

The (Mg,Fe²⁺) substitution in ferri-clinoholmquistite, $\square\text{Li}_2(\text{Mg,Fe}^{2+})_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$

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Abstract: Amphiboles have been synthesized by hydrothermal techniques at 500–600 °C, 1 Kbar $P_{(\text{H}_2\text{O})}$ and low oxygen fugacity (close to NNO) at nominal compositions along the join ferri-clinoholmquistite [$\square\text{Li}_2\text{Mg}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$] – ferri-clinoferroholmquistite [$\square\text{Li}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$]. SEM-EDS and X-ray powder diffraction show that at 500 °C, amphibole is the dominant phase in the run assemblage, together with minor clinopyroxene + quartz, in the Fe-rich side of the join, up to ~50 mol. % ferri-holmquistite component in the system. For higher Mg contents, an assemblage consisting of predominant clinopyroxene + quartz is obtained, and amphibole is only a minor phase. At 600 °C, the situation is reversed: amphibole is the predominant phase in the Mg-rich side of the join (~60–100 mol. % ferri-holmquistite component in the system). X-ray powder-diffraction patterns can be indexed in space group *C2/m* and cell parameters show well-defined linear trends as a function of nominal amphibole composition. Mössbauer spectra show that Fe³⁺ is strongly ordered at the M2 site, whereas Fe²⁺ is disordered over the B and C sites. The infrared OH-stretching spectra of intermediate compositions show fine structure caused by ordering of Mg and Fe²⁺ over the M1 and M3 sites in the amphibole; this fine structure consists of four main bands assigned to the four local combinations of (Mg,Fe²⁺) at M(1,3). The relative intensities of these bands show that there is almost complete Mg-Fe²⁺ substitution at M(1,3) in ferri-clinoholmquistite and that there is no significant short-range ordering (cluster and/or anti-clustering) between these two cations at the M(1,3) sites. The IR spectra show, in addition, four minor components that are assigned to (Fe²⁺,Mg) at M(4), indicating that the amphibole composition departs from the nominal one following the vector ${}^{\text{M4}}\text{Fe}^{2+} {}^{\text{M2}}\text{Mg} {}^{\text{M2}}\text{Fe}^{3+} {}^{\text{M4}}\text{Li}_{-1}$.

Key-words: ferri-clinoholmquistite, synthesis, cell-parameters, infrared and Mössbauer spectroscopy, short-range order.

Introduction

Holmquistite is a member of the Mg-Fe-Mn-Li amphibole group and has ^[B]Li > 1.00 apfu (atoms per formula unit) (Leake *et al.*, 2004). It has been reported from several localities around the world (*e.g.* Deer *et al.*, 1999), typically occurring at the contact of Li-rich pegmatites with country rocks (Deer *et al.*, 1999; London, 1986). During the last few years we have devoted much effort to the crystal chemistry of this amphibole as a function of *T*, *P* and *f*_{O₂} (Iezzi *et al.*, 2003a, 2003b, 2004). Iezzi *et al.* (2003a) showed that, in the Mg-free system, ferri-clinoferroholmquistite is obtained up to 500 °C; at 600 °C, the Li-bearing amphibole is completely replaced by Fe³⁺-rich spodumene, magnetite and quartz. Iezzi *et al.* (2004) showed that, in the Mg-bearing system, ferri-clinoholmquistite crystallizes at *T* ≥ 600 °C, whereas for lower temperatures (500 °C), it is replaced by Fe³⁺-rich

spodumene, taeniolitic mica and quartz. The upper thermal limit of ferri-clinoholmquistite is 800 °C; at 900 °C, the amphibole disappears and is replaced by Fe³⁺-rich spodumene and enstatite (Iezzi, 2001). According to Iezzi (2001), the pressure conditions in the range 0.1 < *P* < 0.7 GPa have no significant effect on the stability of the amphibole, whereas the oxygen fugacity during synthesis plays a major role on the final composition (particularly the Fe²⁺/Fe³⁺ ratio) of the mineral (Iezzi *et al.*, 2004).

In this paper, we report the synthesis of amphiboles along the join ferri-clinoholmquistite – ferri-clinoferroholmquistite, and characterize the obtained products by means of infrared and Mössbauer spectroscopies. Taking into account the results of Iezzi *et al.* (2003a, 2004), we planned two sets of experiments at 500 and 600 °C, and at constant *P*_{H₂O} = 0.1 GPa and NNO *f*_{O₂} conditions. It is known that at 500 °C, the oxygen fugacity of the experiment cannot be properly con-

trolled, due to the low permeability of the gold capsule to hydrogen at this temperature. Thus at 500 °C, the synthetic system is “internally buffered” and the redox conditions inside the charge are not determined (Chou, 1987; Iezzi *et al.*, 2003a). At 600 °C and a run duration of several days, kinetic equilibrium between the buffer (either a solid-state buffer or an Ar-H₂ gas mixture) and the charge within the capsule is attained, allowing control of the redox condition of the experiment. In the present work, 600 °C experiments were buffered at NNO for two reasons: (1) the redox conditions of the 500 °C synthesis are probably very close to the NNO buffer, considering the Fe²⁺/Fe³⁺ ratio of the resulting amphiboles (Iezzi *et al.*, 2003a), and (2) the work of Iezzi *et al.* (2004) showed that at $f_{O_2} < \text{NNO} + 1$, the final amphibole yield is maximized and the occurrence of Fe³⁺-rich spodumene and other additional phases is minimized; this allowed us to use the bulk powder for spectroscopic analysis.

A common problem in amphibole synthesis is the very small size of the crystals obtained, which normally prevents EMP analysis and/or single-crystal X-ray diffraction. A second problem with regard to amphiboles is the need to characterize short-range order (SRO) in addition to long-range order (LRO), as knowledge of SRO is essential in developing reliable geological applications in geothermometry or geobarometry based on amphibole composition. As shown

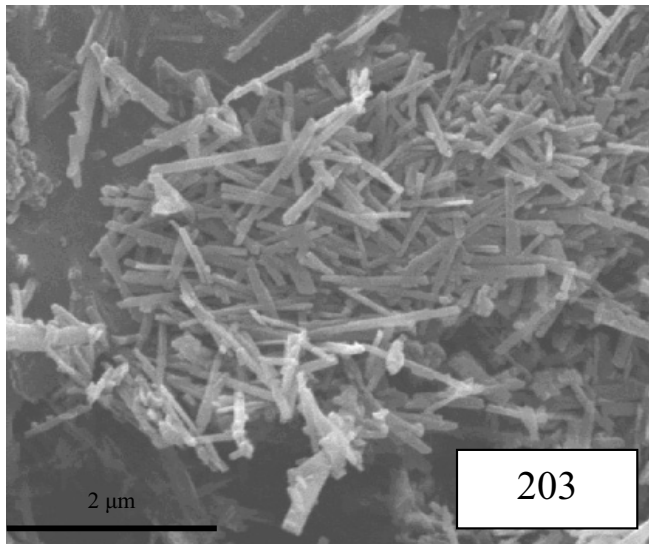


Fig. 1. SEM image of sample 203. The scale bar is 2 μm.

by Della Ventura *et al.* (1999), IR spectroscopy has great potential in this regard, even if several problems still persist, especially when attempting quantitative treatment of the data (Hawthorne *et al.*, 2000; Reece *et al.*, 2002). Iezzi *et al.* (2003a, 2004) recently showed that combined use of IR and Mössbauer spectroscopies allows characterizing the composition of the synthetic product with a high degree of confidence. This work represents further application of this approach for intermediate (Mg,Fe)-holmquistite, where the analytical problems are exacerbated by the simultaneous presence in the system of a multi-valence cation (Fe) and two light elements (H and Li), which cannot be directly measured.

Experimental methods

Starting products were prepared as gels, following the method of Hamilton & Henderson (1968). Iron was added by mixing stoichiometric amounts of metallic Fe (Fe⁰) and Fe-nitrate (Fe³⁺) (Monier & Robert, 1986; Iezzi, 2001). Intermediate compositions were prepared along the (pseudo)-binary join ferri-clinoferroholmquistite [□Li₂Fe²⁺₃Fe³⁺₂Si₈O₂₂(OH)₂] – ferri-clinoholmquistite [□Li₂Mg₃Fe³⁺₂Si₈O₂₂(OH)₂] by mixing end-member gels in steps of 0.6 apfu of the substituent cation. Compositions and sample labels are given in Table 1. Hydrothermal synthesis was done using internally heated pressure vessels equipped with a Shaw membrane (Ag₆₀Pd₄₀), for duration of 12 days (see Iezzi *et al.*, 2004 for details).

Run products were studied using X-ray powder-diffraction, SEM-EDS, Mössbauer spectroscopy and FTIR spectroscopy in the principal OH-stretching region. A complete description of the analytical techniques used was given in Iezzi *et al.* (2003a, 2004).

Results

Run products

The amphibole crystals obtained along the studied join are systematically acicular with a width between 0.2–0.5 μm, and a length between 2–3 μm (Fig. 1); very few crystals exceeded these dimensions. It must be noted that Iezzi *et al.* (2004) were successful in obtaining larger crystal in this system only at temperatures much higher (800 °C) than those used here; one of their samples could be studied by

Table 1. Sample labels, nominal compositions, experimental conditions and run products along the join □Li₂(Fe²⁺_xMg_{3-x})Fe³⁺₂Si₈O₂₂(OH)₂. Amph = amphibole, cpx = clinopyroxene, tc = talc, qz = quartz, i. b. = internally buffered (see text).

Label	Nominal octahedral composition	Temperature (°C)	Pressure (GPa)	Oxygen fugacity	Time (days)	Obtained assemblage
201	Fe ²⁺ ₃ Fe ³⁺ ₂	500	0.1	i. b.	12	amph, qz
202	(Fe ²⁺ _{2.4} Mg _{0.6})Fe ³⁺ ₂	500	0.1	i. b.	12	amph, qz
203	(Fe ²⁺ _{1.8} Mg _{1.2})Fe ³⁺ ₂	500	0.1	i. b.	12	amph, qz
204	(Fe ²⁺ _{1.5} Mg _{1.5})Fe ³⁺ ₂	500	0.1	i. b.	12	amph, qz
13f4	(Fe ²⁺ _{1.5} Mg _{1.5})Fe ³⁺ ₂	600	0.1	NNO	12	cpx, amphib, qz
13f5	(Fe ²⁺ _{1.2} Mg _{1.8})Fe ³⁺ ₂	600	0.1	NNO	12	amph, cpx, qz
13f6	(Fe ²⁺ _{0.4} Mg _{2.4})Fe ³⁺ ₂	600	0.1	NNO	12	amph, cpx, qz
13f8	Mg ₃ Fe ³⁺ ₂	600	0.1	NNO	12	amph, tc, cpx, qz

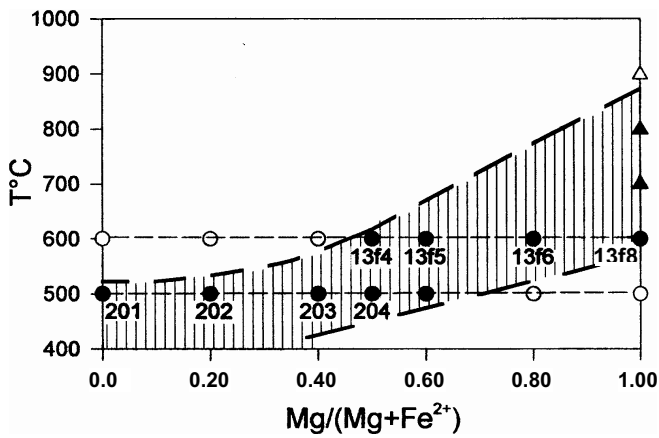


Fig. 2. Schematic thermal stability field (stippled area) of ferri-clinoholmquistite as a function of the Mg content in the system. For experimental conditions and sample labels, see Table 1. Filled symbols: amphibole dominant, hollow symbols: clinopyroxene dominant. Circles: this work, triangles: data from Iezzi (2001).

single-crystal X-ray diffraction, and some of their results will be used below as a basis of comparison. Optical- and electron-microscopy, coupled with powder X-ray diffraction, show that the run products obtained at 500 °C in the range $0 \leq \text{Mg}/(\text{Mg}+\text{Fe}^{2+}) \leq 0.5$ consist of more than 90% amphibole, plus additional quartz and very minor pyroxene (Table 1). For higher Mg contents in the system, the amount of amphibole in the run assemblage decreases significantly, and clinopyroxene is the dominant phase. Experiments at 600 °C gave an assemblage of amphibole (~80%), Fe³⁺-rich spodumene (10–15%) (Cámara *et al.*, 2003) and quartz (10–5%) in the range $0.5 < \text{Mg}/(\text{Mg}+\text{Fe}^{2+}) \leq 1.0$ (Table 1). A slightly higher yield was obtained for the nominal ferri-holmquistite end-member, and at this composition, a minor amount of talc is also present in the assemblage. At this temperature, clinopyroxene is the dominant phase for $\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) < 0.5$. A schematic stability field for (Mg,Fe)-ferri-clinoholmquistite is given in Figure 2.

At the 50:50 Mg-Fe²⁺ composition (samples 204 and 13f4, Table 1), the same kind of amphibole is obtained at both 500 and 600 °C, judging from their cell parameters and IR spectra. However, at higher T (600 °C, sample 13f4, Table 1), a lower yield was obtained. Therefore, we selected the 500 °C run-powder (204) for further analysis.

Cell dimensions

Table 2 gives the unit cell parameters for the amphiboles synthesized in the Mg-Fe series, and Figure 3 shows their variation as a function of nominal $X_{\text{Fe}^{2+}} = \text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+})$. All cell dimensions show a well-defined linear increase as a function of increasing Fe in the system (Fig. 3), reflecting a continuous increase in Fe²⁺ ($r = 0.78 \text{ \AA}$) substituting for Mg (0.720 \AA , Shannon, 1976) in the amphibole structure. A slight linear decrease is observed for the β angle, suggesting a change in M4 occupancy along the series, since it is known that the β angle is particularly sensitive to the aggregate size of the M4 site (*e.g.* Iezzi *et al.*, 2003b).

Mössbauer spectra

The 500 °C samples only (201, 202, 203 and 204, Table 1) were analysed by Mössbauer spectroscopy (Fig. 4), as these run-powders consist of amphibole with minor quartz (see

Table 2. Refined cell parameters for synthetic amphiboles along the join □Li₂(Fe²⁺_xMg_{3-x})Fe³⁺₂Si₈O₂₂(OH)₂.

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
201	9.482(3)	18.006(7)	5.320(2)	101.32(5)	890.63
202	9.476(4)	17.984(9)	5.317(3)	101.40(5)	888.23
203	9.469(3)	17.955(8)	5.314(3)	101.62(5)	884.95
204	9.469(3)	17.947(7)	5.308(2)	101.64(4)	883.49
13f5	9.452(3)	17.948(7)	5.305(2)	101.82(4)	881.14
13f6	9.445(3)	17.909(7)	5.298(2)	101.91(4)	876.86
13f8	9.445(4)	17.882(10)	5.295(3)	102.04(5)	874.63

Table 3. Mössbauer parameters for ferri-clinoferroholmquistite 202, 203 and 204.

Sample	Isomer shift δ (mm/s)	Quadrupole splitting Δ (mm/s)	Γ FWHH (mm/s)	Site	I Relative site distribution (%)	χ^2
	1.12±0.01	2.23±0.01	0.32±0.01	M3 Fe ²⁺	25(2)	
	0.40±0.01	0.26±0.01	0.32±0.01	M2 Fe ³⁺	39(1)	
202	1.13±0.01	2.81±0.02	0.28±0.01	M1 Fe ²⁺	34(4)	1.31
	1.11±0.01	2.32±0.01	0.31±0.01	M3 Fe ²⁺	18(7)	
	1.22±0.01	1.78±0.1	0.44±0.01	M4 Fe ²⁺	6(4)	
	0.37±0.01	0.28±0.01	0.34±0.01	M2 Fe ³⁺	42(1)	
203	1.13±0.01	2.80±0.01	0.26±0.01	M1 Fe ²⁺	31(1)	1.03
	1.12±0.01	2.38±0.01	0.29±0.01	M3 Fe ²⁺	15(3)	
	1.12±0.06	1.95±0.1	0.43±0.01	M4 Fe ²⁺	6(2)	
	0.38±0.01	0.26±0.01	0.32±0.01	M2 Fe ³⁺	48(1)	
204	1.13±0.01	2.82±0.01	0.27±0.01	M1 Fe ²⁺	28(5)	1.28
	1.13±0.01	2.42±0.01	0.31±0.01	M3 Fe ²⁺	17(7)	
	1.26±0.03	1.79±0.05	0.42±0.01	M4 Fe ²⁺	7(3)	
	0.37±0.01	0.28±0.01	0.34±0.01	M2 Fe ³⁺	48(1)	

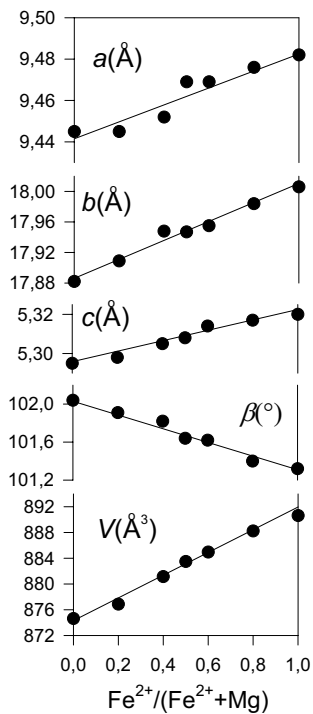


Fig. 3. Variation in unit cell parameters along the (Mg,Fe²⁺) – ferri-clinoholmquistite join.

above). The 600 °C samples contain variable but significant amounts of Fe-bearing clinopyroxene in addition to the amphibole, and these were not analysed. Four Lorentzian quadrupole-doublets were fitted to adequately describe the resonance absorption patterns, and the refined parameters are given in Table 3. These doublets are assigned to Fe³⁺ and Fe²⁺ at the available sites (*e.g.*, Iezzi *et al.*, 2003a, 2003b; Della Ventura *et al.*, 2005 and references therein). In particular, the doublet with the largest quadrupole splitting (QS 2.7–2.8 mm/s) is assigned to Fe²⁺ at the M1 site, the doublet with QS in the range 2.4–2.5 mm/s is assigned to Fe²⁺ at the M3 site, and the doublet with QS in the range 1.98–1.75 mm/s is assigned to Fe²⁺ at the M4 site (Hawthorne, 1983; Redhammer & Roth, 2002; Iezzi *et al.*, 2003a). The doublet with the smallest isomer shift and quadrupole splitting (QS around 0.25 mm/s) is assigned to Fe³⁺ at the M2 site. Relative Fe²⁺-Fe³⁺ site-populations at the B and C sites, calculated from the fitted band intensities, are given in Table 3.

OH-stretching FTIR spectra

The OH-stretching spectra of ferri-clinoholmquistites with variable (Mg,Fe²⁺) contents at the M(1,3) sites are shown in Figure 5. The spectrum of end-member ferri-ferroclino-holmquistite (sample 201, Fig. 5 bottom) shows a single sharp band at 3614 cm⁻¹, which is assigned to the local configuration ^{M(1)}Fe²⁺ ^{M(1)}Fe²⁺ ^{M(3)}Fe²⁺-OH-A□ (Iezzi *et al.*, 2003a). This spectrum indicates that this amphibole has an ordered structure, with Fe²⁺ at M(1,3), Fe³⁺ at M2 and Li at M4. As expected (Strens 1966; Burns & Strens, 1966; Della Ventura, 1992; Della Ventura *et al.*, 1996; Reece *et al.*, 2002), intermediate compositions give rise to four main

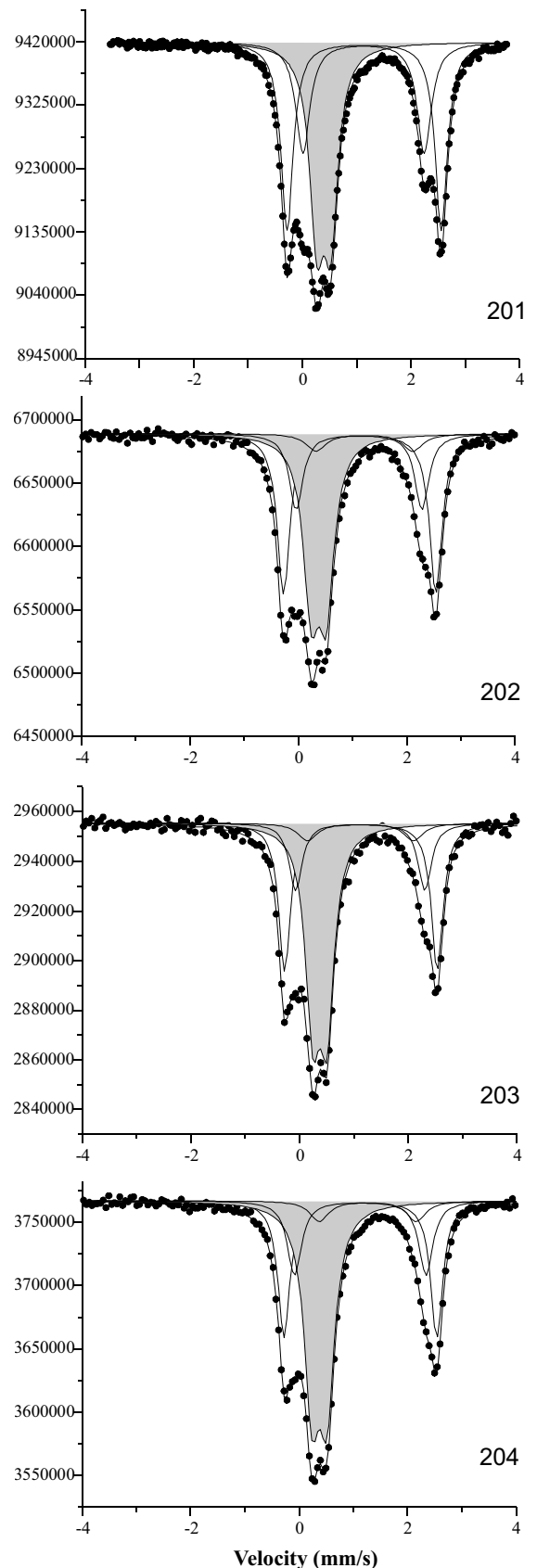


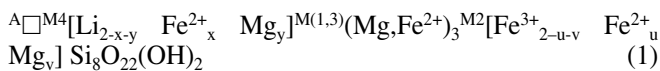
Fig. 4. Selected Mössbauer spectra for the amphiboles synthesized at 500°C. The doublet with the smallest quadrupole splitting, which is assigned to ferric iron, is shown in grey.

bands (labelled A to D) at 3662, 3647, 3631 and 3614 cm⁻¹, respectively (Fig. 5); these bands can be assigned to the four combinations of (Mg,Fe²⁺) cations distributed over the M(1,3) sites. The separation of the components is not constant, but increases slightly with decreasing wave number, from ^{A-B}Δ_v = 15 to ^{C-D}Δ_v = 18 cm⁻¹. Similar behaviour was noted by Della Ventura *et al.* (1997), and is probably related to the increasing aggregate covalence of the M(1,3)-O3 bonds in the A configuration (MgMgMg-OH-^A□) relative to the D configuration (Fe²⁺Fe²⁺Fe²⁺-OH-^A□). The spectrum of end-member ferri-clinoholmquistite (sample 13f8, Fig. 5, top) shows the same quartet of bands, indicating that this sample has Fe²⁺ at M(1,3), and hence its composition departs from the nominal composition (^{M(1,3)}Mg₃). It also shows a very sharp band at 3675 cm⁻¹ and a very broad low-frequency component centred at 3608 cm⁻¹. The sharp band at 3675 cm⁻¹ is due to talc (Wilkins & Ito, 1967), which was identified, in the run assemblage by powder X-ray diffraction (see above). The broad band at 3608 cm⁻¹ is assigned to small amounts of a Fe³⁺-bearing phase, possibly Fe(OH)₃ in the run-powder, but in insufficient quantity to be detected by powder X-ray diffraction.

The composition of the synthesised amphiboles

General considerations

The *nominal* composition of the system examined here is as follows: □^{M4}Li₂^{M(1,3)}(Mg,Fe²⁺)₃M²Fe³⁺₂Si₈O₂₂(OH)₂. The spectroscopic results indicate that the amphiboles synthesized depart from this ideal composition, and we need to carefully examine the constraints that this data and the electroneutrality principle provide in calculating the compositions of these amphiboles. A key observation is that the infrared spectra show no sign of any Li at the A site or at the M3 site in these amphiboles (see Iezzi *et al.*, 2004), and thus ^A□ = 1.0. Similarly, neither the Mössbauer nor the infrared data show any sign of ^TFe. This being the case, we may write the possible range in structural formulae of these amphiboles in the following way:



where all the variable terms involving possible heterovalent substitutions are enclosed in square brackets. Note that the electroneutrality principle requires that $x + y = u + v$; in other words ^{M4}Li apfu must be equal to ^{M2}Fe³⁺. Unlike the experiments of Iezzi *et al.* (2004), the syntheses described in this work did not provide crystals of a size suitable for X-ray single-crystal refinement and/or micro (EMP) analysis, thus estimation of their composition must be based exclusively on spectroscopic methods. However, single-crystal X-ray structure refinement done by Iezzi *et al.* (2004) on a sample (amphibole 152) with a composition very close to those related here, shows that in this amphibole ^{M2}Mg >> ^{M4}Mg, whereas Fe²⁺ is completely ordered at M(1,3) and M4. The Mössbauer spectra of Figure 4 do not exclude minor amounts of ^{M2}Fe²⁺ in the samples, due to the extensive band

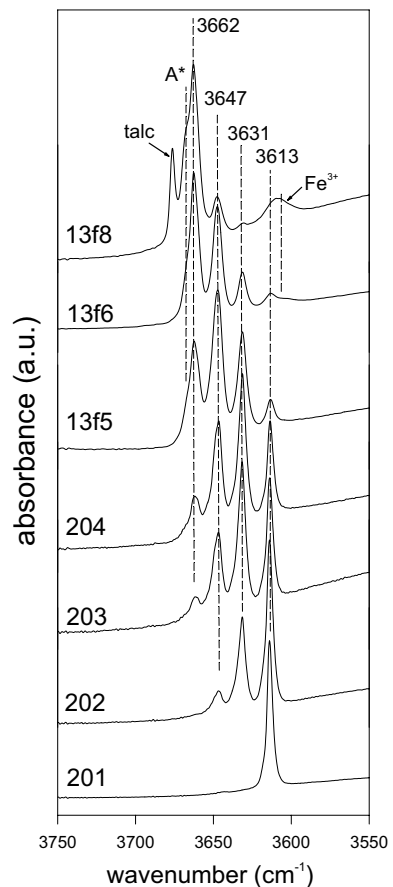
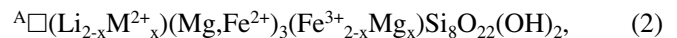


Fig. 5. FTIR spectra in the OH-stretching region for amphiboles synthesized along the (Mg,Fe²⁺) – ferri-clinoholmquistite join.

overlapping. However, coupling our Mössbauer data with the X-ray diffraction data of Iezzi *et al.* (2004), we can confidently assume $u = 0$ in our samples. This being the case, the electroneutrality requirement reduces to $x + y = v$, and the above equation can be simplified as:



where ^{M4}M²⁺ = (Fe²⁺,Mg), with strong preference for Fe²⁺ (Iezzi *et al.*, 2004). This formula shows that the composition of the synthesized amphiboles is ultimately ruled by the ^{M2}Mg ^{M4}(Mg,Fe²⁺) ^{M2}Fe³⁺ ^{M4}Li₁ exchange vector already described by Iezzi *et al.* (2004) and Della Ventura *et al.* (2005).

Cation distribution at M(1,3)

Hawthorne *et al.* (1996) showed that the binary site-occupancies x (=Mg/Mg + M²⁺) and y (= M²⁺/Mg + M²⁺) at M1 and M3 in the amphibole structure are related to the observed intensities of the four component bands in the principal IR OH-stretching spectrum, provided that there is no variation in molar absorptivity with frequency (Skogby & Rossman, 1991) within a single sample. Using the original equations of Burns & Strens (1966):

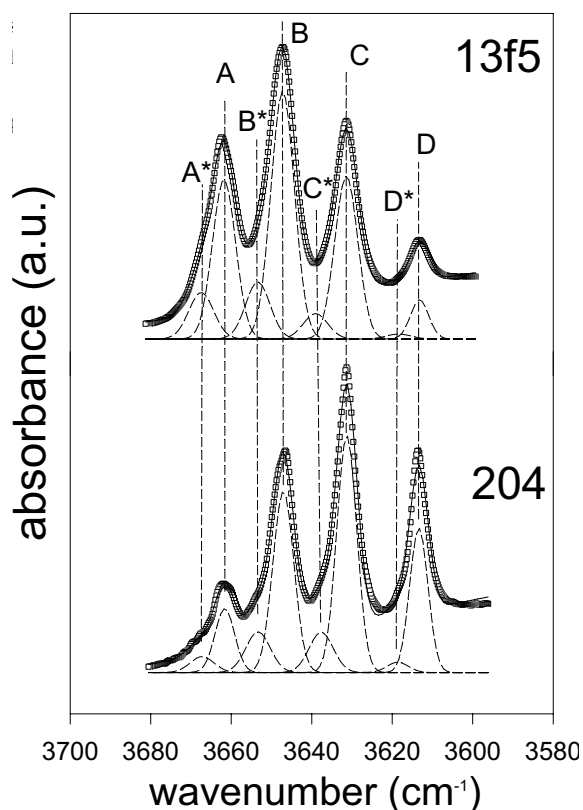


Fig. 6a. Example of resolved spectra for two intermediate amphiboles synthesized along the (Mg,Fe²⁺) – ferri-clinoholmquistite join (samples 13f5 and 204, see Table 1). Resolved bands are vertically displaced for clarity; observed intensities are shown by the hollow squares, and the line following the observed intensities is the envelope of the sum of the fitted component bands.

$$M^{(1,3)}\text{Mg} = 3I_A + 2I_B + I_C$$

$$M^{(1,3)}\text{M}^{2+} = I_B + 2I_C + 3I_D \quad (\text{with } M^{2+} = \text{Fe}^{2+})$$

where I_{A-D} are the intensities measured for the corresponding A to D bands, one can derive the (Mg, M²⁺) site occupancies at M(1,3) with a high degree of confidence (*e.g.* Della Ventura *et al.*, 1996). The digitised spectra were fitted by interactive optimisation followed by least-squares refinement (Della Ventura *et al.*, 1996); the background was treated as linear and all bands were modelled as symmetric Gaussian curves (Strens, 1974). The spectra were fitted to the smallest number of peaks needed for an accurate description of the spectral profile.

Typical examples of fitted spectra are shown in Figure 6a. Preliminary refinement, fitting four components only, gave significant residuals (Fig. 6b), and careful examination of the results showed the presence of resolvable shoulders on the higher-frequency side of each main band, suggesting the presence of additional minor peaks. A satisfactory reproduction of the spectral envelope could be achieved only with the introduction of four minor peaks (A*-D*, Fig. 6a, b), each one associated with a main band. Peak-shape parameters for these minor absorptions were fixed during the first refinement cycles; at convergence, peak positions were released and the peak widths were constrained to be approximately similar to those of the corresponding main bands. It

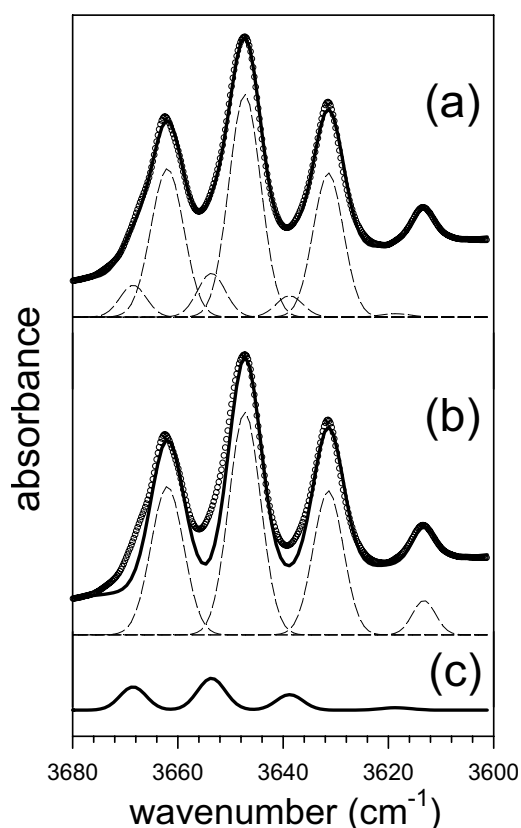


Fig. 6b. The FTIR spectrum of sample 13f5 resolved using (a) an eight-band or (b) a four-band model. The residual from the four-band fitting shown in (b) is given in (c), and corresponds to the additional A*-D* bands needed for a complete description of the experimental profile (see text for an explanation). Observed intensities are shown by the hollow squares, and the line following the observed intensities is the envelope of the sum of the fitted component bands.

is worth noting that the presence of additional minor peaks was noted in the spectrum of natural holmquistite (Law & Whittaker, 1981). Final refined peak positions, widths and relative band-intensities are summarized in Table 4.

The results of the application of the Burns & Strens (1966) equations to the data of Table 4 are given in Table 5 and Figure 7 for both the A-D and A*-D* (normalized) data. Inspection of Table 5 shows that the amount of Mg at M(1,3), calculated using the A-D data, is slightly underestimated, whereas the amount of Mg at M(1,3) calculated using the A*-D* data is generally slightly overestimated; this is not surprising, considering the severe overlap between the two sets of components. However, Figure 7 shows that there is excellent agreement between the nominal and IR-derived Mg/Fe²⁺ contents at M(1,3). This suggests complete Mg/Fe²⁺ substitution at the M(1,3) sites in ferri-clinoholmquistite, in agreement with the variation in cell parameters (Della Ventura *et al.*, 1996). In addition, as already observed for (Mg-Ni-Co)-substituted richterite (Della Ventura *et al.*, 1996), Figure 7 suggests that there is no significant variation in integrated molar absorptivity with absorption frequency in these synthetic amphiboles. Note also that the linear 1:1 trend of Figure 7 implies that there is not SRO (clustering or anti-clustering, *e.g.* Law, 1976) between Mg/Fe²⁺ at M(1,3).

Table 4. Positions (cm⁻¹), widths (cm⁻¹) and relative intensities for the component bands in the OH-spectra of synthetic amphiboles along the join □Li₂(Fe²⁺_xMg_{3-x})Fe³⁺₂Si₈O₂₂(OH)₂.

Band	Parameter	201	202	203	204	13f5	13f6	13f8
A	Position	–	–	3662	3662	3662	3662	3662
	Width	–	–	5.9	6.1	7.0	6.5	6.8
	Intensity	–	–	0.06	0.09	0.23	0.40	0.55
B	Position	–	3647	3647	3647	3647	3647	3647
	Width	–	6.3	6.3	6.2	6.9	6.4	6.2
	Intensity	–	0.08	0.21	0.26	0.34	0.31	0.12
C	Position	–	3631	3632	3631	3631	3631	3631
	Width	–	5.5	5.6	5.9	6.8	5.9	5.8
	Intensity	–	0.29	0.33	0.32	0.23	0.09	0.01
D	Position	3614	3614	3614	3613	3613	3612	–
	Width	5.0	4.9	4.9	5.3	5.5	6.6	–
	Intensity	1.00	0.48	0.25	0.18	0.04	0.03	–
A*	Position	–	–	3668	3668	3668	3668	3668
	Width	–	–	5.1	6.5	6.6	6.7	6.6
	Intensity	–	–	0.01	0.02	0.05	0.09	0.27
B*	Position	–	3653	3654	3653	3653	3654	3654
	Width	–	6.6	6.6	6.4	6.7	6.6	5.9
	Intensity	–	0.01	0.05	0.06	0.07	0.05	0.05
C*	Position	–	3637	3637	3638	3639	3640	–
	Width	–	6.4	6.5	6.6	6.7	6.5	–
	Intensity	–	0.07	0.07	0.06	0.03	0.02	–
D*	Position	–	3619	3619	3619	3618	3618	–
	Width	–	6.2	5.3	6.2	6.7	6.6	–
	Intensity	–	0.07	0.02	0.01	0.01	0.01	–

The A*-D* bands

The A*-D* bands (Fig. 6a) deserve further attention. The frequency separation between each minor band and the corresponding main band (^{A-A*}Δ_v, ^{B-B*}Δ_v, etc.) is close to 6 cm⁻¹ and tends to increase (up to 8 cm⁻¹) with decreasing wave number. Visual inspection of the fitted spectra suggests that the minor peaks A*-D* closely follow the same distribution of relative intensities as the main peaks. Figure 7b shows that the same result regarding the long-range order of Mg-Fe²⁺ is obtained when using the relative intensities of the A*-D* bands. This fact, coupled with the rather low-frequency separation noted above, suggests that these bands are related to some NNN (next-nearest-neighbour) local configuration that affects all four A-D bands in the same manner. Given the restricted chemistry of the system, the only possibilities are: (1) the distribution of Fe³⁺-M²⁺ (where M²⁺ = Mg, Fe²⁺) at M2, or (2) the presence of (bivalent) cations other than Li at M4. This point has been discussed recently by Iezzi *et al.* (2004) who noted the same minor component associated with the main absorption in the spectrum of end-member ferri-clinoholmquistite and assigned it to the presence of small divalent cations at M4 and M2, *i.e.*, to the local ^{M1}Mg^{M1}Mg^{M3}Mg-OH-A□-[^{M4}(M⁺)]-[^{M2}(M⁺)] configuration. In our case, an additional piece of evidence is provided by the Mössbauer spectra (Fig. 4), which show the presence of Fe²⁺ at M4. Therefore, in agreement with Iezzi *et al.* (2004), we assign the

Table 5. Nominal and IR-derived Mg contents (apfu) at M(1,3) for the amphiboles synthesized.

Sample	13f8	13f6	13f5	204	203	202	201
Mg at M(1,3) nom	3	2.40	1.80	1.50	1.20	0.60	0.00
Mg at M(1,3)	1.90	1.91	1.60	1.11	0.93	0.45	0.00
A-D bands							
Mg at M(1,3)	0.91	0.39	0.32	0.24	0.20	0.09	0.00
A*-D* bands							
Mg at M(1,3)*	2.81	2.30	1.92	1.35	1.13	0.54	0.00
Fe ²⁺ at M(1,3)*	0.19	0.70	1.08	1.65	1.87	2.46	3.00
M ²⁺ at (M4,M2)**	0.32	0.20	0.16	0.19	0.18	0.18	0.00

* calculated from the Burns & Strens (1966) equations considering that I_A = I_A+I_{A*} etc.

** calculated from the data of Table 4, as (I_{A*}-I_{D*})/(I_A-I_D)

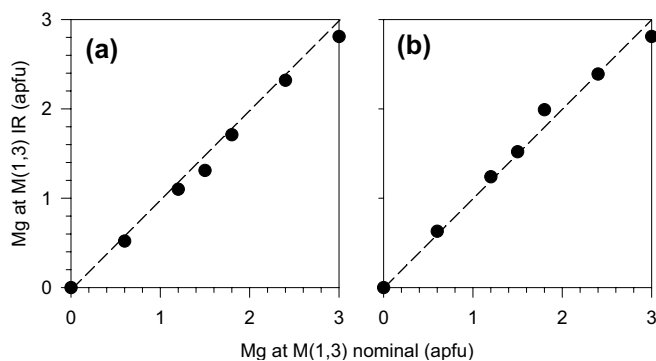


Fig. 7. Nominal vs IR-derived Mg at M(1,3), using (a) the A-D set of bands and (b) the A*-D* set of bands.

A*-D* bands to the NNN effect due to the coupled and simultaneous presence of a divalent cation (Mg and/or Fe²⁺) at M4 and Mg at M2. We conclude that this coupled exchange determines a shift of the OH-stretching bands by ~7 cm⁻¹ upward in frequency, in agreement of the work of Iezzi *et al.* (2004). Note that this assignment also implies that the IR spectra allow evaluation of the M4 and M2 populations.

The chemical composition of the synthesized amphiboles

The chemical composition of the synthesized amphiboles can be determined by combining the IR and Mössbauer spectroscopic data. Regarding Mössbauer, we note however that the area of the ^{M4}Fe²⁺ as well as that of ^{M1}Fe²⁺ and ^{M3}Fe²⁺ doublets have very large standard deviations (Table 3), due to the severe band overlap. Hence, the evaluation of Fe²⁺ at M1-, M3- and M4-sites from Mössbauer has a large error, but the evaluation of the bulk Fe³⁺/Fe²⁺ ratio in the amphibole is reliable.

The amount of M²⁺ at M4 and M2 can be derived from the relative intensity ratio of the (A*-D*)/(A-D) components in the IR spectra. Table 5 shows that it is 0 for the Fe end-member (sample 201, Table 5), it remains rather constant (0.16–0.2 apfu) across the whole join and increases to about 0.3 apfu for the Mg-rich ferri-clinoholmquistite (sample 13f8, Table 5). Since the general composition of the amphiboles in this system is ruled by the ^{M2}Mg^{M4}(Mg,Fe²⁺)^{M2}Fe³⁺₋₁^{M4}Li₋₁

exchange vector, these data suggest that the Mg-Fe²⁺ substitution affects primarily the M(1,3) octahedra, in agreement with the trends of Figure 7.

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References

- Burns, R.G. & Strens, R.G.J. (1966): Infrared study of the hydroxyl bonds in clinoamphiboles. *Science*, **153**, 890-892.
- Cámara, F., Iezzi, G., Oberti, R. (2003): HT-XRD study of synthetic ferrian magnesian spodumene: The effect of site dimension on the $P2_1/c \rightarrow C2/c$ phase transition. *Phys. Chem. Minerals*, **30**, 20-30.
- Chou, I.M. (1987): Oxygen buffer and hydrogen sensor technique at elevated pressures and temperatures. in "Hydrothermal experiments techniques". H.L. Barnes & G.C. Ulmer, eds., Wiley, New York.
- Deer, W.A., Howie, R.A., Zussman, J. (1999): Rock Forming Minerals, Double-chain Silicates. Longman Scientific & Technical, 692 p.
- Della Ventura, G. (1992): Recent developments in the synthesis and characterization of amphiboles. Synthesis and crystal chemistry of richterite. *Trends in Mineralogy*, **1**, 153-192.
- Della Ventura, G., Robert, J.L., Hawthorne, F.C. (1996): Infrared spectroscopy of synthetic (Ni,Mg,Co)-potassium-richterite. in "Mineral Spectroscopy: a Tribute to Roger G. Burns". M. D. Dyar, C. McCammon, M. W. Schaefer, eds., The Geochem. Soc. Spec. Publ., No. 5, 55-63.
- Della Ventura, G., Robert, J.L., Raudsepp, M., Hawthorne, F.C., Welch, M.D. (1997): Site occupancies in synthetic monoclinic amphiboles: Rietveld structure refinement and infrared spectroscopy of (nickel, magnesium, cobalt)-richterite. *Am. Mineral.*, **82**, 291-301.
- Della Ventura, G., Hawthorne, F.C., Robert, J.-L., DelBove, F., Welch, M.D., Raudsepp, M. (1999): Short-range order of cations in synthetic amphiboles along the richterite-pargasite join. *Eur. J. Mineral.*, **11**, 79-94.
- Della Ventura, G., Iezzi, G., Redhammer, G., Hawthorne, F.C., Scaillet, B., Novembre, D. (2005): Synthesis and crystal-chemistry of amphiboles along the magnesioriebeckite – magnesio-arfvedsonite series as a function of f_{O_2} . *Am. Mineral.*, in press.
- Hamilton, D.L. & Henderson, C.M.B. (1968): The preparation of silicate compositions by a gelling method. *Mineral. Mag.*, **36**, 832-838.
- Hawthorne, F.C. (1983): The crystal chemistry of the amphiboles. *Can. Mineral.*, **21**, 173-480.
- Hawthorne, F.C., Della Ventura, G., Robert, J.L. (1996): Short-range order and long-range order in amphiboles: a model for the interpretation of infrared spectra in the principal OH-stretching region. *Geochim. Cosmochim. Acta*, Spec. Vol. **5**, 49-54.
- Hawthorne, F.C., Welch, M.D., Della Ventura, G., Shuangxi Liu, Robert, J.-L., Jenkins, D.M. (2000): Short-range order in synthetic aluminous tremolites: an infrared and triple-quantum MAS NMR study. *Am. Mineral.*, **85**, 1716-1724.
- Iezzi, G. (2001): Cristallographie des amphiboles à lithium, approche expérimentale. Unpublished PhD Thesis, University of Orléans.
- Iezzi, G., Della Ventura, G., Pedrazzi, G., Robert, J.-L., Oberti, R. (2003a): Synthesis and characterisation of ferri-clinoferroholmquistite, $\square Li_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH)_2$. *Eur. J. Mineral.*, **15**, 321-327.
- Iezzi, G., Della Ventura, G., Cámara, F., Pedrazzi, G., Robert, J.-L. (2003b): ^BNa-^BLi solid-solution in A-site vacant amphiboles: synthesis and cation ordering along the ferri-clinoferroholmquistite – riebeckite join. *Am. Mineral.*, **88**, 955-961.
- Iezzi, G., Cámara, F., Della Ventura, G., Oberti, R., Pedrazzi, G., Robert, J.-L. (2004): Synthesis, crystal structure and crystal-chemistry of ferri-clinoferroholmquistite, $\square Li_2Mg_2Fe_3Si_8O_{22}(OH)_2$. *Phys. Chem. Minerals*, **31**, 375-385.
- Law, A.D. (1976): A model for the investigation of the hydroxyl spectra of amphiboles. in "The physics and chemistry of minerals and rocks". Strens R.G.J., ed., J. Wiley and Sons, London.
- Law, A.D. & Whittaker, E.J. (1981): Studies of the orthoamphiboles 1 – The Mössbauer and infrared spectra of holmquistite. *Bull. Minéral.*, **104**, 381-386.
- Leake, B.E., Woolley, A.R., Birch, W.D., Burke, E.A.J., Ferraris, G., Grice, J.D., Hawthorne, F.C., Kisch, H.J., Krivovichev, V.G., Schumacher, J.C., Stephenson, N.C.N., Whittaker, E.J.W. (2004): Nomenclature of amphiboles: additions and revisions to the International Mineralogical Association's amphibole nomenclature. *Can. Mineral.*, **41**, 1355-1362.
- London, D. (1986): Holmquistite as a guide to pegmatitic rare metal deposits. *Econ. Geol.*, **81**, 704-712.
- Monier, G. & Robert, J.-L. (1986): Muscovite solid solutions in the system K₂O-MgO-FeO-Al₂O₃-SiO₂-H₂O: an experimental study at 2 kbar PH₂O and comparison with natural Li-free white micas. *Mineral. Mag.*, **50**, 257-266.
- Redhammer, G.J. & Roth, G. (2002): Crystal structure and Mössbauer spectroscopy of the synthetic amphibole potassic-ferri-ferro-richterite at 298 K and low temperatures (80 K-110 K). *Eur. J. Mineral.*, **14**, 105-114.
- Reece, J.J., Redfern, S.A.T., Welch, M.D., Henderson, C.M.B., McCammon, C.A. (2002): Temperature-dependent Fe²⁺-Mn²⁺ order-disorder behaviour in amphiboles. *Phys. Chem. Minerals*, **29**, 562-570.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751-767.
- Skogby, H. & Rossman, G.R. (1991): The intensity of amphibole OH bands in the infrared absorption spectrum. *Phys. Chem. Minerals*, **18**, 64-68.
- Strens, R.S.J. (1966): Infrared study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. *Chem. Comm.*, **15**, 519-520.
- (1974): The common chain, ribbon and ring silicates. in "The Infrared Spectra of Minerals", Farmer V.C., ed., Mineral. Soc. Monogr., **4**, 305-330.
- Wilkins, R.W.T. & Ito, J. (1967): Infrared spectra of some synthetic talcs. *Am. Mineral.*, **52**, 1649-1661.

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