

8.1.4.2 Carpholite, shattuckite and related silicates

In this chapter we present the physical properties of inosilicates from groups VIIID03 and VIIID04 – Table 1 [91N1].

8.1.4.2.1 Crystal structures. Lattice parameters

Carpholites

The chemical compositions of carpholites can be represented by the end members $MA_2Si_2O_6(OH)_4$ with $M = \text{Mn}$, **manganocarpholite**, $M = \text{Fe}$, **ferrocarpholite** and $M = \text{Mg}$, **magnesiocarpholite**. The natural silicates occur preferentially as binary solid solutions, the third component being generally less than 5% [77M1, 79V1]. Magnesiocarpholite, $MgAl_2Si_2O_6(OH)_4$, is a high-pressure/low-temperature mineral characteristic of the blueschist metamorphic associations [79V1, 83C1]. Potassium and fluorine-bearing carpholites have been also reported [73C1]. All these minerals have common crystal structures [81V1, 92F1] with slight differences in the M1 site (the one hosting Mg, Fe and Mn) and the way by which fluorine replaces hydroxyl [89G1]. In [56M1] the basic structural principles of carpholites were defined by determining the structure of an iron-rich carpholite, $(\text{Fe}^{2+}_{0.8}\text{Mg}_{0.2})(\text{Al}_{0.95}\text{Fe}^{3+}_{0.05})\text{Si}_2\text{O}_6(\text{OH})_4$. Later on, [75N1, 79L1] analyzed the structure of an almost pure manganocarpholite. The structure of Mg-rich carpholite was also studied [81V1]. The structures of the above silicates are orthorhombic of space group Ccca. The structure of magnesio-rich carpholite consists of pyroxene-like slabs, having the composition $\text{Si}_4\text{Al}_2\text{O}_{12}(\text{OH})_4$, [79V1] which cause it to be fibrous. Such slabs are linked to each other by pyroxene-like octahedral metal layers which are oriented perpendicular to the slabs. Smaller Mg (Mn, Fe) atoms occupy the outer octahedra of the metal layers – Fig. 1. As a result, the pyroxene-like slabs are brought closer to each other along [010] and [100], thus explaining the contraction of the unit cell with substitution of Mg^{2+} for Fe^{2+} or Mn^{2+} . The structures of Mg, Mn and Fe carpholites closely resemble, suggesting complete miscibility.

In [89G1] a member of the carpholite family was analyzed which is characterized by the coupled substitutions $\text{K}^+ + \text{Li}^+ \leftrightarrow \text{Mn}^{2+}$ and the ordered replacement of half of the $(\text{OH})^-$ ions by F^- giving rise to the nonstoichiometric composition $\text{K}_x(\text{Mn}_{2-x}\text{Li}_x)\text{Al}_4\text{Si}_4(\text{OH})_4\text{F}_4$ with $x \approx 0.65$. As before mentioned, the crystal structure can be described as formed from pyroxene-like T-O-T slabs consisting of two sets of single silicate chains and an Al1 octahedral band parallel to the c -axis, cross linked by mixed octahedral bands of (Li, Mn) and Al2 octahedra. Half of the $(\text{OH})^-$ ions, in normal carpholite, are replaced by F^- ions in an ordered fashion. Li^+ , replacing Mn^{2+} in a distorted octahedral coordination, occupies a site distinct from the Mn^{2+} position. The K^+ ions partially occupy a large cavity with sixteenfold coordination $[\text{O}_8\text{F}_8]$, which can be described as a truncated octagonal bipyramid. These cages share rectangular faces with adjacent ones to form channels parallel to c , which are peculiar to the carpholite structure. There is an additional channel site comparable to the A site in the amphiboles (see Chaps 8.1.4.1, 8.1.4.3). The carpholite type is amenable to a large variety of cationic and anionic substitutions. The structures of carpholites were further studied in [92F1, 01F1]. According to [01F1] the average structural arrangement of magnesiocarpholite confirms both the apparent Ccca symmetry and the bonding pattern for differently substituted carpholite-like minerals. One more structural evidence is the occurrence of residual maxima corresponding to the K site of non stoichiometric potassium and fluorine-bearing carpholite [89G1, 01F1]. Contradictory data still exist. In [92F1] the real symmetry of magnesiocarpholite was investigated and it was suggested that order/disorder involving hydrogen atoms and cationic or “anionic” impurities might lead to a real symmetry lower than the one revealed by X-rays. In [01F1] contradictory results were shown regarding the long-range ordering behaviour (i.e. the one revealed by X-ray diffraction) and the short-range ordering behaviour (i.e. the one revealed by FTIR and Raman spectroscopy). Since HRTEM studies did not find cluster defects [00G1], short-range ordering was suggested to originate from local arrangements like point defects [01F1].

The atomic sites of a Mg-carpholite are given in Table 2 and lattice parameters are listed in Table 3.

Balipholite, $\text{BaMg}_2\text{LiAl}_3(\text{Si}_2\text{O}_6)_2(\text{OH})_8$

The silicate crystallizes in an orthorhombic-type structure having space group Ccca [75W1, 76F1].

Shattuckite, plancheite

The shattuckite [64N1, 66M1, 67L1, 76K1, 77E1] and plancheite [68V1, 77E1] crystallize in an orthorhombic-type structure (see Table 3 for lattice parameters and Table 2 for atomic sites). Both silicates are chain structures in terms of silicate components. Shattuckite – Fig. 2 – contains zig-zag $(\text{SiO}_3)^{2-}$ chains that are quite similar to those found in the pyroxenes. Plancheite contains such chains joined in parallel pairs, forming double chains $(\text{Si}_4\text{O}_{11})^{6-}$ analogous to those found in amphiboles (see Chaps 8.1.4.1, 8.1.4.3) [77E1]. Thus, the c -axis of these silicates is about 5.3 Å, representing the repeat unit of the silicate chains. Aside from these features, however, there is no analogy between copper silicates and the pyroxene-amphibole structures. In both shattuckite and plancheite, the apices of silicate chain tetrahedra are condensed on both sides of an extended copper-oxygen layer $(\text{CuO}_2)^{2-}$ that topologically is similar to that of brucite $\text{Mg}(\text{OH})_2$. The oxygen sites in the layer that are not supplied by the silicate tetrahedra are occupied by OH groups. The CuO_2 layer is strongly bent at the region of contact of adjacent silicate chains (the angle of bent $\cong 33^\circ$) giving the layers, which lie parallel to the (ac) -plane, a corrugated aspect. The structures may thus be considered as sheet structures in terms of the compact silicate–Cu-silicate triple layers, referred to above. The triple layer (two per unit cell) stack against each other along the b -axis in both structures, with their corrugations nested, and the silicate chains in contact base-to-base [77E1]. The triple layers are linked together by additional copper atoms having an unusual linkage. The copper atoms are bonded to the outer unshared oxygen atoms of the silicate chains from adjacent triple layers to form square-planar CuO_4 groups that are joined in ladder-like ribbons parallel to the c -axis – Fig. 3. There are thus three levels of integrity in these structures. In terms of the overall bonding scheme, they are network structures; in terms of compact triple layers, they are sheet structures; in terms of their strongest elements, the silicate chains, they are chain structures. The physical properties (fibrous character, optical properties) emphasize the last interpretation [77E1].

Apachite, gilalite

Apachite, $\text{Cu}_9\text{Si}_{10}\text{O}_{29} \cdot 11\text{H}_2\text{O}$ and gilalite, $\text{Cu}_5\text{Si}_6\text{O}_{17} \cdot 7\text{H}_2\text{O}$, were reported to crystallize in monoclinic-type lattice [80C1] – Table 3.

Chrysocolla

Chrysocolla, $\text{Cu}_{2-x}(\text{Al},\text{Fe})_x\text{H}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$, was reported to crystallize in a unit cell with a dioctahedral net of octahedra joined to a net of tetrahedra rotated to different sides from the plane of their base [68C1, 69F1].

See Table 3 for lattice parameters.

8.1.4.2.2 Nuclear gamma resonance (NGR) data

Carpholites

The ^{57}Fe NGR spectra of (Fe, Mg)-carpholites were studied [79S1, 96W1, 01F1]. The spectra were generally interpreted as due to one octahedral site for both ferrous and ferric iron. Ferrous iron largely dominates over ferric iron. The ^{57}Fe NGR spectrum for $\text{Mg}_{1-x}\text{Fe}^{2+}_x(\text{Al}_{2-y}\text{Fe}^{3+}_y)\text{Si}_2\text{O}_6(\text{OH},\text{F})_4$ with $x = 0.52$ and $y = 0.05$ are plotted in Fig. 4 [96W1]. In case of a sample with $x = 0.70$ and $y = 0.10$, since of broad linewidth, two doublets were expected for Fe^{3+} ions. These were attributed to iron in both Al octahedra. The high quadrupole splitting values were attributed to the localization of iron in the M1 site, which deviates from the ideal octahedral configuration having two short, two intermediate and two long bonds. Although similar, the two Al sites have slightly different sizes. Therefore, if any Fe^{3+} occurs within this site, Al2 would be favoured in terms of atomic radii [01F1]. For NGR data see Table 4.

8.1.4.2.3 Optical properties

Carpholite

The FTIR and Raman spectra of magnesiocarpholite⁴⁾ are plotted in Fig. 5 [01F1]. The O-H stretching vibrations characterize the 3800...3400 cm⁻¹ spectral region. The strongest absorption bands in FTIR occur at 3630...3621 cm⁻¹ and 3581...3583 cm⁻¹. The first one was attributed to the OH1-H1 stretching vibration and the second one to OH2-H2. In fact, H1 does not form hydrogen bonds and H2 forms weak bonds with O3. The above assignment was confirmed by polarized Raman spectroscopy – Fig. 5c. Considering that the OH1-H1 bond lies almost along *c* and the OH2-H2 bond along *a*, it is expected that the first vibration will be enhanced for sections containing the *c*-axis and polarizer parallel to *z*, the second one will be excited for sections containing the *x*-axis and polarizer parallel to it. This is experimentally verified. The other bands in this spectral region were tentatively explained assuming different local octahedral environments, responsible for the FTIR and Raman shifts. The region of 1200...900 cm⁻¹ of the FTIR spectrum corresponds to the stretching vibrations of the Si-O bonds. In the FTIR region 650...400 cm⁻¹ there are frequencies at 635, 610 and 538 cm⁻¹ [01F1].

Carpholite, $\text{Mg}_{1-x}\text{Fe}^{2+}_x(\text{Al}_{2-y}\text{Fe}^{3+}_y)\text{Si}_2\text{O}_6(\text{OH},\text{F})_4$

The diffuse reflectance spectra for the samples with $x = 0.52$, $y = 0.05$ and $x = 0.70$, $y = 0.10$ are similar. Two sharp lines observed in NIR at 7000 and 7110 cm⁻¹ are overtones of the two nonequivalent OH-species, whose fundamental OH-stretching vibrations occur at 3570 and 3620 cm⁻¹, respectively [96W1] – Fig. 6. A third line, at 5210 cm⁻¹, was attributed to the combination band of molecular water. The broad band centered around 10000 cm⁻¹ with a shoulder at the low energy wing, was attributed to electronic transitions. The band can be resolved into two bands with centers at 7510 and 9380 (or 9340) cm⁻¹, respectively. The Fe²⁺ ions occupy the octahedral M site (2 point symmetry). All degeneracies will be lifted at that symmetry. This suggests the presence of two transitions from the split ⁵T_{2g} ground state to ⁵E_g, as experimentally observed. The energy splitting of the E_g term is rather high (~ 2000 cm⁻¹). This suggests that the high quadrupole splitting for the ⁵⁷Fe²⁺ doublet determined by NGR may be not due to the extremely high symmetry of the M octahedron. The broad absorption band at ≅ 15200 cm⁻¹ was suggested to be caused by spin forbidden Fe-transitions; it is also suspicious to an IVCT transition. From these observations it was concluded that Fe³⁺ is enriched in the edge-sharing Al2 octahedron, neighbouring to the M site having Fe²⁺.

Shattuckite, plancheite

The IR spectra of the above silicates show absorptions at 3 μm corresponding to the OH groups in the structure. The absorption at 6 μm was observed only for plancheite, suggesting that this crystal also contains H₂O [77E1].

The refractive indices for some carpholites, shattuckite and related silicates are listed in Table 5.