed in Table 1b and the modifiers and their suggested ranges in Table 1c [97L2]. We note that in [03M1] was shown that in addition to approved species for which K is a dominant A site cation, other minerals correspond to new end-members (unapproved).

Amphiboles belong to five principal structure types with space groups C2/m, P2/a P2₁/m, Pnma and Pnmm, but the C2/m and Pnma structures are the most common. We follow in this section mainly the excellent description of the amphibole structures given by Hawthorne [83H1]. As pointed out by [83H1] the essential feature of the amphibole structure is a double chain of corner-linked tetrahedra that extends infinitely in one direction and has the general stoichiometry $(\text{T}_4\text{O}_{11})_{\infty}$ – Fig. 3a. The direction of infinite polymerization of the double-chain unit defines the z -axis of the amphibole cell in the normal direction. The value of the repeat distance in the z -direction is the c -dimension of the unit cell and is dependent on the type of tetrahedrally-coordinated cation and stereochemistry of the tetrahedra. These factors produce only minor perturbation from the ideal value (≈ 5.3 Å) for an $(\text{Si}_4\text{O}_{11})_{\infty}$ chain. Two different types of oxygen anions exist in this double-chain element. The oxygen atoms lie approximately in two planes parallel to the chain direction; all oxygen atoms lying in the plane containing the linkages between adjacent tetrahedra are called **basal** oxygens, whereas the oxygen atoms lying in the other plane are called **apical** oxygen. Oxygen atoms bonded to two tetrahedrally-coordinated cations are called **bridging** (linking two TO_4 tetrahedra together, O_{br}), whereas oxygen atoms bonded to one tetrahedrally-coordinated cation are called **nonbridging** (O_{nbr}) [78H1]. The $(\text{T}_4\text{O}_{11})_{\infty}$ chains are linked together by divalent and trivalent cations that bond to the O_{nbr} anions of the chains. The SiO_{nbr} bridging bonds often are as much as ≈ 0.05 Å shorter than SiO_{br} bonds. It has also been observed that $\text{O}_{\text{nbr}}\text{-Si-O}_{\text{nbr}}$ angles that involve SiO_{nbr} bonds tend to be wider than the $\text{O}_{\text{nbr}}\text{-Si-O}_{\text{br}}$ angles, which in turn tend to be wider than $\text{O}_{\text{br}}\text{-Si-O}_{\text{br}}$ angles [81H1]. This trend in the tetrahedral angles of the silicate tetrahedral oxy-anion has been explained in terms of the (d-p) π bonding model [61C1]. It has been argued that the bonding in chain silicates is largely ionic in character and that the differences between the SiO_{br} and SiO_{nbr} bonds and tetrahedral distortions can also be explained on the basis of an ionic model and ionic SiO bond strength considerations without resorting to (d-p) π -bonding effects [69P1]. Later on, [73C2] completed minimum basis (no d-type polarization functions on Si) semiempirical molecular orbital calculations on the silicate chains in clinoamphiboles and found that the observed SiO bond lengths are inversely correlated with the Mulliken overlap populations, $n(\text{SiO})$, calculated for the SiO bonds. They also observed that the $n(\text{SiO})$ values of the SiO_{nbr} bonds tend to be larger than those of the SiO_{br} bonds and that the tetrahedral angles that involve the SiO_{nbr} bond tend to be wider than those that involve the longer SiO_{br} bonds (see above [81H1]). The calculations suggested that SiO_{nbr} bonds possess a greater buildup

of electron density in their bonds than do the SiO_{br} bonds. In [98S1] the electron density distributions, the bond paths and the bond critical properties of protoferro-anthophyllite, protomangano-ferro-anthophyllite, grunerite and protoamphiboles were calculated. It was shown that in these amphiboles the M4 cation is 4-coordinated. The values of the electron density at the bond critical points, $\rho(r_c)$, for the SiO_{nbr} bonds are larger on the average ($0.93 \text{ e}\text{\AA}^{-3}$), than that of the SiO_{br} bonds ($0.90 \text{ e}\text{\AA}^{-3}$). The observed SiO bond lengths decrease linearly with increasing $\rho(r_c)$ while the magnitudes of the curvatures of $\rho(r_c)$ both perpendicular and parallel to the bonds and the Laplacian of $\rho(r_c)$ each increases. These trends were associated with an increase in the electronegativity of the Si cation, a possible increase in the covalent character of the SiO bond and tendency for SiO_{nbr} bonds to be involved in wider O-Si-O angles than SiO_{br} .

Two types of interchain linkages were recognized. A strip of the divalent and trivalent cations is intercalated between two layers of apical oxygen atoms belonging to double chains that adjoin each other orthogonal to the plane of the basal oxygen atoms. The adjacent double chains are staggered in the z -direction so that the apical oxygen atoms of the adjacent chains assume a pseudo-octahedral arrangement around each of the linking divalent and trivalent cations. In order to complete the coordination of these cations in the center of this strip, it is necessary to add a monovalent anion [83H1]. These adjacent double chains are tightly bounded together and form a modular unit (I-beam) – see also Chap. 8.1.4.1. The second type of interchain linkage joins these modular units together in a three-dimensional array – Figs. 3b, c. The divalent and trivalent cations at the edge of the I-beam unit link laterally the nonbridging basal oxygen atoms on an adjacent I-beam. An I-beam may be thought of as a strip of edge-sharing octahedra sandwiched between two double chains of corner-sharing tetrahedra [83H1].

The essential topological aspects of the crystal structures appearing in amphiboles are shown in Fig. 4 [76P1, 88P1]. The tetrahedral-octahedral-tetrahedral (T-O-T) strips (I-beam) are packed in a pseudo-body centered fashion in the (ab) -plane and are interconnected by ions localized at the M4 site [61G1, 69F1]. The different types of structures differentiate by the arrangement of T-O-T units. As mentioned in case of pyroxenes (Sect. 8.1.4.1.1), the rotational aspects of the tetrahedral chains relative to octahedral strip, is **S** if the tetrahedra and octahedra have the same orientation and is **O** if the tetrahedra and octahedra have opposite orientations [70P1, 70T1, 88P1]. A stacking sequence of octahedral layers is defined as positive or negative depending on whether the apex of an octahedron points to $+a$ or $-a$ when viewed in the $+c$ direction. The designations A and B refer to two tetrahedral sheets in a T-O-T unit, that are symmetrical distinct. The absence of these designations indicates that the tetrahedral sheets in a T-O-T unit are symmetrically equivalent and are related by a twofold axis parallel to b .

A comparison of the pyroxenes and amphiboles structures may be made. In both silicate types, interlocking cation-containing tetrahedral and octahedral chains run parallel to c and form layers parallel to (100) with adjacent layers being staggered $t \cong c/3$ with respect to one another to satisfy the bonding requirements of the octahedral and tetrahedral cations. Chemically similar amphiboles and pyroxenes with identical stacking sequences are virtually indistinguishable when viewed down b . For the $C2/c$ clinopyroxenes and $I2/m$ clinoamphiboles, the staggering vectors paralleling the layers are always in the same direction (...+++...) or (...---...) as displayed by the grunerite structure. The stacking sequence for $Pbca$ enstatite and $Pnma$ anthophyllite is always (...++-...). The stacking sequence for $Pbcn$ protoenstatite and $Pnmn$ protoanthophyllite is always (...+-+...). The $P2_1/m$ has the same stacking sequence as the $C2/m$ ($I2/m$) structure. In [59S1] was reported that the crystal structure of $Pnmn$ amphibole could be derived from that of protoenstatite by: (1) inserting a reflexion isometry into the protoenstatite structure parallel to (010) so as to double its single chain of SiO_3 composition into a chain of Si_4O_{11} composition; (2) by centering the 6-membered rings of the doubled chain with F anions (analogous to O3 anions in hydroxy-amphiboles); (3) by placing an Mg cation at the origin of the unit cell. A similar strategy was used to derive the structure of tremolite from that of diopside [29W1]. According to [83H1] the idealized protoamphibole structure ($Pnmn$) can be regarded as alternating layers of protoenstatite and 1M talc (with talc in adjacent M slabs in different orientations). The idealized anthophyllite structure ($Pnma$) can be regarded as alternating layers of orthoenstatite and 2O talc [83H1]. The a lattice parameters are similar in length for the $C2/m$, $P2_1/m$ and $Pnmn$ amphiboles. In case of $Pnma$ orthoamphiboles along a , the distance that must be traversed before arriving at a symmetrically identical point, is twice as long because of the different octahedral stacking sequence. We note that one or more mistakes in any one of the above stacking sequences can result in either a twinned crystal with (100) as its composition plane or in a stacking fault [98S1].

Further linkage between the modular units is provided by the A and B cations. The B cations are situated at the margins of the octahedral strips, where they provide additional linkage both within individual I-beams and between adjacent I-beams [83H1]. The interchain linkage provided by the B cations differs from the second type of interchains linkage described above. The C-type cations all bond to nonbridging anions whereas the B-type cations bond both to nonbridging and bridging anions. The B cations are surrounded by eight anions, not all of which are necessarily bonded to the central cation. These anions are arranged in a distorted square antiprism, the exact configuration of which is a function of the central cation and local structure requirements [83H1]. Between the back-to-back double chains is a large cavity in which A-type cations are situated. The number and configuration of the surrounding anions to which they are bonded are a function of local stereochemical requirements and vary with the composition. The A cations thus provide additional linkage between adjacent double chains orthogonal to the plane of the double chain. The A sites may be split in some amphiboles (Am, A1, A2).

There were different notations of the β -angle in amphiboles. Thus, in I-centered notation, the β -angle was described as acute angle between x - and z -axis [29W1] or the obtuse angle between x and z [55Z1, 60H1, 60H2]. In these studies the signs of z -coordinates must be reversed. In [83H1] the crystallographic data were presented in a C-centered notation with β obtuse.

The site nomenclature of the amphiboles is shown in Table 1d [83H1]. The sites occupied by C and B cations are denoted M sites and those occupied by A and T cations are denoted by A and T, respectively. The site nomenclature by [73H1, 73H2, 73R1] was adopted for C2/m amphibole structure, for Pnma from [70F1, 70P1]. For the site nomenclature of Pnma structure [69G1], Si(1) \rightarrow T1, Si(2) \rightarrow T2 notations were introduced. For P2₁/m structure, that of [69G1] was used, while for P2/a structure, that proposed by [69M1] was revised. Through this chapter all the notations, as for examples M(1), M(1)A, O(1), O(1A) were changed in M1, M1A, O1, O1A, respectively. In Table 2 are also given the atomic coordinates for some representative structures. A nice description of the crystal structure types of amphiboles was given by [83H1]. In the following we reproduce the above basic features of the structure types. Then, we analyze the peculiarities of structural aspects of various amphiboles. As function of composition some sites can be splitted. The amphiboles structural topology is given in Fig. 4. The amphiboles crystal structures C2/m – Fig. 3 and of P2₁/m, P2/a, Pnma and Pnma – Fig. 5 are also presented.

The C2/m-type structure consists of double T₄O₁₁ silicate chains with six-membered rings, two of which sandwich an edge-sharing octahedral band parallel to the c -axis – Fig. 3. There are three nonbridging anions (apical O1 and O2 and basal O4) and three bridging anions (O5, O6, O7 basal oxygens). The O5 and O6 bridge along the length of the T₄O₁₁ double chain and O7 links the two pyroxene-like components of the double chains together. The O3 site is bounded to three octahedrally-coordinated cations and may be occupied wholly or in part by OH⁻, F⁻, Cl⁻ or O²⁻. The anions are arranged in layers parallel to the (100) plane. There are two T sites (T1 and T2) having point symmetry 1. The T1 site is coordinated by three bridging and one nonbridging anions, while the T2 site is coordinated by two bridging and two nonbridging anions. There are three sites with pseudo-octahedral symmetry (M1, M2, M3) having point symmetry 2 (M1, M2) and 2/m (M3). Both the M1 and M3 sites are coordinated by four oxygen atoms and two O3 anions. The O3 anions around M1 site are in cis-arrangement, whereas around the M3 site they are in trans-arrangement. The M2 site is coordinated by six oxygen atoms and is situated at the margin of the octahedral strip. The M4 site (point symmetry 2) is surrounded by eight cations and it is coordinated by both nonbridging and bridging anions. The M1, M2, M3 octahedra are rather regular, whereas M4 is strongly distorted and occurs, as above mentioned, on the outside of the octahedral band. The tetrahedral-octahedral-tetrahedral strips or “I-beams” are packed in a pseudo-body centered fashion in the (ab)-plane and are interconnected through the M4 site. The twelve anions surrounding the A site are all bridging anions and form two ditrigonal rings on opposite sides of the cavity. The ditrigonal rings point in opposite directions [83H1].

The P2₁/m-type structure – Fig. 5a – is characterized by the presence of six nonbridging anions – apical (O1A, O2A, O1B, O2B) and basal (O4A, O4B). There are six bridging anions-basal oxygen atoms (O5A, O6A, O7A, O5B, O6B, O7B) with O7A and O7B cross-linking the double chains and the remainder bridging along the length of the T₄O₁₁ double chains [83H1]. The O3A and O3B sites are generally occupied by OH and are coordinated to three octahedrally-coordinated cations. There are four cation sites (T1A, T2A, T1B, T2B) having point symmetry 1 with the same coordination as in the C2/m-type structure (pseudo-tetrahedral). The back-to-back double chains (A, B) are not equivalent, the B chain showing a more greater deviation from the extended chain configuration than does the A chain with the average chain kinking similar to that found in the C2/m-type structure (in structures with similar composition). The double chains in the structure still have mirror symmetry and retain the same linkage configurations as in C2/m-type in regard of the labeling of the atoms of the chains [83H1]. The M1, M2 (point symmetry 1) and M3 (point symmetry m), as in C2/m-type structure, have pseudo-

tetrahedral coordination. Similar, at the margins of the octahedral strip, is M4 site (point symmetry 2) surrounded by eight anions arranged in a very distorted square antiprism. The site A (point symmetry m) is located between the back-to-back A and B chains.

The *P2/a-type structure* – Fig. 5b – is characterized also by the presence of six nonbridging anions: apical (O1A, O2A, O1B, O2B) and basal (O4A and O4B). There are five bridging (basal) oxygens (O5A, O6A, O5B, O6B and O7); the O7 cross-links the double chains and the other bridge along the length of the double chain. The O3 site is occupied by OH and is coordinated to three octahedrally-coordinated cations. The coordination of T1A, T2A, T1B and T2B sites (point symmetry 1) is pseudo-tetragonal and similar as in the *P2₁/m-type structure*, but in the *P2/a-type structure* form only one double chain. The relative configurations and their coordinating anions for M1A, M2A, M1B, M2B and M3 sites (point symmetry 2 – pseudo-octahedral) are analogous to those of similar sites in the *C2/m-type structure*. There is only one type of octahedral strip [83H1]. At the margins of the octahedral strip are the M4A and M4B sites (point symmetry 2). The anions surrounding each site are arranged in a distorted square antiprism, with all the anion bonded to the central cation. Sandwiched between back-to-back double chains is the A site, surrounded by twelve anions.

In case of the *Pnma-type structure* – Fig. 5c – there are also six nonbridging anions: apical (O1A, O2A, O1B, O2B) and basal (O4A, O4B) and six bridging anions: basal (O5A, O6A, O7A, O5B, O6B, O7B). The O7A and O7B bridge across the chains and the remainder along the length of the chains. The O3A and O3B anions are occupied by OH[−], F[−], Cl[−] or O^{2−} and are coordinated to three octahedrally-coordinated cations. The T1A, T2A, T1B and T2B sites (point symmetry 1) have pseudo-tetrahedral coordination. T1A and T1B sites are coordinated by three bridging and one nonbridging anions and T2A and T2B sites by two bridging and two nonbridging anions. There are two crystallographically distinct double chains (A, B) which have mirror symmetry; the intrachain linkages are analogous to those in the *C2/m-type structure* [83H1]. The M1, M2 and M3 sites with point symmetry 1, 1 and m, respectively have pseudo-octahedral coordination. Apart from the differences in the point symmetry, the coordination of these sites is similar to those of corresponding sites in the *C2/m-type structure*. The anions on one side of the octahedral strip are of A type and on the other side B type and thus, there is only one type of octahedral strip. The M4 site (point symmetry 1) is situated at the edges of octahedral strip and is surrounded generally by eight anions. The coordination number varies with cation occupancy of this site. The cations located in M4 site may be bond to bridging anions of both the A and B tetrahedral double chains. The A site (point symmetry m) is situated between the back-to-back A and B double chains and is coordinated by six bridging anions. In [83H1] was mentioned that there seems to be no significant positional disorder of the cations occupying these sites.

The protoamphiboles crystallize in a *Pnmm-type structure* [60G1, 69G1, 83H1] – Fig. 5d –. There are three nonbridging anions: apical (O1, O2) and basal (O4) and three bridging anions: basal (O5, O6, O7), with O7 bridging across and O5 and O6 bridging along the tetrahedral double chain. The O3 site, occupied by F[−], is coordinated to three octahedrally-coordinated cations. The T1 and T2 sites (point symmetry 1) have pseudo-tetrahedral coordination; the T1 site being coordinated by three bridging and one nonbridging anions and T2 site by two bridging and two nonbridging anions. There is only one symmetrically distinct tetrahedral double chain with distinct tetrahedra alternating along the chain. The M1, M2 and M3 sites (point symmetry, 2, 2 and 2/m, respectively) have pseudo-octahedral coordination, similar as in *C2/m* amphibole structure and there is only one symmetrically distinct octahedral strip. At the edge of the octahedral strip there is the M4 site (point symmetry 2), surrounded by eight anions, only six of which are bonded to the central M4 cation. Unlike M1, M2 and M3 sites, the M4 central cation bonds both to bridging and nonbridging anions. The A site (point symmetry 2/m) is situated in a large cavity between the back-to-back double chains and is surrounded by twelve anions [83H1].

The site occupancies in some amphiboles are given in Table 3 and the lattice parameters for representative amphiboles are listed in Table 4.

As above discussed, the amphibole structures can be distinguished by the chain types and the sequence of stacking vectors ($\pm c/3$) in the *a** direction:

	C2/m		P2 ₁ /m		Pnmm		Pnma			
Stacking sequence	(+c/3)(+c/3)		(+c/3)(+c/3)		(+c/3)(−c/3)		(+c/3)(+c/3) (−c/3)(−c/3)			
<i>a</i> * direction										
chain types	A	A	A	B	A	A	A	B	A	B
<i>a</i> [Å]	≅ 9.5		≅ 9.5		≅ 9.5		≅ 18.6			

Many natural and synthetic amphiboles contain chain-multiplicity faults (CMFs), in which a regular module stacking sequence is interrupted by one or more stacking faults resulting in changes in polysome chain-multiplicity. The most common CMFs in amphiboles and pyroxenes are triple chains. Studies of polysomatism in biopyriboles have sought to establish empirical chain-replacement rules and to recognize important reaction mechanisms: for example the link between topotactic replacement and channel development leading to ultrafast diffusion pathways [92W1]. In [79V1] the statistical significance of runs of various long period polysomes in natural orthorhombic amphiboles was assessed, and it was concluded that some consisting of double and triple-chain multiplicities, such as 232233 are highly non-random occurrences. These non-random sequences were interpreted as kinetically stabilized intermediates formed in the hydration of amphiboles to talc. In [92W1] the polysomatic transformation between amphibole and hydrous triple-chain silicate (TCS) in the $\text{Na}_2\text{O-MgO-SiO}_2\text{-H}_2\text{O}$ system was studied by XRD, HRTEM and ^{29}Si MAS NMR. The reaction is $4\text{Na}_2\text{Mg}_4\text{Si}_6\text{O}_{16}\text{OH}_2$ (TCS) \leftrightarrow $3\text{Na}_{2.67}\text{Mg}_{5.33}\text{Si}_8\text{O}_{21.33}(\text{OH})_{2.67}$ (amphibole). The sample is a fine scale lamellar intergrowth of double- and triple-chain structures, lamellae are 27 Å to hundreds in Å wide. The ^{29}Si MAS NMR spectrum of the intergrowth was analyzed as a superposition of the individual amphibole and TCS spectra. The relative amounts of double- and triple-chain structures are 42(5) and 58(5) mol %, respectively.

1. Iron-magnesium-manganese amphiboles

Amphiboles, chemically approaching the join $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, occur naturally as **anthophyllite** and as **cummingtonite – grunerite** groups. The silicates from above series crystallize in different types of structures, depending on their Mg/Fe ratio. Mg end member anthophyllites are orthorhombic with Pnma symmetry, Mg-rich cummingtonites are monoclinic $\text{P2}_1/\text{m}$ and Fe-rich cummingtonite end members are monoclinic $\text{C2}/\text{m}$ [79C1].

Along the joint series $\text{Mg}_{7-x}\text{Fe}_x\text{Si}_8\text{O}_{22}(\text{OH})_2$ the entire range of amphiboles can be synthesized [71F1, 76P2]. The silicates with $1 \leq x \leq 7$, synthesized hydrothermally, were found to crystallize in an orthorhombic-type structure of Pnma type [76P2]. Variation of the unit-cell parameters with composition suggested that they are member of a single continuous solid solution – Fig.6.

The anthophyllites exhibit long-range, non convergent order of Fe^{2+} and Mg^{2+} over the four sites M1, M2, M3 and M4. A strong preference of Fe^{2+} for the M4 site has been shown [89W2, 97D3]. As an example in $\text{Na}_{0.01}\text{Ca}_{0.02}\text{Mg}_{5.71}\text{Fe}_{1.24}\text{Mn}_{0.02}(\text{Si}_{7.95}\text{Al}_{0.05})\text{O}_{22}(\text{OH})_2$, the M2 site is only occupied by Mg and M1, M3 sites contain also little iron. M4 is greatly enriched in iron ($0.62\text{Fe} + 0.38\text{Mg}$) [89W2]. The coordination of M4 is highly irregular with five next oxygens and two longer M4-O distances. The A site was found to be empty – Table 3. In this table we report also the site occupancy for other representative amphiboles. Lattice parameters are given in Table 4.

The temperature dependence and kinetics of the order-disorder processes was studied [75S1, 77S2, 78S1]. For anthophyllite and cummingtonite – grunerite series, quantitative assessment of their mutual stabilities was attempted [01E1]. The site preferences of Fe^{2+} are $\text{M4} \gg \text{M1}$, $\text{M3} > \text{M2}$. They are smaller at higher temperatures of equilibration. End-member thermodynamic properties of ferro-anthophyllite and cummingtonite were derived from those known for the anthophyllite and grunerite, respectively, using intercrystalline K_D data and a fit of the $T\text{-}x_{\text{Fe}}$ phase loop to two critical field constants: middle amphibole-facies amphibolites and upper amphibolite-facies metaperidotites. Amphibolites suggest a transition temperature in the system Fe-Mg-Si-H at 555°C and $x_{\text{Fe}} \leq 0.3$, whereas metaperidotites suggest a transition temperature of $\cong 650^\circ\text{C}$ at $x_{\text{Fe}} \leq 0.1$. The $\ln K_D$ for Fe-Mg exchange between cummingtonite and anthophyllite passes through zero at $x_{\text{Fe}} = 0.7$, and as a result the $T\text{-}x_{\text{Fe}}$ phase loop shows a minimum at this composition. Extrapolated end-member transition temperatures were estimated to be $\cong 800^\circ\text{C}$ (Mg) and $\cong 450^\circ\text{C}$ (Fe) [01E1].

In anthophyllite, like in other Pnma amphiboles, the stacking vector, in alternate paired tetrahedral layers, is (...++—...). The various combinations of stacking vectors along the *a*-axis result in different amphibole polymorphs. Protoamphibole stacking sequence was described in synthetic [60G1, 69G1] or in natural [98S1] samples. In [02K2] a natural Mg-rich protoanthophyllite was reported having $\text{Mg}/(\text{Mg}+\text{Fe}) \cong 0.90\text{...}0.92$ and space group Pnma (or Pn2n). The protoanthophyllite and anthophyllite have similar composition and orthorhombic symmetry. A method was provided to identify protoanthophyllite and differentiate it from its polymorphs using selected area electron diffraction and HRTEM methods [02K2].

The crystal structure of aluminian ferro-anthophyllite, $\text{Fe}_5\text{Al}_2\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$, was analysed [57S1]. The existence of the continuous solid solution series between the aluminian anthophyllite and the usual anthophyllite was discussed [57S1].

The oxidation and dehydrogenation processes for heat treated anthophyllite were investigated by using the ^{57}Fe NGR method and infrared spectroscopy [98I2]. At temperatures from 350°C to $\approx 650^\circ\text{C}$, Fe^{2+} at the M1 and M3 sites oxidizes, yielding Fe^{3+} and one electron. A proton from the OH^{1-} is liberated and combines with this electron to form a hydrogen atom, and some Fe^{2+} ions at the M2 and M4 sites exchange with Mg at the M1 and M3 sites and then are oxidized in a similar way. At higher temperature, OH^- , remaining in the $(\text{MgMgMg}/\text{Fe}^{3+})$ -OH-configuration, is dehydrogenated by the decomposition of the amphibole to orthopyroxene and quartz. During oxidation and dehydrogenation of anthophyllite, there is disordering of Mg and Fe at the M1, M2, M3 and M4 sites. When all Fe^{2+} ions are oxidized, the M4 and M1, M2, M3 site occupancy become identical, showing that Mg and Fe^{3+} are completely disordered at these sites.

Cummingtonite, $(\text{Mg},\text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, crystallizes in two distinct polymorphs (C2/m and P_2_1/m). Along the cummingtonite – grunerite series where cummingtonite refers to the fraction of the solid solution $\square(\text{Mg}, \text{Fe}^{2+}, \text{Mn}, \text{Li})_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ with $\text{Li} < 1.0$ apfu and $\text{Mg} \geq 0.5$ apfu and grunerite to that with $\text{Li} < 1.0$ and $\text{Mg} < 0.5$ apfu. Mg-rich compositions generally have P_2_1/m symmetry, whereas Fe-richer compositions have C2/m symmetry [94H2, 98Y1]. The P_2_1/m -type structure was considered to represent an important link between the two most abundant amphibole structure types, the monoclinic C2/m and the orthorhombic Pbnm [64K1, 68R1, 69P1, 69R1, 70P3, 88M1]. As already stated, the crystal structures of both P_2_1/m and C2/m cummingtonites are characterized by double silicate chains running parallel to c , each chain consisting of two nonequivalent SiO_4 tetrahedra, T1 and T2. The silicate chains are linked together along [100] by cations occupying M1, M2, M3 and M4 octahedral sites. The two structures differ in two major aspects. One is that the C2/m structure contains one crystallographically distinct O-rotated silicate chain, whereas the P_2_1/m structure contains two, designated as the S-rotated A chain and O-rotated B chain. The other is that the respective site symmetry of M1, M2, M3 and M4 are 2, 2, 2/m and 2 for the C2/m structure but 1, 1, m and 1 for the P_2_1/m structure [70P1, 79C1, 80L1, 81C1, 83H1]. In [68R1, 69R1] was suggested that the P_2_1/m cummingtonite is the analog of pigeonite (see Chap. 8.1.4.1) and would undergo a $\text{P}_2_1/\text{m} - \text{C}_2/\text{m}$ phase transition at high temperatures. The transition behaviour as function of temperature has been studied in various cummingtonites [96Y2, 98Y1] and in manganocummingtonite [70P1, 70P3, 72S1, 00R2]. In [70P1] was found that P_2_1/m manganocummingtonite ($x = (\text{Fe} + \text{Mn})/(\text{Fe} + \text{Mn} + \text{Mg}) = 0.15$) inverts to the C2/m structure at ≈ 318 K and that transition is reversible and unquenchable. From high-temperature studies it was shown that the $\text{P}_2_1/\text{m} - \text{C}_2/\text{m}$ transition takes place at ≈ 373 K and crystal structure refinement of the C2/m phase at 540 K was reported [72S1]. A cummingtonite having $x = 0.37$ transforms from C2/m symmetry at RT to P_2_1/m symmetry at 240 K and crystal structure refinement at 140 K was given [96Y2]. Generally, it has been agreed that the effective M4 cation size, $\langle r_{\text{M4}} \rangle$, which can be affected by temperature and the Mg/Fe site occupancy, plays a critical role in the relative stabilities of the C2/m and P_2_1/m structures. However, the M4 composition depends both on the overall chemistry of the amphibole [94H2, 95Y1] and on non-convergent order-disorder between the B and C group sites which occurs during annealing above $T \approx 673$ K for Fe^{2+} [72G1] or ≈ 823 K for Mn^{2+} containing samples [00R2]. In any case, the overall fraction of larger dominant cation (e.g. $x_{\text{Fe}} = \text{Fe}/(\text{Mg} + \text{Mn} + \text{Fe})$) can be used as a useful indicator.

The C2/m – P_2_1/m transition induced by temperature was studied also in [01B1, 04B1]. Analysing the annealed cummingtonite – grunerite natural system, the long-range order parameters describing the non-convergent order parameters [94C1] of MgFe among the different octahedral sites have been calculated from the site occupancies [01B1]. The local strains arising from the cation substitution, ordering and phase transition have been quantified by means of the autocorrelation function. The displacive phase transition seems to occur in order to reduce local distortions and the P_2_1/m samples are as homogeneous as orthorhombic anthophyllite. The orthorhombic structure however appears less flexible than the monoclinic one in accommodating cations larger than Mg at the octahedral sites. According to [00B2, 04B1] the temperature variations in the intensity of the superlattice reflections above RT were consistent with the transition being thermodynamically continuous and conform to the solution to a 2-4-6 Landau potential. Parameters extracted from IR spectra, collected both above and below RT, suggested that local structure evolution differs slightly from the average macroscopic behaviour observed by X-ray diffraction. Changes in wavenumber of an isolated absorption band at ≈ 1130 cm^{-1} and changes in the integrated intensity of a band at ≈ 760 cm^{-1} can be described by the solution to a 2-4 Landau potential with saturation below RT. Absorption bands due to O-H vibration and libration, however, appear to

show discontinuities in the variation of their wavenumber at the transition point. A local mechanism for the transition might involve a framework distortion as the main driving force, with coupling to an order-disorder process for protons [04B1].

Studies on the effect of pressure on the $P2_1/m - C2/m$ phase transition in cummingtonites were also performed [92Z2, 98Y1, 00R2]. At normal pressure, the $P2_1/m$ structure is stable up to $x_{Fe} = 0.38$ [94H1, 94H2] or $x_{Mn} = 0.29$ [89G2]. In [01B1], at RT, a study of cummingtonites equilibrated at 700°C and then quenched was carried out, and they concluded that $x_{Fe} = 0.57(1)$ is the critical composition under which the $P2_1/m$ phase is stable under the above treatment. Decreasing x_{Fe} decreases the transition pressure, p_c [98Y1, 00B2]. A second order (or close to second order) character, for both the $C2/m - P2_1/m$ phase transition occurring with increasing p [00B2], and the $P2_1/m - C2/m$ phase transition occurring with increasing T [00R2] as well as with increasing x_{Fe} , was shown. The critical temperatures and pressures are proportional to x_{Fe} at both the microscopic and macroscopic scales [98Y1, 01B1, 02B1]. By using the data of [92Z1, 92Z2, 96Y2], in [98Y1] a linear dependence of the $C2/m - P2_1/m$ transition pressure on x_{Fe} was assumed and it was shown that the $P2_1/m$ polymorph is only stable for $x_{Fe} < 0.33$ [95Y1], obtaining p_c [GPa] = $-1.23 + 4.52 x_{Fe}$.

All the cummingtonite crystals examined at high pressure display continuous variations of spontaneous strains and intensities of superlattice ($h + k = 2n + l$) reflections trough the $C2/m - P2_1/m$ transition. In [98Y1] the cummingtonites with $x = 0.50$ and $x = 0.89$ were studied where $x = (Fe + Mn)/(Fe + Mn + Mg)$. It was concluded that the $C2/m - P2_1/m$ transition is of weakly displacive first order or of tricritical character with apparent slope changes in the plots of the axial ratio a/b and a/c as a function of pressure. The unit-cell compression is considerably anisotropic with the a -dimension in both $C2/m$ and $P2_1/m$ phases being the most compressible one. Major structural changes include [98Y1]: (1) one crystallographically distinct silicate chain becomes two, discontinuously coupled by the splitting of the M4-O5 bond, as well as M4-O6, into two nonequivalent bonds, and (2) the M4 cation coordination increases from sixfold to sevenfold. A change in the sense of rotation for the A chain was observed while the crystal structure maintains $P2_1/m$ symmetry. It is **O**-rotated, as the B chain, at 1.32 GPa, but **S**-rotated at 2.97 GPa and higher pressures. As pressure increases from 1.32 to 7.90 GPa, there is a switching of the nearest bridging O atoms coordinated with the M4 cation. The M4-O5B distance contracts from 2.944 Å to 2.551 Å, whereas the M4-O6B distance increases from 2.754 to 2.903 Å. Compression mechanisms for the low- and high-pressure polymorphs appear to be slightly different. In the $C2/m$ phase, the behaviour of the A and M4 site controls the compression of the structure, whereas the response of the M1, M2 and M3 octahedra to pressure also plays a role in determining the compression of the $P2_1/m$ structure. The phase transition was regarded as primarily driven by the differential compression between the M4 and T sites, and the symmetry breaking provides a necessary tighter coordination for the M4 site. According to [98Y1], the changes in the hyperfine parameters of ^{57}Fe in grunerite between 1.0 and 3.4 GPa [92Z1] are likely the result from the $C2/m - P2_1/m$ structural transformation.

The composition dependence of lattice parameters for some unheated and heated cummingtonites are plotted in Fig. 7.

Single crystal X-ray structure refinements of natural members of the cummingtonite series [61G1, 66F1, 69F1, 82G1, 94H2] have shown that Fe^{2+} strongly prefers the M4 site, Mg prefers M2 and the M1 and M3 sites have similar sites occupancies. The ^{57}Fe NGR spectra at 298 K and 77 K do not separately resolve M1, M2 and M3, but they confirm the strong preference of Fe^{2+} for M4 [67B2, 71B1, 71H1, 73B1]. It was also shown that ordering between M4 and M1,2,3 sites is temperature dependent [72G1]. The combination of ^{57}Fe NGR and IR absorption spectroscopy also shows that Fe^{2+} ferrous ions prefer M1,3 over M2 [67B2, 71B1, 89Y1].

In zincian manganocummingtonite (zincian tirodite), Mn is strongly ordered into the M4 site, whereas Fe^{2+} is ordered into the M4 and M2 sites [77H1]. Zn shows octahedral site preference of type $M1 > M3 > M2 > M4$ and Mn shows the site preference $M4 > M3 > M1 > M2$ – Table 3. The silicate is isotypic with other C-centered cummingtonites.

Grunerite is the end member of the $(Mg,Fe)_7Si_8O_{22}(OH)_2$ grunerite – cummingtonite series of amphiboles with monoclinic $C2/m$ symmetry. As already mentioned, the T-O-T strips or I-beams are packed in a pseudo-body centered fashion in the (ab)-plane and are interconnected through the Fe^{2+} ion at the M4 site [61G1, 69F1]. In some respect, the structure of grunerite is similar to that of pyroxene, particularly ferrosilite and to some extent the 2:1 layer silicate [87G1]. Hence similarities in their magnetic properties are expected (section 8.1.4.3.2). The very strong site preference of Fe^{2+} over Mg^{2+} for M4 site in the cummingtonite – grunerite series has been ascribed to the difference in the covalency effect at the M4 versus M1, M2 and M3 sites [61G1, 82G1]. The stronger covalent bonding of Fe^{2+} at the M4 site was suggested by the M4-O4 bonds which are considerably

shorter than the sum of the respective ionic radii [61G1, 82G1]. The stronger covalent bonding was further confirmed by the smaller isomer shift of Fe^{2+} at this site as compared to the values at M1, M2 and M3 sites, as determined by the ^{57}Fe NGR method [71H1]. The effect of temperature of the ordering was studied also in the cummingtonite – grunerite (CG) series [94H2]. Relative to Mg, Fe^{2+} is strongly concentrated in the M4 site and weakly depleted in the M2 site in all crystals, but the degree of fractionation is less pronounced in the samples equilibrated at high temperatures. Fe shows a weak preference for M3, relative to M1 in heat treated C – G, but no significant preference is observed in unheated crystals. According to [94H2] the site preferences expressed in terms of an ideal ordering energy, $-RT\ln K_D$, show no temperature dependence over the range of temperature of heat treatment (600...750°C). The ideal ordering energy between M1 and M4, $-RT\ln K_{14}$, is 18.2(3) kJ and independent of composition except for very magnesian compositions, for which the degree of ordering decreases. The ideal ordering energy between the M1 and M2 sites; $-RT\ln K_{12}$, decreases from –2 kJ at pure $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ to –6 kJ at pure $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. With the assumption that Ca is restricted to the M4 site and that Mn is strongly ordered into M4 site, M1, 2, 3 vs. M4 preferences determined by ^{57}Fe NGR are consistent with X-ray studies [94H2].

Following the prediction of strong site preference of Mn^{2+} for the M4 site in amphiboles [65G1], it has been confirmed in Fe-Mn-Mg amphiboles by ^{57}Fe NGR [67B2], X-ray diffraction [69P1] and a combination of these two techniques [77H1]. The larger size of Mn^{2+} (0.83 Å) as compared to Mg^{2+} (0.60 Å) was shown to be the most important driving force for the site preference of Mn^{2+} for the M4 position. A high degree of covalency of Mn^{2+} at this site plays also an important role, as in case of Fe^{2+} . Further evidence for increased covalent bonding comes from EPR spectra of small amounts of Mn^{2+} in tremolite, in which Mn^{2+} shows a strong preference for the M4 site [82M1]. The super-hyperfine splitting parameter, for Mn^{2+} , at the M4 site, is smaller by about 10 MHz than that at the M1, M2 and M3 sites, indicating a much stronger covalency of Mn^{2+} -O bonds. According to [89G2] in Mn-Mg amphiboles, a combination of both ionic size and relative covalency effects are responsible for the much stronger preference of Mn^{2+} for the M4 site.

In Mn-Mg amphibole with 0.96 Mn per formula unit and $P2_1/m$ -type structure, Mn^{2+} was reported to be exclusively located at the M4 site [69P1]. This amphibole inverts to $C2/m$ symmetry above 373 K [72S1]. In $\text{Ca}_{0.24}\text{Mn}_{2.41}\text{Mg}_{4.20}\text{Fe}_{0.15}\text{Si}_8\text{O}_{22}(\text{OH})_2$, the M4 site is nearly filled with Mn^{2+} , whereas small amounts of Mn^{2+} also occur at the smaller octahedral M1, M2 and M3 sites, the sequence of the site preference being $\text{M4} \gg \text{M1} > \text{M2} > \text{M3}$ [89G1]. The site preference of Mn^{2+} of the M4 site in Mn-Mg amphiboles is nearly twice as strong as that of Fe^{2+} in the Fe-Mg amphibole and is much stronger than that of Fe^{2+} with respect to Mg^{2+} [67B2, 69P1, 77H1, 89G2]. The composition limit for the $P2_1/m$ to $C2/m$ phase transition, at ambient temperature, is presumably close to $\text{Mn}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, at which the M4 site is nearly filled with Mn^{2+} . This corresponds to a Mn/Mg = 2/5 ratio [89G1].

The partitioning of Fe and Mn between the large M4 site and the octahedral sites M1-M3 was also studied in $\text{Ca}_{0.1}\text{Mn}_{1.9}\text{Mg}_{1.25}\text{Fe}^{2+}_{3.56}\text{Fe}^{3+}_{0.38}\text{Si}_{7.81}\text{O}_{22}(\text{OH})_2$ and $\text{Ca}_{0.24}\text{Mn}_{1.57}\text{Mg}_{2.27}\text{Fe}^{2+}_{2.76}\text{Fe}^{3+}_{0.32}\text{Si}_{7.84}\text{O}_{22}(\text{OH})_2$ manganogrunerites by neutron diffraction [02R1]. Site occupancy refinements suggest that the Mn is ordered with a site preference $\text{M4} \gg \text{M2} > \text{M1} > \text{M3}$. On heating, the partitioning of Mn from M4 into the octahedral sites begins at 350°C with site exchange energies of –16.6 kJ/mol and –14.9 kJ/mol in samples containing 1.90 and 1.57 Mn apfu, respectively. The high-temperature cation distributions are retained during cooling.

The elastic properties of cummingtonite [98Y1] and of grunerite [92Z2] were also studied – Table 5. Grunerite exhibits strong anisotropic compression in the low-pressure region ($p < 1$ GPa). With increasing pressure, the compression becomes more isotropic. This behaviour and large volume compressibility compared to that of Ca-rich clinopyroxenes, in the pressure range studied, were attributed to the strong compression of the empty A cavities, in the crystal structure, at low pressure.

The structural defects were studied in natural and synthetic Fe-Mg-Mn amphibole. The synthetic Fe-Mg-Mn amphiboles revealed two types of structural defects at the unit-cell scale: chain-multiplicity faults (CMFs) and chain-arrangement faults (CAFs) [83M1]. CMFs occur when the number of subchains that are linked to form a multiple chain is different from the two normal double-chain amphibole structures. This type of defect has also been called chain width disorder and has been described in natural amphiboles [79V1, 80V1]. CAFs are faults in the stacking sequence of the chains in the a^* -direction. This type of defect is usually (100) twin planes and can cause synthetic monoclinic amphibole to appear orthorhombic in optical and X-ray studies.

A natural grunerite, $\text{Na}_{0.03}\text{Mg}_{0.02}\text{Al}_{0.03}\text{Mn}_{0.23}\text{Zn}_{0.06}\text{Fe}_{6.68}\text{Si}_{7.97}\text{O}_{22}(\text{OH})_2$, consists mainly of $C2/m$ grunerite with minor amounts of $Pnma$ ferro-anthophyllite [01B2]. Selected area electron diffraction show four types of SAED patterns: (1) defect free $C2/m$ grunerite; (2) twinned $C2/m$ grunerite; (3) twinned grunerite intergrown with

Pnma ferro-anthophyllite and (4) Pnma ferro-anthophyllite. The observed structures were interpreted as a result of partial transformation of ferro-anthophyllite to grunerite. The possibility was suggested that grunerite, ferro-anthophyllite and protoferro-anthophyllite may all possess true stability fields [01B2].

The **gedrite** series are described by $\text{Na}_x\text{Li}_z(\text{Mg},\text{Fe}^{2+},\text{Mn})_{7-y-z}\text{Al}_y(\text{Si}_{8-x-y+z}\text{Al}_{x+y-z})\text{O}_{22}(\text{OH},\text{F},\text{Cl})_2$ where $x+y-z \geq 1.00$ and $\text{Si} < 7.00$, the last requirement being the distinction from anthophyllites [97L2]. The gedrites crystallize in the Pnma-type structure [70P2]. Octahedral aluminum is concentrated in the M2 site, while ferrous iron prefers the M4 site over the M1, M2 and M3 sites. Tetrahedral aluminum is disordered over three of the four distinct tetrahedral sites. The fourth is mainly occupied by silicon. The tetrahedron occupied by the silicon shares an edge with an M4 octahedron and is inherently small in size.

As mentioned in Table 1 the root name **holmquistite** defines a series of orthorhombic Pnma amphiboles whose composition can be expressed as ${}^{\text{A}}\square{}^{\text{B}}\text{Li}_2\text{C}[(\text{Mg},\text{Fe}^{2+})_3(\text{Al},\text{Fe}^{3+})_2]{}^{\text{T}}\text{Si}_8\text{O}_{22}(\text{OH})_2$. The structures of natural holmquistites were studied [60N1, 65G3, 69W1, 75I1, 81L1]. In [61V1] was concluded that Li is ordered at the M4 site, Fe^{2+} at the M1 and M3 sites and Al (with minor Fe^{3+}) is somewhat disordered between the M2, M1 and M3 sites. They also noted an unusual separation of ${}^{57}\text{Fe}$ NGR doublets and a strong Fe^{2+} preference for the M3 site (0.52 apfu vs. 0.74 apfu at the 2M1 sites). This scheme (except for the disorder of octahedral Al) was confirmed in case of a natural sample [89W1].

The investigations of monoclinic Li-bearing amphiboles have shown that Li occurs at the M3 site in sodic amphiboles, but partitions itself between the M4 and M3 sites in group 1 and 5 amphiboles [03O2, 03O3, 04O1]. For holmquistite, a remarkable constancy of composition, both in terms of charge arrangement and of limited homovalent ${}^{\text{M1,3}}(\text{Mg},\text{Fe}^{2+})$, ${}^{\text{M2}}(\text{Al},\text{Fe}^{3+})$ and ${}^{\text{O3}}(\text{OH},\text{F})$ exchange was shown [05C1]. There is a remarkable constancy in the unit-cell dimensions, with the Fe^{3+} content at the M2 site being the only factor affecting the *b*-edge. A complete ordering of Li at the M4 site and of trivalent cations at the M2 site was shown as well as an inverse relationship between the Fe^{2+} and Fe^{3+} contents, which was interpreted as a way to keep the size of the octahedral strip constant. There is also a strong distortion of the octahedral sites, both in terms of angular variance and quadratic elongation [05C1]. ${}^{\text{A}}\square{}^{\text{B}}\text{Li}_2\text{C}(\text{Mg}_3\text{Al}_2){}^{\text{T}}\text{Si}_8\text{O}_{22}(\text{OH})_2$ is the amphibole composition of the smallest possible structural moduli. Crystallization in Pnma symmetry, where the two double chains of tetrahedra can assume different conformations, is probably required by the need to obtain a more suitable [5+1]-coordination for ${}^{\text{B}}\text{Li}$ and to shrink the cation-cation distances. This arrangement does not allow for extensive incorporation of larger homovalent substituents, which are hosted by a mechanism implying distortion of the octahedral sites.

The **sodic ferripedrizite**, $\text{Na}(\text{LiNa})(\text{Fe}^{3+}_2\text{Mg}_2\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$, crystallizes in the C2/m-type structure [00O1]. The structure refinement assessed that Li is partitioning among the B and C group sites. Li is ordered at the [6+2]-coordinated position in the M4 cavity and at the M3 site. Two different sites are available for cations in the B cavity. The larger cations (Na^+ and Ca^{2+}) occur at the eightfold-coordinated M4 site at 0, $\cong 0.28$, $\frac{1}{2}$ and the smaller cations (Li^+ , Mg^{2+} , Mn^{2+} and Fe^{2+}) occur at the [6+2]-coordinated M4 site at 0, $\cong 0.24$, $\frac{1}{2}$. The electron density distribution around the M4 site is shown in Fig. 8a [00O1]. The electron density within the B cavity was shown to be asymmetric, with lobe pointing toward the M1 site. Extensive immiscibility of the two groups of B cations is the mean distinction between the two main amphibole groups. Sodic ferripedrizite encompasses the different site preferences and crystal-chemical mechanisms observed for Li in Mg-Fe-Mn-Li amphiboles (clinholmquistite series) and the NaCa group (leakeite series). Sodic ferripedrizite has the same charge distribution pattern as leakeite, but with Li instead of Na at the B cavity. In the A group of sites, Na is preferentially ordered at the Am position, in line with the local association of ${}^{\text{Am}}\text{Na}$ with ${}^{\text{B}}\text{Na}$ in both amphiboles and fluoro-amphiboles [96H2] and with the observation that small cations in the B cavity further enhance this ordering via underbonding at the O5 anions [99O1]. The distance of Am from the center of the A cavity is much longer in sodic ferripedrizite than in leakeite and fluoro-ferroleakeite (0.84...0.85 vs 0.54...0.59 Å). Thus, Na is forced to order at Am and it has to move further in the direction of the tetrahedral basal oxygen atoms (O5 and O6) so as to increase its incident bond strengths. This crystal chemical role is confirmed by the very unusual shape of the electron density – Fig. 8b – which, in the crystal of ferripedrizite, assumes a butterfly like configuration with lobes pointing in the direction of the basal O atoms. In sodic amphiboles (including leakeite) the shape of the electron density is that of a regular 8, with two lobes partly overlapping [96H2]. Significant Li is present in C group sites and is completely ordered at the M3 site. Fe^{2+} is another prevalent substituent at M3 site. M1 site is occupied by Fe^{2+} and Mg^{2+} . All high charge cations are ordered at M2 site.

Complete solid solution between ferripedrizite and leakeite (ideally ${}^A\text{Na}{}^B\text{Na}_2{}^C(\text{Fe}^{3+}{}_2\text{Mg}_2\text{Li})^T\text{Si}_8\text{O}_{22}(\text{OH})_2$) has been found [02C1]. Samples with ${}^B(\text{Mg}+\text{Fe}+\text{Mn}+\text{Li}) \geq 1.0$ apf and $0.0 \leq {}^B\text{Na} \leq 0.50$ apfu were termed **ferripedrizite**. Samples with ${}^B(\text{Mg}+\text{Fe}+\text{Mn}+\text{Li}) \geq 1.0$ apfu and $0.50 < {}^B\text{Na} \leq 0.99$ apfu were called *sodic ferripedrizite*. Samples with ${}^B(\text{Mg}+\text{Fe}+\text{Mn}+\text{Li}) < 1.0$ apfu and ${}^B\text{Na} \geq 1.50$ were named **leakeite**. Samples with ${}^B(\text{Mg}+\text{Fe}+\text{Mn}+\text{Li}) < 1.0$ apfu and $1.0 \leq {}^B\text{Na} < 1.50$ belong to the sodic-calcic group.

We note that lithium may be incorporated in the amphibole structure in two different ways. It can enter the B site in clinoholmquistite series (ideally $\text{Li}_2(\text{Mg},\text{Fe}^{2+})_3(\text{Al},\text{Fe}^{3+})_2\text{Si}_8\text{O}_{22}(\text{OH},\text{F})_2$) or the C sites in the leakeite (ideally $\text{NaNa}_2(\text{Mg},\text{Fe}^{2+})_2(\text{Al},\text{Fe}^{3+})_2\text{LiSi}_8\text{O}_{22}(\text{OH},\text{F})_2$). In ${}^C\text{Li}$ -bearing amphiboles the definition of constraints and crystal chemical mechanisms of lithium incorporation is given [92H1, 93H1, 94H1, 96H1, 96H4, 98H1]. Sodian fluorian clinoholmquistite is a ${}^B\text{Li}$ clinoamphibole [75L1]. Sodic ferri-clinoferroholmquistite (ideally $\text{Li}_2(\text{Fe}^{2+},\text{Mg})_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$) was also studied [98C1]. The pedrizite is an amphibole enriched in both Na and Li, such that their charge arrangement is that of leakeite, but the B site composition is ideally (LiNa) [00O1].

Analysing Li-bearing monoclinic samples from Pedriza massif (Spain) revealed extensive solid solutions between ferri-ottoliniite, ideally ${}^A\Box(\text{Na}_1\text{Li}_1)^C(\text{Mg}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$, ferriwhittakerite, ideally ${}^A\text{Na}{}^B(\text{Na}_1\text{Li}_1)^C(\text{Mg}_2\text{Fe}^{3+}_2\text{Li}_1)\text{Si}_8\text{O}_{22}(\text{OH})_2$, ferri-clinoholmquistite, ideally ${}^A\Box{}^B\text{Li}_2{}^C(\text{Mg}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$, sodic ferripedrizite, ideally ${}^A\text{Na}{}^B\text{Li}_2{}^C(\text{Mg}_2\text{Fe}^{3+}_2\text{Li}_1)\text{Si}_8\text{O}_{22}(\text{OH})_2$ and the ferro counterparts of the two latter end members [03O2, 03O3, 04O1]. [05O1] reexamined the natural holotype “clinoholmquistite”, ideally ${}^A\Box{}^B\text{Li}_2{}^C(\text{Mg}_3\text{Al}_2)^T\text{Si}_8\text{O}_{22}{}^X(\text{OH})_2$ [65G3]. The structure refinements showed that the sample consists of a mixture of two distinct amphibole compositions, tremolite and an amphibole new member fluoro-sodic pedrizite, ideally ${}^A\text{Na}{}^B\text{Li}_2{}^C(\text{Mg}_2\text{Al}_2\text{Li})^T\text{Si}_8\text{O}_{22}{}^X\text{F}_2$. The last silicate crystallizes in space group C2/m [05O1] – Table 4.

2. Calcic amphiboles

Edenite, $\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}(\text{OH})_2$ is a calcic amphibole having high magnesium content [55K1, 97L2].

Both **pargasite** [69G2, 73H5, 77B1, 77H3, 80O1, 81W2, 87R2, 94W1, 98W1, 99D1] and **fluoro-pargasite** [81W2, 87R2, 95O3] have been synthesized and characterized. In [00R1] the synthetic pargasites, $\text{NaCa}_2(\text{Mg}_{4+x}\text{Al}_{1-x}\text{Si}_{6+x}\text{Al}_{2-x})\text{O}_{22}[(\text{OH})_{1-y}\text{F}_y]_2$ were studied. By x is denoted the edenite content. The lattice parameters as function of y are plotted in Fig. 9. There is a strong decrease of the a -edge with $y = \text{F}/(\text{OH} + \text{F})$ up to $y = 0.5$. The b -edge decreases slightly in the same composition range and then increases slightly for $y > 0.5$. The c -edge increases slightly up to $y \cong 0.5$ and then remains constant for higher F content. The β -angle decreases in the range $0.0 < y < 0.5$ and is almost constant for $y > 0.5$. Thus, for hydrothermally prepared samples, the incorporation of F is restricted to about 1.0 apfu. For $y > 0.5$ the data are in agreement with increasing the amount of edenite component. Pargasite is more easily synthesized than tremolite, but displays deviation from the ideal composition [91R1].

Amphiboles of the joint **pargasite – ferropargasite** $\text{NaCa}_2\text{Mg}_{4-x}\text{Fe}_x\text{AlSi}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$ have been prepared [80C1]. No changes in cell parameters were observed with temperature on a given buffer. The essentially linear trend of lattice parameters vs. composition indicates disorder of Mg and Fe in M1, M2 and M3 sites.

Long-range ordering of cations in **pargasite** was discussed [87R2, 94W1, 95O1, 98O1, 99W1] even if there is little knowledge about short-range ordering [99D1]. In [99W1] synthetic end-member pargasite was studied by neutron diffraction on powders and found ${}^{[6]}\text{Al}$ disordered over M2 and M3, but not M1, in agreement with single crystal X-ray data on natural pargasite [95O1]. The ordering of octahedral cations in pargasite is significantly affected by the presence of F, such that trivalent cations are strongly ordered at the M2 site in fluoro-pargasite [87R2, 95O3, 98O1]. Cation distribution in synthetic pargasite has been studied by NMR and IR [94W1], or using single XRD analysis [95O1].

Tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, is one of the chemically simple end-members of calcic amphiboles and was possible to be synthesized. For more recent data see: [94M1, 95H1, 96Y1, 96Z1, 97Z2]. In [87J1] tremolite (TR) – magnesio-cummingtonite (MC) was synthesized, at 850°C. The 6 kbar series produced the maximum yield of tremolite $\text{TR}_{90}\text{MC}_{10}$ bulk composition. The phase relations along the join indicate that synthetic tremolite either has the fixed composition $\text{TR}_{90}\text{MC}_{10}$ or a very narrow compositional range about this value. This suggests that synthetic tremolite always has a cummingtonite component of 10 %. In [83M1] was shown that many synthetic amphiboles may have higher concentrations of chain-multiplicity faults (CMFs) and chain-arrangement faults (CAFs) than their natural counterparts and thereby have different stability phase relations. CMFs commonly decrease the $\text{M4}/(\text{M1}+\text{M2}+\text{M3})$ ratio to less than the ideal 2/5 by formation of “wide-chain pyribole”. Because M4 is the only site that can accept Ca, the resulting “pyribole” is unstable to accommodate as much Ca as the

ideal double-chain amphibole. In synthesis experiments, the compositional change causes a residual composition equivalent to diopside to be left over from a mixture of tremolite composition. High concentration of CMFs in synthetic calcic amphiboles could in this way explain the problems in obtaining the Ca end member.

The temperature dependent Fe-Mg distribution in natural tremolite was investigated [87S1]. The standard free energy change for the exchange reaction $\text{Fe}^{2+}(\text{M4}) + \text{Mg}(\text{M2}) = \text{Mg}(\text{M4}) + \text{Fe}^{2+}(\text{M2})$ decreases with increasing temperature. The substitution of F^- for OH^- in the tremolite structure reduces the size of octahedral layer and accordingly the a and b cell parameters [73C2]. The double chains of tetrahedra in the structures are very similar, and the small differences within the individual tetrahedra were explained in terms of differences in the octahedral layers. The higher thermal stability of fluor tremolite was attributed in part to the stronger Mg-F bonds and in part to an instability created by excessive charge unbalance in the structure during the dehydration of hydroxyl tremolite.

The thermodynamics and synthesis of tremolites were reported [63R1, 72T1, 84K1, 85S2, 87J1, 89G3, 90J1, 91J1, 91W1, 93P3, 94M1, 95H1, 96Y1, 96Z1, 98C2, 99G1]. The composition of tremolitic amphibole as a function of p , T and mineral assemblage was discussed [96Y1, 99G1, 00E1, 04B2].

Hastingsite crystallizes in space group C2/m [77H2, 81W1]. The A site is positionally disordered in two sites, one on the mirror plane and the other on the twofold axis. In [73S1] was shown by analyzing ^{57}Fe NGR and IR spectra in **magnesiohastingsite** that, except at high values of f_{O_2} , iron occurs both as Fe^{2+} and Fe^{3+} , contrary to the ideal formula. The amount of Fe^{2+} produced is a function of the oxygen fugacity of synthesis. A mechanism to produce Fe^{2+} in synthetic magnesiohastingsite which involves an excess of two protons (and/or anionic defects at low f_{O_2}) per formula unit was analyzed. For crystal structure of fluoro-magnesiohastingsite see [01G1].

The crystal structure of **sadanagaite** and **magnesiosadanagaite** were also reported [84S1]. In sadanagaite the A site of the amphibole is occupied almost entirely by K and Na [89S1].

The **kaersutites** crystallize in a monoclinic C2/m-type structure [71K1, 73H2, 73K2, 75K1] – see Table 4. In ferrikaersutite Ti^{4+} was found to be strongly ordered at the M1 site, but that minor Ti may also distribute between M2 and M3 [75K1]. Fe-free kaersutites with different titanium contents were synthesized [99T2]. Single crystal structure refinements show that $^{[6]}\text{Ti}^{4+}$ enters all the three independent octahedral sites. The resulting site population can be related to two different crystal chemical mechanisms, which can be described by means of the $^{M1}\text{Ti}^{4+}_{-1} \text{O}_3^{2-} \text{Mg}^{2+}_{-1} \text{O}_3 \text{OH}^-_{-2}$ and $\text{M}^{2,3}\text{Ti}^{4+}_{-1} \text{Al}^{3+}_{-2} \text{Mg}^{2+}_{-1} \text{Si}^{4+}_{-2}$ exchange vectors. They both increase the amphibole stability at higher temperatures. When Ti^{4+} occupies an M3 site, short $\langle \text{M3-O} \rangle$ distances couple with shorter M3-O1 and longer M3-O3 than expected in the presence of $^{M3}\text{Fe}^{3+}$ balancing for dehydrogenation. Reconsideration of previous refinements showed that the $^{M3}\text{Ti}^{4+}$ is always related to low amounts of $^{[6]}\text{Al}$. The entrance of Ti^{4+} at the M3 site is thus far less favoured than that of Al and Fe^{3+} . According to [99T2] this fact was probably a consequence of steric constraints and electrostatic repulsion due to the simultaneous presence of small tetravalent cation in all the three independent sites of the octahedral strip.

The Fe-free **tremolite** – **pargasite** join was studied [80O1, 90O1, 99S1]. In addition to confirming the higher thermal stability of pargasite relative to tremolite, [80O1] reported the presence of an extensive miscibility gap existing along this join at 1 kbar but not at 5 kbar. At 10 kbar was shown [90O1] complete miscibility even at a temperature $T = 800^\circ\text{C}$ that was well inside the miscibility gap at 1 kbar. The pressure dependence of the miscibility gap was analyzed [92B1]. In [99S1] amphiboles were synthesized hydrothermally, at $750\ldots 1000^\circ\text{C}$ and $1\ldots 6$ kbar, in ternary tremolite (TR) – pargasite (PG) – Mg-anthophyllite (MC), near the join tremolite – pargasite. The lattice parameters as function of composition are shown in Fig. 10. Structural studies confirm that amphiboles form the most part conform to “pargasite” substitution. The only exception are amphiboles formed near $80\ldots 90$ mol % PG which display a small excess of Na in structure and difficulties in synthesizing. The data show a nonlinear trend in the unit-cell volume with composition with a maximum at the ≈ 80 mol % PG. A positive correlation was shown between $\text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+})$ and $\text{K}/(\text{K}+\text{Na})$ ratios in the joint ferro- and potassium pargasite, suggesting that the increase of Fe^{2+} serves to stabilize high-K pargasites [85M1].

The effect of pressure on the lattice parameters in tremolite, glaucophane (see "4. Sodic amphiboles" below) and pargasite was studied [91C1] – Fig. 11. The above silicates show anisotropic compression – Table 5. The most evident effect of the pressure is the reduction of bowing of the tetrahedral double chains, which assumes a flatter configuration. This effect is greater for glaucophane, followed by tremolite and pargasite. Opposite movements have been reported for tremolite on heating. Minor variations in the dimensions of the I-beam occur

along [001], that is the extension direction of the tetrahedral chain, and along [010] across the M4 sites. The tetrahedral double chain shows an increase in ditrigonal character with increasing pressure. The A-polyhedron is the softest, followed by M4 and by M1, M2 and M3. The M2 octahedron is the hardest polyhedron in glaucophane, where it is occupied by trivalent cations, but it is softest in tremolite and pargasite. The values of polyhedral bulk moduli are in the order $K_{M2} > K_{M1} > K_{M3} > K_{M4}$ in glaucophane and $K_{M3} > K_{M1} > K_{M4} > K_{M2}$ in tremolite and pargasite.

Cation distribution among the four nonequivalent M1 to M4 sites in natural **calcic amphiboles** have been studied by X-ray single crystal refinements [69P1, 71M1, 83U1, 89S2] and spectroscopic methods [71B2]. Usually, the M4 site was assumed to be completely occupied by Ca in ideal **tremolite – actinolite**, $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. Fe^{2+} on the M4 site of calcic amphiboles has also been confirmed by X-ray structure refinements [83U1]. The accommodation of Fe^{2+} and Mg on the large M4 site in calcic amphibole reflects the solubility of the grunerite – cummingtonite component. Incomplete yields of synthetic calcic amphiboles with formation of pyroxene have also been reported [80O1, 86O1, 87R2].

The analysis by ^{57}Fe NGR of synthetic actinolites showed that Fe^{2+} prefers the M4 site relative to M1 and M3 sites and discriminates against the M4 site [79G1]. The distribution of iron in natural, low Fe actinolites annealed over the range 550...800°C was also analysed by the same method [85S1, 87S1]. They reported that iron has a stronger preference for the M2 site than Mg and that iron exchanges primarily between the M2 and M4 sites with no clear evidence that it exchanges on the M1 and M3 sites. In case of Mg-rich synthetic actinolite, made from bulk compositions with variable Ca contents, again it was found that Fe exchanges primarily between the M2 and M4 sites with no change in the Fe content at the M1 and M3 sites [89S2]. An increase in the iron content at the M4 sites and a decrease at the M2 site with decreasing temperature was also observed, similarly as found for natural actinolites [85S1]. In case of the natural, low Al actinolites, a slight preference of Fe for the M1 and M3 sites, that was essentially independent on temperature, was reported [98E1]. Mg is slightly favoured at the M2 relative to M1 sites, but this minor partitioning becomes completely disordered at 700°C. Because the M4 site was dominated by calcium (> 87 %) and since the presence of minor amounts of competing elements (Mn and Na) was not possible to determine accurately Fe-Mg partitioning at this site. The refinements were, however, consistent with the M4 site having a higher Fe/Mg ratio than at any of the other sites. The site occupancy as function of bulk composition were studied in low calcium actinolites with 0...30 mol % ferro-actinolite when projected onto the tremolite – ferro-actinolite join [05D1]. The Fe/(Fe+Mg) ratio in the M1, M2, M3 and M4 sites versus bulk Fe/(Fe+Mg) content are given in Fig. 12. According to [05D1] there is no significant preferential partitioning of Fe and Mg relative to the bulk Fe content at the M1 and M3 sites, weak partitioning of Mg relative to Fe into the M2 site and strong partitioning of the Fe relative to Mg at the M4 site. No ferric iron was detected – Fig. 12. The partitioning of the Fe and Mg at the M4 site was modeled by a simple ideal activity, two-site exchange reaction by using the data of [05D1] as well as actinolites with bulk $\text{Fe}/(\text{Fe}+\text{Mg}) \leq 0.3$ and low Al, Mn, Na contents. A reasonably good fit to the observed Fe/(Fe+Mg) ratio in the M4 site was obtained using ΔG° and ΔS° values ($p = 1$ bar, at 298 K) of 62 kJ and 54 J/K, respectively.

A smaller miscibility gap than in case of tremolite – pargasite, at 1 kbar, was reported in the **actinolite – pargasite** join, where each member had 20 mol % Fe^{2+} substituted for Mg^{2+} [87O1]. They observed that the miscibility gap was smaller in extent compared to the iron-free system and was displaced toward the actinolite end-member.

In amphiboles, the Mg tschermakite substitution of the type $\text{Mg}^{2+} + \text{Si}^{4+} = \text{Al}^3 + \text{Al}^{3+}$ is quite common [03N1]. The content of the tschermakite component in amphibole has been studied [72J1, 78O1, 81J1, 83J1, 86C1, 88J1, 91C2, 94J1, 94S1, 95H4, 97J1, 98Q1, 00H2, 03N1] by using the simplified system **tremolite – aluminotschermakite** $\text{Ca}_2\text{Mg}_5[\text{Si}_8\text{O}_{22}(\text{OH})_2] - \text{Ca}_2\text{Mg}_3\text{Al}_2[\text{Al}_2\text{Si}_6\text{O}_{22}(\text{OH})_2]$. As mentioned already, the main feature of the amphibole structure is two double chains of SiO_4 tetrahedra connected by a strip of octahedra which form an I-beam in the z -direction. In tremolite, the octahedral sites M1, M2 and M3 are occupied by Mg^{3+} , M4 by Ca^{2+} and the tetrahedral sites T1 and T2 by Si^{4+} . From analysing natural monoclinic amphiboles it was deduced that octahedral aluminum (^{61}Al) is strongly ordered on the M2 site [81H1]. IR and NMR studies on synthetic pargasite indicated ^{61}Al disorder over M2, M1 and/or M3 site [87R2, 94W1]. The X-ray structure refinements on natural pargasites and pargasitic hornblende showed that ^{61}Al is distributed over the M2 and M3 sites [95O1]. This result is in agreement with neutron diffraction study of synthetic pargasite [99W1] and an IR investigation of synthetic richterite – pargasite solid solutions [99D1]. The IR and NMR studies of synthetic tremolite – magnesiohornblende solid solutions indicated that ^{61}Al occupies two different octahedral sites (M2 and M1 or M3) [00H2].

In monoclinic amphiboles, $^{[4]}\text{Al}$ is preferentially incorporated at the T1 site [81H1]. In calcic amphiboles having $^{[4]}\text{Al} < 2$ apfu, Al^{3+} strongly prefers the T1 site in order to avoid reducing the incident bond-valence to O4 [95O2]. However, Al^{3+} on T1 and T2 sites was observed in amphiboles with $^{[4]}\text{Al} > 2$ apfu. Al^{3+} disorder over T1 and T2 sites is also a function of temperature [95O2]. This is in agreement with ^{29}Si MAS NMR investigations of pargasite synthesized at 930 °C and 100 MPa [98W1]. Al^{3+} ordering on the T1 site was observed in fluoroedenite synthesized at 1000°C and 200 MPa [98W1]. In [97J1] synthetic tremolite – tschermakite solid solutions were investigated up to the composition of magnesiohornblende. It was concluded that Al^{3+} is distributed over all T and M sites in the Al-tremolites. The ternary system tremolite – tschermakite – cummingtonite was synthesized [03N1]. Along the Tschermaks vector $\text{Si}_{-1}\text{Mg}_{-1}\text{Al}_2$, amphibole compositions between 11 and 54 mol % tschermakite were obtained. The lattice parameters were described by: a [Å] = $9.8345x_{\text{Tr}} + 9.7438x_{\text{Ts}} + 9.4700x_{\text{Cum}}$; b [Å] = $18.0562x_{\text{Tr}} + 17.936x_{\text{Ts}} + 17.925x_{\text{Cum}}$; c [Å] = $5.2768x_{\text{Tr}} + 5.2995x_{\text{Ts}} + 5.2700x_{\text{Cum}}$; β [°] = $104.74x_{\text{Tr}} + 105.68x_{\text{Ts}} + 102.18x_{\text{Cum}}$. A model with random distribution at M2 and M3 including Al avoidance at the tetrahedral and octahedral sites yielded the best agreement with spectroscopic results [03N1] – see section 8.1.4.3.9.

The crystal structure of ferrotschermakite was also reported [73H1].

The magnesio**hornblende** crystallizes in the C2/m-type structure [71L1, 71L2, 72L2, 97J1]. The crystal structures of iron-rich hornblende [72L3] and ferroan pargasitic hornblende [80H1] were also studied.

Cannilloite, a hyper calcic amphibole with Ca at the A site was reported [96H6].

3. Sodic-calcic amphiboles

The crystal structures of natural and synthetic **richterites** were studied by X-ray diffraction and IR spectroscopy [62A1, 66P1, 89R1, 90D1, 91D1, 91R1, 92R1, 93D1, 93D2, 93P1, 93R1, 96D1, 96H1, 97D1, 98G1]. The final compositions of synthetic samples were also analyzed [93P2, 97Z1, 97Z2, 98G1]. Richterites are monoclinic amphiboles (C2/m-type structure) composed of double chains of silicon tetrahedra as shown in natural potassic richterite [69P1]. The structure is rather flexible with respect to cation and/or anionic substitutions. The cation sites linking these chains contain Na in the eightfold A site, Na and Ca in the eightfold M4 sites and Mg and Fe in the remaining sixfold M sites. The phase relations of the amphiboles richterite and ferrichterite, $\text{Na}(\text{NaCa})(\text{Mg}_{5-x}\text{Fe}_x)\text{Si}_8\text{O}_{22}(\text{OH})_2$, have been studied [75C1]. Richterite is stable up to 1030(10)°C at 1 kbar. Ferrichterite on the iron wüstite buffer is stable up to 715(5)°C at 1 kbar. In synthetic richterite, the octahedral sites are filled with Mg. The Ca and Na are distributed over the M4 sites. To balance the 46 negative charges of O^{2-} and $(\text{OH}, \text{F})^-$, one additional alkali atom is needed per formula unit and fills the A site, which is located between two tetrahedral double chains. The A site is large and irregular; the A site alkali is coordinated by 8 to 12 oxygen neighbours. Hydroxyl or fluorine occupies the O3 site, which is in the octahedral strip adjacent to the A site alkali [70H1].

The crystal structures of natural [69P1, 83C1, 92O1] and synthetic [98G1] potassium richterites were refined from single crystal X-ray diffraction data. Natural potassium richterites are close to end-member composition $\text{KNaCaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ with $\text{K} = 1.0$ apfu [77D1]. High-pressure experiments [90S1, 97K1, 97L1, 98G1] have produced potassium richterites with K in the M4 site of amphibole structure, a crystallographic position that has been considered too small to accommodate such a large cation [69P1]. The refinement of potassic richterite, $\text{K}(\text{KCa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (KK), shows that the M4 site is occupied by K and Ca at the ratio 1:1 with no site splitting [99Y1]. Entrance of K into M4 site mainly affects the local environment: the M4-O2, M4-O4 and M4-O6 bond lengths in KK richterite are 3.4, 3.7 and 3.1 % larger, respectively, than the corresponding ones in potassium richterites, whereas the M4-O5 distance is 1.2 % shorter, giving rise to a more regular M4 polyhedron. Three major structural adjustments allow the M4 site to accommodate larger K: a shift of the M4 cation along the twofold **b**-axis, a modification of the double chain configurations and relative displacements of the two back-to-back tetrahedral chains. K at the A site is completely ordered on the Am position [93R1, 94B1, 96H2, 99Y1].

The lattice parameters of synthetic potassic ferri-ferrichterite were determined in the low-temperature range [02R2]. The silicates crystallize in the C2/m-type structure. No crystallographic phase transition down to 110 K was observed. The two nonequivalent T sites and the octahedral M1 and M3 sites behave very rigidly upon cooling. Bond lengths for the distorted M sites slightly decrease as temperature is lowered. The tetrahedral chain kinking increases by 0.9° between 298 K and 110 K [02R2].

HRTEM investigations show that synthetic amphiboles tend to grow structurally disordered depending on synthesis conditions, in contrast to their well ordered natural analogues [83M1, 88M1, 91A1]. According to

[98G1], despite the fact that the synthesis was done on bulk compositions along the richterite – K-richterite, the amphiboles are not simple solid solutions of the two richterite end members but tremolite and Mg-cummingtonite components are also present. HRTEM observations show that they are structurally well ordered; only very few chain multiplicity faults are present. The unit cell parameters of (Na-K) richterites vary linearly with composition [98G1]: a [Å] = $9.9055 + 0.1731x_{K(A)} - 0.1300(x_{Ca(M4)} - 1/2) - 0.2795x_{Mg(M4)}$; b [Å] = $17.9844 + 0.0032x_{K(A)} + 0.1372(x_{Ca(M4)} - 1/2) + 0.12875x_{Mg(M4)}$; c [Å] = $5.2689 + 0.0025x_{K(A)} + 0.0188(x_{Ca(M4)} - 1/2) + 0.0159x_{Mg(M4)}$; β [°] = $104.212 + 0.666x_{K(A)} + 1.176(x_{Ca(M4)} - 1/2) - 0.288x_{Mg(M4)}$. By $x_{K(A)}$ is denoted a vacancy concentration on A, Ca^{2+} concentration by $x_{Ca(M4)}$ and Mg^{2+} concentration by $x_{Mg(M4)}$.

The behaviour of titanium in richterite was analyzed [83M2, 86W1, 87T1, 90P1, 91D1, 92O1]. According to [91D1], the substitution limit of Ti in synthetic potassium richterite is $0.6 \leq Ti < 0.8$ apfu, similar as observed in natural samples [83M2, 86W1, 87T1]. The studies show that Ti^{4+} preferentially enters the tetrahedral chain in richterite [90P1, 91D1, 92O1] and it is fully ordered at the T2 site [92O1]. The presence of $[4]Ti^{4+}$ is related to the very high temperature–low pressure conditions of crystallization of lamproitic richterites. Octahedrally-coordinated Ti^{4+} can also occur in some richterites where it is strongly ordered at the M1 site. According to [92O1] the entrance of Ti^{4+} at M1 seems to be associated with the occurrence of O^{2-} at the O3 site. The ordering of $[6]Ti^{4+}$ is therefore related to local charge-balance requirements. The amount of Ti^{4+} is inversely related to the pressure conditions of crystallization, whereas its site preference is most likely related to the (H_2O, F^-) contents of the liquid. If no hydrogenation occurs, Ti^{4+} and other high-charge cations order at M2 so to balance for the presence of $[4]Al^{3+}$ [92O1]. In dehydrogenated samples, Ti^{4+} enters, as above mentioned, in M1 in order to satisfy the bond strength requirement at the O3 site. The exchange vector is $^{M1}Ti^{4+} + ^{O3}O_2^{2-} \rightarrow ^{M1}Mg_2^{2+} + ^{O3}OH_2^-$

(kaersutite substitution). According to [91D1], the progressive decrease in the tremolite-type band intensities in the OH-stretching region with increasing Ti content, seen by IR studies, confirms that the A site cation splitting over A subsites is a function of the geometry of the A cavity, controlled by the major cationic substitutions. There is a regular increase of lattice parameters (a , b , c , β) as a function of titanium content.

In richterite there is a complete exchange between OH^- and F^- at the O3 site and linear contraction of the cell volume as function of F^- occurs, because F^- is smaller than OH^- [89R1, 99R1]. The refinements of $NaCaNaMg_5Si_8O_{22}F_2$ and $CaNaNaMg_{3.41}Fe_{1.59}Si_8O_{22}F_2$ fluor richterites showed that Fe^{2+} strongly orders on the M2 site [71C1]. It was argued that this preference is due to the Fe^{2+} avoidance rule, which according to [77R1] was explained in terms of lower crystal field stabilization energy when F^- is the coordinated anion instead of OH^- . In [83C1] the structures of fluor richterite and potassium fluor richterite were refined at several temperatures.

The crystal structure and site occupancies of manganoan richterites have been studied [93O1]. In case of low-Fe manganoan richterites, there is significant occupancy at the B group of sites by Mn^{2+} , which enters a position displaced towards the octahedral strip relative to the M4 site. The latter is occupied only by Ca and Na. The split position, M4', has a coordination similar to that observed in Fe-Mg-Mn amphiboles. At the octahedrally-coordinated M1, M2, M3 sites, Mn is present as Mn^{2+} and is strongly ordered at the M2 site. The increase in the M2-O distance due to Mn^{2+} substitution prevents high-charged octahedral cations from entering the richterite structure in significant amounts [93O1].

The temperature dependence of the lattice parameters for $K(NaCa)Mg_5Si_8O_{22}F_2$ (KR) and $Na(NaCa)Mg_5Si_8O_{22}F_2$ (NaR) are plotted in Fig. 13 [83C1]. The A atoms were approximated by split-atom model at all temperatures. The K atom, in the A site of KR, was refined by using a half atom model with K randomly occupying to special positions (4i) within the (010) mirror plane. The Na atom in the A site of sodium richterite was refined using a quarter atom model, in which Na randomly occupies four general positions (8j) off both the (010) mirror plane and the twofold axis parallel to b . In the studied temperature range, the interatomic distances T1-O and T2-O remain statistically identical, but all other mean polyhedral distances increase significantly. Mean thermal coefficients (MTEC) for mean bond lengths increase as follows: $T1 = T2 \ll M3 < M1 < M2 < [8]M4 < ^xA$ (K richterite) and $T1 = T2 \ll M1 < M2 < M3 \ll [8]M4 < ^xA$ (Na richterite). This differential polyhedral expansion is accompanied by straightening of the tetrahedral chains and by increased displacement of the double chains relative to each other. Expansion of three of the four M polyhedra in K richterite is slightly greater than for Na richterite and the MTEC of its unit-cell volume is larger (3.39 vs. $3.10/^\circ C \cdot 10^{-5}$). The behaviour of the richterite structure, at elevated temperatures, is generally similar to that of tremolite – Fig. 13.

The crystal structure of synthetic amphiboles along the **tremolite** – **richterite** series were studied [93P2, 97H1]. The compositions of synthetic $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ amphiboles synthesized at 1023 K and 1 kbar, are displaced towards magnesiocummingtonite, $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, such that average compositions are better represented by the pseudobinary (tremolite_{0.92} – Mg-cummingtonite_{0.08}) – richterite [93P2]. The amphiboles are highly ordered, with only the tremolite-rich compositions containing any chain multiplicity faults. According to [86G2, 93P2], the A site controls the mixing energetics of tremolite – richterite and F-tremolite – F-edinite amphiboles, with A site positional ordering and interactions with other cations playing an important role. The lattice parameters of the K richterite – tremolite join, synthesized at 1023 K and 1 kbar, vary linearly with composition – Fig. 14 [97H1]. The cell volume decreases regularly from K richterite to tremolite in response to the decreasing amount of K at the A site (K, \square) and decreasing size of the constituent cations (Na, Ca) at the M4 site. The *a*-dimension shows by far the greatest variation across the series, decreasing as the amount of tremolite component increases in the amphibole. This observation is in accord with the idea that K at the A site holds the back-to-back – double chains apart, and removal of K allows the chains to relax toward each other. Relaxation in the *b* and *c* directions is much less as it is expected from this particular substitution.

In **ferritaramite**, the small trivalent cations are ordered into the M2 site [78H3]. Mn^{2+} is strongly or completely ordered into the M3 site as shown in **arfvedsonite** [76H1]. The atoms occupying the A site show positional disorder – Table 2. The best results were obtained from occupancy of the Am(4i) and A2(4g) positions, although a model involving a disorder over Am and A1(8j) positions could not be rejected [78H3]. The potassium ferritaramite crystallizes in the C2/m-type structure [73L2].

The potassium magnesiokataphorite crystallizes in C2/m-type structure [69P1]. The crystal structures of **winchite** [81L3] and **barroisitic** hornblende [57H1] were also studied.

4. Sodic amphiboles

Glaucophane crystallizes in C2/m-type structure [68P1, 69B1]. The refinement of the crystal structure shows that trivalent cations occupy the M2 site, when univalent cations are located in M4 [60W1, 68P1] – Table 3. In **ferroglaucophane**, site population refinement indicates that Al is strongly ordered on M1 site [79H1]. (For pressure effect on glaucophane see text above).

Riebeckite is a Na amphibole with ideal chemical formula $\text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$. The structure contains four different cation sites M1, M2, M3 and M4 with relative abundance 2:2:1:2, respectively. The first three are octahedrally coordinated (O_6 for M2, $\text{O}_4(\text{OH})_2$ for M1, M3) whereas the last one shows a strongly deformed six- to eightfold coordination and is occupied by Na^+ . The sites form ribbons of alternately three (M2-M3-M2) and four (M4-M1-M1-M4) polyhedra wide. These ribbons are sandwiched by double Si_4O_{11} -chains which run parallel to the crystallographic *c*-axis. In **magnesioriebeckite** [49W1, 65C1] and glaucophane [63E1, 66C1, 68P1] the trivalent ions (Fe^{3+} , Al^{3+}) are ordered to a considerable extent and its ordering may be regarded as a consequence of the effect of the confinement of the monovalent ions to a single neighbouring site. In **fluor riebeckite** a portion of the OH^- group is replaced by F^- . In this silicate, some Fe^{3+} cations seem to exist in the M1 site [78H1, 83H3]. In fluor riebeckite, the Li is located in M3 site. Tetrahedral Al is strongly ordered in T1 and octahedral trivalent cations strongly ordered in M2 [78H1]. The atoms occupying the A site show positional disorder in the mirror plane, suggesting that the A site K occupies Am, whereas A site Na occupies A2 or A1 sites. Complete ordering of Li in M3 minimizes deviations from Pauling's rule of local compensation of charges.

The riebeckite ($\square\text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$) – ferri-clinoferroholmquistite ($\square\text{Li}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$) series were synthesized, where the exchange vector is NaLi_{-1} at the B site [03I2]. The lattice parameters decrease when increasing the Li content – Fig. 15.

Obertiite, $\text{NaNa}_2(\text{Mg}_3\text{Fe}^{3+}\text{Ti}^{4+})\text{Si}_8\text{O}_{22}\text{O}_2$, crystallizes in C2/m-type structure [00H1]. The M1 site is split into two subsites along the *b*-axis (M1 and M1A). The M1 site is occupied by Mg and M1A is occupied predominantly by Ti^{4+} and Mn^{3+} – Table 3. M2 is occupied by Mg, Fe^{2+} and Fe^{3+} and M3 is occupied by Mg. Local bond valence considerations suggest that O^{2-} at O3 is linked to $\text{Ti}^{4+}\text{Mg}^{2+}$ or $\text{Mn}^{3+}\text{Mn}^{3+}$ at the adjacent M1 and/or M1A sites and that OH^- or F^- at O3 is linked to $\text{Mg}^{2+}\text{Mg}^{2+}$ at adjacent M1 sites. Obertiite may be formally derived from magnesio-arfvedsonite $\text{NaNa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$ by substitution $^{\text{M1A}}\text{Ti}^{4+} + ^{\text{H}}\square_2 \rightarrow ^{\text{M1}}\text{Mg} + ^{\text{H}}\text{H}_2$. A splitting model for the A site was reported. The Am and A2 sites both show significant electron density. According to A site stereochemistry in monoclinic amphiboles containing Na, K [96H2], Na was assigned to the A2 site and a mixture of K and Na to the Am site.

Arfvedsonite crystallizes in the monoclinic C2/m-type structure [76H1]. The structure exhibits double chains of SiO_4 tetrahedra and octahedral strips along [001], Fe^{3+} and Fe^{2+} are commonly entering octahedral sites M1, M2, M3; occasionally, Fe^{2+} is observed on 8-coordinated M4 positions in larger concentrations. Between the tetrahedra of the double chains are large cavities, the A sites, which are partly occupied by cations (Na^+ , K^+). Oxygen on O3 of M3 octahedra are in part or fully replaced by OH^- , F^- , Cl^- . **Magnesio-arfvedsonites** both naturally [74M2] or synthesized hydrothermally [68K1] were reported. Both crystallize in the C2/m-type structure. In [70F2] the crystal structure of **fluor arfvedsonite** was analyzed. Fluoro-magnesio-arfvedsonite crystallizes also in the C2/m-type structure [00B1].

Nyböite, crystallizes in a monoclinic-type structure [81U1]. Fluoro-nyböite crystallizes in a monoclinic structure of C2/m type [03O1].

Kozulite is a Mn-rich amphibole which crystallizes in C2/m-type structure [72K1]. The site occupancy is given in Table 3. No Al was found in tetrahedral sites in spite of the presence of alkali cations in A sites. This fact was explained considering the long T1-O7 bond distance, cation distributions and the splitting atom model in A site.

Ungarettiite is an anhydrous amphibole having an ideal composition $\text{NaNa}_2(\text{Mn}^{2+}_2\text{Mn}^{3+}_3)\text{Si}_8\text{O}_{22}\text{O}_2$ [95H3]. In natural samples, the M1, M2 and M3 sites are occupied dominantly by Mn. The determined M-O distances are compatible with the site occupancy $\text{M1} \equiv \text{M3} \equiv \text{Mn}^{3+}$, $\text{M2} \equiv \text{Mn}^{2+}$. All bonds to the O3 anion are very short and a bond valence analysis indicates that O3 site is occupied by a divalent anion O^{2-} as suggested by the overall electroneutrality requirement of the structure formula. In [02K1] ungarettiite was reported close to the ideal composition.

Dellaventuraite, $\text{NaNa}_2(\text{MgMn}^{3+}_2\text{LiTi}^{4+})\text{Si}_8\text{O}_{22}\text{O}_2$, crystallizes in a monoclinic-type structure having space group C2/m [05T1]. The M1 site is occupied by Ti^{4+} , Mn^{3+} and Mg^{2+} in approximately equal amounts, the M2 site is occupied primarily by Mg^{2+} and Fe^{3+} and M3 site is occupied by Li with minor content of Mg^{2+} and Mn^{2+} . Local bond valence configurations suggested that O^{2-} at O3 is linked to $\text{Ti}^{4+}\text{Mg}^{2+}$ or $\text{Mn}^{3+}\text{Mn}^{3+}$ at the adjacent M1 sites and that OH (when exit) at O3 is linked to $\text{Mg}^{2+}\text{Mg}^{2+}$ at the adjacent M1 sites. Dellaventuraite is an anhydrous amphibole such as ungarettiite [95H3] and obertiite [00H1].

The ideal composition of **leakeite**, $\text{NaNa}_2(\text{Mg}_2\text{Fe}^{3+}_2\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$, may be derived from end-member ferri-eckermannite by the substitution $\text{Fe}^{3+} + {}^{\text{M3}}\text{Li} \leftrightarrow \text{Mg} + {}^{\text{M3}}\text{Mg}$ [92H1]. This is a heterovalent cation substitution taking place completely within the octahedral strip, that is, completely within the C group of cations. Alternatively, leakeite may be considered to be derived from end-member magnesioriebeckite by the substitution ${}^{\text{A}}\text{Na} + {}^{\text{M3}}\text{Li} \leftrightarrow {}^{\text{A}}\square + {}^{\text{M3}}\text{Mg}$. The sites occupancies are given in Table 3.

The $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ amphibole has been synthesized [91M1, 96L1]. In [91M1] a complex monoclinic to triclinic phase transition at 373...433 K was observed. Above 433 K the structure was shown to be monoclinic with space group C2/m [91M1]. However, electron diffraction patterns and unit-cell refinements from X-ray diffraction data do not rule out space group Cm or C2. Below 373 K, $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ is triclinic with space group $\text{C}\bar{1}$ or C1 and has a superstructure with triple *b* parameter. According to [91M1] two thermal transitions were shown, quite different in character. An upper transition at 426 K has a little or no hysteresis and is probably displacive. The lower transition at 373...403 K has a significant hysteresis, suggesting that a kinetic barrier is involved and that it is in some way „reconstructive“. According to [96L1] the $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ undergoes a complex triclinic to monoclinic $\text{C}\bar{1} \rightarrow \text{C2/m}$ phase transition in the 373...433 K temperature range.

A fibrous phase $\text{NaMg}_4[\text{Si}_6\text{O}_{15}\text{OH}](\text{OH})_2$ was synthesized at 500°C and 1000 atm [75D1]. A structural model was suggested based on strips of three pyroxene chains. In the projection of the (010) plane, the structure of this phase is similar to that of monoclinic pyroxenes and amphiboles.

$\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ amphibole has not been found in nature but synthesized and investigated [62G1, 64G1, 69W2, 91R1, 96L1, 04I1]. Despite of the simple chemical composition and easy synthesis, there were different proposals for the crystal structures. Two different monoclinic space groups C2/m [69W2] and $\text{P2}_1/\text{m}$ [96L1] have been suggested. The $\text{NaNa}_2\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$, is related to $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ by the $\text{Na}_1\text{H}_1\text{Mg}_{-1}$ exchange. As mentioned already, the space group $\text{P2}_1/\text{m}$ in amphiboles is rare. Besides the cummingtonite it has been reported for a synthetic amphibole $\text{Na}_{0.95}(\text{Na}_{0.64}\text{Mg}_{0.97}\text{Li}_{0.27}\text{H}_{0.12})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ sample with an excess of OH located at the M4 site [00O2]. In [03I2, 05I1] was shown that samples with compositions varying from $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ($T = 750^\circ\text{C}$, $p = 4$ kbar) to $\text{Na}_{0.82}(\text{Na}_{0.81}\text{Mg}_{1.19})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ($T = 900^\circ\text{C}$, $p = 5$ kbar) all have $\text{P2}_1/\text{m}$ symmetry under ambient conditions. In [04I1] $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ was synthesized at different temperatures. There is a progressive departure

of amphibole from the nominal composition with increasing temperature although $P2_1/m$ crystal structure is maintained. The active exchange vector is ${}^A\Box_1{}^B\text{Mg}_1{}^A\text{Na}_{-1}{}^B\text{Na}_{-1}$. The most composition sensitive parameters are the α -dimension (the values of which mostly depends on the A site occupancy) and the β -angle (the value of which strongly depends on the site population, or more accurately on the aggregate ionic radius and charge at the B site). The b and c -dimensions depend mainly on octahedral and tetrahedral site populations, respectively, therefore they are virtually constant. Although it has, at RT, the same crystal structure as Mg-rich cummingtonite ($P2_1/m$), there are several peculiar features [03C1, 04I1]: (1) two cations, one mono- and one divalent with very different sizes, at the M4 site; (2) a fully occupied A site, and (3) a rather ordered structure, with only Si at the T site and Mg at the C sites. Like cummingtonite, the A and B double-chains have **S** and **O** rotations, respectively. However, the degrees of kinking of the A and B double chains are, respectively, the largest and the smallest so far reported for $P2_1/m$ amphiboles [03C1]. The cell parameters as function of temperature were determined. The temperature dependence of kinking angle is plotted in Fig. 16 [05I1]. At 573 K, the symmetry is $C2/m$ and the double chains are equivalent and both extended with O5-O6-O5 angle $\cong 174^\circ$. With decreasing temperature, down to 298 K, the amphibole converts to $P2_1/m$ and the chains are not longer equivalent: the A chain lengthens as function of T (the O5A-O6A-O5A angle increases to 189.9°), while the B chains shrink (the O5B-O6B-O5B angle decreases to 158.6°) [03C1]. By decreasing the temperature down to 8 K, the independent chains keep the same trend, however, the rate of variation of the degree of kinking is less steep. We note that according to [03C1] the evolution of order parameter with T yields $T_c = 530$ K and the Landau coefficient is compatible with a second order transition. The shapes of electron density at the A and M4 sites are plotted in Fig. 17. There is only one cation position in the $P2_1/m$ symmetry, which is significantly off centered ($\cong 0.25$ Å) almost along the imaginary line joining the two farthest O7A and O7B oxygen atoms (the O7 sites are those connecting the two chains thus forming the rings). There are two nearly equal short A-O7A, B distances and two different long A-O7A, B distances. In the $C2/m$ symmetry Na is ordered at the analogous Am site and is increasingly displaced from the center of the cavity with increasing T . Therefore, the electron density has been modeled by means of two different cation positions. Analyzing the shape of electron density at the B group sites it was shown that at $T < T_c$ a split model was required with the smaller Mg in a position closer to the octahedral strip (M4) and the larger Na shifted towards the double chain of tetrahedra (M4'). After the transition, the electron density must be more symmetric. The residual elongation along the b -axis does not require a split model in the high- T refinements. Mg changes its coordination from fivefold in $P2_1/m$ to [6+2] fold in $C2/m$ as in analogous cummingtonites and clinopyroxenes. Na changes its coordination from sevenfold to [6+2] fold [03C1]. The two geometrically different M4 sites (Mg and Na) help to reduce strain fields, an effect which would be further enhanced by short-range ordering of ${}^A\text{Na}-{}^{M4}\text{Na}$ and ${}^A\Box-{}^{M4}\text{Mg}$ clusters, which is forced by bond-valence and local charge balance requirements. The pattern of order within the A cavity is different in the two long-range symmetries. In the space group $C2/m$, the two distinct Am positions related by the diad are alternatively occupied along each “sandwich” of double chains running parallel to [001]. In space group $P2_1/m$, the position of the A cation repeats itself by a translation parallel to [001] within the “sandwich”, whereas adjacent “sandwiches” have A sites related by the 2_1 diad [03C1].

As for richterite [92O1] a crystal chemical model for the ${}^{63}\text{Ti}^{4+}$ partitioning has been proposed for Li-bearing sodic amphiboles [94H1]. If no dehydration occurs, Ti^{4+} and other high-charge cations order at M2 so as to balance for the presence of ${}^{[4]}\text{Al}$. In dehydrogenated samples, Ti enters also at M1 in order to satisfy bond-strength requirement at the O3 site.

5. Na-Ca-Mg-Fe-Mn-Li amphiboles

The members of group 5 that have ${}^B\text{Li} > 0.50$ apfu derive from the finding ferriwhittakerite, ${}^A\text{Na}^B(\text{NaLi})^C(\text{LiMg}_2\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$ with $A \geq 0.50$ apfu and ferri-ottoliniite, ${}^A\Box^B(\text{NaLi})^C(\text{Mg}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$ with $A < 0.50$ apfu [04O1]. Usually, there is also significant ${}^C\text{Li}$ [04L1]. The members of this group are listed in Table 1. The second subgroup has ${}^B\text{Li} \leq 0.50$ apfu. In the calcic and sodic-calcic groups it is usual, for the total of the cations initially allocated to C, to exceed the limit of 5.00 apfu and the excess of the larger ions to overspill into B. This is particularly common where a „cummingtonite solid solution” in calcic amphiboles occurs. In some cases the ${}^B(\text{Mg}+\text{Fe}^{2+}+\text{Mn}^{2+}+\text{Li})$ slightly exceeds 0.50 apfu although ${}^B\text{Li} < 0.50$ apfu. Such samples (according to present known miscibility limit) have only slightly greater cationic content at B site than ${}^B0.50$ apfu. In order to avoid a rash of new root names for such compositions of small cations in B (and small or zero Li content), the prefix **parvo** should be prefixed to the root names for a

species in the calcic, sodic-calcic and sodic groups [04L1]. This preserves familiar names, makes no distinction as to what the dominant type ion is in B and avoid making new names as a consequence of creating group 5 to deal with certain Li-rich amphiboles. As example, a usually large $^B(\text{Mg, Fe, Mn, Li})$ value of 0.74 apfu occurs in silicate $^A(\text{K}_{0.03}\text{Na}_{0.30})^B(\text{Na}_{0.87}\text{Ca}_{0.39}\text{Mn}_{0.68}\text{Li}_{0.06})^C(\text{Mn}_{0.27}\text{Mg}_{4.01}\text{Fe}^{3+}_{0.72})\text{Si}_{7.88}\text{Al}_{0.12}\text{O}_{22}\text{F}_{0.40}(\text{OH})_{1.60}$ [93O2]. According to the old nomenclature [97L2], the name was winchite or with modifiers, a fluorian manganian winchite. According to [04L1] it becomes parvowinchite or fluorian manganian parvowinchite. Similarly, rare $^B\text{Li} \leq 0.50$ apfu amphiboles, previously included in group 2, now fall in group 5. For the calcic amphibole $^A(\text{K}_{0.02}\text{Na}_{0.65})^B(\text{Ca}_{1.17}\text{Mn}_{0.83})^C(\text{Mn}_{0.27}\text{Fe}^{2+}_{0.09}\text{Mg}_{4.46}\text{Ti}_{0.01}\text{Al}_{0.16})\text{Si}_{7.18}\text{Al}_{0.82}\text{O}_{22}(\text{OH}_{1.91}\text{F}_{0.09})$ [91S1], if there was no mixture of phases the name mangano-edenite is to be changed now in parvo-mangano-edenite [04L1]. To avoid new root names for rare amphiboles with compositions $^B\text{Li} \leq 0.50$ apfu which were in group 1, according to [04L1], they fall into group 5; because of significant $^B(\text{Ca, Na})$ these should be named as previously with group 1 root names and prefixes but prefixed **magno** to indicate the entry of large cations at B position, in group 5.

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* *

A characteristic feature of the amphiboles is the substitution of Al for Si in the tetrahedral double chain. In natural samples, the amount of $^{[4]}\text{Al}$ seems to be a function of both bulk-rock composition and the intensive parameters at equilibration. These relationships are not straightforward as the $^{[4]}\text{Al} - \text{Si}$ substitution is heterovalent and couples to other heterovalent substitutions in the structure to maintain electroneutrality. Some general trends are apparent. Amphiboles very enriched (> 2.5 apfu) in $^{[4]}\text{Al}$ are characteristic of Si-deficient environment [75A1, 84S1]. Amphiboles with high $^{[6]}\text{Al}/^{[4]}\text{Al}$ ratios are characteristic of high-pressure/low-temperature conditions in metamorphic rocks [89C1] and the $^{[6]}\text{Al}/^{[4]}\text{Al}$ ratio in calcic amphiboles from granitic plutons is sensitive to the pressure of crystallization, to the extent that was used as geobarometer [92A1]. The ordering behaviour of $^{[4]}\text{Al}$ was examined in terms of bond balance requirements [95O2]. In most amphiboles $^{[4]}\text{Al}$ occurs completely at T1 in order to avoid reducing the incident bond-valence to O4, the only 3-coordinated nonbridging oxygen. The normal limit $^{[4]}\text{Al} \equiv 2$ apfu observed in amphiboles occurs so as to avoid Al-O7-Al linkages that are very unfavorable from a bond-valence view point, and to avoid the occurrence at T2. When $^{[4]}\text{Al} > 2$ apfu, the additional $^{[4]}\text{Al}$ normally occurs at the T2 site.

In [78H2] the relationships between mean bond length and the mean constituent cation and anion radii were analysed. There is a linear dependence for the M1, M2 and M3 octahedra in clino-amphiboles.

For crystal structures and lattice parameters see also:

Amphiboles [30W1, 70B1, 72H1, 88M2]; Anthophyllite [30W1, 75S1, 78S1]; Holmquistite [58V1]; Cummingtonite [59G1, 71G1, 91P1]; Tremolite [66E1]; Pargasite [73B3, 97D2]; Richterite [92D2]; Hornblende [78D1]; Riebeckite [64C1]; Eckermannite, Nyböite [87R1].

8.1.4.3.2 Magnetic properties

Cummingtonite – grunerite series

The $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ grunerite – cummingtonite series (sect. 8.1.4.3.1) have monoclinic symmetry of space group C2/m. The magnetic properties of this system were investigated [83L1, 87G1, 88L1]. The samples having a composition close to the end member grunerite ($x = 1.0$) were particularly studied, namely with $x = 0.95$ [83L1, 88L1] or 0.955 [87G1]. The thermal variation of reciprocal susceptibilities for the $x = 0.95$ sample is plotted in Fig. 18. Well defined peaks are located at $T_N = 45.0(5)\text{K}$ and $T_{sc} = 8(1)\text{K}$. The higher temperature peak was attributed to the magnetic ordering temperature, while the presence of the lower temperature peak was related to spin canting (sc) away from the *b*-axis at the distorted M4 site and the neighbouring M1 site. The paramagnetic Curie temperature, Θ , is positive and the Curie constant is $3.9 \text{ K emu (g atom Fe)}^{-1}$. Thus, the dominant exchange interactions are ferromagnetic.

The high-field measurements on a sample with $x = 0.95$, up to 15 T revealed a metamagnetic transition with an extrapolated saturation moment of $4.1 \mu_B/\text{atom}$ and a critical field $\mu_0 H_c = 1.4 \text{ T}$ for $T < 12 \text{ K}$ – Fig. 19. Another critical field H_s also appears at 0.5 T which looks like a spin-flop field. The above magnetic behaviour is characteristic of antiferromagnetic ordering, as also confirmed by neutron diffraction studies (see sect. 8.1.4.3.3). Between T_{sc} and T_N , all the Fe^{2+} ions are ferromagnetically coupled within a ribbon and the spins of neighbouring ribbons are oriented antiparallel giving rise to the overall antiferromagnetic structure. Below T_{sc} ,

the anisotropy energy overcomes the intra-ribbon ferromagnetic interaction and spin canting occurs. The effective exchange coupling constant between ribbons was estimated to be $z'J/k_B = -0.48(5)$ K where z' is the effective number of Fe^{2+} neighbours. The effective intra-ribbon exchange coupling is $zJ/k_B = 12.2$ K, where z is the effective number of Fe^{2+} neighbours inside a ribbon. The ratio $z'J/zJ \cong 0.04$ is characteristic for a quasi-one-dimensional system.

The magnetic ordering temperatures, T_N , for $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ system with $x < 1.0$ are low and decrease when the x values diminish – Table 6. The low T_N values result, in a first step, from weak superexchange interactions due to the superexchange bond Fe-O-Fe angle close to 90° but also, for samples with $x < 0.50$, to the low Fe^{2+} content inside the ribbons.

The magnetic measurements were made also on $(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ natural anthophyllite (amosite), but the composition has not been mentioned [75E1]. The temperature dependences of the susceptibilities parallel (χ_c) and perpendicular (χ_{ab}) to the fibre axis, as well as of the powdered sample (χ_p) are plotted in Fig. 20. The powder susceptibility shows two peaks at 25 K and 10 K. The χ_{ab} values have a maximum at 25 K and decreased essentially to zero at about 11 K. The peaks at 10 K and 25 K can be associated with spin canting and magnetic ordering temperatures, respectively.

Riebeckite

Two samples of crocidolite, which is a fibrous form of riebeckite were studied [83M3]. Their compositions are given in Table 6 (A^7 and B^8). The susceptibilities and reciprocal susceptibilities for sample B^8 are plotted in Fig. 21. There is a sharp peak at $T_N = 30$ K, suggestive of an antiferromagnetic order. However, the intercept of the linear portion of the reciprocal susceptibility gives a paramagnetic Curie temperature, $\Theta = 26.5(1.0)$ K, which indicates that ferromagnetic interactions predominate. Some magnetization isotherms are plotted in Fig. 22 [83M3]. Those at 4.2 K, marked with \parallel and \perp were obtained with the field applied parallel and perpendicular to the axes of oriented bundles of fibres whereas the others were measured on randomly oriented samples. Except for the easily saturated component in sample A, due to the magnetite impurity, the curves of the two samples at 4.2 K are similar. There is a sharp increase in slope at $\mu_0 H_s \cong 1.5$ T. This jump in magnetization is absent above $T_N = 30$ K. We note that a jump in the magnetization of riebeckite has been also found previously [80B1]. The data suggest a model for the magnetic structure consisting of ferromagnetic ribbons coupled by weaker antiferromagnetic interactions. The data obtained by analysis of the spin-flop transition and other magnetic properties, in the effective field approximation, in terms of four fields representing in-plane and inter-plane exchange (H_E^\perp and H_E^\parallel) and the anisotropy fields H_A^\parallel created by the trigonal crystal field and an anisotropy field H_A^\perp which picks out a preferred orientation within the plane of the strips (when the local symmetry is lower than trigonal), leads to values given in Table 6. The ratio of in-plane to inter-plane exchange coupling is very high ($\cong 25$); so the magnetic interactions have a distinctly two-dimensional character.

The magnetic properties of a riebeckite, having essentially the chemical formula $\text{Na}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH,F})_2$, have been reported [75B3]. The magnetic susceptibility for a powdered sample shows a sharp peak at $T_N = 31.5$ K – Fig. 23a. At $T > 40$ K the data were analysed considering a modified Curie-Weiss law $\chi = \chi_0 + C(T - \Theta)^{-1}$ with $\Theta = 22.4$ K, $\chi_0 = 3.6 \cdot 10^{-6}$ emu/g and $C = 2.26 \cdot 10^{-2}$ emu K/g. Some magnetization isotherms are given in Fig. 23b. The value of the saturation magnetization at 5 K in the highest field suggests that the antiferromagnetic interactions have been broken up, leading to the resulting nearly saturate ferromagnetic state.

Other studies on magnetic properties of amphiboles were performed. The temperature dependences of magnetic susceptibilities for some amphiboles were also analyzed by [60S1, 68B3, 72E1, 82B1, 82C1].

8.1.4.3.3 Neutron diffraction data

Grunerite

Powder neutron diffraction measurements between 8...45 K, reveal that all the Fe^{2+} spins within an octahedral band are ferromagnetically coupled parallel to the *b*-axis with each band antiferromagnetically coupled to neighbouring bands. Below 8 K, Fe^{2+} spins at the M1 and M4 sites are canted away from the *b*-axis, whereas those at the M2 and M3 sites are not significantly affected – Fig. 24 [87G1]. The ordered Fe^{2+} moment on the M4 site is substantially lower than those of other sites – Table 6 – most likely indicating a strong correlation effect, i.e. considerable spin transfer to neighbouring oxygen atoms. Thus, the magnetic behaviour of grunerite and ferrosilite (Chap. 8.1.4.1) is similar, as expected, since they are based on similar crystal structures and M-O-M superexchange paths, which have angles close to 90° . The very strong site preference of Fe^{2+} over Mg for the M4 site in the cummingtonite – grunerite series, has been ascribed to the difference in the covalency effects at the M4 versus the M1, M2 and M3 sites [61G1, 82G1].

Riebeckite

Crocidolite, the fibrous form of riebeckite, was studied by neutron diffraction at 5 K and 40 K [83M3]. The magnetic contribution to the neutron scattering pattern at 5 K is shown in Fig. 25. All the magnetic reflections occur in positions quite separate from the nuclear reflections, but they can be indexed on the crystallographic unit cell. The iron ions in the ribbons parallel to *c* are all coupled ferromagnetically but the moments of adjacent ribbons are oppositely aligned. The iron moments are oriented at angles of about 69° , 36° , 69° with the *a*, *b*, *c* axes, respectively – Table 7. The magnetic structure is sketched in the insert to Fig. 25. The temperature dependence of the sublattice magnetic moment agree with that of the average iron hyperfine field.

8.1.4.3.4 Nuclear gamma resonance (NGR) data

Iron-magnesium-manganese-lithium amphiboles

The ^{57}Fe NGR spectra taken at 298 K and 77 K on cummingtonites and grunerites do not separately resolve M1, M2 and M3 sites, but they confirm the strong preference of Fe^{2+} for M4 sites [67B2, 71B1, 71H1, 73B2, 75E1]. The ordering between M4 and combined M1, M2 and M3 sites is temperature dependent [72G1]. The combination of ^{57}Fe NGR and IR absorption spectroscopy also shows that Fe^{2+} favors M1, M3 over M2 [67B2, 67B3, 71B1, 89Y1]. The doublets with larger quadrupole splitting were attributed to octahedrally-coordinated M1, M2 and M3 sites and the smaller splitting to the eightfold-coordinated M4 site [73K1, 75E1]. In [71H1] 26 cummingtonites with atomic ratios $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.98\ldots 0.18$ were studied by ^{57}Fe NGR. The quadrupole splittings, ΔQ , increase with decreasing temperature between 300 and 77 K whereas the splitting at the M4 site is nearly invariant. The ΔQ and isomer shift, δ , values exhibit a correlation with the radial distortion of the oxygen octahedra at the (M1, M2, M3) and M4 sites, in accord with similar trends observed in pyroxenes. The isomer shift at the M4 site is indicative of an enhanced covalent participation in the Fe^{2+} -O bonding compared to the other sites. The Fe^{2+} distribution over (M1, M2, M3) and M4 is generally quite ordered. Samples with composition $\text{Fe}/(\text{Fe}+\text{Mg}) < 0.7$ have disordering parameters $p = 0.1\ldots 0.2$.

The effect of pressure, *p*, on the hyperfine parameters of grunerite⁵⁾ – Table 8 – was studied [92Z1]. The ^{57}Fe NGR spectrum at ambient conditions consists of two apparent doublets – Fig. 26a. The doublet with the larger splitting was ascribed to Fe^{2+} in M1, M2, and M3 sites and that with smaller splitting to Fe^{2+} in M4. The spectra do not change significantly with increasing pressure up to 8.5 GPa. A small fraction of resonant absorption with traces of Fe^{3+} was observed in all the spectra, but this component was ignored [92Z1]. The isomer shifts, δ and the quadrupole splittings, ΔQ , of the two resolved paramagnetic Fe^{2+} doublets change significantly: $\Delta Q(\text{M1, M2, M3})$ decreases by 2.9 % and $\Delta Q(\text{M4})$ increases by 21 % with increasing pressure. The δ of M1, M2 and M3 decreases and δ at M4 increases with increasing pressure indicating a crossover at about 10 GPa. Linear relationships between δ , ΔQ and *p* were found at RT – Fig. 26b, c. At pressures smaller than ≈ 1 GPa, the electronic structure of Fe^{2+} in M sites is practically independent of compression of the unit cell. The Fe^{2+} ions remain in high-spin configuration up to at least 8.5 GPa. The nuclear electron density of Fe^{2+} in M1, M2, and M3 sites increases, whereas that in M4 decreases. The pressure dependences of $\delta(\text{M1, M2, M3})$ - and $\Delta Q(\text{M1, M2, M3})$ – Figs. 26b, c – were mainly attributed to electronic changes in the Fe^{2+} valence shell and overlap with the ligands. The increase of $\delta(\text{M4})$ was ascribed to 4s, 3d electron transfer. For the change of $\Delta Q(\text{M4})$, the lattice

contribution is predominant. The electronic states of Fe^{2+} in the M octahedra become more similar and the M4 octahedra less distorted at high pressures [92Z1].

The M1, M2 and M3 doublets, generally, cannot easily be resolved. However, a smaller discrepancy index has been obtained when the ^{57}Fe NGR spectrum of a grunerite sample at 77 K was fitted with three quadrupole doublets associated, after consideration of the relative distortion of the four octahedral sites, with the M4 site, the M2 site and the (M1, M3) group of sites [88L1] – Table 8. As evidenced in $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ samples with $0.36 \leq x \leq 0.95$, the quadrupole splitting ΔQ of Fe^{2+} in the M4 site is almost independent of temperature [88L1]. In connection with the strong distortion of the M4 site, this suggests that the ground state of Fe^{2+} ion is an orbital singlet, well separated from the first higher excited state ($\Delta > 1000 \text{ cm}^{-1}$). This situation leads to a complete quenching of the orbital momentum if one neglects the $\Gamma_3 - \Gamma_5$ orbital mixing ($\langle L \rangle = 0$ to first order). The small value of ΔQ in this site is due to an important lattice contribution to the electric field gradient and also to a strong covalency effect. The ΔQ value of M1, M2 and M3 sites have significant temperature dependences. The variation in ΔQ in these sites between 4.2 and 300 K indicated that the separation from the ground state, Δ , is about 150 cm^{-1} . In this case, the orbital momentum is not completely quenched. The isomer shift, δ , at the M4 site is indicative of an enhanced participation in the Fe^{2+} -O bonding compared to other sites. A positive sign for the electric field gradient, V_{zz} , was determined for the M4(Fe^{2+}) site at 250 K. The sign of V_{zz} in the M1, M2 and M3 sites has not been completely determined. However, a smaller discrepancy index has been obtained in the fitting procedure when a positive sign has been considered [88L1]. In grunerite, ($x = 0.95$), just below the ordering temperature, $T_N = 46 \text{ K}$, the ^{57}Fe NGR spectra show the presence of some quadrupolar component indicating that parts of ferrous ions have still paramagnetic behaviour. For $T < 39 \text{ K}$ all the Fe^{2+} ions present in the four different sites are magnetically ordered [83L1, 88L1] – Fig. 27. The ^{57}Fe NGR spectra change in the 8.2...5 K temperature range. The changes were attributed to the variation of the θ -angle between the direction of B_{hf} and the principal axis of the electric field gradient. The spectrum at 4.2 K was fitted considering four different hyperfine fields attributed to M1, M2, M3 and M4 sites. The hyperfine fields associated with the above sites by [83L1] were reconsidered later – Table 8 [88L1]. According to [88L1], the B_{hf} values of Fe^{2+} in M1, M3 and M2 sites (6.3, 11.4 and 15.3 T) are smaller than $B_{\text{hf}}(\text{M4}) = 24.5 \text{ T}$ because in these sites the orbital momentum is not completely quenched leading to a substantial anisotropic orbital contribution to the hyperfine field. The value of $B_{\text{hf}}(\text{M4})$ reflects the sum of a negative Fermi contact contribution, sensitively reduced by covalency effects, and a very weak positive orbital contribution ($\langle L \rangle = 0$ to first order within the ground orbital singlet of the Fe^{2+} at M4). So, the sign of $B_{\text{hf}}(\text{M4})$ must be negative. The anomalous low value of $2.4 \mu_B$ of the magnetic moment in M4 site at 12 K [87G1] supports the above conclusions: a quenched orbital momentum and strong covalency effects, i.e. considerable spin transfer to the neighbouring oxygen atoms. The magnetic moments on Fe^{2+} in the M1, M2 and M3 sites fall in the range typical of Fe^{2+} values ($3.8 \mu_B \dots 4.5 \mu_B$) which confirms the presence of a substantial orbital contribution to the momentum, in agreement with the corresponding B_{hf} values (6.3...15.3 T).

The $\text{C2/m} - \text{P2}_1/\text{m}$ transition in cummingtonite was studied also by the ^{57}Fe NGR method. As mentioned already, the transition mechanism involves rotations of SiO_4 tetrahedra in double chains such that the chains are extended parallel to c in the C2/m structure, but are contracted in the $\text{P2}_1/\text{m}$ structure – section 8.1.4.3.1. These rotations cause changes in the oxygen atom positions around the M4 crystallographic sites and it is these changes in coordination which can be detected by ^{57}Fe NGR of Fe^{2+} . In the C2/m structure, there are four oxygen atoms at distances between 2.0 and 2.2 Å from the M4 cations and two oxygen atoms at distances between 2.7 and 2.8 Å. In the $\text{P2}_1/\text{m}$ structure the 4+2 coordination changes to 4+1+1 coordination with two more distant oxygen atoms at $\approx 2.5 \text{ Å}$ and $\approx 2.8 \text{ Å}$ from the position of the M4 cation. Fe^{2+} ions are located also at the M1, M2 and M3 sites, but their coordination is closer to a regular octahedron and is not significantly affected by the symmetry change. The quadrupole splitting corresponding to (M1, M2, M3) sites varies smoothly with temperature, but at the phase transition is a strong change of ΔQ at the M4 site – Fig. 28 [02B1]. The difference between ΔQ of the low-symmetry phase and the values obtained, at the same temperature, by extrapolating ΔQ of the C2/m phase has been used as a measure, proportional to the local order parameter, Q , associated with the phase transition. The transition was close to being second order in character with $T_C = 270(2) \text{ K}$ but the sixth order term in the Landau expansion was shown to be significant when the transition is followed as function of pressure [00B2].

In case of **ferri-clinoholmquistite**, $\square\text{Li}_2\text{Mg}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$, four doublets were used to describe the ^{57}Fe NGR pattern [04I2]. The doublet with the largest quadrupole splitting, i.e. 2.7...2.8 mm/s was assigned to Fe^{2+} at the M1 site, that with $\Delta Q = 2.4 \dots 2.5 \text{ mm/s}$ to Fe^{2+} at the M3 site and that with $\Delta Q = 1.98 \dots 1.75 \text{ mm/s}$ to Fe^{2+} at the M4 site [83H1, 02R2, 03I2, 04I2]. The doublet with the smallest δ and $\Delta Q \approx 0.25 \text{ mm/s}$ was assigned to Fe^{3+}

at the M2 site. According to [04I2] the Fe^{3+} is strongly ordered at the M2, whereas Fe^{2+} is disordered over B and C sites.

We note that in anthophyllites, at 15 K, a broad magnetic hyperfine structure was observed, while at 11 K the hyperfine magnetic structure is more clearly defined [75E1].

For ^{57}Fe NGR studies on gedrite see [89L1].

Calcic amphiboles

The ^{57}Fe NGR studies were also performed on calcic amphiboles as hastingsite [82T1], magnesiohastingsite [73S1, 90H1], pargasite [90H1], kaersutite [90H1], actinolite [66B1, 67B3, 71B2, 71G2], tremolite – actinolite [71B2, 77G1, 79G1, 89S2, 91G1], hornblende [75B1, 76G1, 79G1], etc.

Synthetic **hastingsites**, ideally $\text{NaCa}_2\text{Fe}^{2+}_4\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$, and natural samples having nearly similar compositions, were studied by ^{57}Fe NGR at room temperature [82T1]. All the spectra, both for natural and synthetic samples, are similar and were fitted with four doublets, three for octahedral ferrous and one for octahedral ferric iron – Fig. 29. The synthetic end-member hastingsite was inferred from compositional constraints to have the M1, M2 and M3 sites filled entirely with iron and to have little or no iron in the M4 site. Thus, these samples were considered to provide a test of peak-to-site correspondence. The areas of the Fe^{2+} doublets in synthetic samples, however, were not in the same proportions as the abundances of the sites to which they were conventionally assigned, as would be expected if each doublet uniquely represented the contribution from one single site. On the other hand, the fractional areas of the three Fe^{2+} doublets relative to the total Fe^{2+} absorption normalized to unity, show relatively uniform values of 0.55(3), 0.29(3) and 0.16(2) for the outer, intermediate and inner doublets, respectively, in the synthetic and natural hastingsites as well as for other hornblendes – Table 8. By inference from their chemical analyses, the natural samples were also considered to contain little or no iron in the M4 site. According to [82T1], the ferrous absorption has a characteristic shape, independent of iron concentration, and ferrous doublets cannot be assigned to sites uniquely to yield accurate site population for hornblendes. The observed ferrous area fractions cannot be explained by peak broadening due to an octahedral next-nearest neighbour effect, although it is possible that the presence of neighbouring tetrahedral aluminum may be a factor in perturbing the areas of the ferrous doublets [79G1].

The ^{57}Fe NGR method was used to analyze the **actinolites** [66B1, 67B3, 71B2, 77G1, 79G1]. In [71B2] the spectra were decomposed into three quadrupole-split ferrous doublet assigned to Fe^{2+} ions in M1, M2 and M3 sites. A fourth peak, due to Fe^{3+} , was broad and it was suggested that Fe^{3+} ions were distributed over several sites. The relative enrichment of Fe^{2+} ions of various sites follows the sequence $\text{M1} > \text{M3} \geq \text{M2}$.

In [77G1, 79G1] a ^{57}Fe NGR spectrum of **tremolite** was presented which is unlike from other spectra of calcic amphiboles [63D1, 67B2, 69H1, 71B2, 75B1, 76G1] because it has two well separated Fe^{2+} doublets. As shown in Fig. 30 it bears a striking similarity to the spectra of the cummingtonite – grunerite series – see Fig. 26. Thus, the spectra of the tremolite – actinolite series were reinterpreted in terms of Fe^{2+} in M1 and M3 sites ($\Delta Q \cong 2.8$ mm/s), the M2 site ($\Delta Q \cong 2.2$ mm/s) and M4 site ($\Delta Q \cong 1.8$ mm/s). These assignments indicate that Fe^{2+} prefers to enter the M4 site prior to the M1 and M3 sites, and it discriminates against the M2 site. This is the same ordering scheme found in the cummingtonite – grunerite series. Increasing the Al and Fe^{3+} contents in calcic amphiboles, reduces ΔQ for Fe^{2+} in the M1, M2 and M3 sites from the values determined in the tremolite – actinolite series, and separates the M1 and M3 doublets. It was also suggested that next-nearest-neighbour effects on the already closely-overlapping peaks limit the accuracy of determining site populations from ^{57}Fe NGR method.

The low-calcium actinolites have been studied by ^{57}Fe NGR [05D1]. The ^{57}Fe NGR measurements were performed also on the series tremolite – ferro-actinolite [02I1]. Depending on compositions $\text{Fe}^{2+}(\text{M2})$, $\text{Fe}^{2+}(\text{M1,3})$; $\text{Fe}^{3+}(\text{M2})$, $\text{Fe}^{2+}(\text{M2})$, $\text{Fe}^{2+}(\text{M1,3})$, $\text{Fe}^{3+}(\text{M1,3})$; $\text{Fe}^{3+}(\text{M2})$, $\text{Fe}^{3+}(\text{M1,3})$; $\text{Fe}^{3+}(\text{M2})$, $\text{Fe}^{2+}(\text{M2})$, $\text{Fe}^{2+}(\text{M1,3})$; $\text{Fe}^{3+}(\text{M2})$, $\text{Fe}^{3+}(\text{M2,M1,3})$, $\text{Fe}^{2+}(\text{M2})$, $\text{Fe}^{2+}(\text{M1,3})$; $\text{Fe}^{3+}(\text{M1,3,M2})$, $\text{Fe}^{2+}(\text{M2})$, $\text{Fe}^{2+}(\text{M1,3})$, doublets were reported.

Amphiboles described as **kaersutite**, **magnesiohastingsite** and **pargasite** were also studied by ^{57}Fe NGR spectroscopy. According to [90H1], all the spectra can be decomposed into four doublets corresponding to Fe^{2+} and Fe^{3+} in different crystallographic sites. The two Fe^{2+} subspectra were associated with (M1, M2, M3) as well as M4 octahedral sites [73B1, 88H1]. In case of spectra recorded up to very high counts, the M1, M2 and M3 positions occupied by Fe^{2+} were possible to be distinguished [90H1]. In some investigations only one doublet was evidenced for Fe^{3+} [73B1, 82L2, 88H1]. The correspondence of the doublets to crystallographic sites is a

difficult matter to be analyzed because (M1, M2, M3) sites, corresponding to only one doublet, were expected to be occupied by Fe^{3+} [78L1]. A significant change in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be observed for different natural amphiboles, which reflects different fugacity at the formation conditions. A high $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio reflects a low fugacity at the formation conditions.

The natural pargasites, kaersutites and ferrikaersutites were also analysed by the ^{57}Fe NGR method [99T1].

Sodic-calcic amphiboles

The ^{57}Fe NGR spectra of **winchites** were fitted with one doublet characteristic of Fe^{3+} ions in fairly regular octahedral sites. In **arfvedsonite (juddite)**, in addition to the principal doublet due to Fe^{3+} ions in a regular octahedral site, a small doublet was found [86G1] – Table 8. In winchite all the Fe^{3+} ions were assigned to the octahedral M2 site. In arfvedsonite (juddite), most of the Fe^{3+} ions occur in the M2 site with a small amount on the M1 site. In both amphiboles, the structure refinements indicate nearly total absence of Fe^{3+} or Mn^{3+} ions in the M3 sites. A small amount of Fe^{3+} ions in M1 sites may explain the larger linewidths observed in the clinoamphiboles. The isomer shift and quadrupole splitting in winchite and arfvedsonite (juddite) are in agreement with those found in riebeckite [65G2, 67W1, 69B1].

The ^{57}Fe NGR spectra of synthetic **ferrorichterite** were decomposed in two doublets attributed to Fe^{3+} and Fe^{2+} [74V1]. The potassic ferrorichterite was also studied by ^{57}Fe NGR [97S1]. According to [02R2], for initial refinements of the ^{57}Fe NGR spectra in potassic ferri-ferrorichterites, a quadrupole splitting distribution model with two generalized sites f_2 (for Fe^{2+}) and f_3 (for Fe^{3+}) was chosen. Approximate refinements can be obtained with one ferric ($\Delta Q = 0.42$ mm/s) and two ferrous ($\Delta Q = 2.78$ and 2.26 mm/s) components contributing to f_3 and f_2 , respectively. However, a distinct amount of resonance absorption was observed at ≈ 1.1 mm/s, which was indicative for an additional Fe^{2+} component and there also were problems which arise in the assignment of Fe^{2+} to the M sites. Some residual resonance absorption was observed for ferric iron showing that Fe^{3+} occupies more than one M site. The best refinements were obtained using three Fe^{3+} and Fe^{2+} components contributing to f_3 and f_2 , respectively. The most intense Fe^{3+} component with $\Delta Q = 0.45$ mm/s was assigned to the M2 site. The two other Fe^{3+} components with $\Delta Q = 1.17$ and 1.70 mm/s were weak in intensity (2 % and 3 %, respectively) and were assigned to the M3 and M1 sites. The ferrous quadrupole splitting distribution curve is shown in Fig. 31 [02R2]. It exhibits rather well resolved probability density maxima at 2.79, 2.37 and 1.93 mm/s. Since there was no extensive overlap of the three ferrous components of the generalized site f_2 , these were assigned to $\text{Fe}^{2+}(\text{M1})$ with $\Delta Q = 2.77$ mm/s, $\text{Fe}^{2+}(\text{M3})$ with $\Delta Q = 2.31$ mm/s and $\text{Fe}^{2+}(\text{M2})$ with $\Delta Q = 1.80$ mm/s. A ferrous component with weak intensity was attributed to $\text{Fe}^{2+}(\text{M4})$ site. This analysis differs from that given by [97S1]. According to [02R2] their assignment is consistent with polyhedral distortion and gives correct site occupancies. The results obtained in four different samples show that the magnitude of the quadrupole splitting of Fe^{2+} on M1 and M3 sites have a dependency on the ferric iron content, through the mean radius of the M2 site, of the sample [02R2].

Sodic amphiboles

A number of ^{57}Fe NGR studies were performed on **riebeckite** and of its asbestous form **crocidolite** [68B1, 72E1, 80B1, 80S1, 83M2, 84C1, 88B1, 92H2, 92P1, 96V1]. Except the last reference, the paramagnetic spectra have been analysed by at least three major components which were almost unanimously attributed to $\text{Fe}^{2+}(\text{M1})$, $\text{Fe}^{2+}(\text{M3})$ and $\text{Fe}^{3+}(\text{M2})$ species. The quadrupole splittings, ΔQ , at room temperature were found in the ranges 2.86(4), 2.37(5) and 0.44(4) mm/s, respectively – Table 8. Only in [83M2] an alternative interpretation was suggested with a reverse assignment of the two ferrous doublets. In [88B1, 92H2] an additional component was resolved for their low-temperature spectra which was they ascribed to Fe^{3+} in M1 sites; however, the reported ^{57}Fe NGR parameters for this component in the above papers seriously disagree. Thus, for F riebeckite three ferrous doublets in M1, M3 and M2 sites and two ferric doublets occupying M2 and M1 sites were considered [88B1]. Most of the Fe^{3+} is located in M2 site and Fe^{2+} in M1 and M3 sites – Table 8. The ^{57}Fe NGR spectra in crocidolite were later analyzed in terms of three doublets, the one with the smallest quadrupole splitting corresponding to Fe^{3+} and the others to Fe^{2+} . In those cases, where more than three components have been considered, the additional doublets were completely hidden beneath the major absorptions and their relative contributions to the total spectrum seems to be marginal. Hence, their hyperfine parameters cannot be determined to any reasonable precision. [96V1].

The ^{57}Fe NGR spectra at 4.2 K of riebeckite (crocidolite) were interpreted in [83M3] in terms of three superimposed sextet components, in line with their results obtained from paramagnetic spectra. For the two ferrous components, a negative sign for V_{zz} and a small asymmetry parameter η , for the EFG acting at the M1 and M3 sites, were evaluated and interpreted as being due to a pseudo-trigonal deformation of the involved coordinations. In contrast to these findings, [92P1] concluded a positive V_{zz} value from the ^{57}Fe NGR study of a pseudo-single crystal of crocidolite, recorded at room temperature, with different angles between the incident γ -beam and the absorber plane. To explain this apparent discrepancy in sign, the latter authors suggested a reorientation of the EFG's principal axes in passing through the magnetic transition temperature. The temperature dependence of the reduced hyperfine field at the ^{57}Fe nucleus in riebeckite is different from the molecular field prediction [75B3]. According to [75B3], the atomic spins associated with ferric ions are canted at an angle of 29° from the [001] axis and are nearly perpendicular to (121) and $(1\bar{2}1)$. The Fe^{2+} ions predominantly occupy sites M1, M3, and M2 is occupied by Fe^{3+} .

A different type of analysis was made for ^{57}Fe NGR spectra of riebeckite by [96V1]. The ^{57}Fe NGR spectra at 80 K are plotted in Fig. 32. Apart from a gradual increase of the degree of overlap in the central part near $\nu = 0$ mm/s, no drastic changes in the shape were observed as temperature increases. In riebeckite²⁸⁾, at $T \leq 110$ K, three ferrous and one ferric components were resolved. The interpretation of the spectra in terms of three or four specific quadrupole doublets did not uncover a satisfactory global behaviour of the various ^{57}Fe NGR parameters. As result, all paramagnetic ^{57}Fe NGR spectra obtained for the riebeckites were described by a model-independent quadrupole splitting distribution for the ferrous component with a superimposed single Lorentzian-shape doublet for the Fe^{3+} site. The ΔQ for Fe^{2+} consists of 50 values with fixed upper limit of 3.70 mm/s and lower limit depending on temperature (1.25 mm/s for $T = 80$ K and 0.85 mm/s for $T = 480$ K) and a linewidth $DH = 0.22$ mm/s. The corresponding distribution profiles for the ferrous quadrupole splitting are also shown in Fig. 32. The fraction area of the ferric component for both riebeckites was found to be scattered within the range 0.47(2) and its linewidth within 0.30(2) mm/s. The ΔQ does not depend upon temperature either, and is slightly lower for riebeckite²⁹⁾, i.e. 0.44(1) mm/s versus 0.48(1) mm/s for riebeckite²⁸⁾. The calculated ferrous histograms, $P(\Delta Q)$, are multimodal and the distinct maxima were associated to different iron sites, their respective quadrupole splitting being distributed as a result of slightly different chemical environments. The obtained profiles were analyzed as three distribution functions (D1, D3, D4) for riebeckite²⁹⁾ and four (D1, D2, D3, D4) for riebeckite²⁸⁾, at $T < 250$ K. Beyond that point the weak component D3 becomes entirely obscured by the major D1 component and therefore remains irresolvable. The positions of ΔQ maxima and the fractional area with respect to the total ferrous absorption are given in Table 8. The D1, D2 and D3 can be attributed to Fe^{2+} at M1, M2 and M3 positions, respectively. The component D4 has $\Delta Q = (1.85 \dots 1.89)$ mm/s at 80 K, which is very close to that of the M4 coordination in actinolites [77G1, 85S1] and in cummingtonites [88L1]. It was therefore suggested that D4 is due to the $\text{Fe}^{2+}(\text{M4})$ species. The ^{57}Fe NGR spectra at 4.2 K are shown in Fig. 33. The Fe^{3+} component is relatively sharp ($\cong 0.4$ mm/s) for both riebeckites^{28,29)}, but broadens significantly as the temperature rises, indicative of hyperfine field distribution. The distribution of B_{hf} values were explained by the sensitivity of ferrous and ferric hyperfine fields upon structural and compositional fluctuations. Also, the magnitudes of the dipolar- and orbital-field contributions, which are both of major importance in the case of Fe^{2+} , are strongly affected by local site distortions and hence fluctuations on these distortions give rise to varying hyperfine field strengths. The 4.2 K spectrum of riebeckite²⁸⁾ was fitted with a superposition of two distributed hyperfine fields, one for Fe^{3+} and a global one for Fe^{2+} since it was not found feasible to resolve the different Fe^{2+} components due to strong overlap combined with the weak contributions of the M2, M3 and M4 sites to overall absorption. This implies that the numerical interpretation of the spectra can only give some conclusive information about the magnetic properties of Fe^{3+} cations and of the dominant contribution of Fe^{2+} cations on M1 site. The obtained distribution profiles $P(B_{\text{hf}})$ are given in Fig. 33 and the relevant parameters are listed in Table 8. The relevant parameters for Fe^{2+} primarily characterize the M1 site, namely $B_{\text{hf}}^{\text{m}} = 16.1$ T, $\Delta Q = 3.11$ mm/s and $V_{zz} < 0$. In case of riebeckite²⁹⁾ the spectrum was fitted with one hyperfine field distribution for Fe^{3+} and two for Fe^{2+} . The two weak high-field maxima in $P(B_{\text{hf}})$ for Fe^{2+} in riebeckite²⁸⁾ – Fig. 32 – were believed to be artifacts [96V1]. The other two Fe^{2+} maxima in riebeckite²⁹⁾ were attributed to M1 ($B_{\text{hf}}^{\text{m}} = 18.9$ T) and M3 ($B_{\text{hf}}^{\text{m}} = 9.8$ T) sites. The $\text{M4}(\text{Fe}^{2+})$ component, found in the paramagnetic spectra, was not resolved for the magnetically split spectrum. Both silicates exhibit negative ferrous V_{zz} values. The $^{57}\text{Fe}^{3+}$ hyperfine fields are 54.8(2) T for both riebeckites. The temperature dependences of the isomer shifts – Fig. 34 – can be described by

$\delta T) = \delta_i + \delta_{\text{SOD}}(T)$, where δ_i is the intrinsic isomer shift and δ_{SOD} is the second-order Doppler shift. The temperature dependences of ferrous quadrupole splittings could not be explained in terms of the point charge model and assuming a temperature independent energy level scheme for the ^5D term. It was suggested that a gradual change with temperature of the orbital-level splittings takes place. All calculations yielded a positive sign for the principal component of the electric field gradient.

The riebeckite – ferri-clinoholmquistite join was studied by ^{57}Fe NGR [03I2]. The ^{57}Fe NGR spectrum of ferri-clinoferroholmquistite was decomposed in three lines: $\text{M1}(\text{Fe}^{2+})$, $\text{M3}(\text{Fe}^{2+})$ and $\text{M2}(\text{Fe}^{3+})$. For the other samples four doublets were considered. A small and significant amount of Fe^{2+} occurs at the M4 site along join.

For natural magnesio-arfvedsonite, a 5 doublets fit was made by considering 3Fe^{2+} and 2Fe^{3+} doublets (symmetrical) [87H1]. One weak Fe^{3+} doublet was attributed to the T site. In arfvedsonite the spectra were decomposed in 4 doublets (Fe^{3+} and 3Fe^{2+} doublets) – Table 8 [96S1].

The ^{57}Fe NGR studies of natural sodic amphiboles suggest that Fe^{3+} is concentrated in the M2 site, whereas Fe^{2+} is ordered in M1 and M3 sites [70E1]. Aluminous sodic amphiboles characteristically display a $\text{Fe}^{2+}/\text{Mg}^{2+}$ fractionation where M3 is enriched in ferrous iron relative to M1; the converse relationship seems to hold for iron-rich analogues [70E1]. Heat treatment of iron-bearing sodic amphiboles in air at $705(2)^\circ\text{C}$ results in rapid loss of hydrogen and concomitant increase in the ferric/ferrous ratio. To the extent that Fe^{2+} ions are available in M1 and M3 sites, electrons are transferred to adjacent bonded hydroxyls, allowing neutralization and expulsion of hydrogen [70E1].

In [92L1] the correlation between ΔQ of Fe^{2+} ions and the distortion of their octahedral coordination in chain silicates were studied. It was found that ΔQ initially increases very steeply with increasing distortion parameters and subsequently shows a moderate lowering. The observed correlations were discussed in terms of the crystal field model.

For arfvedsonite see previous section.

For ^{57}Fe NGR studies on amphiboles see also:

Anthophyllite [66B2, 67B3, 73B1, 74S2, 77S1, 78S1, 80S1, 98I2]; Holmquistite [73L1, 81L1, 02B1]; Cummingtonite [66B2, 67B2, 71B1, 71H1, 72G1, 73B1, 80S1]; Grunerite [66B2, 67B2, 71H1, 73B1, 73K1, 79G1]; Manganocummingtonite (tirodite) [67B2, 77H1]; Dannemorite [73B1]; Tremolite [77G1, 79G1, 91C1]; Actinolite [67B3, 71B2, 78T1, 79G1]; Edenite [69H1]; Pargasite [70R1, 79G1]; Hastingsite [73S1]; Hornblende [69H1, 71B2, 75B1, 75B2, 76G1, 78T1]; Kaersutite [75H1]; Oxykaersutite [75H1]; Richterite [72V1]; Winchite [78T1]; Kataphorite [73L2, 75L1]; Glaucophane [69B1, 70E1, 77S1]; Riebeckite [69B1, 70E1, 73B4, 80S1]; Arfvedsonite [73B4, 75A2, 76L1]; Crossite [69B1, 70E1, 73B4]; Amphiboles [67B1, 78T2, 92H2, 98L1]. – For a review paper on ^{57}Fe NGR in amphiboles see [99C1].

8.1.4.3.5 Nuclear magnetic resonance (NMR) data

The cation order-disorder of tetrahedrally and octahedrally-coordinated cations in **pargasite** was analyzed by NMR and IR studies [87R2, 94W1, 95J1, 95H2, 95O1, 95O3, 98W1]. In [87R2], by using IR studies of pargasite, was concluded that octahedrally-coordinated trivalent cations (Al, Cr, Ga, Sc, In) were significantly disordered with Mg over the M(1, 2, 3) sites of the octahedral strip in OH-bearing pargasites but relatively ordered at the M2 site in F-bearing pargasites. The ^{29}Si MAS NMR spectra on scandium-fluor pargasite $\text{NaCa}_2(\text{Mg}_4\text{Sc})(\text{Al}_2\text{Si}_6)\text{O}_{22}(\text{OH},\text{F})$ were compatible with substantial Si and Al disorder over the tetrahedrally-coordinated T1 and T2 sites, but the authors [87R2] cautioned that their interpretation was not conclusive owing to the complex spectrum overlap and the unknown effect of octahedral-cation variation on the spectra (NMR and IR). A similar observation concerning the degree of ordering of cations was made in the binary series of fluor hydroxy-pargasite with $\text{M} = \text{Al}^{3+}$ in the octahedral site [85M2]. A systematic decrease in the Mg_2Al Raman absorption (corresponding to non- $\text{M2}^{[6]}\text{Al}$) with increasing F content was observed suggesting progressive ordering of Al onto M2 [85M2]. In [94W1] synthetic pargasite $\text{NaCa}_2(\text{Mg}_4\text{Al})(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$ was characterized by multinuclear NMR and IR methods. Two aspects of ordering were considered: (1) $^{[4]}\text{Al}$ ordering over T1 and T2 sites and (2) $^{[6]}\text{Al}$ ordering over the M1, M2, M3 sites. The ^{29}Si spectra show the presence of 5 lines which were attributed to different Si NNN environments. The ^{27}Al MAS NMR spectra show three peaks at 68.5, 8.4 and -5 ppm – Table 9. The 68.5 ppm peak corresponds to $^{[4]}\text{Al}$, the other peaks were attributed to $^{[6]}\text{Al}$ (8.4 ppm to Al in M1 or M3 and -5 ppm to Al in M2). The ^1H MAS NMR spectrum shows two proton NNN environments corresponding to resonances at 0.2 and 1.2 ppm. In addition, the IR spectra show peaks at 3711 and 3678 cm^{-1} due to $\text{Mg}_3\text{-OH}$ and $\text{Mg}_2\text{Al-OH}$ configurations [87R1, 94W1]. The analysis of the MAS NMR

spectra was consistent with $1.5\text{Mg} + 0.5\text{Al}$ on M2 and $0.5\text{Mg} + 0.5\text{Al}$ on M3 sites, ^{41}Al being ordered onto T1 sites without Al avoidance (Al-O-Al linkages being allowed). In [94W1] it thus was concluded that there was disorder of Al and Mg over the M2 and M3 sites but that Al occurred only on the T1 tetrahedral site. The ^{27}Al MAS NMR peak ratios were shown to give a much higher $^{41}\text{Al}/^{61}\text{Al}$ value than expected, from the ideal chemistry (supported by electron microscope analysis) of the synthetic pargasite they studied. It was also suggested that quadrupolar effects for ^{27}Al may be responsible for the abnormally low intensity of the ^{61}Al signal. Later on, it has been reported that MgAl_2OH and Al_3OH configurations do not appear and there is no long-range ordering [95H2]. Thus, the MAS NMR study by [94W1] does not resolve the question of Al ordering over the M1, M2 and M3 sites in synthetic pargasite. The results of [94W1] were also commented by [95H2]. By ^{27}Al MAS NMR spectroscopy [97J1] it was shown that Al in **aluminous tremolite** is always present in the M1, M3 sites, as well as the M2 site, but partitioned among these sites in ways that were not clearly resolved. In addition, ^{29}Si MAS NMR data indicate that Al substitutes essentially equally into both the T1 and T2 sites. The synthetic aluminous tremolite, $\text{Ca}_{1.8}(\text{Mg}_{4.8}\text{Al}_{0.4})(\text{Si}_{7.6}\text{Al}_{0.4})\text{O}_{22}(\text{OH})_2$, was further analyzed by ^{27}Al MAS NMR and triple-quantum (3Q) MAS NMR spectra [00H2]. The fitted NMR and FTIR spectra showed that ^{61}Al occurs at the M2 site and at the M1 or M3 sites. Finally, the occupancy at the M2 and M3 sites was presumed. The fine structure present in the FTIR spectra indicates that they are also affected by NNN interactions. There are two types of NNN arrangements: (1) SiSi or SiAl at adjacent T1T1 dimers; (2) permutation of Mg/Al over M2M2M3 sites. Discounting those arrangements unlikely on bond-valence grounds, there were two arrangements that give rise to five distinct bands in the IR spectra (sect. 8.1.4.3.9). The main conclusions of the study were: (1) IR spectra in the principal OH- stretching region can be affected significantly by NNN effects; (2) the small number of bands due to NNN effects indicates that amphiboles show strong short-range order.

The ^{29}Si MAS NMR studies were also performed on **richterite**, **pargasite** and **fluor edenite** [98W1]. These allowed to quantify the distribution of Al and Si over T1 and T2 sites. We note that X-ray studies indicate that ^{41}Al is highly ordered at T1. This distribution has been explained as arising from the bonding requirements of the very underbonded O4 atom, which is bonded to T2, M2 and M4 cations, so that a strong preference exists for a tetravalent element (Si^{4+}) at T2 over a trivalent element (Al^{3+}). Seven configurations are possible in amphiboles with ^{41}Al : $\text{T1} = \text{Q}^3(0\text{Al})$, $\text{Q}^3(1\text{Al})$, $\text{Q}^3(2\text{Al})$, $\text{Q}^3(3\text{Al})$ and $\text{T2} = \text{Q}^2(0\text{Al})$, $\text{Q}^2(1\text{Al})$, $\text{Q}^2(2\text{Al})$. Here $\text{Q}^3(n\text{Al})$ refers to an Si at T1 with $n\text{Al}$ NNNs and $\text{Q}^2(n\text{Al})$ refers to an Si at T2 with $n\text{Al}$ NNNs. Some ^{29}Si MAS NMR spectra of **richterites** are given in Fig. 35 [98W1]. Since richterites have only Si in tetrahedral sites, ^{29}Si peaks were referred for brevity as Q^3 and Q^2 rather than $\text{Q}^3(0\text{Al})$ and $\text{Q}^2(0\text{Al})$. Thus Q^3 corresponds to T1 and Q^2 to T2. The single Q^3 peak of tremolite at -92 ppm is split in the richterite spectrum into two peaks of equal intensity. The Q^2 peak is unsplit. The preferential splitting of T1 was explained in terms of ordering of the A cation at Am site. The fluor edenite and pargasite spectra contain five peaks. The effect of M4 and A site chemistry upon the richterite spectra were used for assignment of these peaks for pargasite and fluor edenite – Table 9. The long-range ordering of Al and Si over T1 and T2 sites in fluor edenite synthesized at 2 kbar and 1000°C and pargasite synthesized at 1 kbar and 930°C has been calculated from their ^{29}Si MAS NMR spectra assuming that the Al avoidance rule operates. From the intensities of the $\text{Q}^2(2\text{Al})$, $\text{Q}^2(1\text{Al})$ and $\text{Q}^2(0\text{Al})$ peaks an equation was obtained that allows the extent of long-range Al-Si order to be calculated from ^{29}Si MAS NMR spectra. The spectrum of fluor edenite is consistent with all ^{41}Al being at T1 with maximal short-range disorder within the constraints of Al avoidance. The pargasite spectrum is more complex because there is a probable peak coincidence of $\text{Q}^2(1\text{Al})$ and $\text{Q}^3(2\text{Al})$ at -82 ppm that must be considered. The presence of a $\text{Q}^3(0\text{Al})$ peak in the pargasite spectrum indicates that some long-range disorder exists, and this implies that $\text{Q}^3(2\text{Al})$ groupings also occur. The calculated extent of long-range disorder in pargasite is 55(10) %, a value in agreement with X-ray data for natural amphiboles extrapolated to $^{41}\text{Al} = 2$ apfu at 900°C [95O2]. The different Al-Si long-range ordering behaviour of fluor edenite and pargasite was explained in terms of bond valence requirements of O4. At high temperatures, configurational entropy becomes an important stabilizing factor, and structural distortion around O4 in pargasite and hornblende allows Al into T2, provided that O4 is coupled to Al at an adjacent M2 site, as in pargasite. The results for fluor edenite which has no ^{61}Al show that the low O4 bond strength sum of the $^{29}\text{Al}^{M2}\text{Mg}^{M4}\text{Ca}$ configuration cannot be accommodated by sufficient structural relaxation, even at 1000°C . Coupling between Al at M2 and T2 is an important control on Al-Si long-range order-disorder.

In [99S2] amphiboles were studied by the ^{29}Si , ^{71}Ga , ^{23}Na MAS NMR method along the **gallian-fluor** analogue of the **tremolite – pargasite** join, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2 - \text{NaCa}_2[\text{Mg}_4\text{Ga}][\text{Ga}_2\text{Si}_6]\text{O}_{22}\text{F}_2$ in order to identify the extent of Ga and Si ordering in tetrahedral sites. In Ga-free samples only two ^{29}Si peaks were observed in the spectrum at -92.4 and -87.8 ppm, assigned to Si in T1(Si_3) and T2(Si_2) sites [83S1, 99S2] – Fig. 36. The relative

central areas have the ratio 49.5/50.5 for peaks at -92.4 and -87.8 ppm, respectively. The inequality of peaks widths was not observed for OH-bearing amphiboles [97J1] and thus the difference in peak width was attributed to dipolar or spin-spin coupling to adjacent magnetic ^{19}F nuclei, even though Si is not directly bonded to the anion O3 site (OH or F^-). With addition of Ga, the two peaks decrease in relative intensity and become broader. There are new peaks which were interpreted as being due to Si in T1 (Si_2Ga) at about -84 ppm, T2 (SiGa) at -80 ppm at T2 (Ga_2) at -76 ppm. The variation in the adjacent octahedral cation distributions would cause broadening and distortion of the peaks due to overlapping peaks that cannot be individually resolved as for example in T1(Si_3) peak at -92.4 ppm. The ^{23}Na MAS NMR spectra, are all similar, with one broad peak at about -23 ppm. There is a slight shift in peak position from -23 ppm from $\text{Na}_{0.2}\text{Mg}_{4.8}\text{Ga}_{0.6}\text{Si}_{7.6}\text{O}_{22}\text{F}_2$ to -27 ppm for $\text{NaCa}_2\text{Mg}_4\text{Ga}_3\text{Si}_6\text{O}_{22}\text{F}_2$. The ^{71}Ga MAS NMR spectra show a single peak at about 230 ppm attributed to tetrahedrally-coordinated site and one octahedrally-coordinated Ga doublet at 40 ppm. The above data agree with models that allow Ga on both T1 and T2 sites, which support also the cation distribution from Rietveld refinement of X-ray data. It was not possible to discriminate between cation distribution models that allowed completely random mixing of Ga and Si vs. the presence of Ga-O-Ga avoidance on tetrahedral sites. The ratio of Ga in octahedral and tetrahedral sites was overestimated from the analysis of NMR spectra due to the large quadrupole effects of the asymmetrical octahedral site. The ^{23}Na MAS NMR spectra of tremolite and Ga pargasites shift to higher frequency and increasing peak width with Ga content and this was related to the reduction in magnetic shielding produced by substitution of Ga for Si and Mg [99S2].

The phase transition in $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ amphibole, which contain one excess OH per formula unit, from C2/m to $\text{C}\bar{1}$ (or C1) type structure at $(100\ldots 160)^\circ\text{C}$ was studied by ^{29}Si , ^{23}Na and ^1H MAS NMR [96L1]. The ^{29}Si MAS NMR spectrum at room temperature has 9 resolved peaks – Table 8 – Fig. 37a. The spectrum at 100°C has at least eight peaks and those at 120°C and 130°C six peaks. The spectrum at 150°C has two distinct sets of peaks corresponding to $\text{Q}^3(\text{T1})$ and $\text{Q}^2(\text{T2})$, each set comprising at least three peaks. At 160°C there are five peaks and at 170°C only four. The 180°C and 240°C spectra consist of two intense peaks, one $\text{Q}^3(\text{T1})$ and one $\text{Q}^2(\text{T2})$, at -85.6 and -89.2 ppm, respectively. The ^1H MAS NMR spectrum shows systematic changes in peak intensity and chemical shift with temperature. The ^{23}Na MAS NMR spectra of $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ show a strong peak at -20 ppm essentially unaltered during heating from 20 to 240°C , while the quadrupolar features with maxima at ≈ 0 and -40 ppm show systematic changes on heating – Fig. 37b. The spectra were correlated with the number of Si tetrahedral sites. The results obtained by the analysis of the spectra were: (a) confirmation that the monoclinic polymorph has space group C2/m , (b) consistence with a triplet superstructure for the triclinic polymorph, (c) suggestion that the phase transition may be caused by a positional disordering of the excess proton, which interacts with A-site Na to cause displacement of the latter from the special position at $2/\text{m}$ onto general position.

For ^1H NMR in hornblende see [77K1].

8.1.4.3.6 Electron paramagnetic resonance (EPR) data

For EPR of Mn^{2+} in tremolite see [66B3].

8.1.4.3.7 Heat capacity

The temperature dependences of the heat capacities for $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ and $\text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2$ are plotted in Fig. 38a [85K1, 85K2]. In the temperature range $298\ldots 700$ K the heat capacities may be described by: $C_p = 3287 - 1.628 T - 1.885 \cdot 10^7 T^{-2} - 41859 T^{-0.5} + 6.527 \cdot 10^{-4} T^2$ [J/mol K] for $\text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2$ and $C_p = 2713 - 0.9630 T + 1.331 \cdot 10^7 T^{-2} - 33473 T^{-0.5} + 2954 \cdot 10^{-4} T^2$ [J/mol K] for $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. The entropy change $S_{298}^\circ - S_0^\circ = 538.9(27)$ J/mol K for $\text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2$ and $537.0(27)$ J/mol K for $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. A Schottky heat capacity anomaly was observed at low temperatures – Fig. 38b.

The temperature dependence of the heat capacity for glaucophane is plotted in Fig. 39. At $T > 298$ K the data can be described by the relation $C_p = 11.4209 \cdot 10^2 - 40.3212 \cdot 10^2/T^{1/2} - 41.00068 \cdot 10^6/T^2 + 52.1113 \cdot 10^8/T^3$ [J/mol K] [89G1].

The heat formation on the pseudobinary join from tremolite $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2$ to magnesiohornblende, $\text{Ca}_{1.8}\text{Mg}_{4.2}\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$ was studied [94S1]. The calorimetric data indicate that the energy change associated with substitution $^{[6]}\text{Mg}$, $^{[4]}\text{Si} \leftrightarrow ^{[6]}\text{Al}$, $^{[4]}\text{Si}$ is small.

For heat capacity in tremolite see also [63R1].

8.1.4.3.8 Electrical resistivity

In [65L1] the electrical resistivity of **riebeckite (crocidolite)** was measured along the fibre direction. During heating, progressive oxidation resulted in systematically different behaviour in repeated experiments, with activation energies $E_a = 0.69$ and 0.33 eV. The resistivity across the fibre direction was very high. In [73T1] activation energies $E_a = 0.54$ eV along the [001] axis and 0.57 eV along [010] were determined for **hornblende**, with a molar concentration $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg}^{2+}) \cong 0.19$ – Table 10. The charge transport was assumed to be controlled by electron hopping between Fe^{2+} and Fe^{3+} . The dielectric constant of fibrous **tremolite** was found to be frequency-dependent [76V1]. A minimum and maximum at higher temperatures were ascribed to a breakdown of amphibole. The resistivity data for some amphiboles were also reported in [82P1]. For $T \leq 600^\circ\text{C}$, measurements along [001] give activation energies $E_a = 0.35 \dots 0.40$ eV for riebeckite and $E_a \cong 0.65$ eV for tremolite.

The $\log \sigma$ versus T^{-1} plots in case of **arfvedsonite** ($\text{Na}_{0.29}\text{K}_{0.71}$)-($\text{Fe}^{3+}_{0.92}\text{Fe}^{2+}_{3.60}\text{Ti}_{0.09}\text{Al}_{0.15}\text{Mg}_{0.11}\text{Mn}_{0.13}\text{Ca}_{0.16}\text{Na}_{1.84}$)($\text{Si}_{7.83}\text{Al}_{0.17}$) $\text{O}_{22}(\text{OH},\text{F},\text{O})_2$ is plotted in Fig. 40. Two different semiconducting charge transfer mechanisms were observed, which are due to volume conduction for measurements parallel and perpendicular to the [001] direction. According to [96S1] they arise probably from conduction mechanisms related to lattice defects, both with an activation energy, $E_a \cong 0.4$ eV – Table 10. The extrapolated dc conductivity, for a fixed temperature, along [001] is about 5...6 times higher than that perpendicular to [001]. From thermopower data (positive and temperature independent) it follows that hole conduction occurs, and a hopping-type charge transport is acting, probably affected by electron hopping $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Possible charge transfer paths were analyzed. It was concluded that the main fraction of Fe^{2+} and Fe^{3+} takes part in long-range charge transport.

The electrical resistivities of **calcic magnesiohornblende**, **calcic-ferro-edenitic hornblende** and **calcic kaersutite** were analyzed [00S1]. The dc resistivity is much smaller for an amphibole with high iron content than for the samples having lower iron concentrations. The temperature dependence of resistivities was described by the relation $\rho = \rho_0 \exp(E_a/k_B T)$. The activation energies E_a were between 0.48 and 1.06 eV. The experimental data, for temperatures $T \leq 600^\circ\text{C}$, are compatible with a charge transport mechanism due to electron hopping between Fe^{2+} and Fe^{3+} . Above 600°C , dehydrogenation and/or beginning amphibole decomposition obviously alter the conduction mechanism [00S1].

8.1.4.3.9 Infrared and Raman spectroscopy

The hydroxyl group in amphibole structure occupies the apex of a pseudotrigonal bipyramid, the base of which is formed by three cations at two M1 and M3 sites. The OH vector lies along the a^* , with the OH bond projecting into the large cavity about the A site. The role of cation occupancy of the M1 and M3 and A sites on the position of the OH infrared bands were studied [68B1, 66H1, 70B3, 81H1, 81L1, 81L2, 82L1, 83H1, 87R2, 89R1, 93D1, 93R1, 96D1, 96H1, 97H1, 98D1, 98G2, 99D1, 99G1, 00H2, 02I1, 03I3, 03J1]. In [66B1] the first overtone of the OH bands was studied in spectra, obtained on single crystals of Fe-Mg and Ca amphiboles, and it was concluded that the OH dipole is aligned close to the a^* -direction. The same OH orientation was reported in alkali amphiboles [66H1].

Infrared OH-stretching bands in orthorhombic (Pnma) **holmquistite**, and the **anthophyllite – gedrite** series were investigated [70B3, 81L1, 81L2, 82L1, 03I3]. The spectra consist of four bands labeled A, B, C, D and were assigned to local configurations M1M1M3-O3H-A, where $A = (\square, \text{Na})$ and $\text{M1M1M3} = \text{MgMgMg}$, MgMgFe_p , MgFeFe_p and FeFeFe for A, B, C, D bands respectively. The symbol p denotes that the configuration includes all permutations of the cations listed. Thus, $\text{MgMgFe}_p = {}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Mg}^{\text{M3}}\text{Fe} + {}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Fe}^{\text{M3}}\text{Mg}$. The two configurations ${}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Mg}^{\text{M3}}\text{Fe}$ and ${}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Fe}^{\text{M3}}\text{Mg}$ stereochemically are fairly similar in terms of the way in which they affect the principal OH-stretching frequency of the locally associated OH group and hence give rise to two bands that have very similar stretching frequencies. This results in a single envelope, labeled B, consisting of two closely overlapping bands. The situation is similar for the band C. In bands (envelopes) B and C, there are actually two component bands, hence the envelope is broader than for a single band. The resulting broadening is known as a **permutation broadening** [74S1]. Configurations MgMgMg and FeFeFe each give rise to only a single band. The four principal OH-stretching bands were observed in holmquistite without any fine structure [81H1] and in the anthophyllite – gedrite series with some shoulder bands [70B3, 81L2, 82L1]. As discussed in Sect. 8.1.4.3.1, there are two crystallographically distinct double chains of tetrahedra in Pnma amphiboles (A, B)

and two crystallographically distinct OH sites (O3A, O3B). The distinct OH groups should, in principle, give rise to two sharp OH-stretching peaks of approximately equal intensity [83H1]. In [03I3] was reported on fine structure observed in principal OH-stretching bands in orthorhombic amphiboles (holmquistite and anthophyllite – gedrite). Up to four well resolved OH-stretching bands from A_A at 3662 cm^{-1} to D_B at 3611 cm^{-1} in holmquistite – Fig. 41 – and from A_A at 3670 cm^{-1} to D_B at 3619 cm^{-1} in anthophyllite – gedrite, respectively, were shown. The fine structure can be ascribed to the O3A-H1- and O3B-H2-stretching bands, respectively. The B chain is more rotated than the A chain and the hydrogen bond to the bridging anion(s) of the B chain is stronger than the hydrogen bond to the bridging anions of the A chain. As a result, there is a shift of the frequency of the principal stretching bands by $\approx 5\text{ cm}^{-1}$ to lower frequency, and this allows resolution of the two bands in the IR spectrum.

For IR spectra of ferri-clinoholmquistite in the OH-stretching region see [04I2].

The IR spectra of cummingtonite with $x = (\text{Fe} + \text{Mn})/(\text{Fe} + \text{Mn} + \text{Mg}) = 0.50$ provide evidence for phase transition $C2/m - P2_1/m$ at 1.21 GPa [98Y1]. A distinct splitting of stretching bands results from an increase from one to two nonequivalent OH positions.

In [00H2] was shown that IR spectroscopy in the OH-stretching region is a valuable tool in understanding particular features of Al incorporation in synthetic **tremolites** $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{Ca}_{1.8}(\text{Mg}_{4.2}\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$. In the amphibole structure, as above mentioned, the OH group is directly bonded to two M1 and one M3 cations, and the H atom projects into the A site cavity in which the A site may be occupied or vacant (\square). The NN configuration directly around the OH group may be represented by the general symbol $\text{M1M1M3-OH-}^A\text{A}$. For ordered end-member tremolite and pargasite, the symbols are $\text{MgMgMg-OH-}^A\square$ and $\text{MgMgMg-OH-}^A\text{Na}$, respectively. The M1M1M3 cluster is surrounded by two M2 and one M3 octahedra within the octahedral sheet and two T1 tetrahedra within the tetrahedral double chain. The triplet of cations at M2M3M2 and the doublet at T1T1 are thus NNN cations to O3. The NNN configuration around the O3 group may be denoted by adding the cation doublet and triplet to the general symbol introduced above: $\text{M1M1M3-O3-}^A\text{A:T1T1-M2M3M2}$. Note that the NN and NNN octahedra within the octahedral sheet have pseudo-trigonal point symmetry. For ideally ordered end-member tremolite and pargasite, the configuration symbols are $\text{MgMgMg-OH-}^A\square$: SiSi-MgMgMg and $\text{MgMgMg-OH-}^A\text{Na}$: SiAl-MgMgAl , respectively. The IR spectra in the principal OH-stretching region of the tremolite – magnesiohornblende series are plotted in Fig. 42. The end-member tremolite spectrum – Fig. 42a consists of a sharp absorption band at 3675 cm^{-1} . This band was assigned to the vibration of an O-H dipole bonded to three $^{[6]}\text{Mg}$ cations and directed along a^* toward an empty A site $\text{MgMgMg-OH-}^A\square$: SiSi-MgMgMg . Both in natural and synthetic tremolites this band is asymmetric suggesting the presence of a second component at around 3670 cm^{-1} . This second band was attributed [96H1, 97H1] to Mg at M4 (a cummingtonite component) that seems ubiquitous in synthetic tremolite [87J1, 91A1, 93P2, 94M1, 98G2, 99G1]. The introduction of Al into the tremolite structure correlates with the appearance of two absorption features (B, C) – Figs. 42b-e. The B ($3655 + 3642\text{ cm}^{-1}$) and C ($3624 + 3608\text{ cm}^{-1}$) are doublets which increase in magnitude with Al content. The sharp band in tremolite (3675 cm^{-1}) broadens and shifts to slightly lower wavenumber. The band splitting in IR spectra in the principal OH-stretching region was attributed to the variation in NNN cation occupancy. In end-member tremolite the band A is extremely sharp and, in amphiboles with significant Al, it is split in two components. The bands denoted in Fig. 42 were attributed to various NNN configurations: A(3675 cm^{-1}) to $[\text{MgMgMg}]\text{-SiSi-MgMgMg}$; A'(3671 cm^{-1}) to $[\text{MgMgMg}]\text{-SiSi-MgMgAl}$; B(3655 cm^{-1}) to $[\text{MgMgMg}]\text{-SiAl-MgMgMg}$; B'(3642 cm^{-1}) to $[\text{MgMgMg}]\text{-SiAl-MgMgAl}$; B''(3642 cm^{-1}) to $[\text{MgMgAl}]\text{-SiSi-MgMgMg}$; C(3625 cm^{-1}) to $[\text{MgMgAl}]\text{-SiSi-MgMgAl}$; C(3625 cm^{-1}) to $[\text{MgMgAl}]\text{-SiAl-MgMgMg}$ and C'(3608 cm^{-1}) to $[\text{MgMgAl}]\text{-SiAl-MgMgAl}$. We note that the configurations $\text{M2M3M2} = \text{MgMgAl}$ and MgAlMg are indistinguishable. By analogy with crystal structure refinement results on natural amphiboles, $^{[6]}\text{Al}$ occupancy of M2 and M3 was presumed (Sect. 8.1.4.3.5). Thus, the fine structure present in FTIR indicates that they are affected by NNN interactions. There are two types of NNN arrangements: (1) SiSi or SiAl at adjacent T1T1 dimers, (2) permutation of Mg/Al over M2M2M3 sites. The IR spectra were concluded to be affected significantly by NNN effects. The small number of bands due to NNN effects suggest that amphiboles show short-range order.

The **tremolite – ferro-actinolite** series crystallize in a monoclinic-type structure. In this case there are four chemically distinguishable NN configurations: A(MgMgMg), B(MgMgFe^{2+}), C($\text{MgFe}^{2+}\text{Fe}^{2+}$), D($\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}$) [66S1]. The fine structures in the principal OH-stretching region is also affected by NNN cations at the M2, M4, T1 and A sites [99D1, 00H2]. As already mentioned, there are two tetrahedrally-coordinated sites in $C2/m$

amphiboles (T1, T2). Normally, tetrahedrally-coordinated Al is strongly ordered at the T1 site [95O1, 95O2]. There is hydrogen bonding between the H atom and the adjacent O7 anion. When O7 is bonded to Si and Al, the hydrogen bond to O7 must be stronger than when O7 is bonded to Si and Si. As the principal OH-stretching frequency is inversely related to the strength of hydrogen bond, the presence of tetrahedrally-coordinated Al gives rise to two bands: a higher frequency band corresponding to ${}^{\text{T1}}\text{Si}^{\text{T1}}\text{Si}$ and a lower frequency band corresponding to ${}^{\text{T1}}\text{Si}^{\text{T1}}\text{Al}$. Thus, OH-stretching bands in the IR region contain information on the chemical composition and short-range order [96H1, 99D1, 00H2]. However, the chemical compositions of the amphibole group are frequently complicated and as a result FTIR spectroscopy has been focused mainly on synthetic silicates [87R2, 89R1, 93D1, 93R1, 96D1, 98D1, 98G2, 99G1]. The fine structure in the principal OH-stretching bands of the natural tremolite – ferro-actinolite series have also been analysed [02I1]. In samples with partially filled A sites, a broad (composite) band was observed at $3725\ldots3680\text{ cm}^{-1}$ – Fig. 43 – and was assigned to two types of configurations (M1M1M3)-OH- ${}^{\text{A}}(\text{Na},\text{K})$: ${}^{\text{T1}}\text{Si}^{\text{T1}}\text{Al}$ in which Al occurs at the T1 site and (M1M1M3)-OH- ${}^{\text{A}}(\text{Na},\text{K})\text{-O}^3(\text{O}^{2-},\text{F},\text{Cl})$. The component corresponding to the first configuration is small because Na and K at the A site are locally associated with Al at an adjacent T1 site. In tremolite, manganian tremolite and Fe^{2+} -poor actinolite, a weak shoulder on the principal A band at $\approx 3669\text{ cm}^{-1}$ (indicated by arrows) was assigned to the configuration ${}^{\text{M4}}\text{Ca}^{\text{M4}}(\text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Na})$: (MgMgMg)-OH- ${}^{\text{A}}\square$: ${}^{\text{T1}}\text{Si}^{\text{T1}}\text{Si}$. Fine structure in the principal bands B(B', B'') and C(C', C'') were observed [02I1]. The higher frequency band B'' was assigned to ${}^{\text{M1}}\text{Fe}^{2+}\text{M}^{\text{M1}}\text{Mg}^{\text{M3}}\text{Mg}$ -OH- ${}^{\text{A}}\square$ and the lower frequency band B' to ${}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Mg}^{\text{M3}}\text{Fe}^{2+}$ -OH- ${}^{\text{A}}\square$. The higher frequency band C' was assigned to ${}^{\text{M1}}\text{Fe}^{2+}\text{M}^{\text{M1}}\text{Fe}^{2+}\text{M}^{\text{M3}}\text{Mg}$ -OH- ${}^{\text{A}}\square$ and the lower frequency band C'' to ${}^{\text{M1}}\text{Mg}^{\text{M1}}\text{Fe}^{2+}\text{M}^{\text{M3}}\text{Fe}^{2+}$ -OH- ${}^{\text{A}}\square$. Some broad OH-stretching bands attributed to (M1M1M3)-OH- ${}^{\text{A}}\square$: ${}^{\text{T1}}\text{Si}^{\text{T1}}\text{Al}$ were observed at $3640\ldots3580\text{ cm}^{-1}$. In amphiboles of the tremolite – ferro-actinolite series that show a substantial B[(MgMgFe $^{2+}$)-OH] band, an OH-stretching band, E ($\approx 3641\text{ cm}^{-1}$) appears near the principal C band ($\approx 3643\text{ cm}^{-1}$) on heat treatment. The shape of band E is similar to that of the original band B, and its local configuration is O^{2-} -(MgMgFe $^{3+}$)-OH. A weak and broad band appears at $\approx 3690\text{ cm}^{-1}$ on heat treatment of some Na-bearing actinolites and was ascribed to the (MgMgMg)-OH- ${}^{\text{A}}\text{Na-O}^{2-}$ configuration [02I1].

The FTIR spectra in the hydroxyl-stretching region of low calcium actinolites are plotted in Fig. 44 [05D1]. For tremolitic amphibole (0.0 Fe apfu), the spectrum was modeled by three component bands at $3674(\text{A})$, $3669(\text{A}')$ and $3664(\text{A}'')$ cm^{-1} . The A, A' and A'' bands were assigned to the configurations CaCa, CaMg and MgMg, respectively in the M4 site. With the addition of iron, bands at $3660(\text{B})$, $3655(\text{B}')$, $3643(\text{C})$, $3638(\text{C}')$, $3625(\text{D})$ and $3620(\text{D}')$ cm^{-1} appear. The B, C and D bands were attributed to Fe substituting for Mg at the two M1 and one M3 sites with configurations MgMgFe, MgFeFe and FeFeFe [66B1]. The B', C' and D' bands were considered as determined by configurations MgMgFe, MgFeFe and FeFeFe, respectively with CaMg or CaFe (for the more Fe-rich samples) in the M4 sites rather than CaCa. The FTIR band intensities were used to determine the amount of Fe at the M1 and M3 (M1,3) sites and to look for short-range order over these sites. The net amount of Fe at the M1, 3 sites is slightly less than the nominal values [05D1].

The IR spectra in the OH-stretching region were also investigated in potassium richterite – tremolite [79H1, 00M1], tremolite – fluoro-tremolite [99R1], richterite – fluoro-richterite [99R1], actinolite [66B1, 70W1, 71B2], tremolite – richterite [98G1], pargasite [96R1, 00R1], tremolite – tschermakite – cummingtonite [03N1], tremolite – pargasite – cummingtonite [03J1], (Na,K) richterite [96S2, 98G1, 01I1], manganian arfvedsonite [01I1], richterite [68B2, 70E1]. For example, the IR spectroscopy was used to analyse the vacancy concentration in synthetic solid solutions **K richterite – richterite – tremolite**, $(\text{K}_x\text{Na}_y\square_{1-x-y})(\text{Na}_{x+y}\text{Ca}_{2-x-y})_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ [00M1]. Two systems of OH-stretching bands were observed. The first band system at wavenumbers $3669\ldots3678\text{ cm}^{-1}$ was attributed to a vacant A site and the second one between 3721 and 3737 cm^{-1} to a filled A site. The fine structures of the bands were attributed to distinct M4 site occupancies by Ca^{2+} , Mg^{2+} and Na^+ . Using pure tremolite as a standard, the vacancy concentration was determined from normalized integral absorbances of the band system at $3669\ldots3678\text{ cm}^{-1}$. The derived vacancy concentrations were consistent with those obtained by electron microscopy. Additional bands at 3659 , 3695 and 3710 cm^{-1} were attributed to triple chains or higher chain multiplicity faults, and from these data the chain multiplicity faults were also determined [00M1].

In case of the **tremolite – tschermakite – cummingtonite** system, three band regions were distinguished at $3664\ldots3676\text{ cm}^{-1}$ (I), $3633\ldots3664\text{ cm}^{-1}$ (II) and $3526\ldots3633\text{ cm}^{-1}$ (III) – Fig. 45 [03N1]. Assuming ${}^{[6]}\text{Al}$ substitution at the M2 and/or M3 and ${}^{[4]}\text{Al}$ at T1, three principal different configurational groups could be assigned as local environments for the proton: (I) only Si^{4+} at T1 and one or two Al^{3+} at M2 and/or M3_{far};

(II) one Al^{3+} at T1 and one to three Al^{3+} at M2 and/or at M3_{far} ; (III) either Al^{3+} at M3_{near} and/or two Al^{3+} on T1 and additional one to four Al^{3+} at M2. It was assumed that these three configurational groups correspond to the three groups of observed bands. The above assumption was quantitatively supported by Monte-Carlo simulations. As mentioned in section 8.1.4.3.1, a model with random distribution at M2 and M3 including Al avoidance at tetrahedral and octahedral sites yielded the best agreement with experimental data [03N1].

The FTIR absorption spectra in the region of hydroxyl stretching frequencies for the joint **tremolite** ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) – **pargasite** ($\text{NaCa}_2\text{Mg}_4\text{Al}_3\text{Si}_6\text{O}_{22}(\text{OH})_2$) – **cummingtonite** ($\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$) were also correlated with the specific cation configurations [03J1]. The extent of short-range order was qualitatively determined by comparing the observed intensities for groups of related bands, corrected for differences in their molar absorptivities to their calculated intensities based on random-mixing probabilities. The intensities corresponding to sodic amphibole configurations are consistently high, tremolite is lowest near the middle of the join and aluminous amphibole configurations crossover from being higher (at low Al contents) to being lower (at high Al content) than expected near the middle of the join. These differences may reflect the presence of deviations in the thermodynamic activities of amphibole components from those predicted on the basis of random-mixing models [03J1].

In **riebeckite**, **magnesioriebeckite** and **glaucothane**, the fundamental bands of OH stretching ($3700\ldots 3600\text{ cm}^{-1}$) were resolved into several absorption peaks, corresponding to different NN cation combinations [70E1].

The IR spectra in α -polarization of natural **tremolites**, **ferro-actinolites** and **grunerites** consist of up to four sharp peaks corresponding to different Fe and Mg occupancy of the two M1 and the M3 positions coordinating OH (i.e. MgMgMg , MgMgFe , MgFeFe , FeFeFe) [66B1, 91S1] – Fig. 46. The intermediate peaks in tremolite (Zillertal) and ferro-actinolite spectra seem to consist of two closely overlapping peaks. This feature was attributed to two slightly different OH environments: $\text{M1M1M3} = \text{MgMgFe}$ and $\text{M1M1M3} = \text{MgFeMg}$. The peak corresponding to two Mg and one Fe can be decomposed in a stronger line at 3661 cm^{-1} and a weaker line at 3658 cm^{-1} . Since the probability of having the Fe ion in an M1 site is twice that of having Fe in the M3 site (assuming random distribution), the 3661 cm^{-1} peak was attributed to $\text{M1M1M3} = \text{MgFeMg}$ and the weaker (3658 cm^{-1}) one to $\text{M1M1M3} = \text{MgMgFe}$. The shoulder on the FeFeMg peak in ferro-actinolite at 3647 cm^{-1} should be due to $\text{M1M1M3} = \text{FeFeMg}$ and the stronger peak at 3647 cm^{-1} to $\text{M1M1M3} = \text{FeMgFe}$. The intermediate peaks in grunerites do not show any splitting. Spectra of the alkali-rich amphiboles consist of broader absorptions, sometimes with overlapping sharper peaks. The broad bands reflect the more diverse local environments for the OH dipole, including partial occupancy of the A site which shifts the absorptions to higher wave numbers [91S1].

The IR studies on amphiboles of **tremolite** – **fluoro-tremolite** series in the principal OH-stretching region show one-mode behaviour, a single band due to a local $\text{MgMgMg-OH}^{\text{A}}\square$ arrangement [99R1]. This behaviour was shown to be consistent with no coupling between NNN O3 anions either through the O3-O3 edge or across the vacant A site cavity. The amphiboles of the **richterite** – **fluoro-richterite** and **potassic richterite** – **potassic fluoro-richterite** series show two-modes behaviour, two bands due to the local arrangements $\text{MgMgMg-OH}^{\text{A}}\text{Na-OH}$ and $\text{MgMgMg-OH}^{\text{A}}\text{Na-F}$ (and their K equivalents). This behaviour was shown to be consistent with coupling between NNN O3 anions across the filled A site cavity through Na or K that occupies the A site. The variation in infrared band intensities was consistent with complete short-range disorder of OH and F in the synthetic amphiboles of richterite – fluoro-richterite and potassic richterite – potassic fluoro-richterite series [99R1].

The variation in relative intensities in the FTIR spectra of OH-F **synthetic pargasites** $\text{NaCa}_2(\text{Mg}_{4+x}\text{-Al}_{1-x})(\text{Si}_{6+x}\text{Al}_{2-x})\text{O}_{22}(\text{OH},\text{F})_2$ – Fig. 47 – were explained also by considering possible local cation arrangements around O3 sites [00R1]. The spectrum of end-member pargasite shows a doublet consisting of two rather broad bands (A, B), of almost equal intensity, centered at 3710 and 3678 cm^{-1} which were conventionally assigned to the MgMgMg-OH-Na and MgMgAl-OH-Na configurations, respectively [73S1, 87R2, 94W1, 99D1] and an additional low-intensity band at 3652 cm^{-1} (A*). Really, the pargasite spectrum was shown to be more complicated due to short-range ordering, both at NN and NNN [99D1] but the authors used a simplified four-band model. The minor A* band was ascribed to $\square\text{-MgMgMg}$ configuration [87R2, 99D1] and suggests that end-member pargasite departs slightly from the ideal composition, toward magnesiohornblende. In the spectra of pargasite having intermediate OH-F contents, each of these two bands (A, B) was replaced by new bands (A', B') of lower wavenumber. The A-A' and B-B' separations are 15 and 20 cm^{-1} , respectively. The spectra of intermediate compositions were decomposed into four symmetrical Gaussian bands. The variation in relative band intensities in the spectra of intermediate (OH-F) amphiboles was explained by considering the possible

arrangements around the O3 sites. The analysis of the relative band intensities suggests complete short-range disorder of OH and F at the O3 anion site.

The infrared OH-stretching bands in some heat-treated A site occupied and $^{[4]}\text{Al}$ -free (or nearly free) **manganoan sodic-calcic** and **sodic amphiboles**, **manganoan magnesio-arfvedsonites** and **richterites** have been analyzed [01I1]. Two OH-stretching bands, $(\text{MgMgMg})\text{-OH-A-O}^{2-}/\text{F}^{-}/\text{Cl}^{-}$ and $(\text{MgMgMg})\text{-OH-}\square$ configurations, persist to high temperatures. With increasing temperature, the OH-stretching band of the $(\text{MgMgMg})\text{-OH-A-OH}$ ($\text{A} = \text{A site cation}$) configuration shifts downward from 3730 to near 3700 cm^{-1} with the formation of the $(\text{MgMgMg})\text{-OH-A-O}^{2-}$ configuration; the repulsive interaction between the proton and the A cation is removed through dehydrogenation of OH at the O3 site, coupled with movement of the A cation toward the dehydrogenated side. In natural F^{-} and Cl^{-} bearing sodic-calcic and calcic amphiboles, two kinds of $(\text{MgMgMg})\text{-OH-A}$ stretching bands were observed at around 3730 and 3700 cm^{-1} , in which A site alkali ions move toward the $\text{F}^{-}(\text{Cl}^{-})$ substituted O3 site. In this manner, $(\text{MgMgMg})\text{-OH-K}$ and $(\text{MgMgMg})\text{-OH-Na}$ bands shift downward 20 cm^{-1} and 26...29 cm^{-1} , respectively, by heat treatment, reflecting the different size of the A site cations.

The $\text{K}(\text{Na,Ca})(\text{Mg}_{5-x}\text{Fe}_x)\text{Si}_{8-y}\text{Ti}_y\text{O}_{22}(\text{OH})_2$ **richterites** investigated by FTIR, in the OH stretching region, indicate a random distribution of Mg and Fe^{2+} over M1 and M3 octahedra and the presence of minor vacancies at the A site [96S2]. The presence of $^{[4]}\text{Ti}^{4+}$ was indicated by the band at 3655 cm^{-1} assigned to OH groups adjacent to 5Si and 1Ti, whose intensity grows with the Ti content. The anisotropy of tetrahedra is reduced as x increases. The data were interpreted in terms of dimensional misfit between tetrahedra and octahedra within the I-beam of amphibole. The replacement of Mg by the larger cation Fe^{2+} requires an expansion of the tetrahedral double chain. It is realized by an expansion of tetrahedra: longer Si-O bonds and more regular SiO_4 tetrahedra in the Ti-free system, and incorporation of the larger $^{[4]}\text{Ti}^{4+}$ in the Ti-bearing one.

According to [96D1], the FTIR spectrum of the **Ti-free potassium richterite** shows a main band at 3734 cm^{-1} assigned to an OH anion bonded to three octahedral Mg cations and directed toward K at the A site, facing a tetrahedral ring of composition Si_6 . When Ti is introduced into the structure, two new overlapping components appear in the IR spectrum. They were resolved into two single bands at 3711 and 3698 cm^{-1} . These two bands were assigned to OH groups facing rings of tetrahedra with compositions Si_5Ti and Si_4Ti_2 , respectively. Their intensities were shown to be linearly related to the Ti content at the T2 site up to 0.8 apfu. The analysis of relative band intensities indicates short-range disorder of Si and Ti over the T2 sites.

In [68B2] the Mg, Fe^{2+} and Fe^{3+} ion distributions in **riebeckite** (crocidolite) were estimated from the hydroxyl stretching frequency in the IR spectrum. It was concluded that the Fe^{3+} ions are enriched in the M2 positions, but a small portion also occurs in M1 and M3 sites with relative enrichment in M1 sites. The majority of Fe^{2+} ions occupy M1 and M3 positions with relative enrichment in M1 sites.

Infrared spectroscopy studies show that the Li end member in the **riebeckite – clinoferroholmquistite** series has a very ordered structure, whereas intermediate compositions show local heterogeneities associated with the presence of two different B sites occupied by Na or Li [03I2].

The IR spectrum of synthetic $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ has two well defined absorption bands at 3742(A) and 3715(B) cm^{-1} which can be assigned to OH bands associated with two independent anion sites (O3A and O3B) in the structure – Fig. 48. The higher frequency band was assigned to shorter O3B-H2 bond and the lower frequency band was assigned to the longer O3A-H1 bond [04I1]. The band at 3667 (C) cm^{-1} was assigned to OH directly bonded to three Mg octahedral cations, facing an empty A site, i.e. to $\text{MgMgMg-OH-A}^\square$ configuration [97H1]. The broader shape of the 3742 cm^{-1} band is consistent with a stronger interaction of the H2 atom with $^\text{A}\text{Na}$ which is confirmed by structure refinement. Increasing T of synthesis causes a progressive departure from the ideal stoichiometry via $^\text{A}\square_1^\text{B}\text{Mg}^\text{A}\text{Na}_{-1}^\text{B}\text{Na}_{-1}$ substitution [04I1]. The O-H and O-D bands, obtained at 300 K and 20 K, are very similar [05I1]. The only notable effect of temperature is a shift toward higher frequency of the A band (by $\approx 15 \text{ cm}^{-1}$) and a very minor shift toward lower frequencies (by $< 5 \text{ cm}^{-1}$) of the B bands. The C band remains practically constant.

Typical IR spectra of **glaucophanes** are shown in Fig. 49a while in Fig. 49b the Raman spectrum is plotted [89G1]. The theoretical analysis shows that there are modes: $30\text{A}_g + 30\text{B}_g$ (Raman active), $27\text{A}_u + 33\text{B}_u$ (IR active) and $1\text{A}_u + 2\text{B}_u$ (acoustic) [72L1]. All the IR and Raman bands occurring above 600 cm^{-1} were assigned (probably) to Si-O related vibrations of the Si_4O_{11} ribbons. Among these bands the following groups can be distinguished [72L1, 87D1]: (1) The bands between 120 and 610 cm^{-1} represent the deformation vibrations of the ribbon and the vibrations involving Na, Mg and Al; (2) from 650 to 800 cm^{-1} , the intense bands seen in the

Raman spectrum and the weak to medium bands observed in the IR spectra are due to the symmetrical Si-O-Si ($10 \nu_s$ Si-O-Si) vibrations and probably also to the four Si-O vibrations; (3) the isolated Raman band at 887 cm^{-1} and IR bands at 885 and 920 cm^{-1} were attributed to the four symmetrical ν_s Si-O-Si vibrations; (4) the group of bands occurring from 960 to 1110 cm^{-1} in the Raman spectrum and from 990 to 1160 cm^{-1} in the IR spectrum represents probably four ν_{as} Si-O-Si and four ν_{as} O-Si-O stretching vibrations; (5) the three bands at 3630 , 3645 and 3658 cm^{-1} were assigned to the two ν_{OH} stretching vibrations. The spectroscopic data were used to compute other physical properties (heat capacity, entropy). The agreement between measured and calculated properties was good [89G1].

Powder IR spectra of synthetic **richterite – tremolite** and **Sr tremolite – tremolite** solid solutions were studied, in order to analyze the internal vibrations of $[\text{Si}_4\text{O}_{11}]_\infty$ complex anion [00A1]. The energy of the internal vibrations of the $[\text{Si}_4\text{O}_{11}]_\infty$ ribbon is a function of the relative bond strengths and masses of the nearby ions. A one-mode behaviour was observed for all the Si-O, Si-O-Si and O-Si-O stretching vibrations, indicating no clustering in the two solid solution series. In both solid solution series the vibrational energy of the stretching vibrations is a linear function of composition. In the system richterite – tremolite, a shift of the stretching frequencies of the $[\text{Si}_4\text{O}_{11}]_\infty$ ribbon over the whole compositional range of up to 30 cm^{-1} was observed. For Sr tremolite – tremolite the maximum shift was only 5 cm^{-1} . These quite small band shifts allow the $[\text{Si}_4\text{O}_{11}]_\infty$ -ribbon to be treated as an isolated entity for factor group analysis. Nevertheless, by the exchange mechanisms, $\text{Ca}(\text{M4}) \leftrightarrow \text{Sr}(\text{M4})$ and $\square(\text{A})\text{Ca}(\text{M4}) \leftrightarrow \text{Na}(\text{A})\text{Na}(\text{M4})$, the full width at half height increased and the amplitude decreased, indicating a slight distortion of the ribbon. For Sr tremolite – tremolite only a linear expansion of the lattice was observed. In the series richterite – tremolite, individual bond angles of the SiO_4 tetrahedra are additionally changed, causing the higher energy shift of the bands. The one-mode behaviour of the Si_4O_{11} -double chain indicates that there is no short-range order of Na/Ca and Ca/Sr at the M4 sites.

For Raman spectra in potassium richterite see [99Y1]. For IR spectra see: amphibole [74S1, 87R1, 94I1].

8.1.4.3.10 Electronic absorption spectra

The electronic absorption spectra were examined in actinolites [66W1, 70B2, 74M1], tremolite [77G1, 79G1], grunerite [77G1, 79G1], pargasite [77G1, 99T1], kaersutite [99T1] magnesio-arfvedsonite [86G1], arfvedsonite (juddite) [86G1].

In [70B2] absorption spectra were presented of two **actinolites** $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ in the $350\text{--}1500 \text{ nm}$ region in which all Fe^{2+} features were attributed to Fe^{2+} in the M1, M2 and M3 sites. It was inferred that the main band at about 1035 nm arises from Fe^{2+} in the M2 site. In [66W1] an unpolarized spectrum of actinolite was presented and they assigned an absorption band at 1020 nm to Fe^{2+} in sixfold coordination, a sharp band at 1399 nm to the first vibrational overtone of the OH^- stretching mode, and a set of sharp bands at 2320 nm and 2392 nm to infrared combination modes. In [70B2], in actinolite, the absorption bands at 727 nm in the γ -spectrum and at 661 nm in the β -spectrum were assigned to $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfer (IVCT), and four sharp absorption bands in the α -spectrum at about 1400 nm were described as arising from OH^- vibrational overtones. In [70B2] the absorption in the $800\text{--}1300 \text{ nm}$ region was attributed to Fe^{2+} in the M1, M2 and M3 sites. The band assigned by [66W1] to tetrahedral Fe^{2+} is located in the α -spectrum at approximately 2470 nm (4050 cm^{-1}). The spectra obtained for natural tremolite are shown in Fig. 50 [77G1]. In addition to features presented by [66W1, 70B2], the sharp peaks of low intensity in the $400\text{--}550 \text{ nm}$ region in Fig. 50 were identified as spin forbidden electronic transitions of Fe^{2+} and Fe^{3+} . Sharp bands at 2297 nm and 2384 nm in the β -spectrum and at 2315 nm and 2387 nm in γ correspond to the localizations of the combination bands described by [66W1]. In [77G1, 79G1] the prominent absorption bands at 1030 nm in β and at 2470 nm in α were assigned to transitions of Fe^{2+} in the M4 site. We note that the spectra of Fe^{2+} in M4 sites of the cummingtonite – grunerite series [70B2] show dominant absorption bands in the 1000 nm region. In case of anthophyllite and gedrite [74M1] bands near 1000 nm and 2500 nm were assigned to Fe^{2+} in the M4 site. The spectra of a wide variety of calcic amphiboles indicate that the Fe^{2+} content in the M4 site is variable.

The optical properties of Ti bearing amphiboles (most pargasites and kaersutites) having Ti- and Fe- contents from 0.111 to 0.729 apfu and from 0.479 to 2.045 apfu , respectively were studied [99T1]. These silicates crystallized in the C2/m-type structure. As mentioned already, the structure consists of infinite bands of edge-shared octahedral M1-M4 sites in the (*bc*)-plane. Therefore it is rather appropriate for IVCT transitions [94B2] and one may expect the appearance of $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$ IVCT bands of the electronic spectra of Fe, Ti

bearing amphiboles. Optical properties of Ti-enriched amphiboles were reported [86L1, 99T1]. As example, in [99T1], on the basis of their electronic spectra, the samples were classified in three groups. The group 1 – Figs. 51a, b – closely resembles the spectra of iron bearing amphiboles [77G1, 94B2]. In addition, the Ti-bearing amphiboles exhibit much more intense high-energy absorption edge causing the characteristic brown colour. The bands, superimposed on the edge were caused by iron. Thus, the broad band at $\approx 14000\text{ cm}^{-1}$ (YZ-polarization) was assigned to $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$ IVCT transition, whereas a band near 10000 cm^{-1} , more intense in Y- and Z- than in X-polarization, was attributed to the spin allowed dd-transition ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ of Fe^{2+} distributed over unequivalent structural positions M1-M4. A ratio of intensities of these latter bands significantly varies from sample to sample showing a different distribution of Fe^{2+} between these sites. The group 2 contains low-iron pargasites. These samples lack an $\text{Fe}^{2+}/\text{Fe}^{3+}$ IVCT band around 14000 cm^{-1} . A broad and intense Y-polarized band superposing the absorption edge – Fig. 51c – occurs near 22000 cm^{-1} . Group 3 contains a sample of dark brown Ti, Fe-enriched kaersutite – Fig. 51d. The polarized electronic spectra consists of an extremely intense pleochroic absorption edge ($Z > Y \gg X$) and four relatively weak bands around (a) 9300 cm^{-1} (Y-polarization), (b) 17200 cm^{-1} (X), (c) 19900 cm^{-1} (Y,Z) and (d) 22900 cm^{-1} (X). The strong pleochroic absorption edge, causing the dark brown colours of Ti-bearing amphiboles was attributed to ligand-metal and metal-metal charge transfer transitions involving both iron and titanium ions ($\text{O}^{2-} \rightarrow \text{Fe}^{3+}$, Fe^{2+} ; $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ and $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$). The broad intense Y-polarized band at $\approx 22000\text{ cm}^{-1}$ ($\nu_{1/2} \approx 3700\text{ cm}^{-1}$), in spectra of low iron amphiboles, with a relatively low $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio was attributed to electronic $\text{Fe}^{2+}(\text{M3}) + \text{Ti}^{4+}(\text{M2}) \rightarrow \text{Fe}^{3+}(\text{M3}) + \text{Ti}^{3+}(\text{M2})$ ICVT transitions. The IVCT bands of other possible iron pairs, involving Ti^{4+} and Fe^{2+} in M2 and M1, M4 sites, respectively, were presumed to be at higher energies being obscured by the absorption edge [99T1].

The Fe^{2+} - Fe^{3+} charge transfer was analyzed in glaucophane [76S1, 87M2]. The Fe^{2+} - Fe^{3+} charge transfer has been assigned to transition at 16130 cm^{-1} with a half width of 6600 cm^{-1} . In gedrite, the band at 10600 cm^{-1} and in grunerite at 9980 cm^{-1} were attributed to Fe^{2+} in M4 sites.

The polarized spectra of **winchite** and **arfvedsonite** (juddite) are shown in Fig. 52 [86G1]. The octahedral M2 site in clinoamphibole, winchite and arfvedsonite (juddite), which principally contains the Mn^{3+} ions, is already distorted due to chemical reasons. Arfvedsonite (juddite) contains the highest amount of Mn^{3+} , which can be incorporated in a clinoamphibole structure, whereas winchite contains much less Mn^{3+} . Hence, the distortion of the M2 site in arfvedsonite (juddite) is much greater than that in winchite. The colors and pleochroic schemes in the above clinoamphiboles were explained on the basis of the locations of the UV absorption “edges” and the d-d transition bands in the polarized optical absorption spectra of Mn^{3+} ions in distorted octahedral coordination. The polarization behaviour in these bands, in the $20000\ldots 15000\text{ cm}^{-1}$ range and near 7000 cm^{-1} , indicates a $2(\text{C}_2)$ symmetry of the crystal field at M2 site in clinoamphiboles. Crystal field stabilization energies of Mn^{3+} in above clinoamphiboles ($140\ldots 142\text{ kJ/g atom}$) at the M2 site are smaller than in the respective sites of other Mn^{3+} silicates. This is due to small Jahn-Teller splitting of the ${}^5\text{E}_g$ ground state of Mn^{3+} in weakly distorted M2 sites. Spin forbidden bands from Fe^{3+} are present.

Reflectance spectra in the **tremolite** – **actinolite** series were used to characterize variations in absorption band parameters as function of composition [95M1].

8.1.4.3.11 X-ray absorption spectra

Polarized X-ray absorption spectra study was performed on **edenite** and **hastingsite** [98L2]. The X-ray absorption tensors were determined at the Fe K-edge by means of polarized fluorescence spectroscopy. Analysis of the energy-dependent tensor elements revealed anisotropic anomalous scattering and, in analogy to visible light optics, energy dependence of the respective absorption tensor orientations.

There were structural refinements by neutron diffraction on Ti-containing amphiboles [71K1, 73H2, 73R1, 75K1]. The Ti was assigned to different sites in different studies. In [92D1] the Ti 2p X-ray absorption spectra were studied. The spectrum of **kaersutite** consists of four structureless peaks, from which it was difficult to extract a clear information. From the absence of asymmetry in the e_g peak it was concluded that the titanium sites were not tetragonally distorted.

The crystal-chemical role of nickel in synthetic **potassium richterites** within the join $\text{K}(\text{CaNa})\text{Mg}_4\text{Ni}[\text{Si}_8\text{O}_{22}](\text{OH})_2 - \text{K}(\text{CaNa})\text{Ni}_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$ system has been investigated by X-ray absorption spectroscopy [00G1]. The XANES spectra recorded at the Ni K edge show variations that can be related to the Ni-Mg substitution at the octahedral M sites – Fig. 53. The XANES calculations showed a relationship between spectral features and the environments around Ni, with increasing Ni contents along the join. In particular: (1) a

cluster size of 4...5 Å is necessary for best reproduction of the experimental spectra. The main edge is correctly reproduced only when including all atoms to within 5 Å from the absorber; peak F is obtained when including all atoms to within 4 Å from the photoabsorber. Peak G is reproduced in the theoretical spectra when taking into account the first coordination shell around the absorber, but it is further modified by including also the second coordination shell (i.e. the octahedral strip). (2) The intensities of peaks C and D are sensible to the Mg substitution around the absorber. (3) The splitting of peak G into two components G' and G'' observed in the experimental spectra is reproducible in the calculations only when Ni is located in the M3 or M1 sites. It thus reflects a low Ni occupancy in M2. (4) Such a splitting is produced by the presence of a sufficient number of Mg atoms located in the second coordination shell around Ni; therefore it is typical of low-Ni compositions. (5) The evident peak G splitting observed in the Ni₂₀Mg₈₀ spectrum depends on both Ni octahedral occupancy and Ni clustering. The absence, or the minor presence, of Ni clustering in the above sample was suggested. In turn, the decrease of the peak splitting towards the Ni end-member reflects both the increasing Ni M2 occupancy and Ni enrichment in the sample.

For absorption spectra see: calcic amphiboles [82A1, 82G2]. For optical properties of amphiboles [67B4].

For charge transfer see: glaucophane [87M2].

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Some refractive indices are listed in Table 11. The shape of crystal indicatrix ($2V$) of the cummingtonite – grunerite series is a sensitive indicator of the Fe-Mg order [97E1]. The correlation of $2V$ in anthophyllite – ferro-anthophyllite versus composition was also studied [98S1, 01E1].