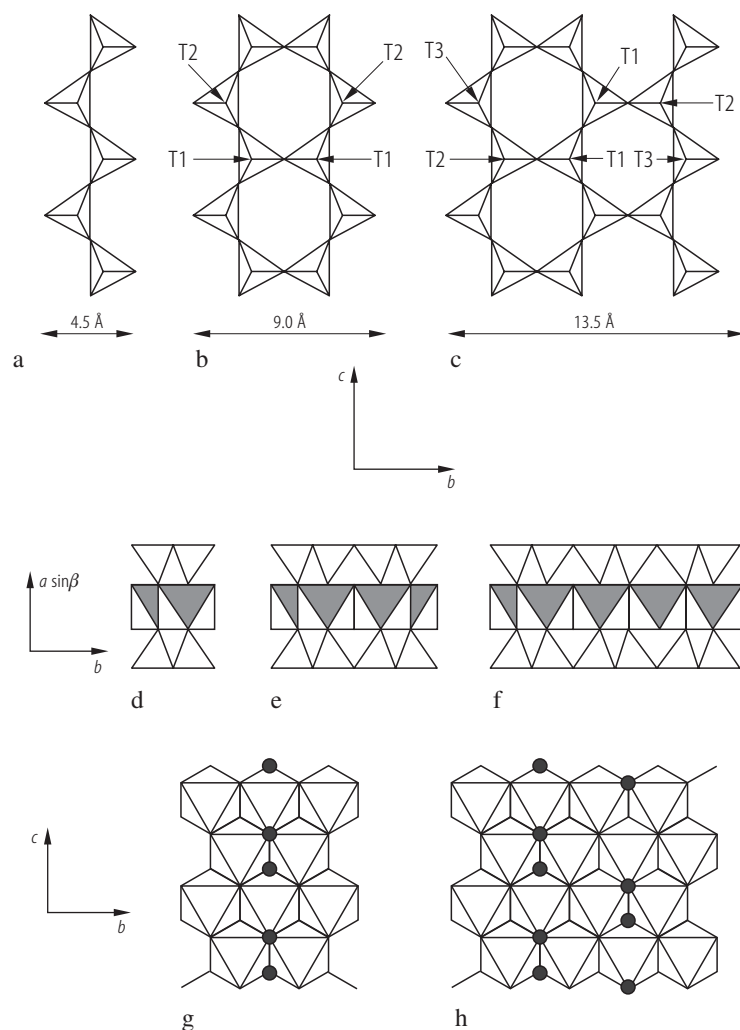
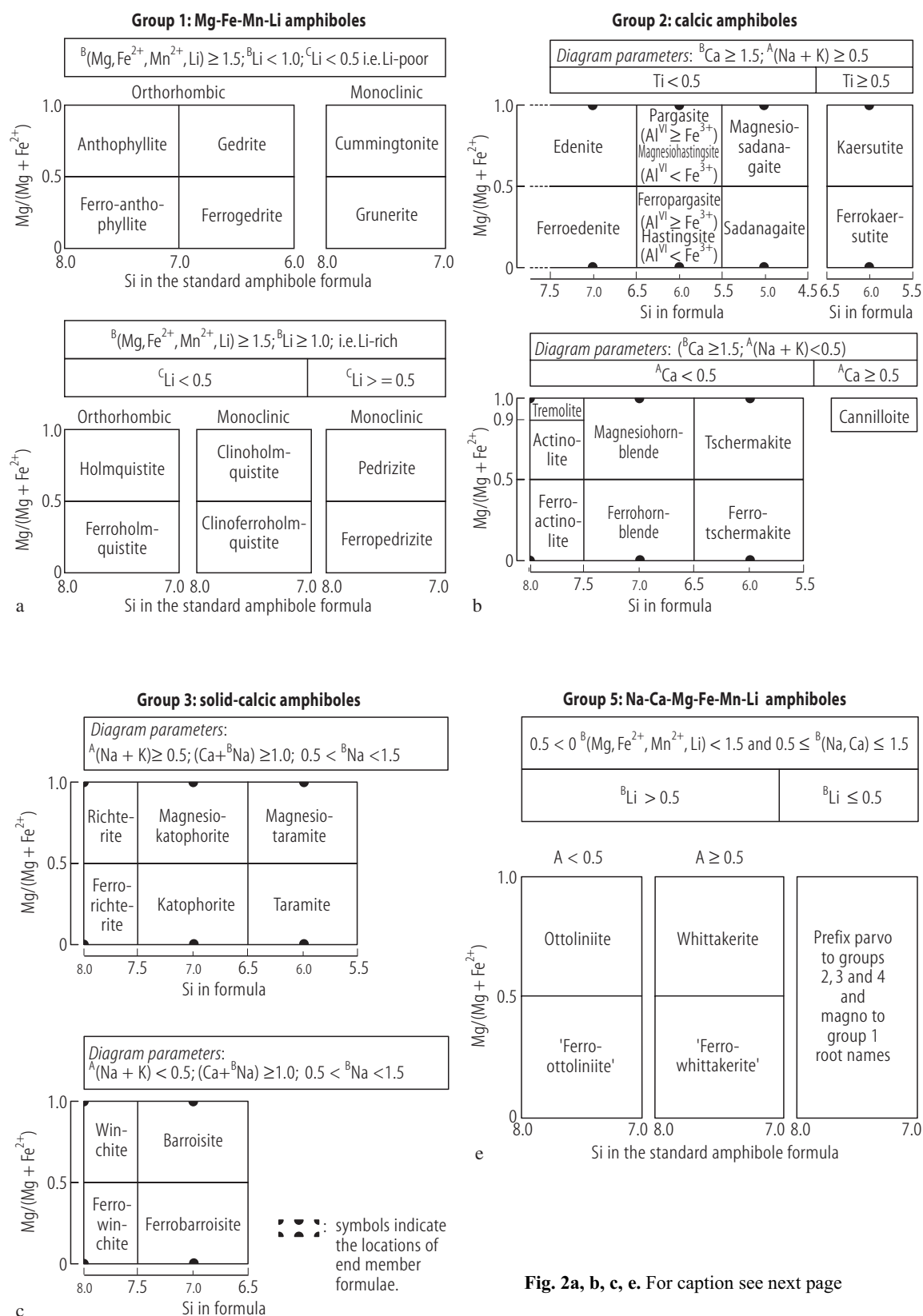
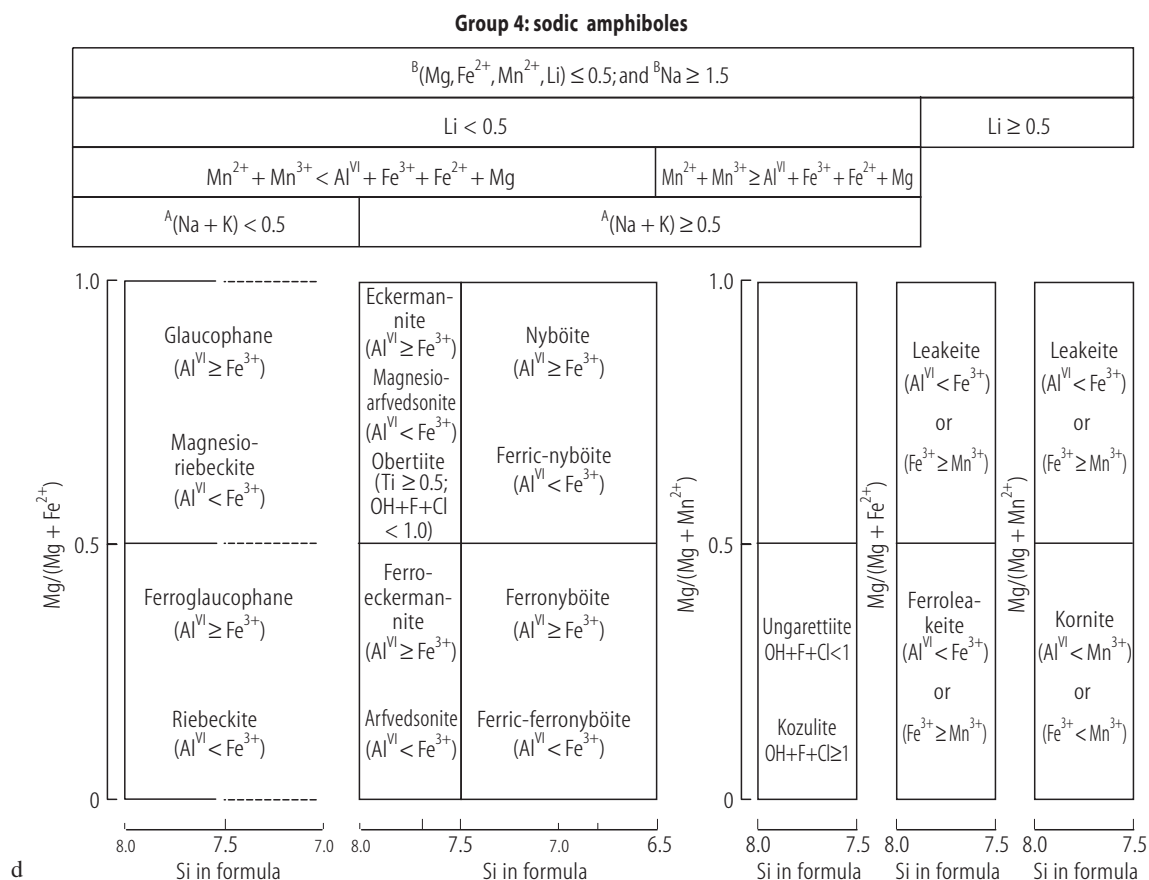


## Biopyriboles



**Fig. 1.** Biopyriboles. Silicate chains formed by sharing  $\text{SiO}_4$  tetrahedra. **(a)** Single-chain (pyroxenes), **(b)** double-chain (amphiboles), **(c)** triple-chain silicates. The chain widths indicated are  $0.5 [010]$ . The tetrahedral sites are labeled using the next-nearest neighbour notation. **(d-f)** The interlayer octahedral ribbons corresponding to structures **(a-c)**. Viewing direction is along the  $c$ -axis parallel to the elongation of the silicate chains. **(g, h)** Parts of the octahedral ribbons of the sodic amphibole and sodium-jimthompsonite (SJT), respectively, showing the normal distribution of OH sites (solid circles) in the two structures [92W1, 77V1].

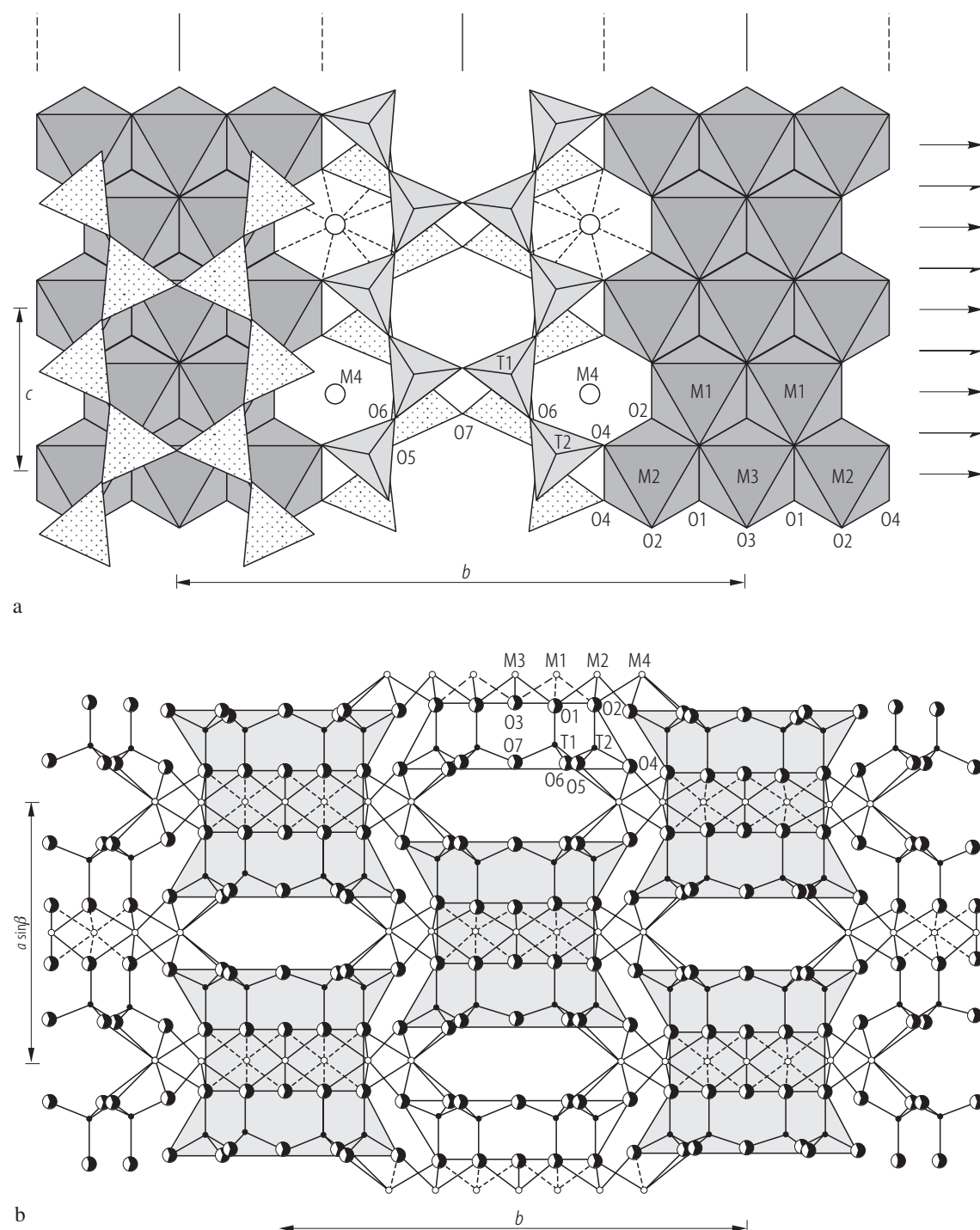




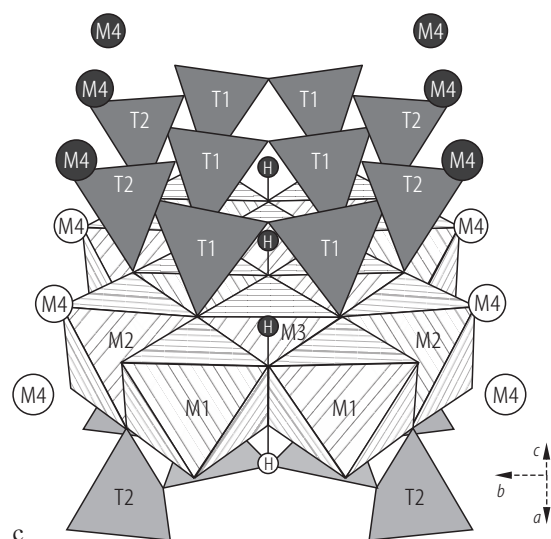
**Fig. 2.** The amphibole groups. (a) Mg-Fe-Mn-Li amphiboles; (b) calcic amphiboles; (c) sodic-calcic amphiboles; (d) sodic amphiboles; (e) Na-Ca-Mg-Fe-Mn-Li amphiboles [97L2, 04L1]. Final names require the relevant

prefixes which are listed in Table 1b and may optionally include the modifiers that are found in Table 1c. - Symbols in (b) and (c) (semi-circles, quarter-circles) indicate the locations of end-member formulae.

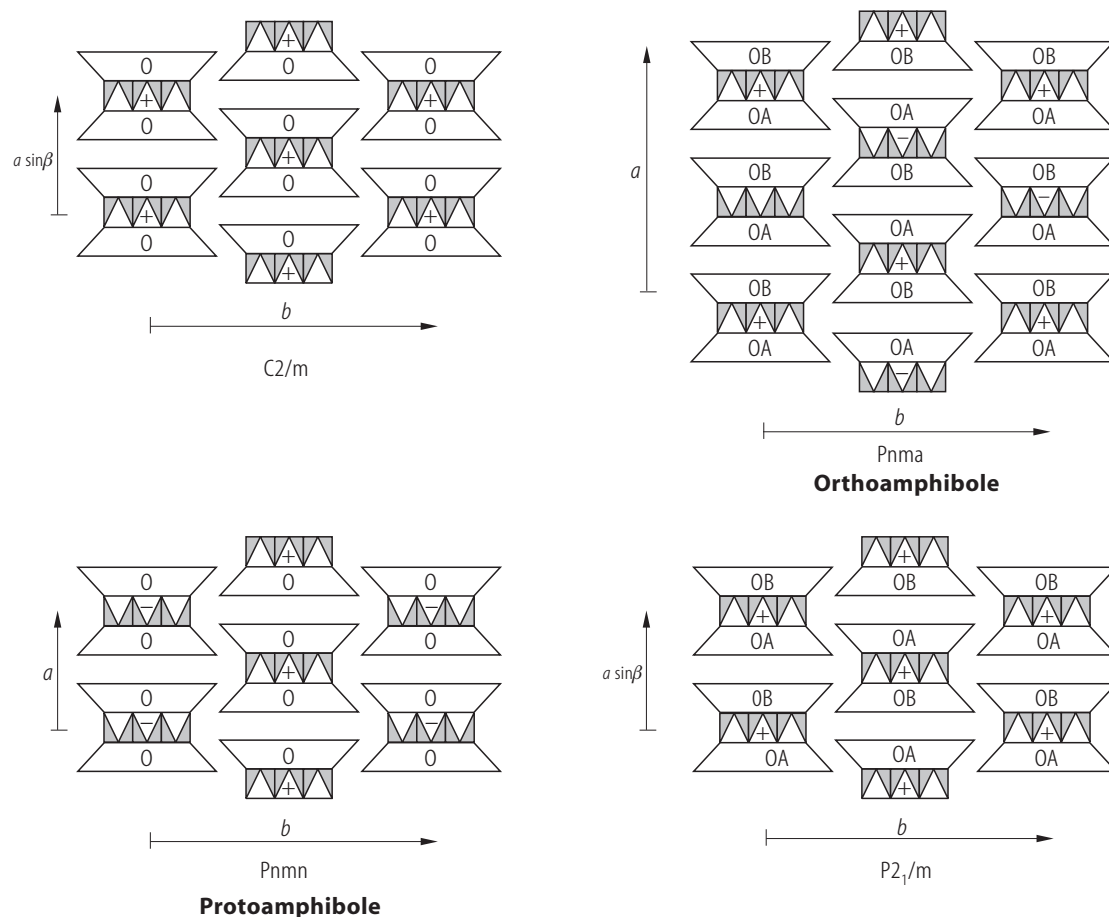
## Amphibole



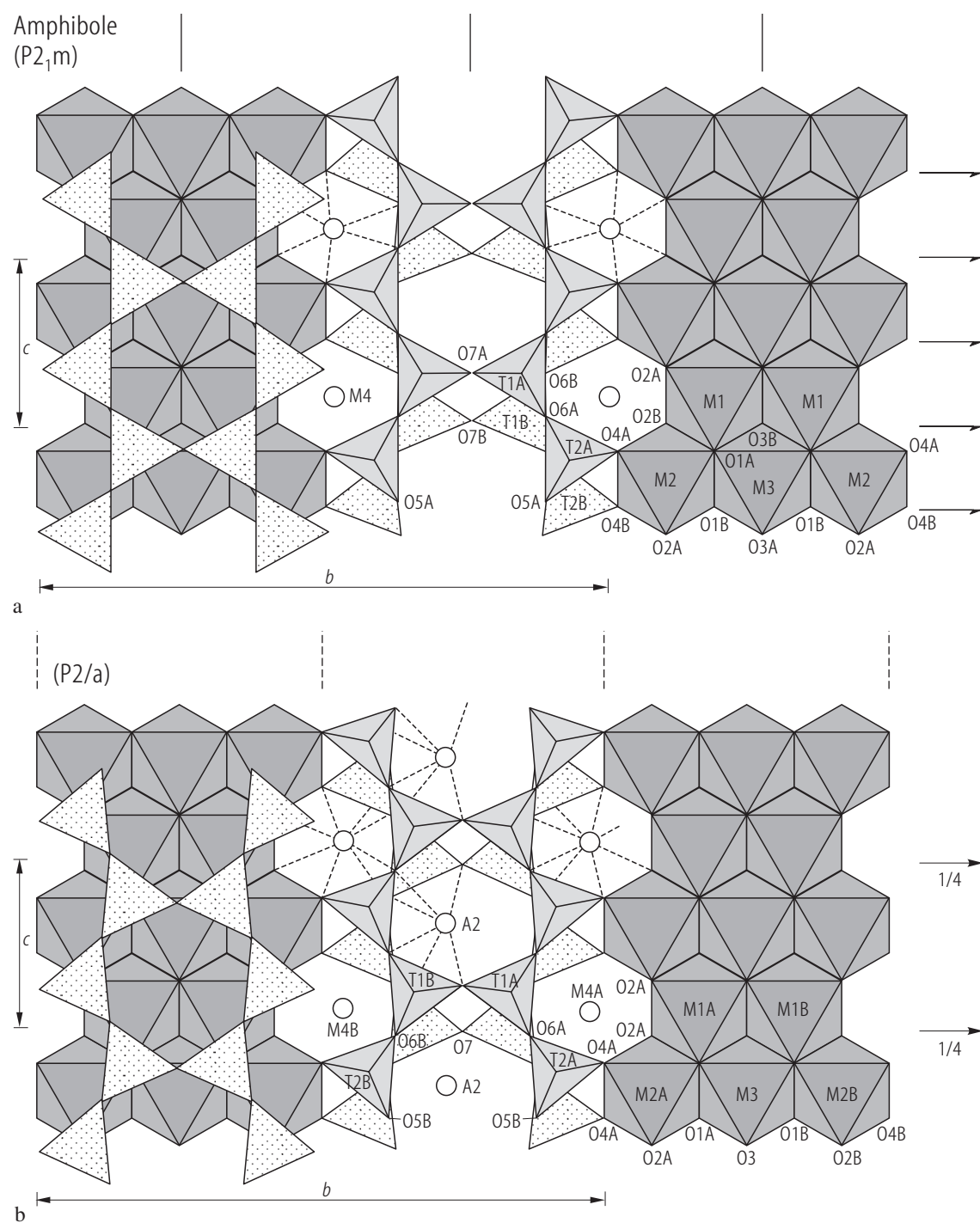
**Fig. 3a, b.** For caption see next page.



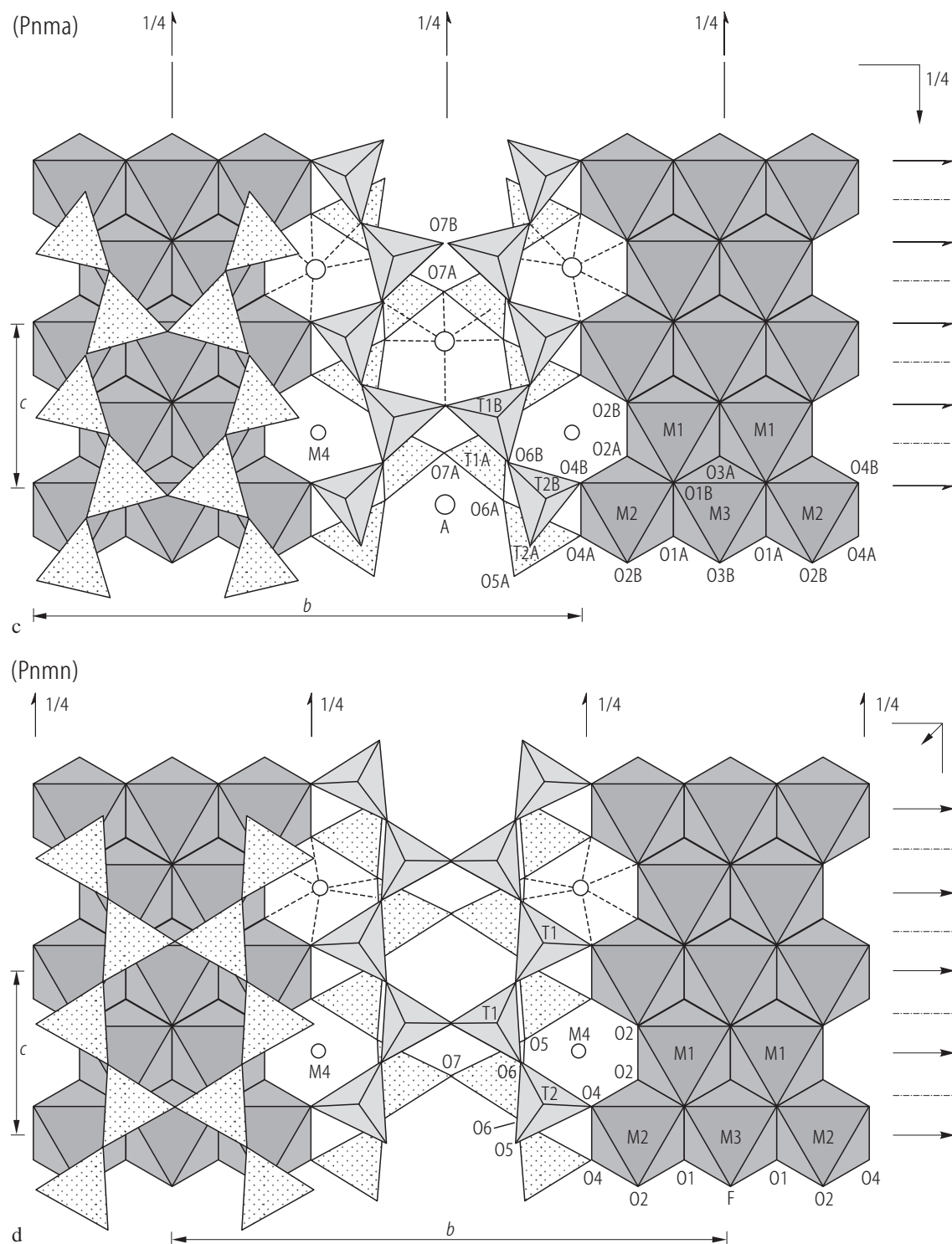
**Fig. 3.** Crystal structure of C2/m amphibole. (a) View along the [100] direction [83H1]; (b) crystal structure projected down [001] [79C1]. Stippled areas outline I-beams depicted in Fig. 4; (c) I-beam with surrounding M4 sites. A strip of edge-sharing octahedra is intercalated between two corner-sharing double tetrahedral chains in apex-to-apex arrangement. The M2 and M4 sites provide the linkages to adjacent I-beams [83H1, 03N1].



**Fig. 4.** Amphiboles. Structural topology [76P1].

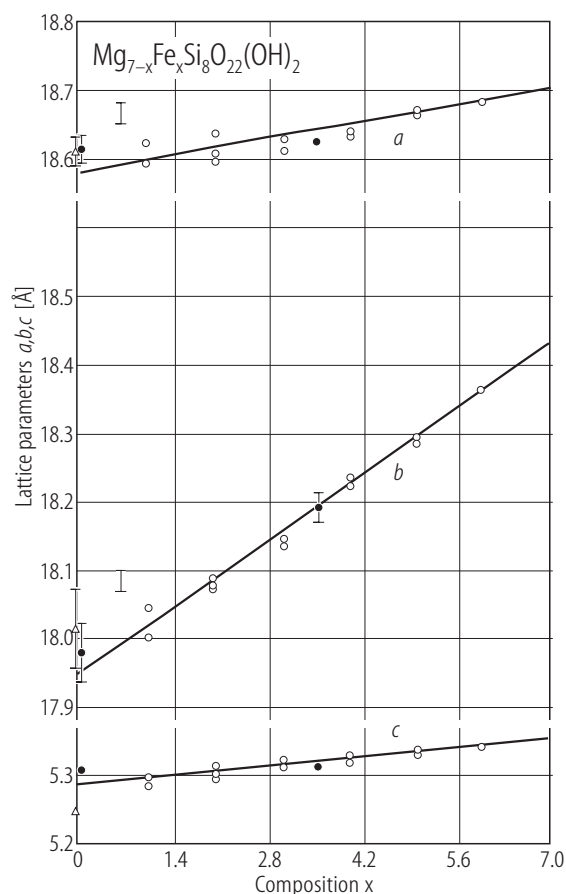


**Fig. 5a,b.** For caption see next page.



**Fig. 5.** Amphiboles. Crystal structures projected on the (100): (a)  $P2_1/m$ ; (b)  $P2/a$ ; (c)  $Pnma$ ; (d)  $Pnmn$ . The space-group symmetry elements are also shown [83H1].

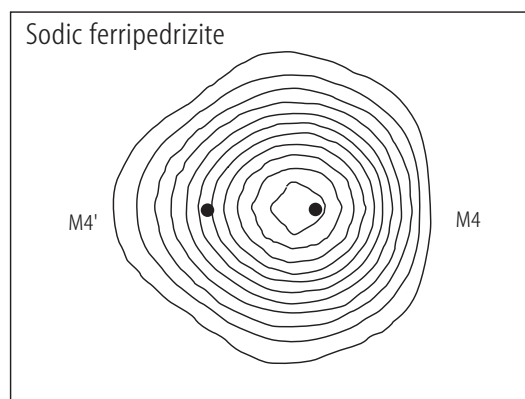
→  
**Fig. 8.** Sodic ferripedrizite. Electron density distribution around (a) the M4 site (projected onto (100); contours at  $1.0 \text{ e}/\text{\AA}^3$ ; dots give positions of M4'(Li) and M4(Na)); (b) the A site (best plane passing through A and Am dots giving their positions; contours at  $1.0 \text{ e}/\text{\AA}^3$ ) [0001].



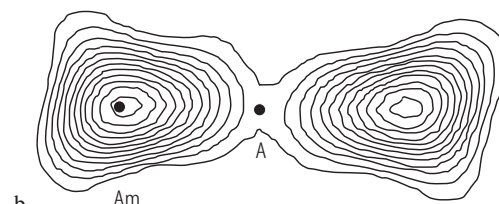
**Fig. 6.**  $\text{Mg}_{7-x}\text{Fe}_x\text{Si}_8\text{O}_{22}(\text{OH})_2$  orthorhombic amphiboles. Composition dependences of the lattice parameters: open circles [76P2]; triangles [63G1]; full circles [75C3].

For Fig. 7 see next page

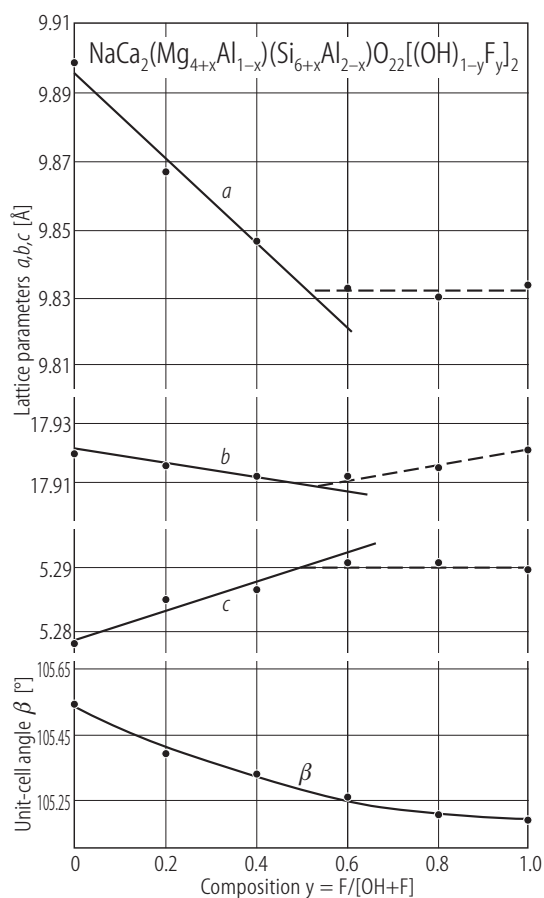
**Fig. 9.**  $\text{NaCa}_2(\text{Mg}_{4+x}\text{Al}_{1-x})(\text{Si}_{6+x}\text{Al}_{2-x})\text{O}_{22}[(\text{OH})_{1-y}\text{F}_y]_2$ . Unit cell parameters along the join pargasite – fluoro-pargasite as function of  $\text{F}/(\text{OH}+\text{F})$  [00R1]. The  $\text{Al}/(\text{Al}+\text{Si})$  content was  $\approx 0.32$  for nominal  $y \leq 0.6$  and  $0.29$  for  $y \geq 0.8$ .



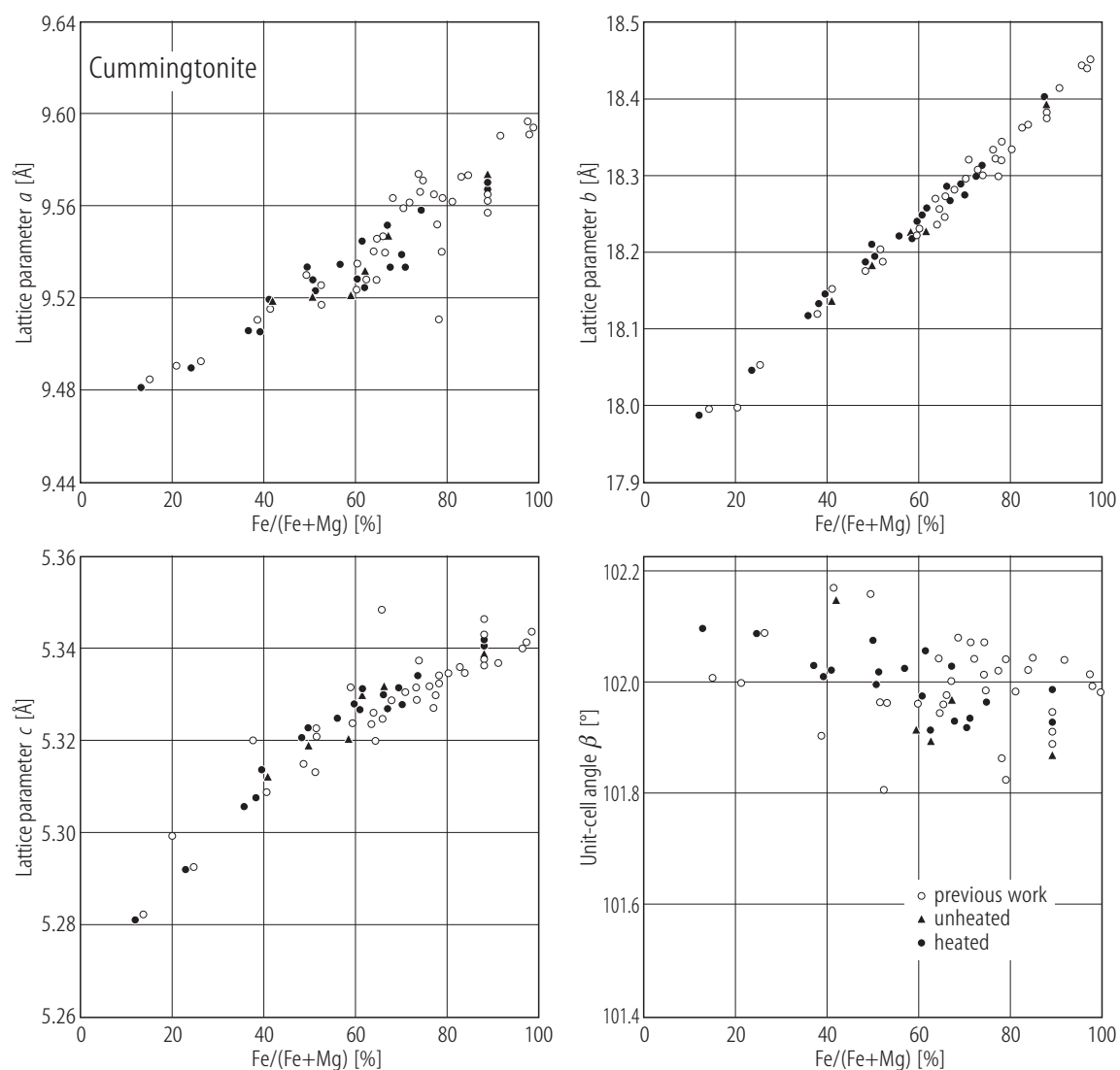
a



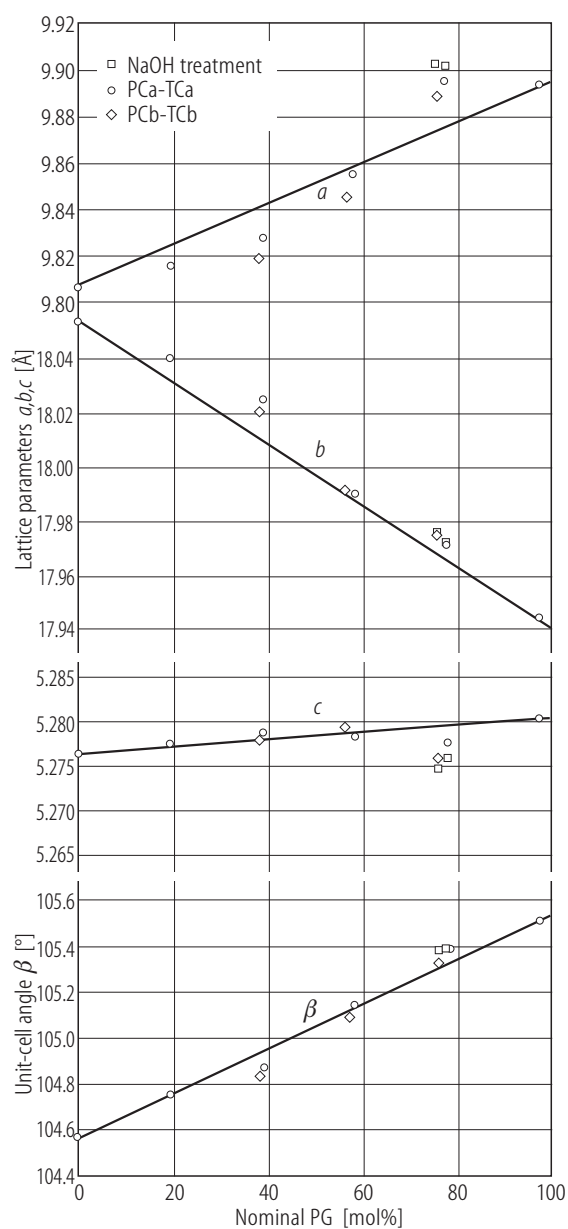
b



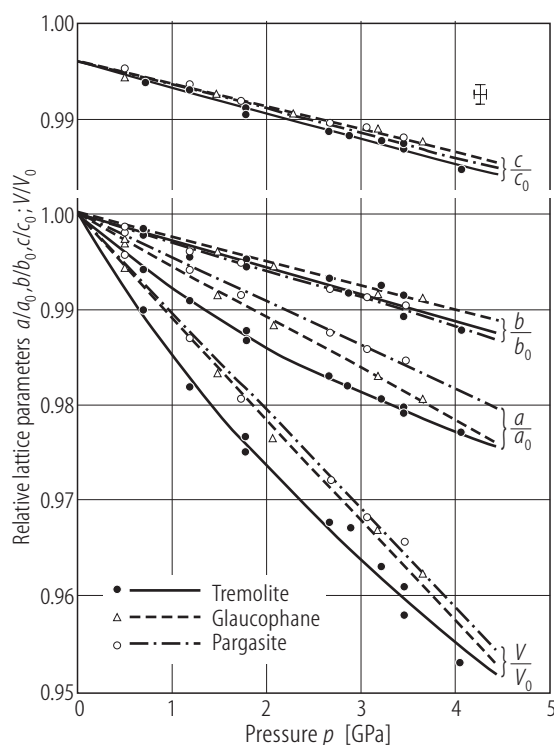




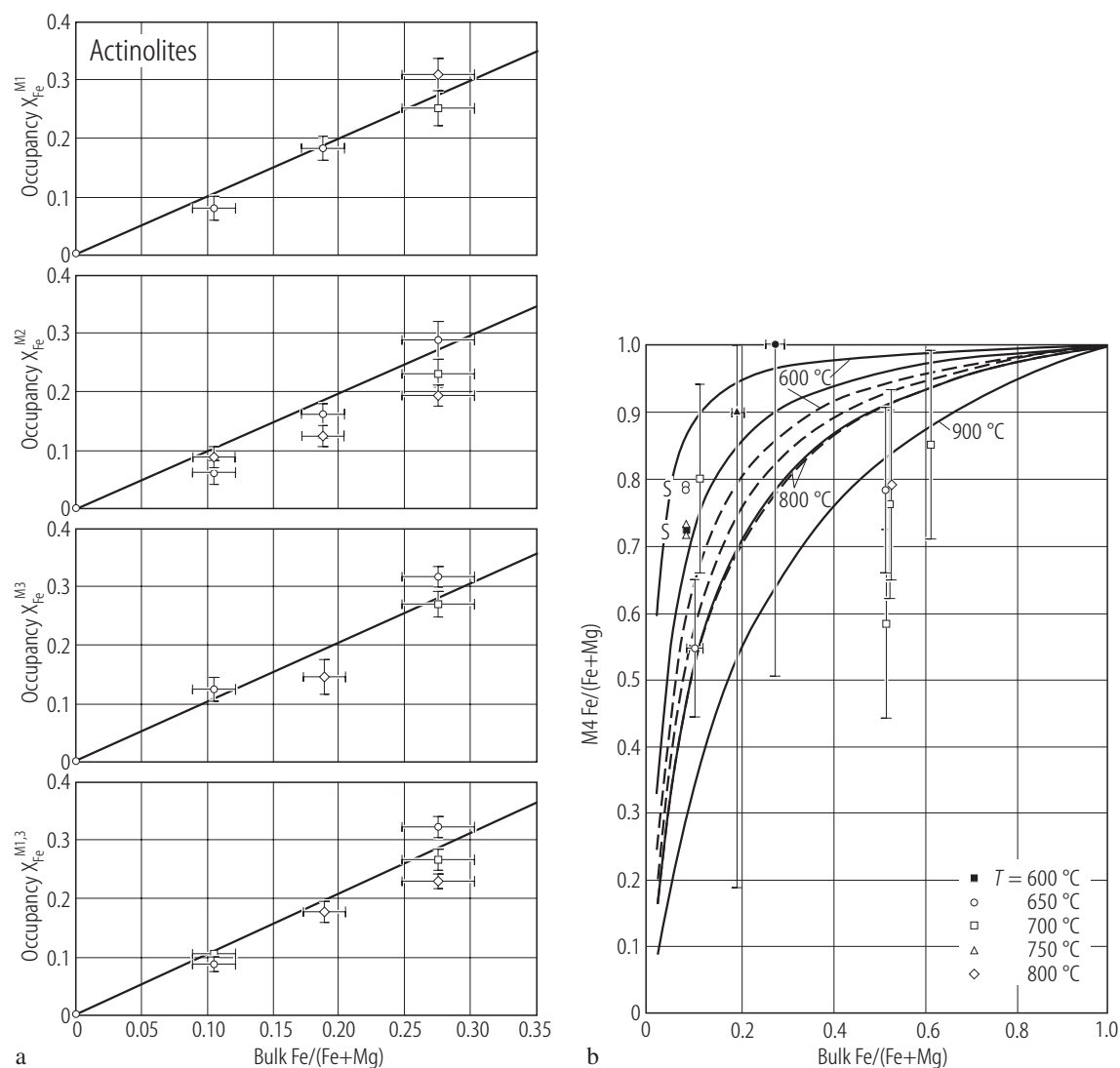
**Fig. 7.** Cummingtonite (natural and heated). Lattice parameters as function of iron content. Data for unheated and heated samples are from [94H2]. Data from previous work on natural cummingtonites are from [67K1, 69K1, 73K1, 74R1, 80H1, 88C1, 92L1, 92Z2].



**Fig. 10.**  $\text{Na}_{0.975}\text{Ca}_{1.95}\text{Mg}_{4.075}\text{Al}_{2.925}\text{Si}_{6.05}\text{O}_{22}(\text{OH})_2$  (PCa) –  $\text{Ca}_{1.8}\text{Mg}_{5.20}\text{Si}_8\text{O}_{22}(\text{OH})_2$  (TCa) (circles) and  $\text{Na}_{0.95}\text{Ca}_{1.90}\text{Mg}_{4.15}\text{Al}_{2.85}\text{Si}_{6.1}\text{O}_{22}(\text{OH})_2$  (PCb) –  $\text{Ca}_{1.7}\text{Mg}_{5.3}\text{Si}_8\text{O}_{22}(\text{OH})_2$  (TCb) (diamond). Composition dependences of lattice parameters. Squares indicate amphiboles formed in a 0.25m NaOH solution [99S1]. The straight lines are without significance.  $x$ -axis is nominal pargasite (PG).

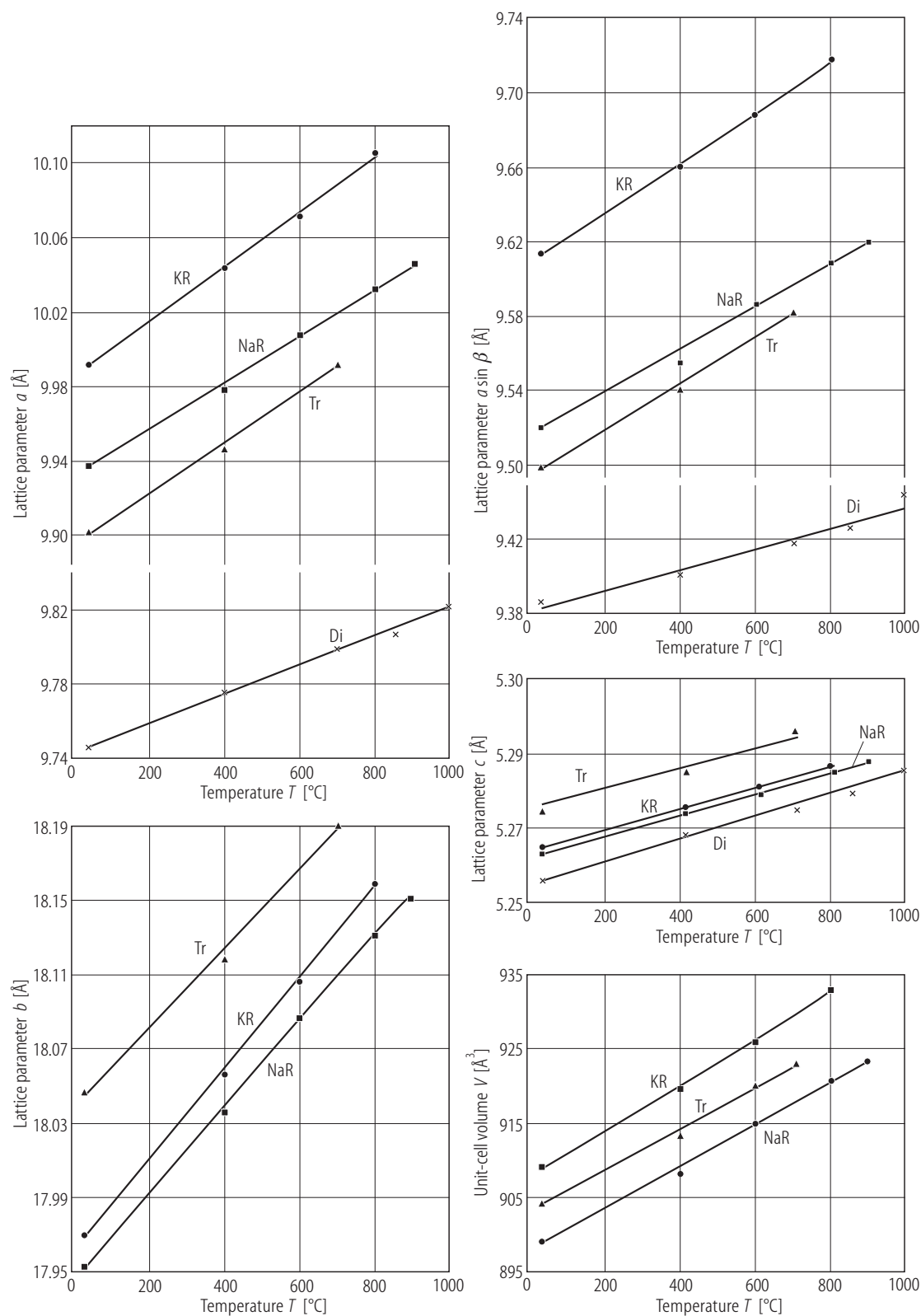


**Fig. 11.** Tremolite, glaucophane, pargasite. Cell volumes and lattice parameters as function of pressure [91C1]. The cross indicates the error bar. Lattice parameters and volume are normalized to the ambient pressure value.

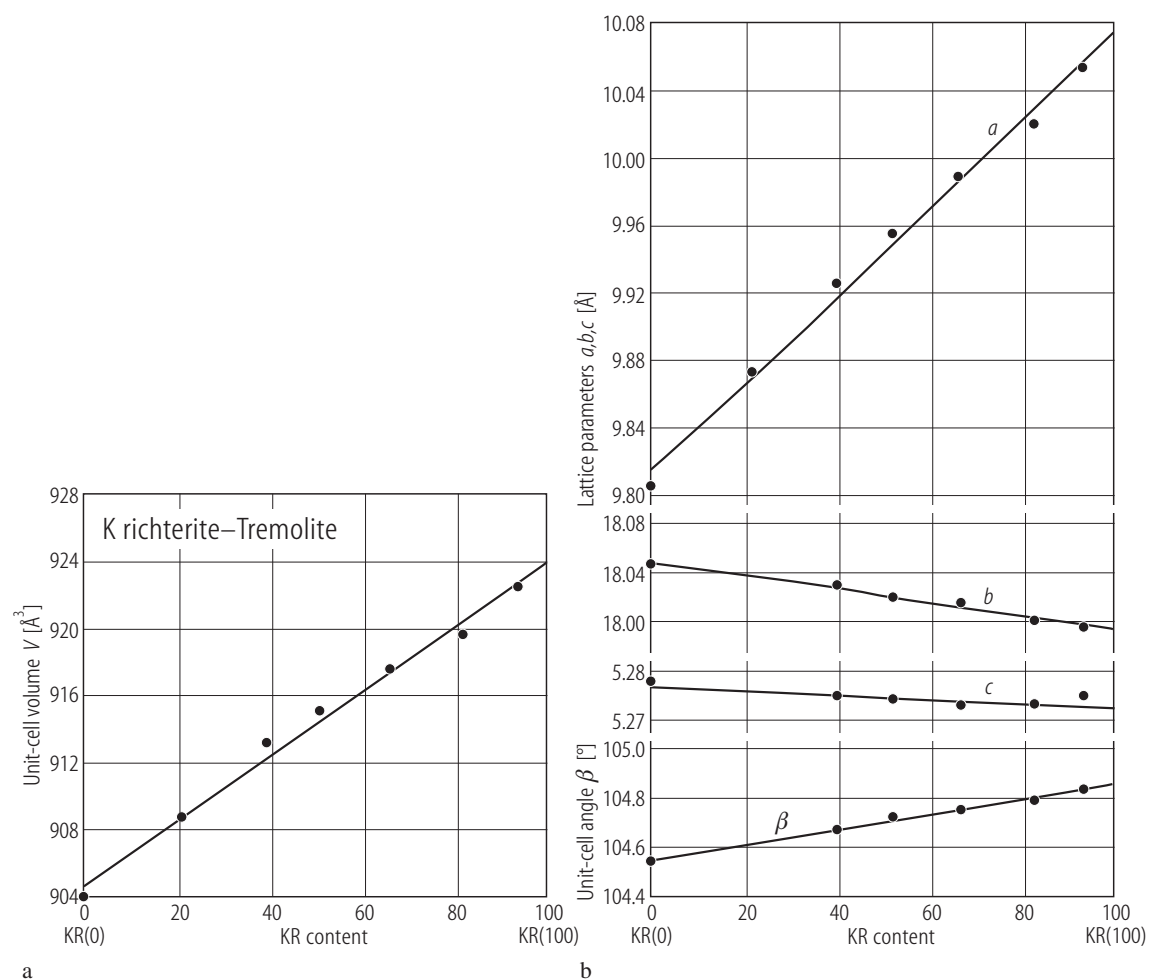


**Fig. 12.** Actinolites. (a) Plots of Fe/(Fe+Mg) ratios at the M1,M2,M3 and M13 (M1+M3) sites determined by Rietveld refinements (o), Rietveld refinements reduced by 20 % (since overestimate the Fe content) ( $\square$ ) and  $^{57}\text{Fe}$  NGR data ( $\diamond$ ). The straight lines represent the 1:1 correlation [05D1]; (b) the same ratios in the M4 site versus bulk

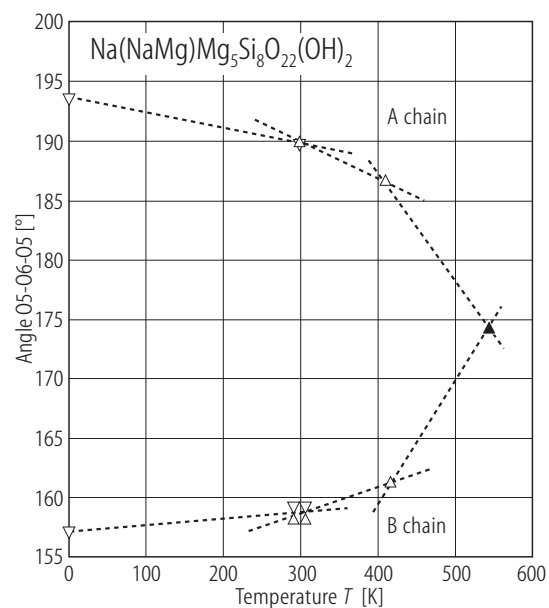
Fe/(Fe+Mg) ratio ( $= x_{Fe}$  in the M1,2,3 sites) from [05D1] (solid symbols) and from [87S1] – S and [98E1, 02G1] (open symbols). Dashed isotherms were calculated from  $\Delta G^0$  (1073 K) = 20 kJ, while the solid isotherms were obtained with  $\Delta G^0$ (298 K) = 62 kJ and  $\Delta S^0$  (298 K) of 54 J/K [05D1].



**Fig. 13.** Na richterite (NaR), K richterite (KR), tremolite (Tr) [83C1], diopside (Di) [79C1]. Temperature dependences of lattice parameters. I-centered cell parameters of the amphiboles are plotted.

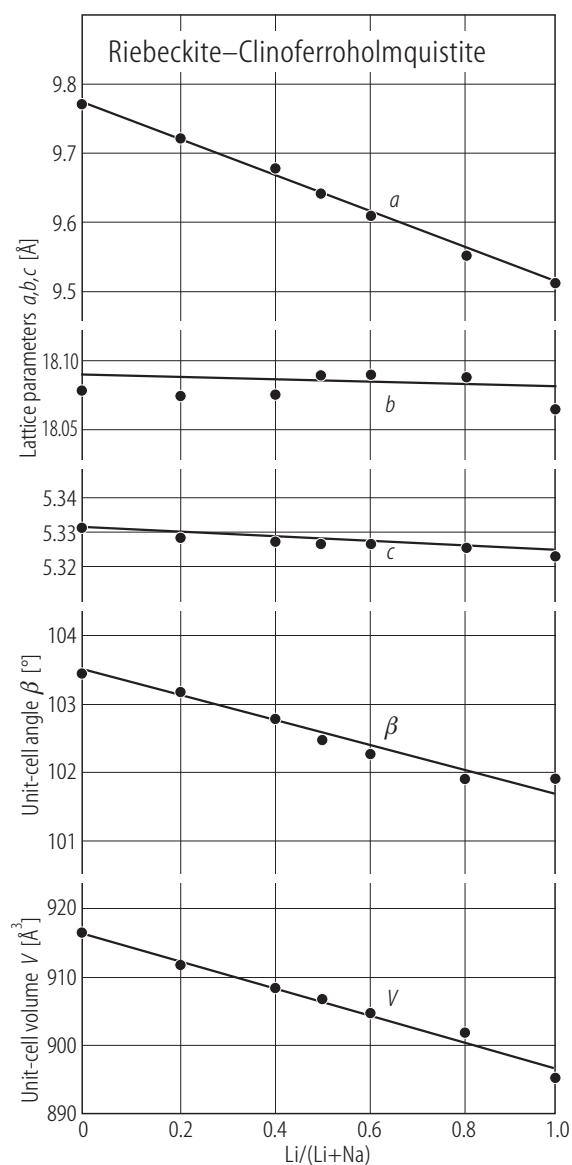


**Fig. 14.** K richterite – tremolite. Composition dependences of the unit-cell volume (a) and lattice parameters (b) [97H1].

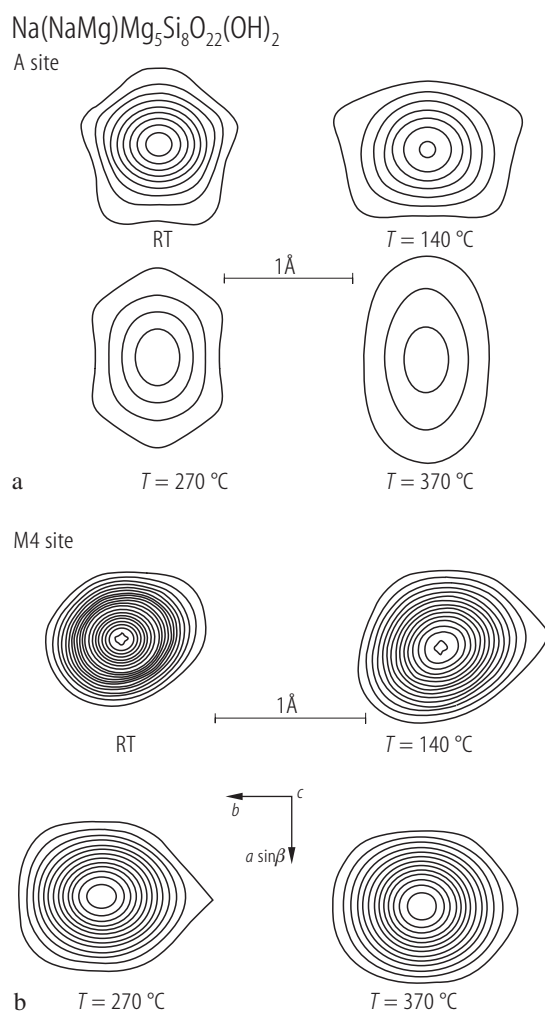


For Fig. 15 see next page

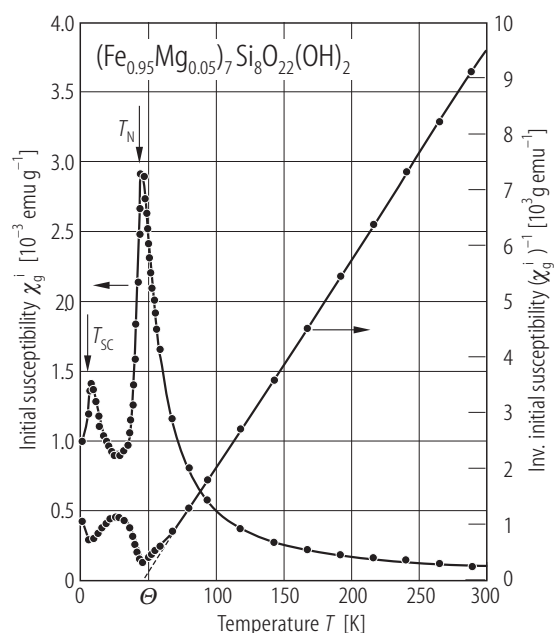
**Fig. 16.**  $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Change in the O5-O6-O5 angles between 8 and 573 K  $\nabla$ -[0511];  $\Delta$ -[03C1];  $\blacktriangle$ -after  $P2_1/m - C2/m$  transition [0511]. The dotted lines are drawn as guide for the eye.



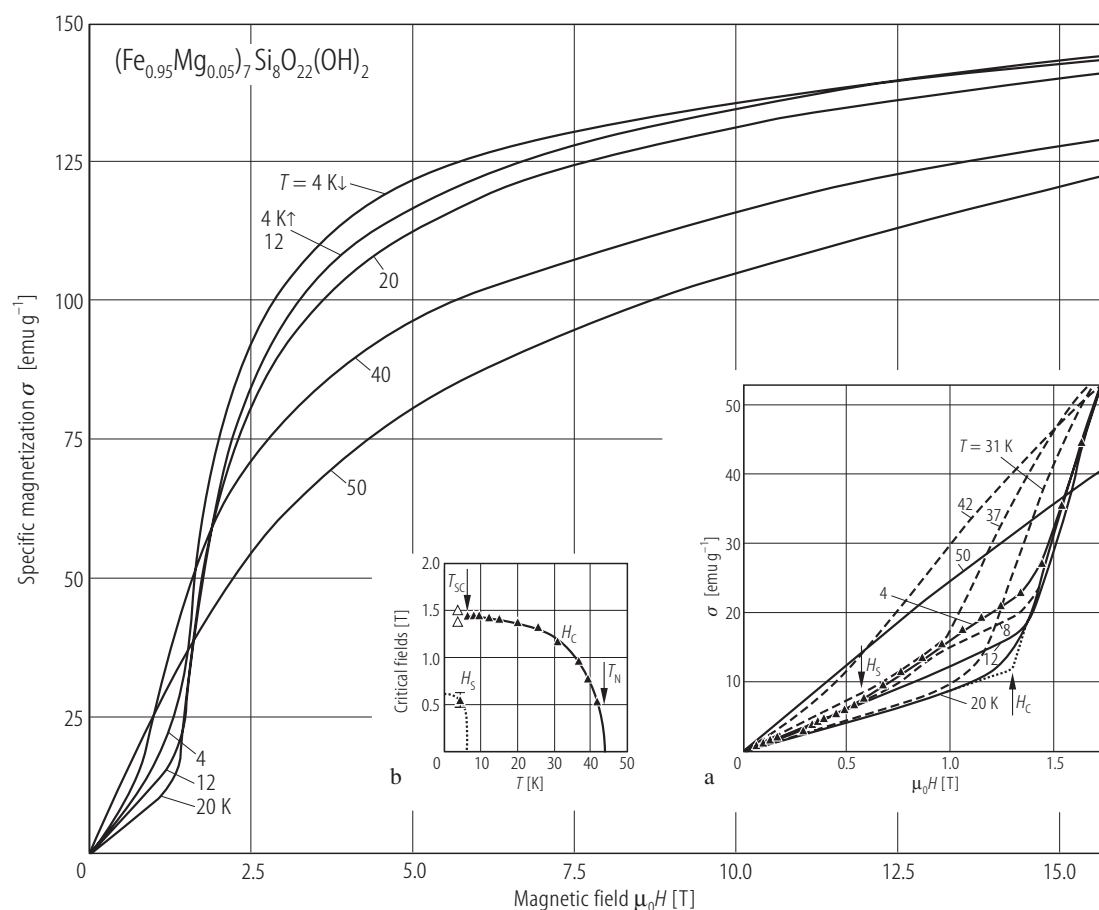
**Fig. 15.** Riebeckite – ferri-clinoferroholmquistite. Composition dependences of the lattice parameters [0312].



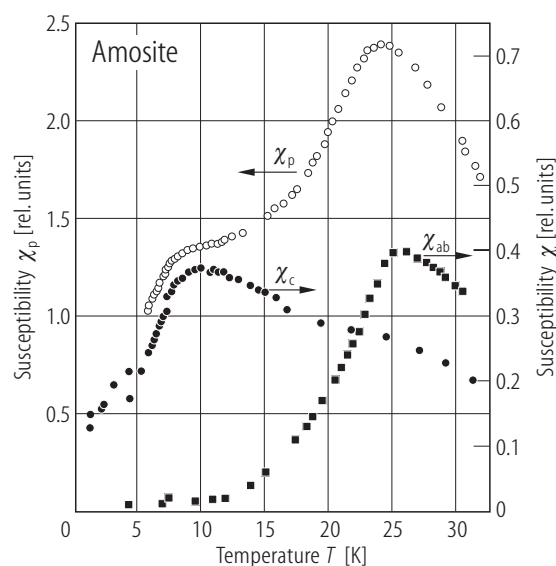
**Fig. 17.**  $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . The shape of the electron densities (a) at the A site in the two symmetries; projection onto  $(-210)$ ,  $b$ -edge on the abscissa; (b) at the M4 site in two symmetries. Contour lines each  $2\text{ e}\text{\AA}^{-3}$ ; first line at  $2\text{ e}\text{\AA}^{-3}$  [03C1].



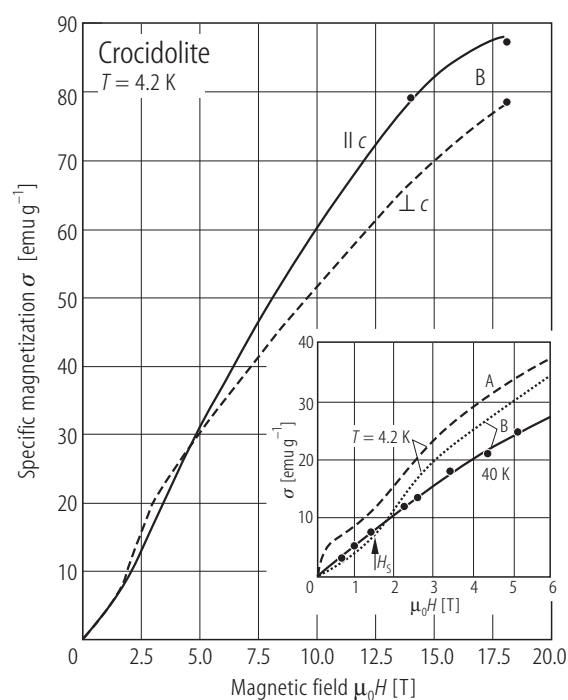
**Fig. 18.**  $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  grunerite with  $x = 0.95$ . Thermal variations of initial and inverse susceptibilities [88L1].  $T_{\text{SC}}$ : spin canting temperature (see text).



**Fig. 19.**  $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  grunerite with  $x = 0.95$ . Magnetization isotherms. Inset (a) shows details of the magnetization curves and inset (b) the variation with temperature of the critical threshold fields  $H_c$  and  $H_s$  (see text). The values noted on curves are  $T$  in K [88L1].

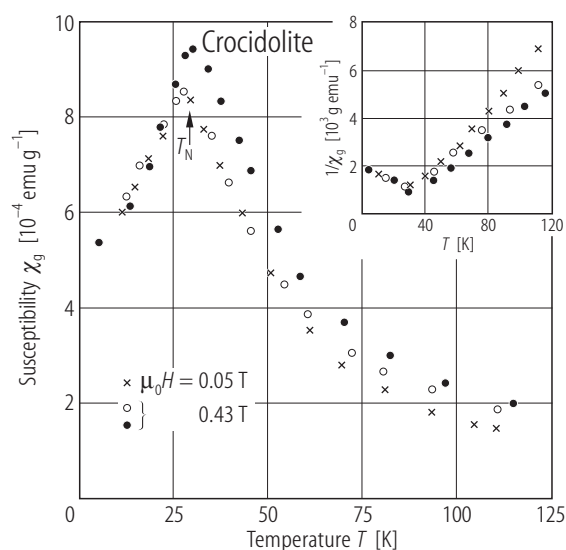


**Fig. 20.** Natural anthophyllite (amosite). Temperature dependence of the magnetic susceptibilities in a field of  $\mu_0 H = 2$  T ( $\chi_c$  – parallel and  $\chi_{ab}$  – perpendicular to the fibre axis and  $\chi_p$  for the powdered sample) [75E1].

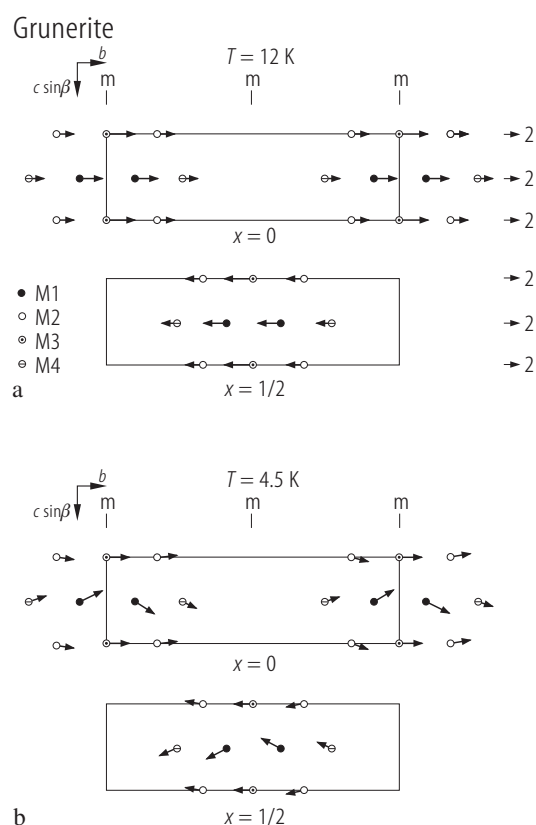


**Fig. 22.** Crocidolites (riebeckites A<sup>7</sup>) and B<sup>8</sup>). Specific magnetization isotherms. Data in high fields were obtained on oriented fibres [83M3]. Composition in Table 6.

For Fig. 23 see next page

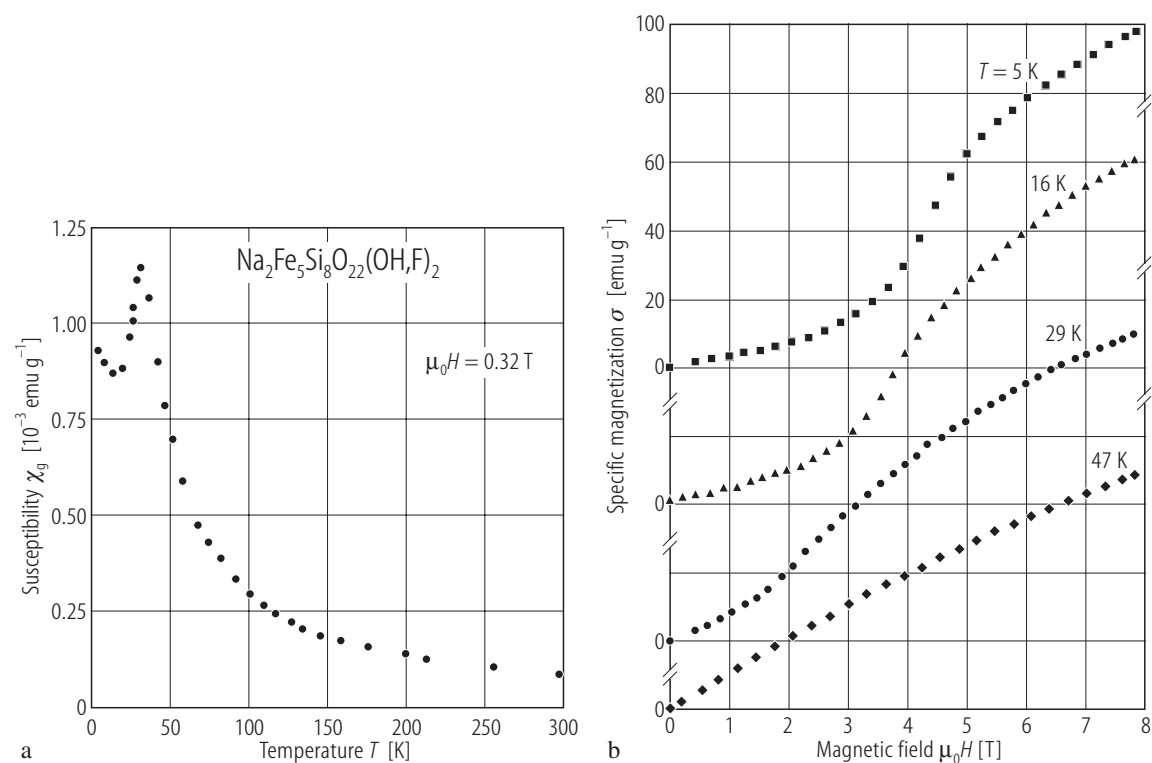


**Fig. 21.** Crocidolite (riebeckite)<sup>8</sup>). Susceptibilities and inverse susceptibilities (inset). Measurements were made with the field applied parallel (•) and perpendicular (o) to the fibre axes and for a randomly oriented sample (×) [83M3]. Composition in Table 6.

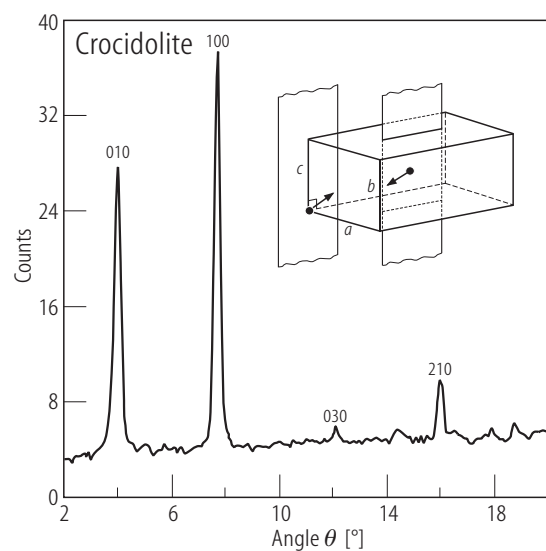


**Fig. 24.** Grunerite. Projection of magnetic structure perpendicular to the  $a$ -axis. Arrows represent direction of the magnetic moments at (a) 12 K and (b) at 4.5 K [87G1].

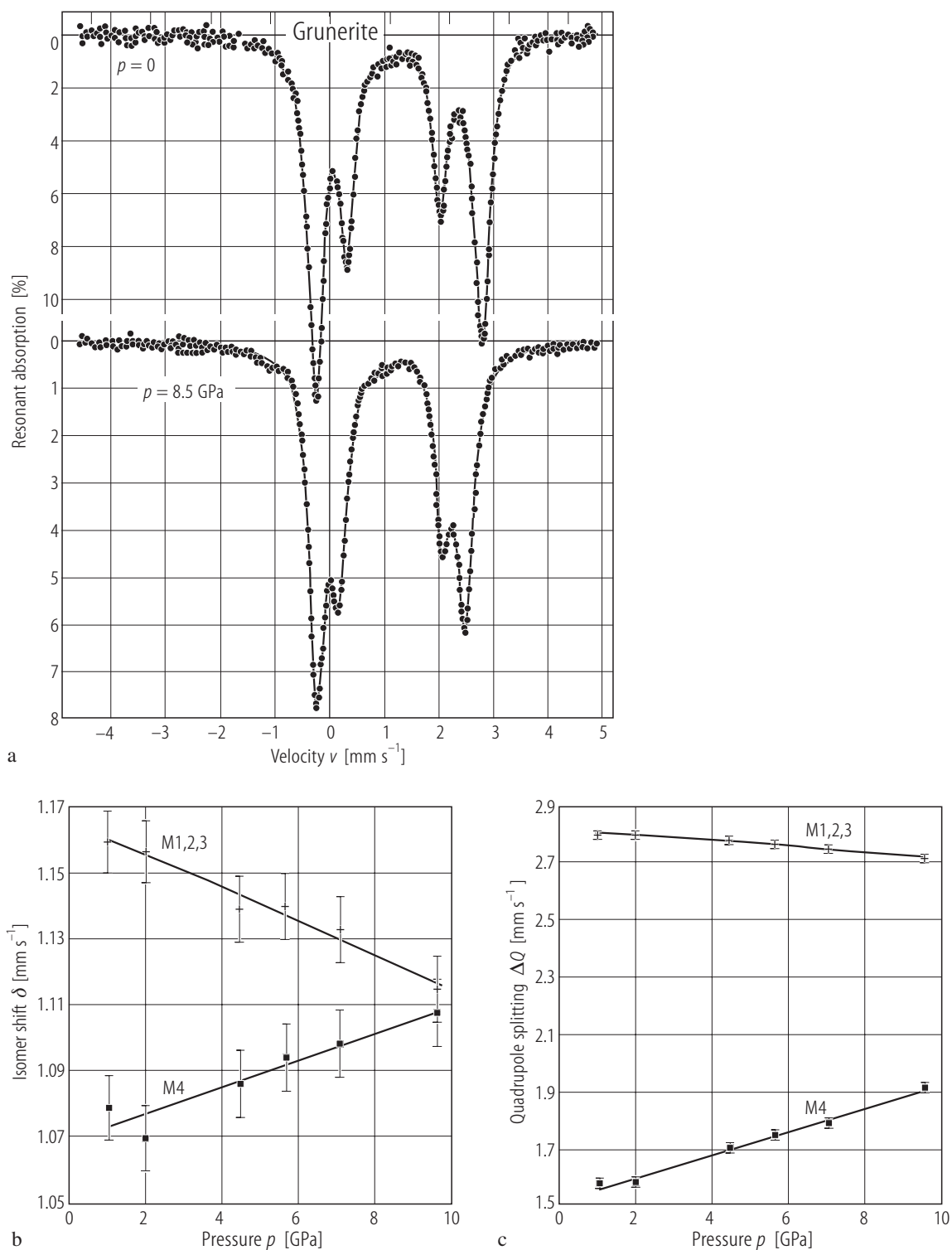




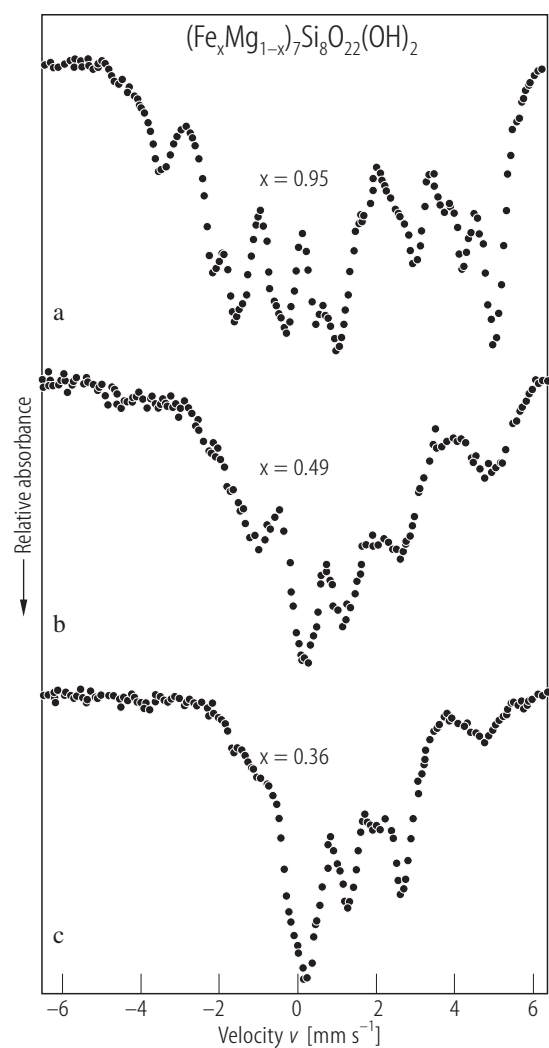
**Fig. 23.**  $\text{Na}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH},\text{F})_2$ . (a) Temperature dependence of the susceptibility in a field  $\mu_0 H = 0.32 \text{ T}$  for a powdered sample, (b) specific magnetization isotherms for a single crystal in a field  $H \parallel [001]$  [75B3].



**Fig. 25.** Crocidolite (riebeckite). Magnetic neutron scattering pattern obtained by subtracting the diffraction pattern recorded at 40 K from that at 5 K. The magnetic structure is shown in the insert [83M3].

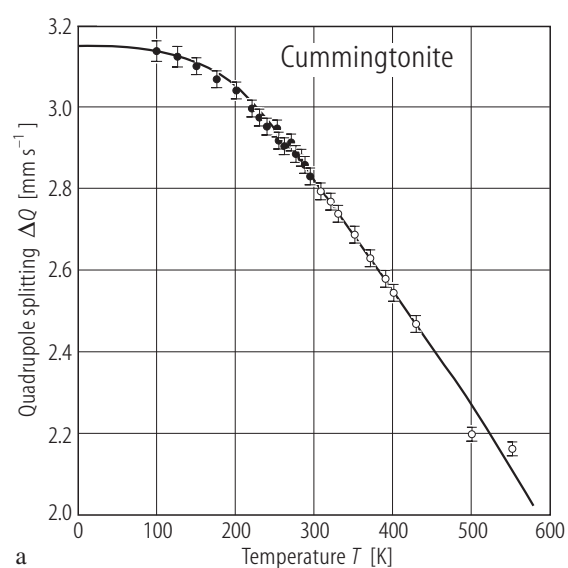


**Fig. 26.** Grunerite<sup>5)</sup>.  $^{57}\text{Fe}$  NGR spectra at ambient pressure and 8.5 GPa (a). Pressure dependences of the isomer shifts (b) and quadrupole splittings (c) [92Z1]. Composition in Table 8.

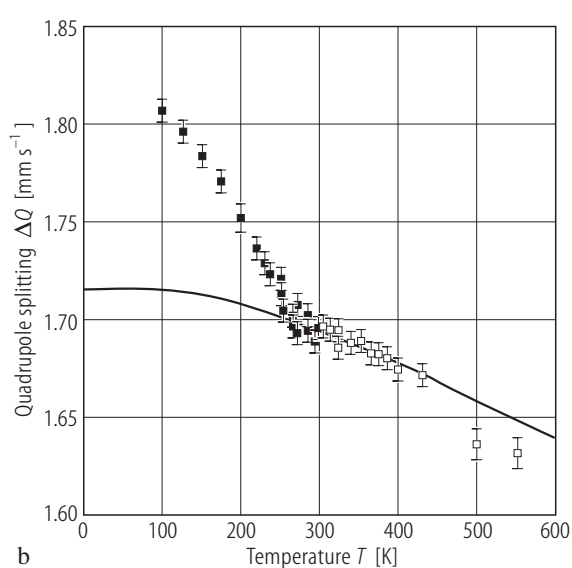


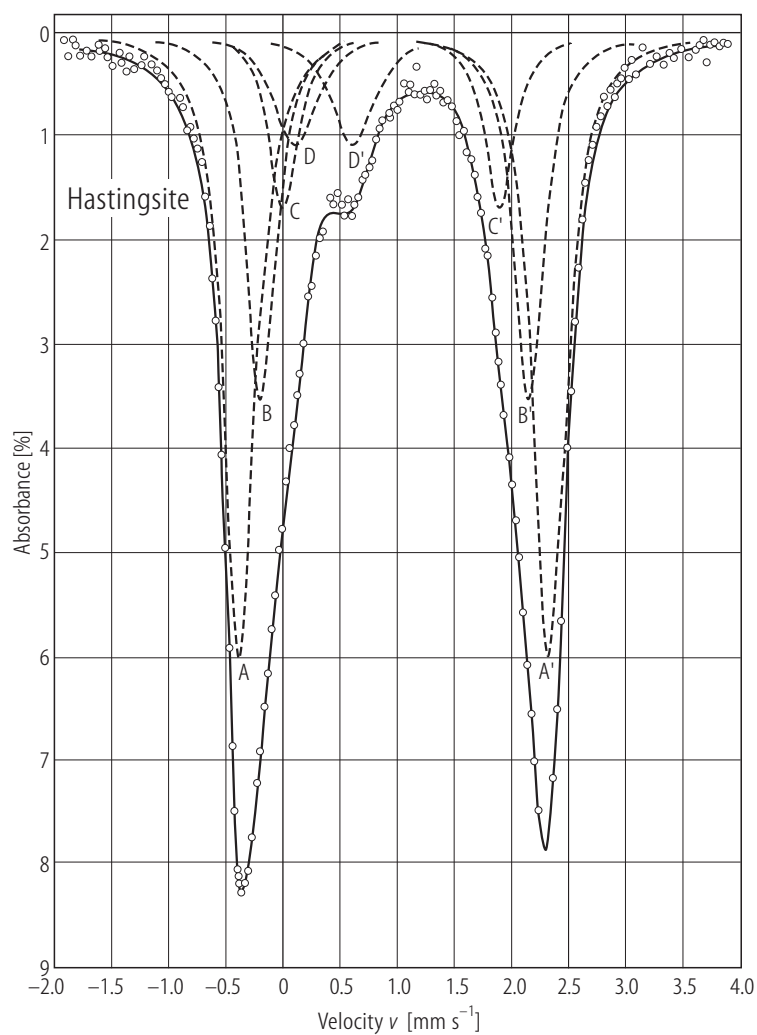
←

**Fig. 27.**  $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ .  $^{57}\text{Fe}$  NGR spectra at (a) 14 K ( $x = 0.95$ ), (b) 4.2 K ( $x = 0.49$ ) and (c) 1.6 K ( $x = 0.36$ ) [88L1].

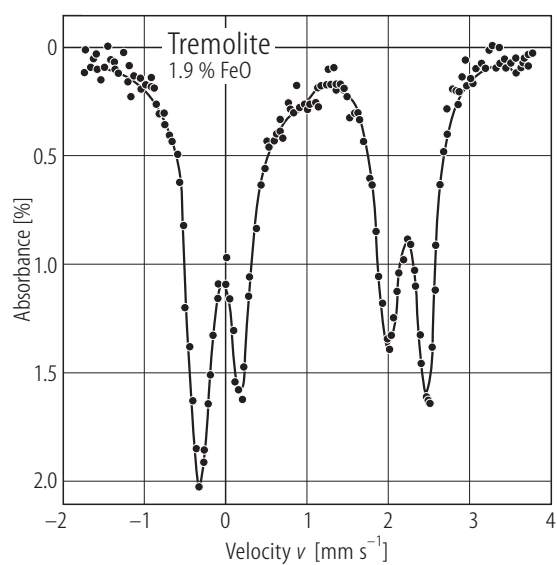


**Fig. 28.** Cummingtonite. Temperature dependences of the quadrupole splittings,  $\Delta Q$  for (a)  $\text{Fe}^{2+}$  at the (M1, M2, M3) sites, (b)  $\text{Fe}^{2+}$  at M4 site [02B1]. Open symbols (C2/m structure), filled symbols (P2<sub>1</sub>/m structure). ↓

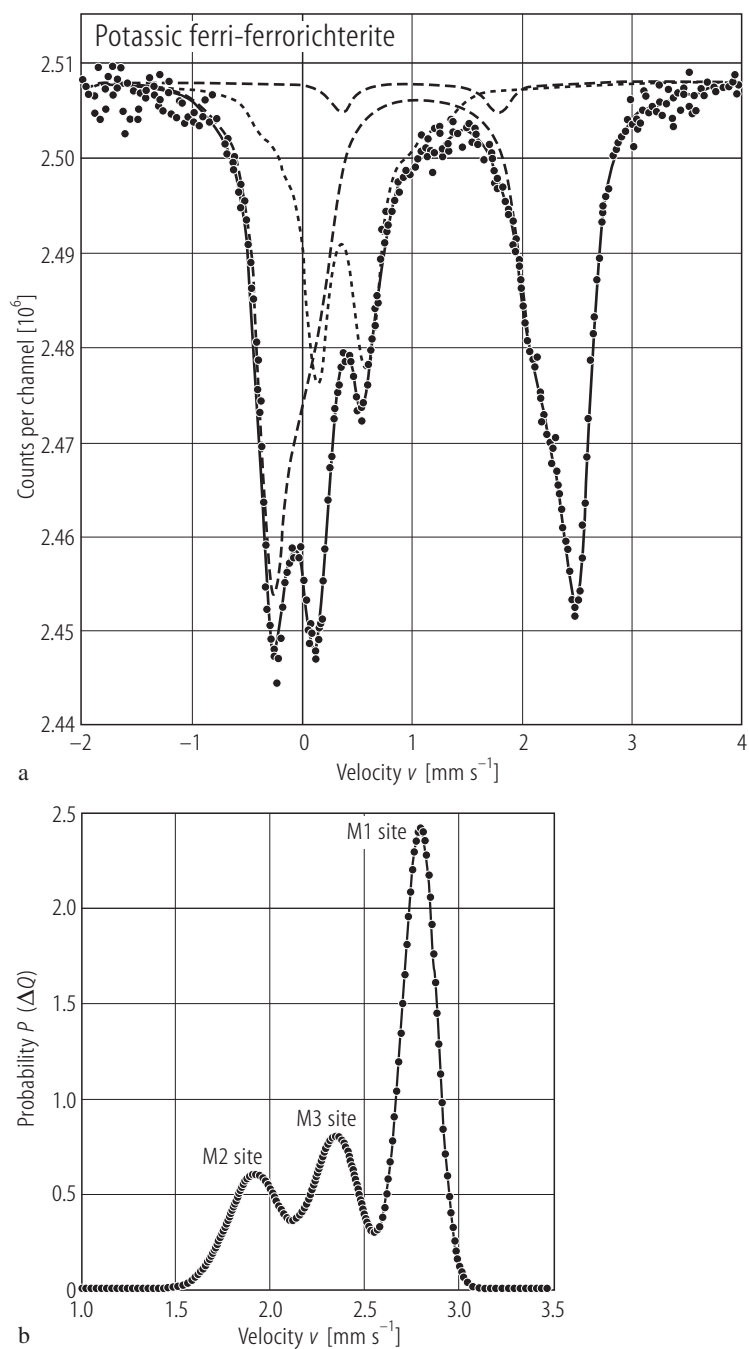




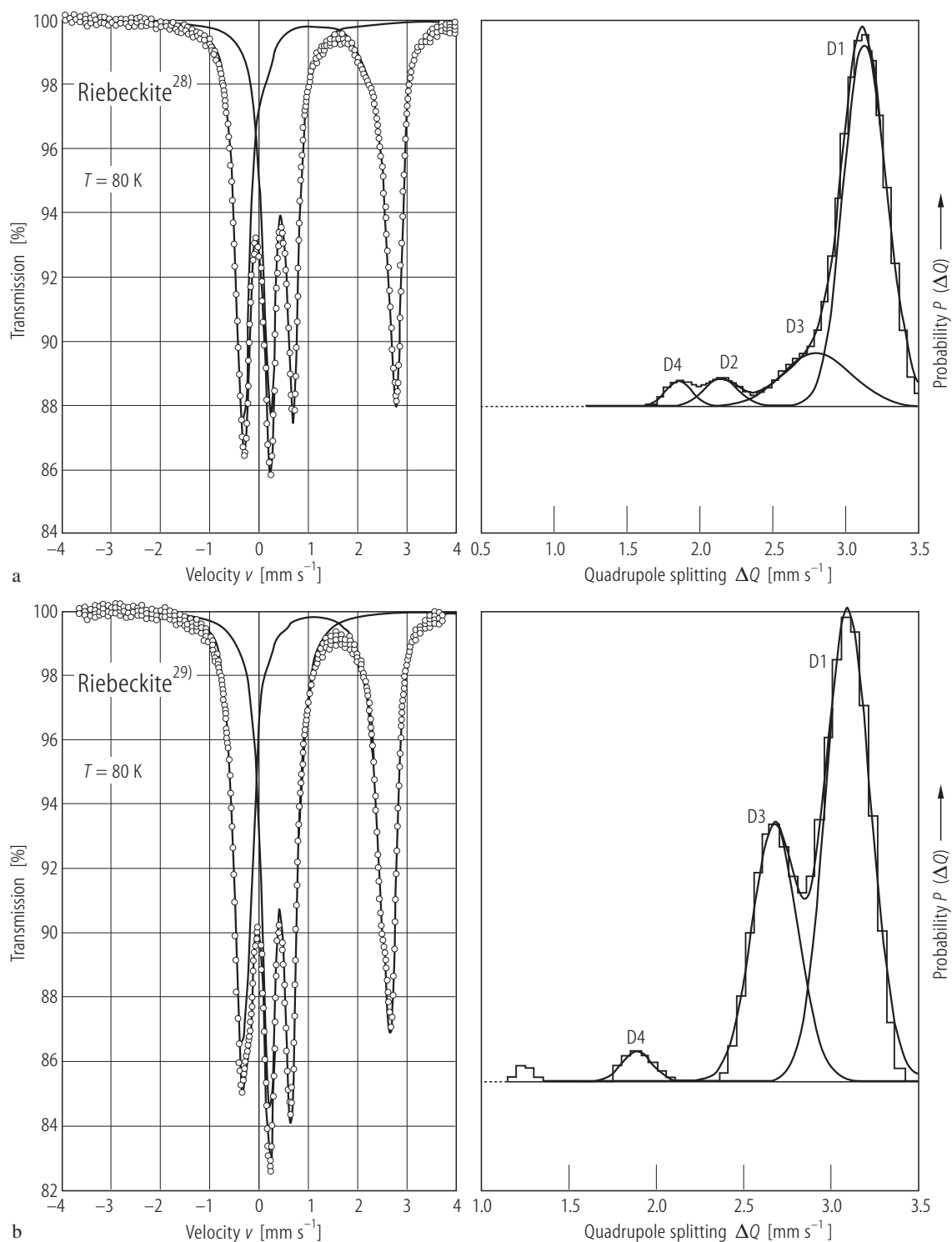
**Fig. 29.** Hastingsite (synthetic).  $^{57}\text{Fe}$  NGR spectrum at room temperature. Doublets AA', BB', CC' are assigned to  $\text{Fe}^{2+}$  and doublet DD' to  $\text{Fe}^{3+}$ , all in octahedral coordination [82T1].



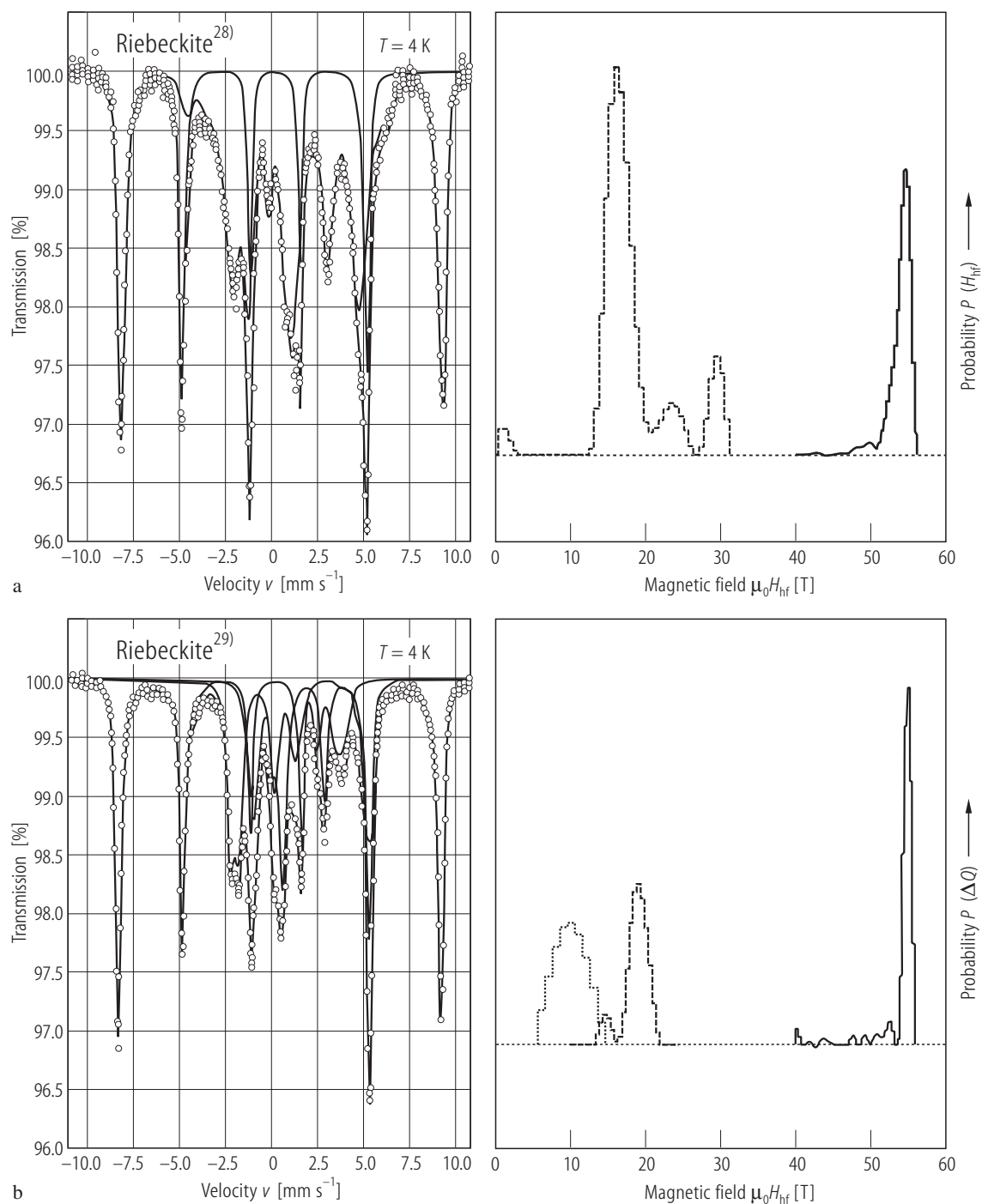
**Fig. 30.** Tremolite.  $^{57}\text{Fe}$  NGR spectrum at room temperature [79G1].



**Fig. 31.** Potassic ferri-ferrorichterite<sup>40</sup>. (a)  $^{57}\text{Fe}$  NGR spectrum at 298 K and (b) the corresponding trimodal  $\Delta Q(\text{Fe}^{2+})$  distribution curve [02R2]. Composition in Table 8.

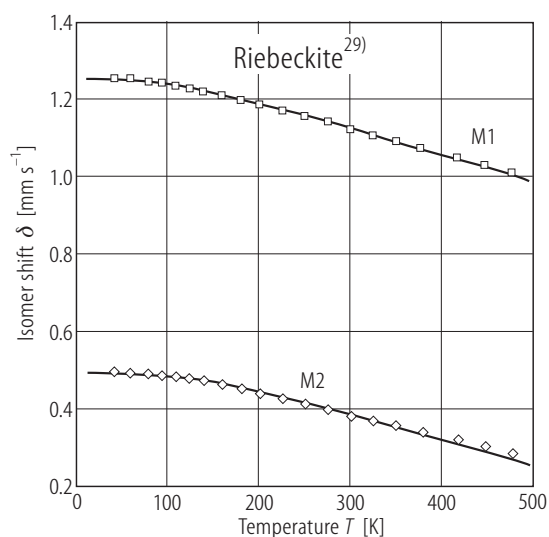


**Fig. 32.** Riebeckite<sup>28</sup> (a) and riebeckite<sup>29</sup> (b).  $^{57}\text{Fe}$  NGR spectra at 80 K. The spectra have been fitted with a superposition of a ferric doublet and a ferrous quadrupole splitting distribution (full lines). The calculated probability distribution,  $P(\Delta Q)$ , is reproduced in the right part of the drawing [96V1]. Composition in Table 8.

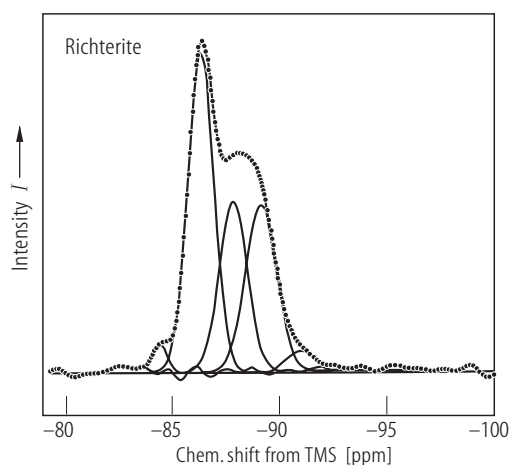
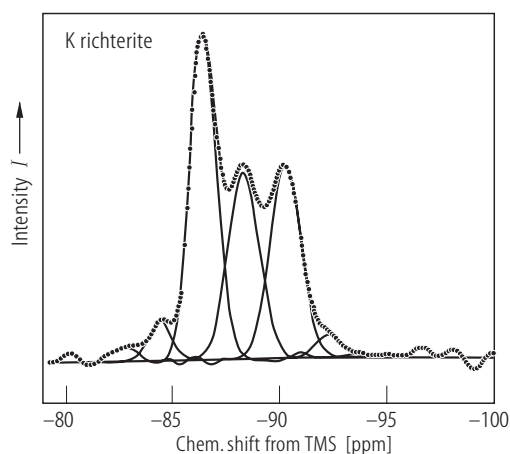
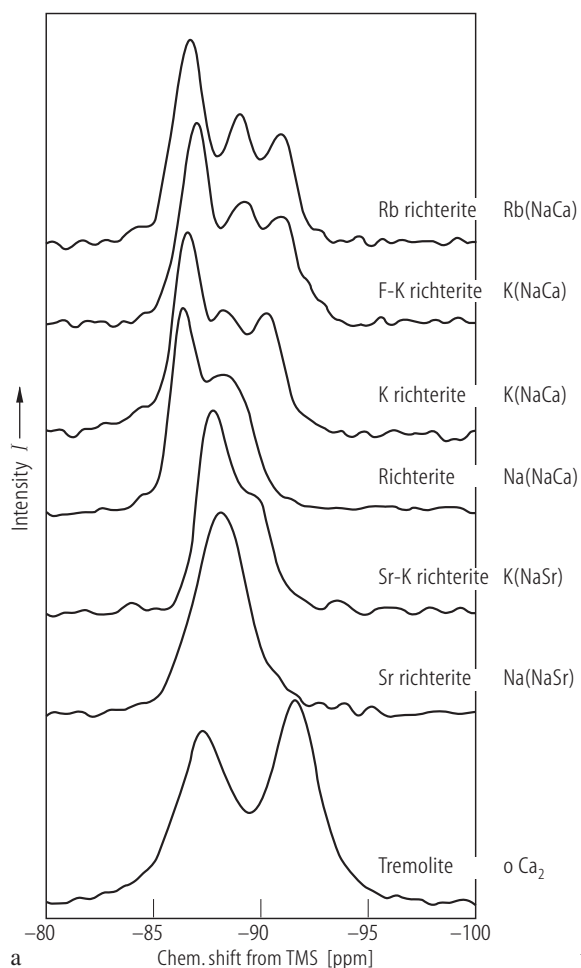


**Fig. 33.** Riebeckite<sup>28</sup> (a) and riebeckite<sup>29</sup> (b). <sup>57</sup>Fe NGR spectra at 4 K fitted with a superposition of one ferric and one ferrous hyperfine-field distribution. The distribution profiles are shown on right side in full line for the ferric

component and dashed line for the ferrous one (a), while in (b) the distribution profiles in dashed are for the Fe<sup>2+</sup>(M1) component and in dotted line for the Fe<sup>2+</sup>(M3) component (full line as in (a)) [96V1]. Composition in Table 8.



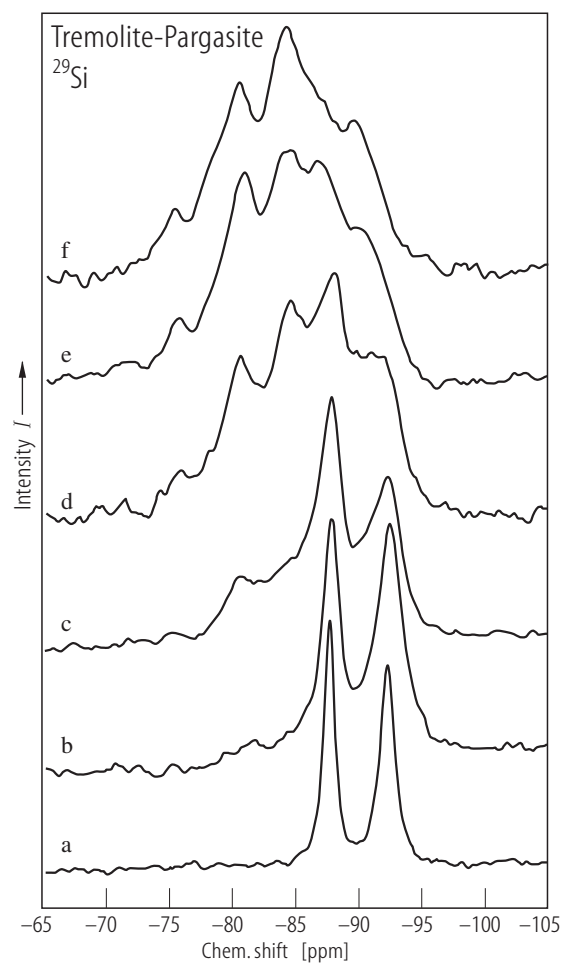
**Fig. 34.** Riebeckite<sup>29)</sup>. Calculated (full line) and experimental isomer shifts as function of temperature for M1(Fe<sup>2+</sup>) and M2(Fe<sup>3+</sup>) [96V1]. Composition in Table 8.



**Fig. 35.** Synthetic richterites and natural tremolite. (a) <sup>29</sup>Si MAS NMR spectra. The small peak at -84 ppm in some spectra is the only peak that does not cross-polarize and is due to a very small amount of clinopyroxene impurity. The

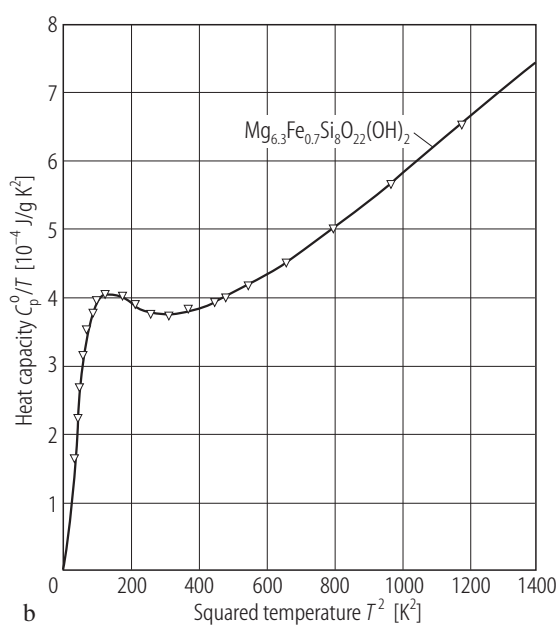
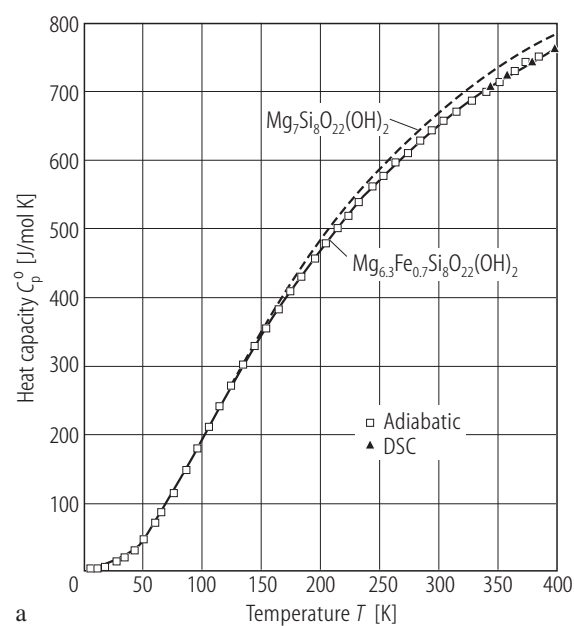
A site and M4 chemistries are indicated in right part. (b) Simulations of the <sup>29</sup>Si MAS NMR spectra of potassium richterite and richterite using a pure Gaussian peak shape. The dots are experimental data [98W1].



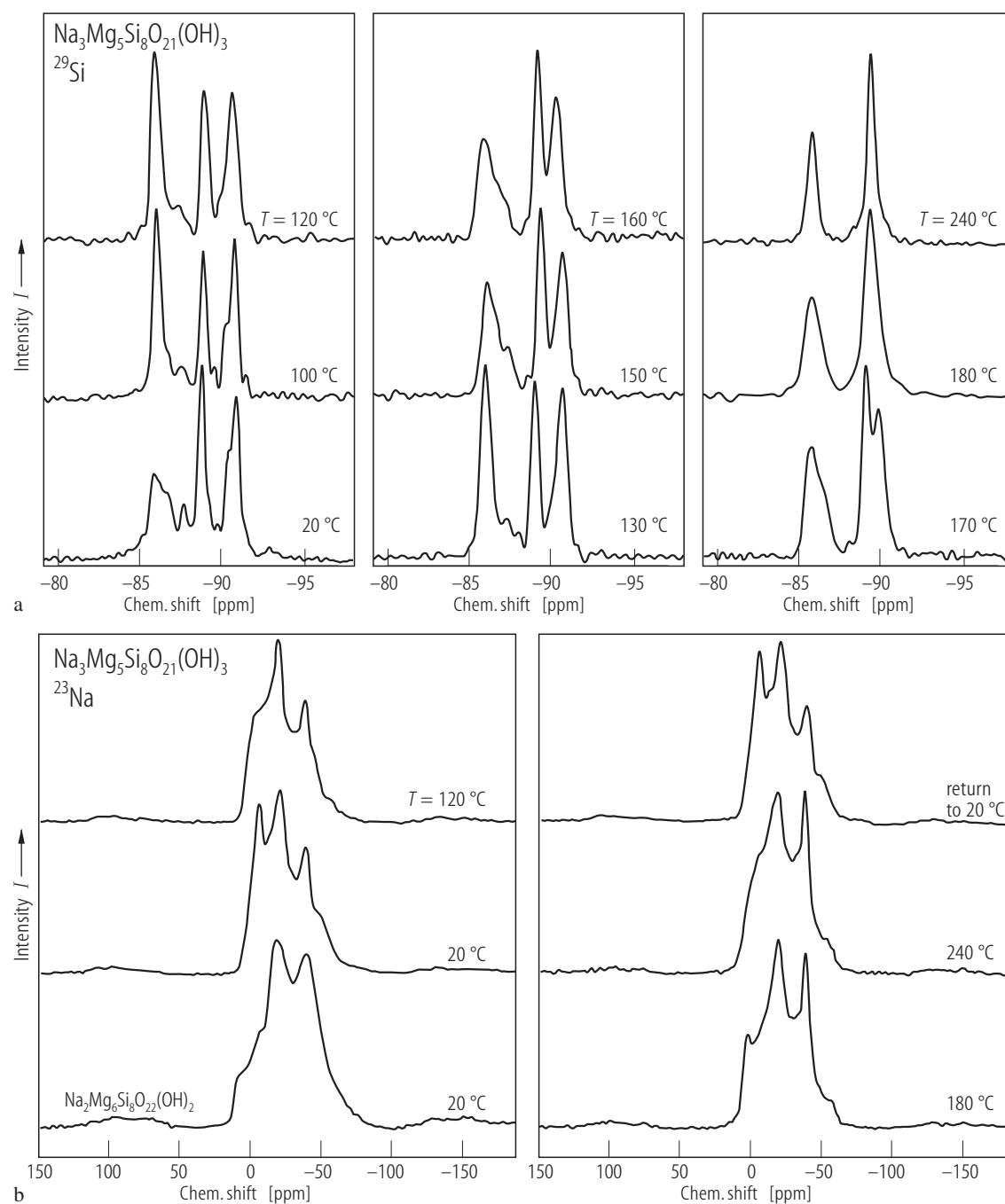
**Fig. 36.**

$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$  (curve *a*);  $\text{Na}_{0.2}\text{Ca}_2\text{Mg}_{4.8}\text{Ga}_{0.6}\text{Si}_{7.6}\text{O}_{22}\text{F}_2$  (*b*);  $\text{Na}_{0.4}\text{Ca}_2\text{Mg}_{4.6}\text{Ga}_{1.2}\text{Si}_{7.2}\text{O}_{22}\text{F}_2$  (*c*);  $\text{Na}_{0.6}\text{Ca}_2\text{Mg}_{4.4}\text{Ga}_{1.8}\text{Si}_{6.8}\text{O}_{22}\text{F}_2$  (*d*);  $\text{Na}_{0.8}\text{Ca}_2\text{Mg}_{4.2}\text{Ga}_{2.4}\text{Si}_{6.4}\text{O}_{22}\text{F}_2$  (*e*);  $\text{NaCa}_2\text{Mg}_4\text{Ga}_3\text{Si}_6\text{O}_{22}\text{F}_2$  (*f*).  $^{29}\text{Si}$  MAS NMR spectra of  $^{41}\text{Si}$  [99S2].

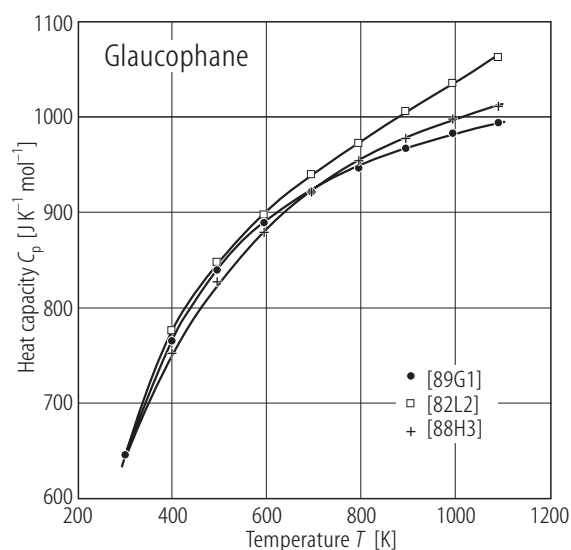
For Fig. 37 see next page



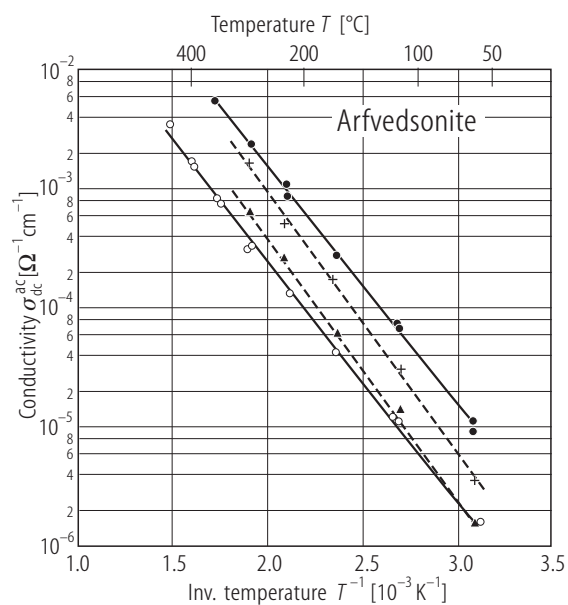
**Fig. 38.**  $\text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2$ ,  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Temperature dependence of the heat capacity (**a**) and  $C_p/T$  vs.  $T^2$  at low temperature (**b**) [85K1, 85K2].



**Fig. 37.**  $\text{Na}_3\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ . (a)  $^{29}\text{Si}$  and (b)  $^{23}\text{Na}$  MAS NMR spectra as function of temperature. In (b) is also shown the spectrum of  $\text{Na}_2\text{Mg}_6\text{Si}_8\text{O}_{22}(\text{OH})_2$  at 20 °C [96L1].

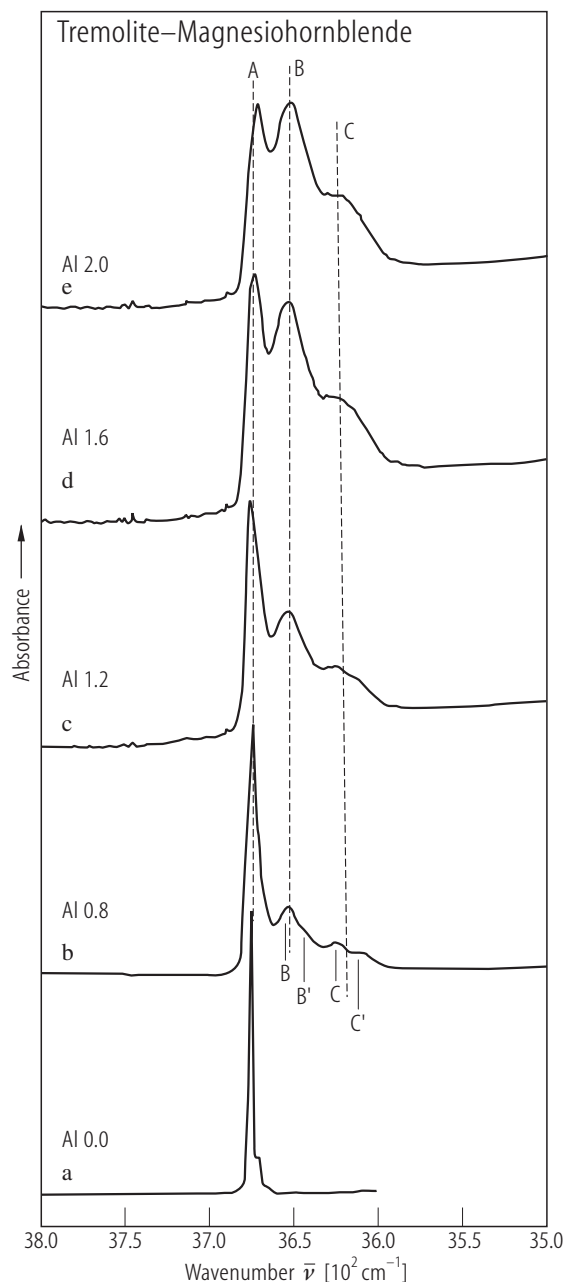


**Fig. 39.**  $\text{Na}_{0.01}(\text{Na}_{1.93}\text{Ca}_{0.05}\text{Fe}_{0.02})\text{-(Mg}_{2.60}\text{Fe}^{2+}_{0.41}\text{Fe}^{3+}_{0.15}\text{Cr}_{0.01}\text{Al}_{1.83})(\text{Si}_{7.92}\text{Al}_{0.08})\text{O}_{22}(\text{OH})_2$  glaucophane. Heat capacity (corrected for composition) vs. temperature [89G1]. The data obtained by [82L2] and [88H3] are also given.

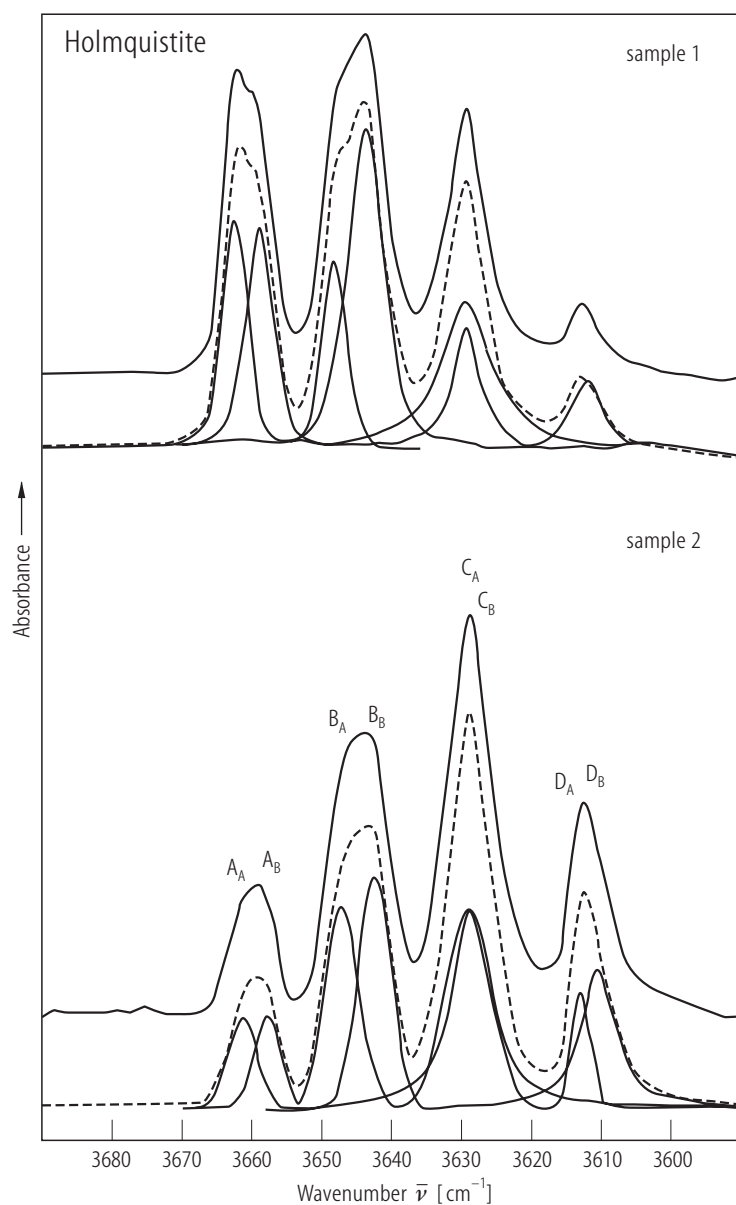


**Fig. 40.** Arfvedsonite. Logarithm of extrapolated conductivity for  $\omega \rightarrow 0$  from impedance plots  $\sigma_{\text{dc}}^{\text{ac}}$  versus  $T^{-1}$ . Volume conductivity: crosses: second run; full circles: seventh run. Conductivity assumed to occur at or across internal surface layers generated by defects of variable kinds: triangles: second run; open circles: seventh run. Current in all cases parallel to [001] [96S1].

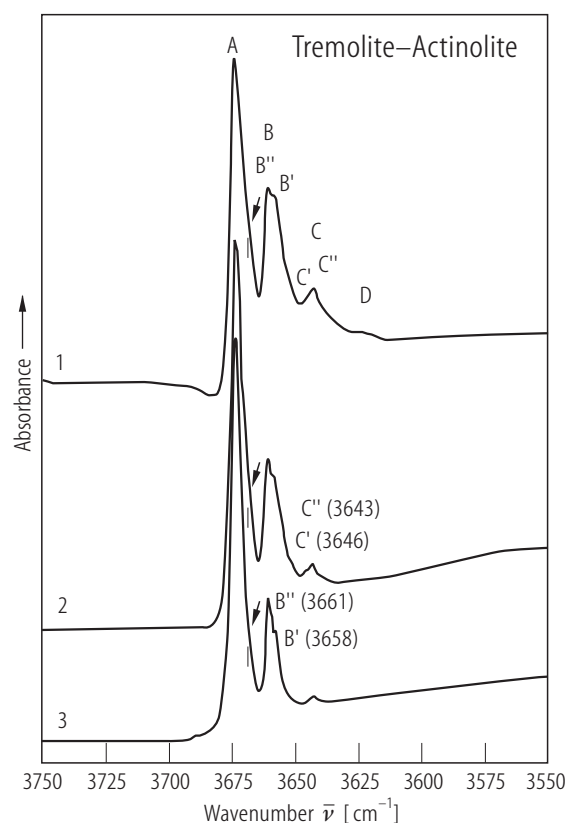
For Fig. 41 see next page



**Fig. 42.**  $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{Ca}_{1.8}(\text{Mg}_{4.2}\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$ . Infrared spectra in the principal OH-stretching region [00H2].

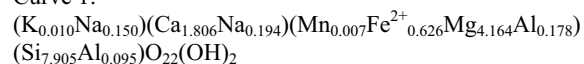


**Fig. 41.** Holmquistite (natural). Infrared OH-stretching spectra of two samples heat treated in air [03I3].

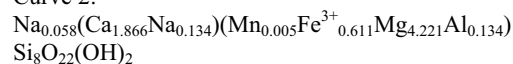


**Fig. 43.** Tremolite –  $\text{Fe}^{2+}$  poor actinolites. IR OH-stretching spectra [0211].

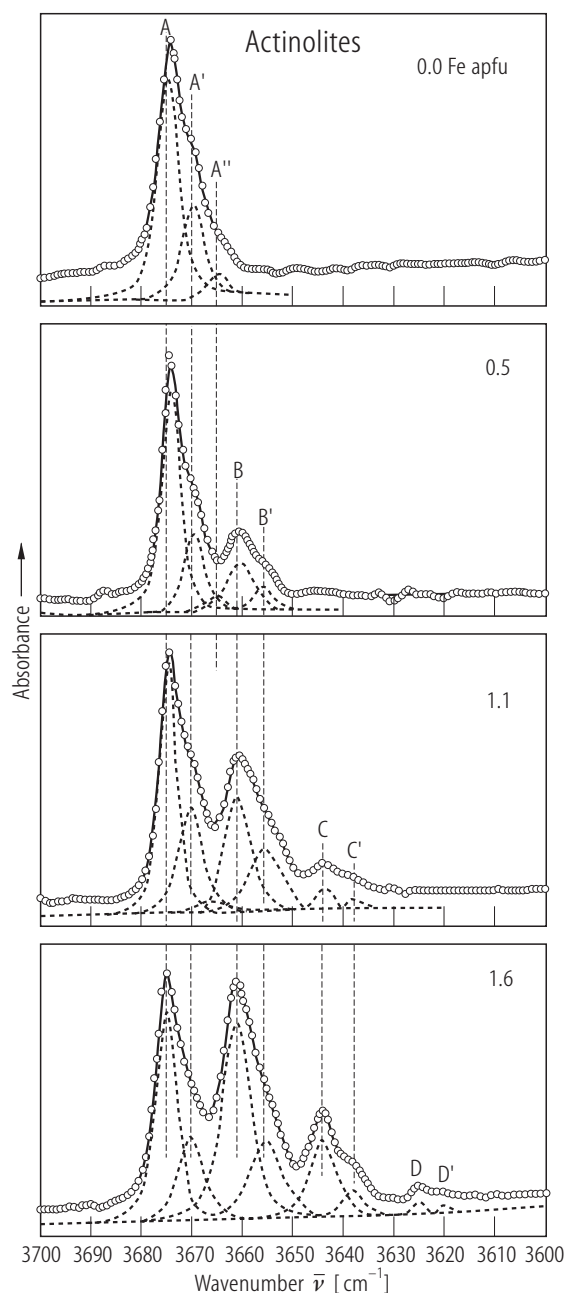
Curve 1:



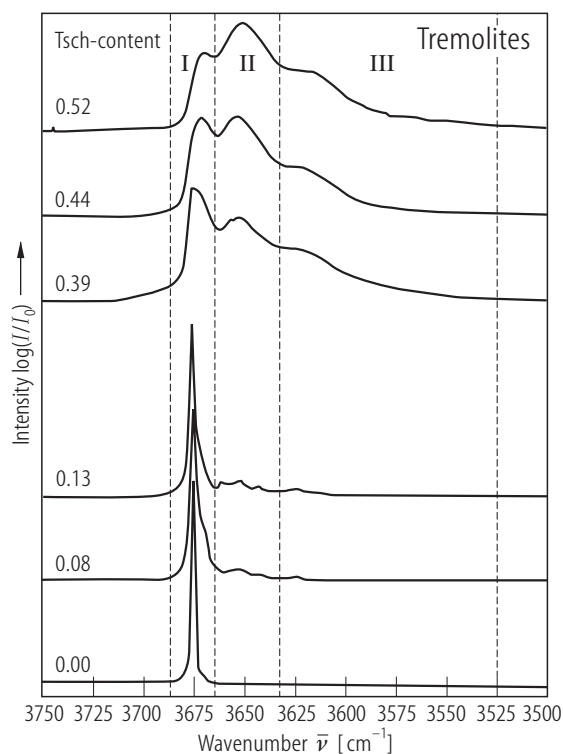
Curve 2:



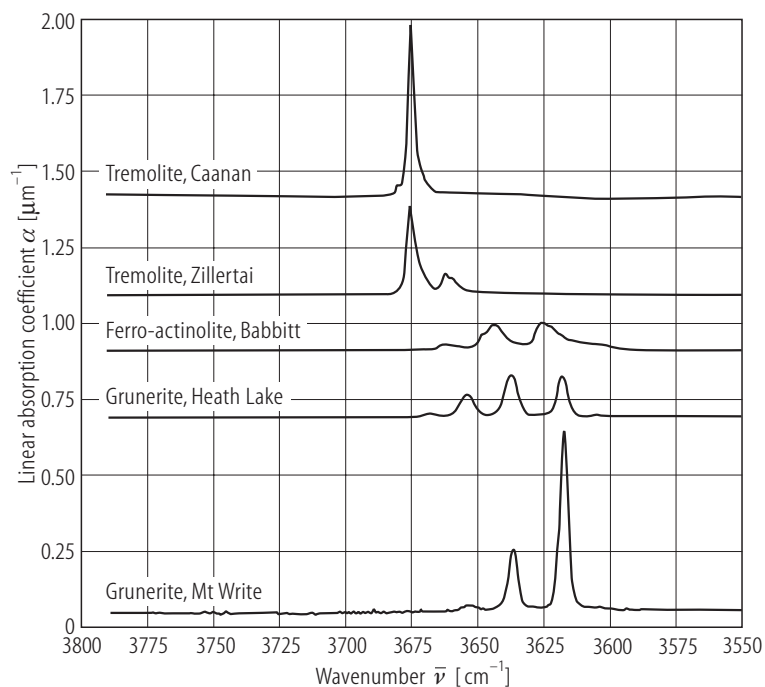
Curve 3:



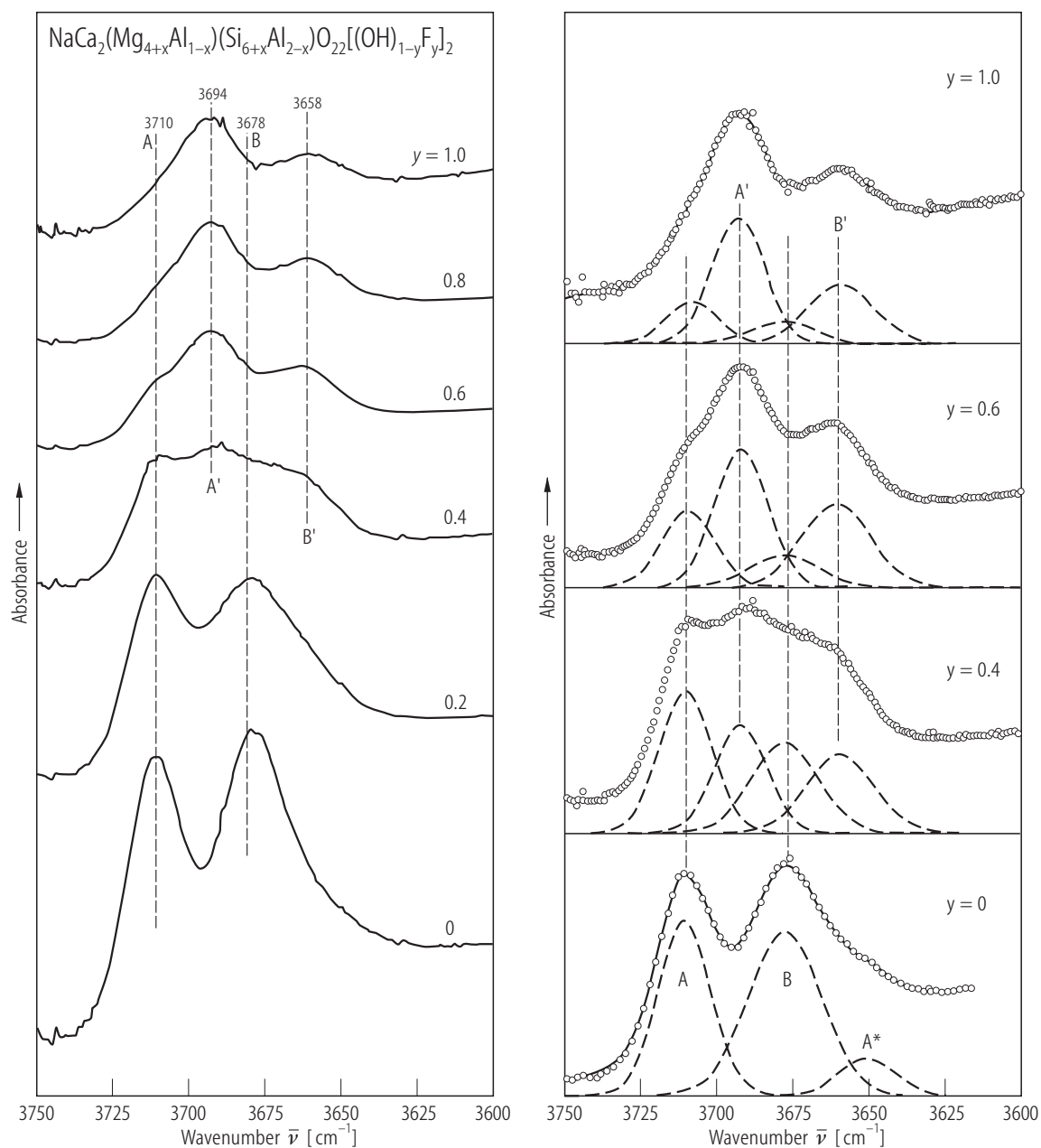
**Fig. 44.** Low calcium actinolites. FTIR spectra. Parameter: Fe content. The solid curves are the calculated fit to the observed data (circles) and dashed curves are the individual bands fitted to the spectra [05D1].



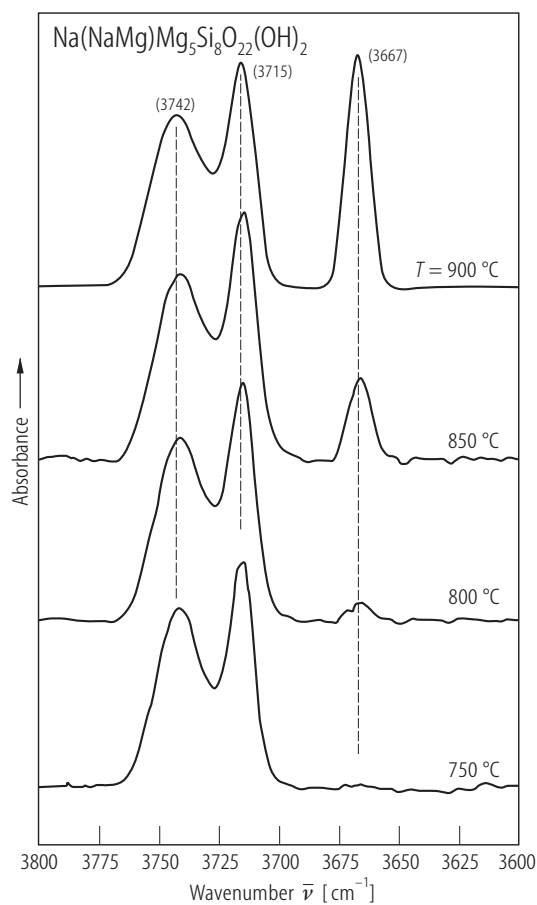
**Fig. 45.** Aluminium tremolites. FTIR spectra of the OH-stretching vibration [03N1]. Tsch: tschermakite.



**Fig. 46.** Natural Ca and Fe-Mg amphiboles. IR spectra obtained on (010) sections polarized in the  $\alpha$ -direction [91S1].

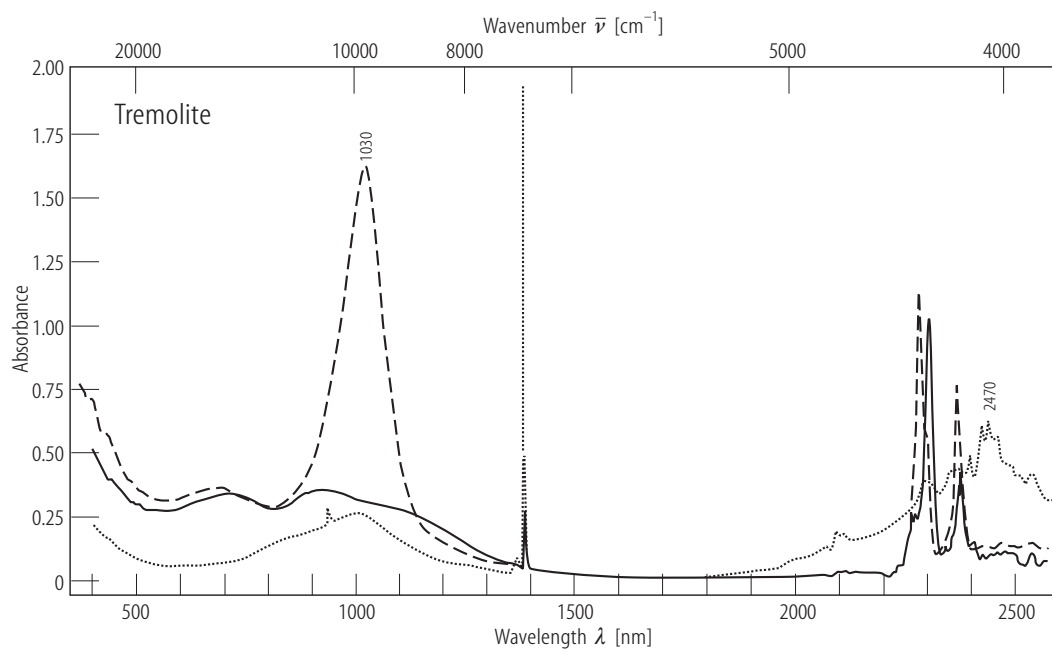


**Fig. 47.** Pargasites  $\text{NaCa}_2(\text{Mg}_{4+x}\text{Al}_{1-x})(\text{Si}_{6+x}\text{Al}_{2-x})\text{O}_{22}[(\text{OH})_{1-y}\text{F}_y]_2$ . FTIR spectra in the OH-stretching region for different F content ( $y$ ) [00R1]. Right part shows spectra of left part resolved into symmetric Gaussian bands.



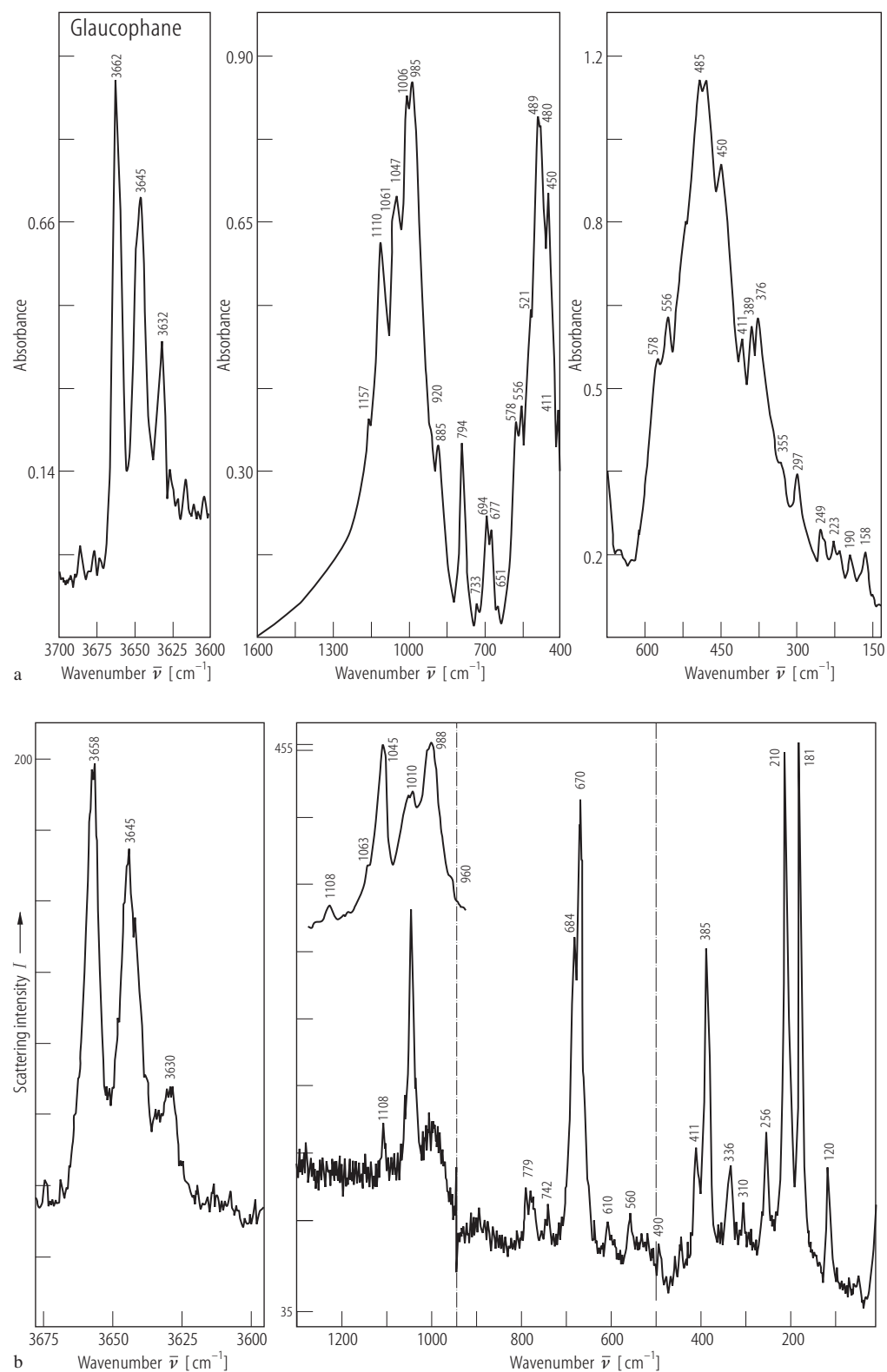
**Fig. 48.**  $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . FTIR spectra in the OH-stretching region for samples with different synthesis temperatures [0411].

For Fig. 49 see next page

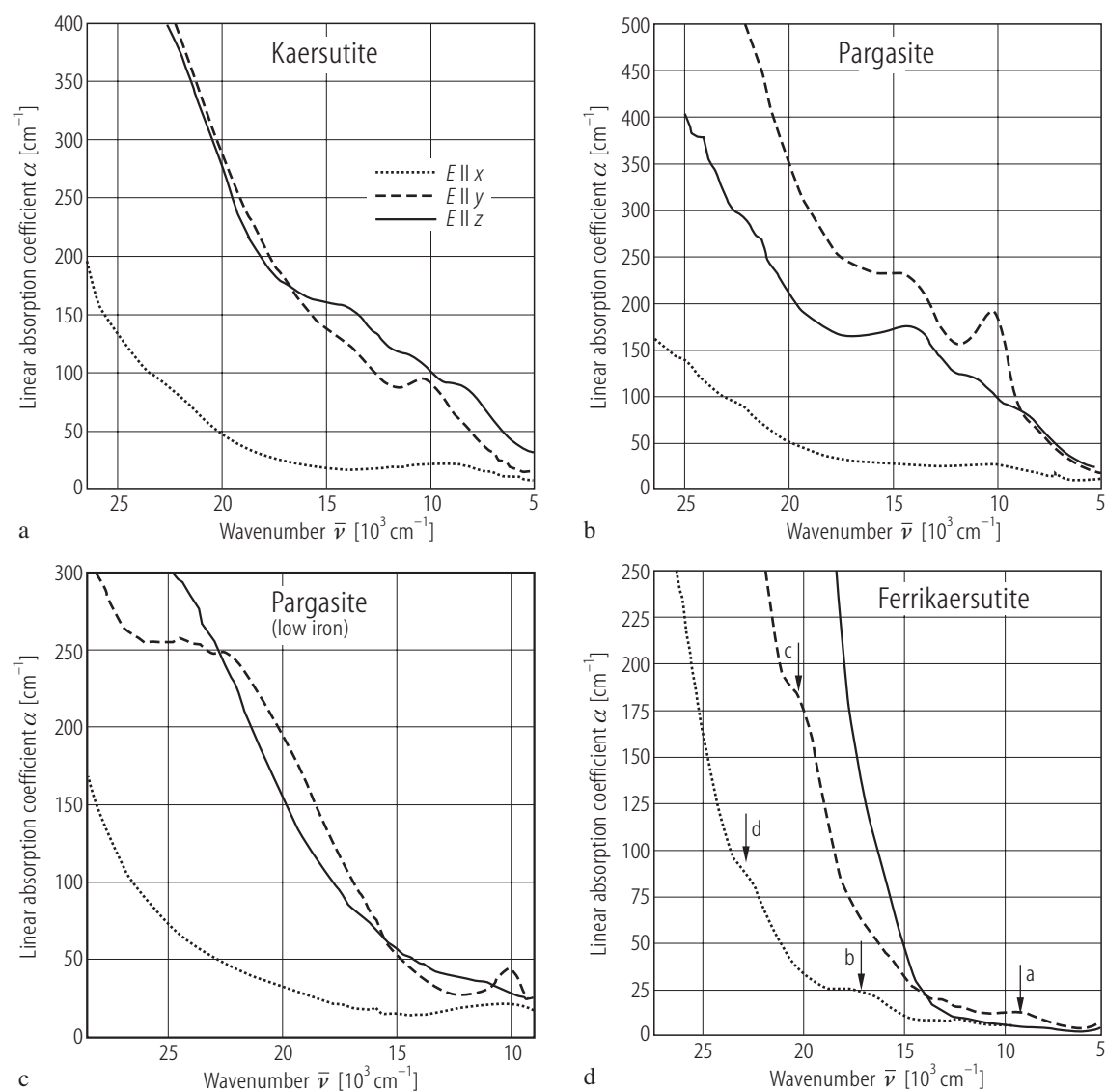


**Fig. 50.** Natural tremolite. Room temperature spectra:  $\alpha$ -spectrum (.....),  $\beta$ -spectrum (---) and  $\gamma$ -spectrum (—).  $\alpha \wedge c = 17^\circ$ ; crystal thickness 1.0 mm [77G1].

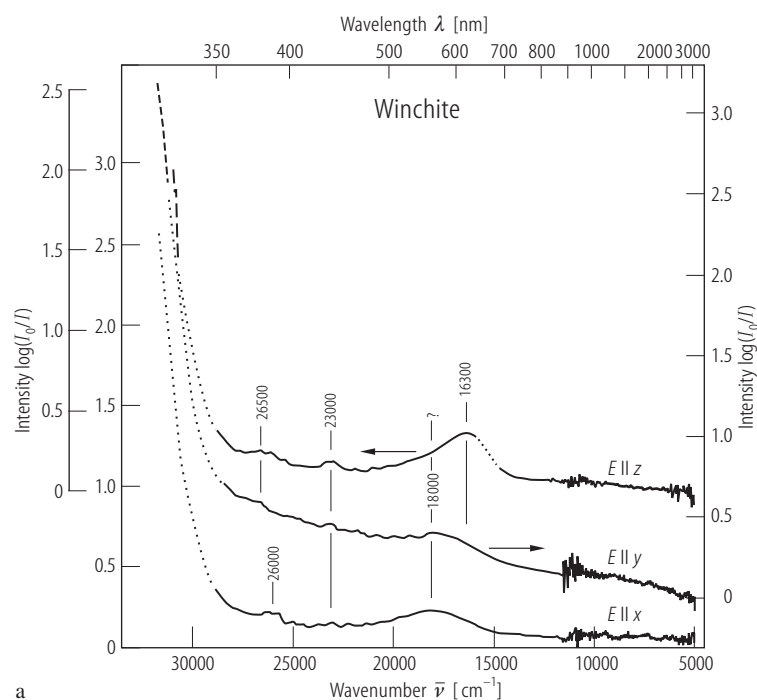




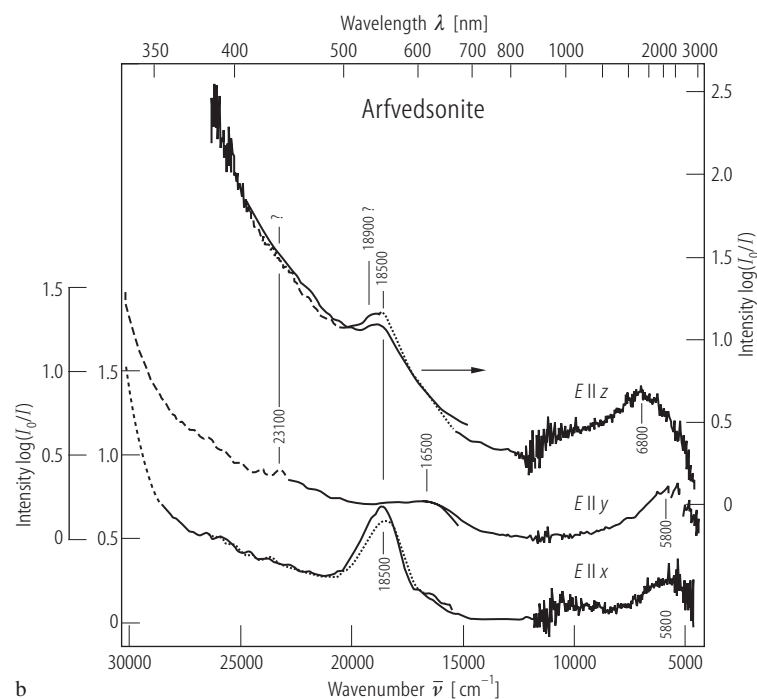
**Fig. 49.** Glaucophane. (a) Infrared spectra, (b) Raman spectra [89G1].

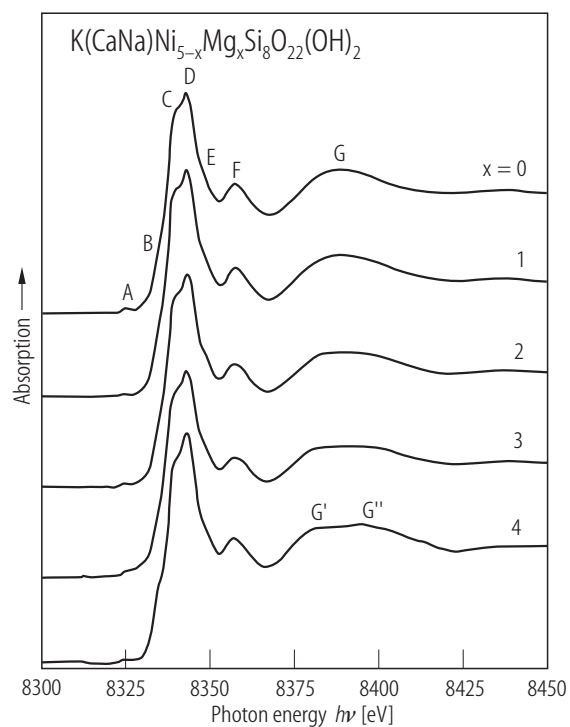


**Fig. 51.** Kaersutite (a), pargasite (b), low iron pargasite (c) and ferrikaersutite (d). Optical spectra [99T1].



**Fig. 52.** Winchite **(a)** and arfvedsonite (juddite) **(b)**. Polarized spectra at 295 K. In **(a)**, spectra  $E \parallel x$  and  $z$  were taken from a crystal slab  $\perp b$  with  $t = 71 \mu\text{m}$ , spectrum  $E \parallel y$  from slab  $\perp c$  with  $t = 77 \mu\text{m}$ . Uncertainties are high below  $12000 \text{ cm}^{-1}$  and above  $30000 \text{ cm}^{-1}$ . In **(b)** data obtained at 110 K are shown by solid lines and those at 295 K by broken lines. Spectra  $E \parallel x$  and  $y$  were obtained from a crystal slab  $\perp b$  with  $t = 75 \mu\text{m}$ , spectra  $E \parallel z$  from slabs  $\perp c$  with  $t = 81 \mu\text{m}$  [86G1].





**Fig. 53.**  $\text{K}(\text{CaNa})\text{Ni}_{5-x}\text{Mg}_x\text{Si}_8\text{O}_{22}(\text{OH})_2$  richterites. Ni K edge XANES spectra [00G1]. Changes as a function of the increasing Ni/Mg substitution in the join are evident in the edge region (peaks C and D) and in the energy range 8375...8400 eV (peaks G, G', G'').