

Synthetic and natural Fe-Mg chloritoid: structural, spectroscopic and thermodynamic studies

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Abstract: Fe-Mg bearing chloritoids were synthesized at 18–35 kbar and 590–720°C in a piston cylinder apparatus under the f_{O_2} defined by the Fe/FeO buffer (IW). We investigated the synthetic crystals by electron microprobe, X-ray powder diffraction, high-resolution transmission electron microscopy, Mössbauer spectroscopy and diffuse reflectance spectroscopy in the UV-NIR (30000–6000 cm^{-1}). Structural studies reveal that the high-pressure chloritoids crystallize in the triclinic space group $C\bar{1}$. The molar volume of the chloritoid solid solutions depends linearly on composition. The crystal lattices are nearly perfect with almost no defects, while some of the triclinic chloritoids may contain minor amounts of monoclinic intergrowths. Mössbauer spectroscopy shows that in the synthetic chloritoids a small amount of Fe_{tot} is incorporated as Fe^{3+} . This result is consistent with estimates from electron microprobe analyses and the results of diffuse reflectance spectroscopy. The diffuse reflectance spectra exhibit a broad band at about 15000 cm^{-1} caused by $\text{Fe}^{2+}\text{Fe}^{3+}$ charge transfer and two small crystal-field bands at about 11000 and 8200 cm^{-1} due to Fe^{2+} in the strongly distorted M1B octahedron (Hålenius *et al.*, 1981). The crystal-field effect on ΔH^{excess} ($\text{CFSE}^{\text{excess}}$) of Fe^{2+} in chloritoid was determined by an analysis of the crystal-field spectra. $\text{CFSE}^{\text{excess}}$ is negative within the whole Fe-Mg chloritoid solid-solution series. It is larger in the Fe-rich than in the Mg-rich part of the system, which indicates a non-ideal, asymmetrical mixing behaviour of Fe-Mg chloritoid.

Key-words: Fe-Mg chloritoid, syntheses, Mössbauer spectroscopy, electron microprobe, diffuse reflectance spectroscopy, crystal-field spectra, $\text{CFSE}^{\text{excess}}$.

Introduction

Chloritoid is a characteristic mineral of low-temperature metapelites. It is an orthosilicate with the general formula $(\text{Fe}^{2+}, \text{Mg}, \text{Mn}^{2+})_2(\text{Al}, \text{Fe}^{3+})\text{Al}_3\text{O}_2[\text{SiO}_4]_2(\text{OH})_4$. Although the most common chloritoids are Fe-rich, an increasing number of Mg-rich chloritoids have been found in the last decade indicating that there is a complete solid-solution series: $(\text{Fe}^{2+}_x \text{Mg}_{1-x})_2\text{Al}_4\text{O}_2[\text{SiO}_4]_2(\text{OH})_4$ (Chopin *et al.*, 1992). Fe-rich chloritoid is characteristically found in rocks of low grade, whereas magnesiochloritoid is a key-mineral in high-pres-

sure pelitic blueschists (Chopin, 1983). Although a lot of work has been done to gain insight into the structure, stability and crystal chemistry of chloritoids there are many open questions. Some of them are summarized below:

i) Polymorphism *versus* polytypism: The most abundant chloritoids occur in two modifications: a monoclinic one, space group $C2/c$ and a triclinic one, space group $C\bar{1}$ (Hanscom, 1975 and 1980; Jefferson & Thomas, 1978). The last mentioned authors investigated natural chloritoids by high-resolution electron microscopy in combination with X-ray precession photographs. They sug-

gested that the triclinic and monoclinic chloritoids should be considered as 1Tc and 2M₂ polytypes. In addition to these polytypes they discovered two new polytypes, a second monoclinic and a trigonal one. Hanscom (1975, 1980) refined the crystal structure of natural monoclinic (2M₂) and triclinic (1Tc) chloritoid by single-crystal X-ray structure refinements. He showed that the monoclinic (2M₂) and triclinic (1Tc) structures cannot be considered as polytypes, but rather as polymorphs. Up to now, there has been no other structure refinement of triclinic chloritoid that could confirm the polymorphic character of the phase transition.

ii) The stability fields of triclinic and monoclinic chloritoids: in nature the monoclinic 2M₂ form has been reported to occur most frequently in rocks metamorphosed at higher temperature than the triclinic 1Tc form, which is assumed to be stable at low temperatures and/or high pressures (Deer *et al.*, 1982). This observation supports the result of Hanscom (1980) since polymorphs – in contrast to polytypes – are structures which have their own stability fields as a function of P, T and x and are therefore limited in number (Baronet, 1997). The stability fields of both types, however, have not yet been experimentally determined.

iii) Scarcity of Mg-rich chloritoid: Ivaldi *et al.* (1988) refined the crystal structure of a natural, monoclinic 2M₂ high-pressure magnesiochloritoid with 35 mole% of the Fe end-member ($x_{\text{Fe}} = 0.35$) by single-crystal X-ray diffraction at 25°C and at 700°C. They observed that the calculated bond lengths in the magnesiochloritoid do not differ very much from those of a Fe-rich chloritoid, even for polyhedra where Fe is replaced by Mg. The only significant difference between the monoclinic Fe-rich chloritoid ($x_{\text{Fe}} = 0.87$) investigated by Hanscom (1975) and the monoclinic Mg-rich chloritoid is a smaller mean cation-oxygen distance, 2.163 Å vs. 2.150 Å at the M1B site. The theoretical M1B-O value for the Mg-rich sample, calculated with Shannon's (1976) ionic radii is 2.121 Å (Ivaldi *et al.*, 1988). This implies that the structure is relatively rigid. Despite this rigidity, the authors observed a higher deficiency in bond-valences of the oxygen atoms in magnesiochloritoid than in Fe-rich chloritoid. They concluded that the chloritoid structure accommodates Fe better than Mg. This may explain why magnesiochloritoid is rather scarce and is restricted to high-pressure conditions. According to Chinner & Dixon (1973), Mg-rich chloritoid breaks down in

the presence of quartz to a more Fe-rich chloritoid plus kyanite and talc.

An experimental study of the structural state and the stability of chloritoid as a function of pressure, temperature and composition is necessary. Experiments involving the Fe end-member chloritoid have been carried out since the sixties (Halferdahl, 1961; Hoschek, 1967; Ganguly, 1968 and 1969; Ganguly & Newton, 1968; Vidal *et al.*, 1994). Chopin & Schreyer (1983) were the first to investigate the synthesis conditions and stability of the Mg end-member chloritoid. However, up to now, no synthetic Fe-Mg-bearing chloritoid solid solutions have been reported.

In a comprehensive experimental study we intend to investigate the crystal structure, crystal chemistry, thermodynamics and the stability fields of triclinic and monoclinic, synthetic Fe-Mg chloritoids (Koch-Müller *et al.*, in prep.). Here, we present results of electron microprobe analyses, powder X-ray diffraction and high-resolution electron microscopy, Mössbauer spectroscopy and diffuse reflectance spectroscopy in the UV-NIR region obtained on Fe-Mg chloritoid solid solutions, synthesized at 590–720°C and 18–35 kbar.

Structure

The structure of natural chloritoid has been investigated by Brindley & Harrison (1952), Harrison & Brindley (1957), Hanscom (1975), Jefferson & Thomas (1978), Hanscom (1980) and Ivaldi *et al.* (1988). Fig. 1 shows a polyhedral plot of a part of the structure of the monoclinic 2M₂ polymorph. It contains alternating layers of edge-connected octahedra, which are perpendicular to c. Layer 2 consists of M2A and M2B oxygen octahedra, while layer 1 consists of M1A and M1B octahedra which are coordinated by 4 OH and 2 O ligands in a trans and cis configuration, respectively. The M1A octahedron is about 25% smaller than the M1B octahedron. According to Hanscom (1975, 1980) and Hålenius *et al.* (1981) the M1A polyhedra are occupied by Al and some Fe³⁺, the M1B octahedron by di-valent cations such as Fe²⁺, Mg and Mn²⁺. The polyhedra of the L2 layer are exclusively occupied by Al. The two layers L1 and L2 are linked by isolated tetrahedra centred on silicon. The structure of the triclinic polymorph 1Tc is very similar to the monoclinic 2M₂ structure. The triclinic structure contains only one of each octahedral layer type in the unit cell, *i.e.* the

c period in the triclinic polymorph is half as long as in the monoclinic form. The reduction in symmetry from monoclinic to triclinic is mainly caused by displacements in the L2 layer: the M2B site is located on two special positions in the triclinic structure, while it occupies a general position in the monoclinic one. Hanscom (1980) transformed the refined triclinic atomic coordinates to the monoclinic cell using the relation given by Halferdahl (1961). This relation is based on the assumption that the monoclinic structure results from twinning of the triclinic structure on a unit-cell scale. Hanscom (1980) noted that, although the positional parameters of the monoclinic and the transformed triclinic atomic coordinates are very similar, there are small but significant differences, so the monoclinic and triclinic structures cannot be considered as polytypes.

Methods

Syntheses were performed at the Technische Universität Berlin in the pressure range of 18 to 25 kbar and at the Bayerisches Geoinstitut Bayreuth at 35 kbar in piston-cylinder devices using stoichiometric oxide mixtures and about 35 wt% water. In two runs, indicated in Table 1, 10 mole% SiO₂ in excess was used. We used rock-salt cells (Technische Universität Berlin) and talc-pyrex cells (Bayerisches Geoinstitut, Bayreuth) as pressure transmitting medium. Details of the experimental set ups used in Berlin and Bayreuth are given in Koch-Müller (1997) and Shaw (1999), respectively. The synthesis experiments for Fe²⁺-bearing chloritoid were buffered by IW using a double-capsule technique with an inner AgPd capsule (3.5 mm in diameter, 7 mm long) and an outer iron capsule (5.5 mm in diameter, 10 mm long). The syntheses of Mg end-member chloritoid were performed in Au capsules (5.0 mm in diameter, 10 mm long). The capsules were sealed with a special cold-sealing technique described by Cemic *et al.* (1990).

Run products were examined by optical and scanning electron microscopy, electron microprobe, powder X-ray diffraction, high-resolution transmission electron microscopy, Mössbauer spectroscopy and diffuse reflectance spectroscopy in the UV-NIR region. For comparison, three natural chloritoids (CldT: Üstüağıksarıncı, Turkey; RO1: Kuçadası, Turkey and RO2: Allalin-Gabbro, Switzerland) were included in the set of samples.

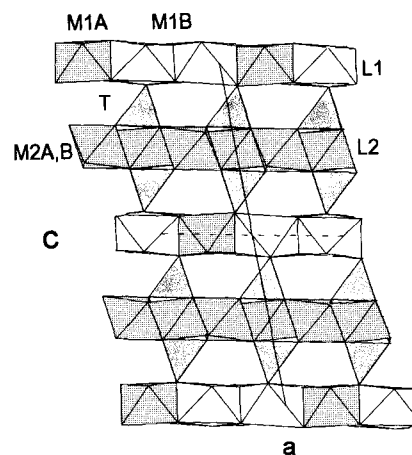


Fig. 1. Polyhedral presentation of the monoclinic 2M₂ chloritoid structure, based on data of Hanscom (1975). The octahedra M2A and M2B in the L2 layer are not distinguished in this presentation. The horizontal broken line and the crossing solid line outline the monoclinic unit cell dimensions in the *a* and *c* direction, respectively.

Electron microprobe analyses

EMP analyses were performed with a Cameca Camebax at the ZELMI laboratory of the Technische Universität Berlin and with Cameca SX50 and SX100 microprobes at the GeoForschungs-Zentrum Potsdam using the wavelength dispersive mode and the PAP correction program (Pouchou & Pichoir, 1985). Operating conditions were 15 kV and 15 nA. Counting time was set at 20 s on peak and 10 s on background. Well characterised natural minerals were used as standards: andalusite, wollastonite (Si), andalusite, K-feldspar (Al), olivine (Mg), spessartine (Mn) and hematite, metallic iron (Fe).

Rietveld refinements of powder XRD data

Powder X-ray diffraction data were collected in transmission mode on a STOE-STADI-P diffractometer with a Ge monochromator in the primary beam (CuKα₁ radiation, 40 kV, 40 mA) at the GeoForschungsZentrum Potsdam. The instrument is equipped with a 7° position-sensitive detector. The samples were fixed between Mylar foils. A 1 mm thick Al-foil was placed in front of the detector in order to reduce fluorescence radiation in the Fe-rich samples. The powder patterns were recorded from 5–125° 2θ in steps of 0.02° using counting

times sufficient to obtain about 3000 counts on the peak maximum of the peak with highest intensity.

Crystal-structure refinements of the natural and the synthetic chloritoids were performed in the monoclinic space group *C2/c* as well as in the triclinic space group *C1* using the program GSAS (Larson & van Dreele, 1998). Starting values were the fractional atomic coordinates, lattice constants and the isotropic displacement parameters as determined by Hanscom (1975, 1980) for the monoclinic and triclinic forms, respectively. The number of profile parameters was 20–22. These consisted of 16 background parameters (radial-distribution peak-function, Larson & van Dreele, 1998), 4–6 parameters to define the variation of peak width with 2θ and to describe asymmetric pseudo-Voigt peak shapes (Howard, 1982; Thompson *et al.*, 1987). Texture effects due to the preferred orientation of the chloritoid plates (strong cleavage parallel to (001) and (110)) were corrected in the refinements using the formalism of March (1932) and Dollase (1986). Soft constraints on the Si-O bond distance based on values refined by Hanscom (1975, 1980) were introduced before the refinement of the atomic coordinates. After convergence of the profile refinements, the atomic coordinates were refined with the isotropic displacement parameters constrained to the data of Hanscom (1975, 1980) and the site occupancies constrained to the results of our microprobe analyses. Quantitative phase analyses were performed on those run products that contain additional phases. In this procedure the structural input data for all impurities except staurolite refer to the International Crystallographic Structural Database (ICSD). The data for staurolite were taken from Koch-Müller *et al.* (1998). Only the lattice parameters, some profile parameters and the preferred orientation parameters were refined for the additional phases corundum, hercynite, diaspore, quartz, kyanite and chlorite. The amount of staurolite was in the range of 15–40 wt% in the Mg-rich samples and, therefore, the fractional atomic parameters of staurolite were refined in these samples in addition to the parameters mentioned above.

High-resolution electron microscopy

One natural chloritoid sample and four synthetic chloritoid samples were investigated by high-res-

olution electron microscopy at the GeoForschungsZentrum in Potsdam. The samples were ground and suspended in ethanol by ultrasonic treatment. The crystallites of the samples were transferred from the suspension onto a holey carbon grid. Usually, the edges of the grains on the grid are electron-transparent. TEM analysis was carried out on the chloritoid crystallites of the samples using a Philips CM200 with twin lens configuration at 200 kV. The electron source was a LaB₆ filament. The lattice fringe images are energy-filtered using the zero-loss electrons and recorded with a Gatan image filtering system (GIF). The width of the energy window was 10 eV and symmetrical with respect to the zero-loss peak. The objective aperture used was 100 μm .

Mössbauer spectroscopy

⁵⁷Fe-Mössbauer spectra were obtained at the Technische Universität Berlin using a Mössbauer spectrometer (driving unit and MCA from Halder Electronic, FRG) equipped with a source of 1.85 GBq ⁵⁷Co in Pd. The velocity scale and isomer shift was calibrated against natural iron (α -Fe foil, 25 μm thickness and 99.99 % purity). Absorbers were prepared from 10–16 mg chloritoid powder, diluted in about 100 mg sugar to yield a concentration of about 0.04–0.07 mg ⁵⁷Fe/cm². Due to the high dilution in sugar and careful preparation avoiding intensive pressure, our Mössbauer spectra show no texture effects due to preferred orientations.

Mössbauer measurements were usually recorded in constant-acceleration mode from –4 mm/s to +4 mm/s in 1024 channels. One sample (MKM-98-9) was measured in the velocity range of ± 10 mm/s to check for traces of magnetically ordered phases such as spinel. Such impurities were not detected. The modified program MBF (Nagel, 1990) and the program package Recoil (Lagarec & Rancourt, 1998) were used to resolve peaks using Lorentzian functions (MBF; Recoil) and to perform a Voigt-based fitting analysis (Recoil). Rancourt & Ping (1991) proposed this analysis as a new approach to fit Mössbauer spectra. The method is based on a continuous quadrupole splitting distribution (QSD) for materials with significant atomic disorder. Rancourt (1994) compared the results of Mössbauer spectroscopy of natural biotite samples fitted with Lorentzian line shapes and with the Voigt-based QSD method. He

Table 1. Synthesis conditions for Fe-Mg chloritoid.

sample	P [kbar]	T [°C]	X _{Fe} ^{start}	run duration [h]	product ¹
MKM-97-8	18	600	1.00	100	cld
MKM-98-1	20	600	1.00	48	cld
MKM-98-9	20	590	1.00	24	cld
MKM-97-16	20	600	0.85	72	cld (sp, crn)
MKM-97-7	18	600	0.75	48	cld (crn)
MKM-98-31 ²	20	600	0.75	72	cld
MKM-97-10	23	600	0.60	45	cld (crn)
MKM-99-2	20	600	0.60	48	cld (crn)
MKM-98-32 ²	20	600	0.55	72	cld (qtz)
MKM-97-4	18	600	0.50	72	cld
MKM-98-4	23	600	0.45	48	cld <u>st</u> (qtz) [chl]
MKM-97-6	25	620	0.35	72	cld <u>st</u> (chl)
MKM-98-23	25	600	0.35	48	cld <u>st</u> , <u>crn</u> (chl) [qtz]
MKM-98-28	25	600	0.35	48	cld, <u>st</u> (qtz, ky)
MKM-98-38	35	680	0.10	40	cld, <u>st</u> [dia, ?]
MKM-98-40	35	650	0.10	50	cld, <u>st</u> [dia, ?]
MKM-98-43	35	690	0.00	47	cld, <u>st</u> [?]
MKM-98-47	35	650	0.00	18	cld, <u>st</u> [?]

¹abbreviations after the suggestions of Kretz (1983): cld (chloritoid);

crn (corundum); dia (diaspore); ky (kyanit); qtz (quartz); spl (spinel); st (staurolite); ? phase not identified. Amount of additional phases obtained in the quantitative phase analyses (see also table 3): [between 1 and 5 wt%], (between 5 and 10 wt%), between 10 and 40 wt%

²oxide mixture with 10 mole% SiO₂ in excess

pointed out that the Lorentzian-based fits of the biotite spectra always overestimate the background, put large wings or tails on the main absorption peaks and give unrealistically large values for the line widths. As a consequence, the Fe³⁺/Fe spectral area ratio obtained with a Lorentzian fit may be different to that obtained by the Voigt-based QSD method.

Diffuse reflectance spectroscopy

The measurements were made at the Technische Universität Berlin on a Perkin-Elmer Lambda 19 spectrometer. The spectra of the synthetic chloritoid powders were recorded in the range 30000 to 5000 cm⁻¹ (333 to 2000 nm). Absorption was measured using the FR-mode which is based on the Kubelka-Munk relation (Kubelka & Munk, 1931, Kortüm & Oelkrug, 1966), using Teflon as the reference white standard. The quantity FR (= f(R_∞)) is directly proportional to absorbance units. The spectra were fitted to obtain the peak positions, half widths and intensities of the bands in the range of 6000 to 20000 cm⁻¹ using the PEAKFIT system of programs by Jandel Corpora-

tion. The baseline for each spectrum was obtained as a straight line interpolation between the background near 6500 and 20000 cm⁻¹. The peak shapes were assumed to be normal Gaussian. The uncertainty in peak position is estimated as ±30 cm⁻¹.

Results and discussion

Products of synthesis

Table 1 compiles the synthesis conditions and the run products obtained. Though pure magnesiochloritoid becomes stable at about 18 kbar at the expense of the paragenesis chlorite and kyanite (Schreyer, 1988), direct synthesis from the anhydrous composition MgOAl₂O₃SiO₂ requires water pressures in excess of 30 kbar and temperatures between 600 and 750 °C (Chopin & Schreyer, 1983). With a maximum pressure of 25 kbar available in the laboratory at the Technische Universität, we were able to synthesize a Mg-rich chloritoid with 65 mole% of the Mg end-member (x_{Fe} = 0.35). With a pressure of 35 kbar, using the equipment at the Bayerisches Geoinstitut, Bayreuth, the synthesis of more Mg-rich chloritoids (x_{Fe} = 0.13

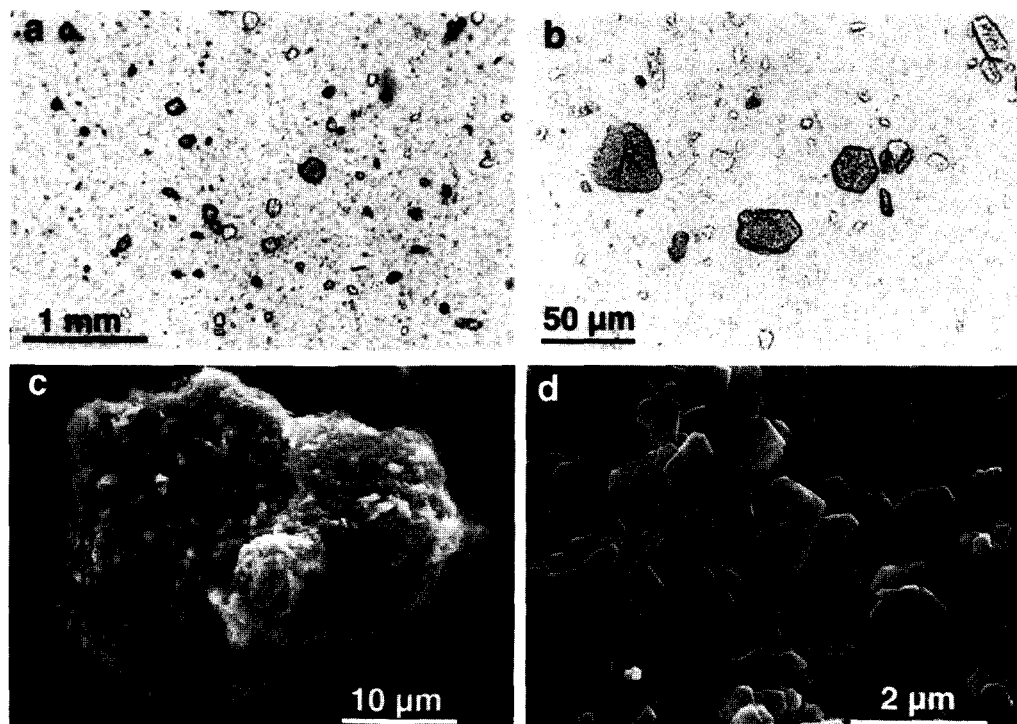


Fig. 2. Photomicrographs of synthetic chloritoid: a and b petrographic microscope (sample MKM-97-4); c and d scanning electron microscope MKM-98-1).

and 0.15) and even of the Mg end-member chloritoid was successful, though not as a single-phase product. Optical examination revealed that some of the run products contain additional phases. In the compositional range $x_{\text{Fe}} = 0.5$ to $x_{\text{Fe}} = 1.0$, some contain traces of corundum. With higher Mg-content, the amount of additional phases, mainly staurolite, increases dramatically (Table 1). According to Chopin (1985), Mg-rich chloritoid never nucleates spontaneously and it seems to be impossible to obtain a single-phase product without seeds. Fig. 2a and b show microphotographs of the chloritoid sample MKM-97-4 obtained at different magnifications. Most of the crystals exhibit pseudo-hexagonal symmetry and have an average size of about 3 μm . However, some of them are up to 50 μm in size. This unusual size distribution of some large crystals together with many small ones was also observed by Chopin (1985).

Fig. 2c and d show SEM images of the Fe end-member chloritoid (MKM-98-1) at different magnifications with the typical pseudo-hexagonal

crystal shapes (performed using a Hitachi S-4000 SEM at the Technische Universität Berlin).

Electron microprobe analyses

Electron microprobe analyses of the synthetic and the natural chloritoid samples are presented in Table 2. Neither a calculation of the structural formulae based on 12 oxygen assuming 4 H per formula unit (pfu) nor a calculation based on 8 cations yielded satisfactory results: in both cases, the calculated number of Si atoms pfu significantly exceeded the ideal value of 2.00. Simon *et al.* (1997) noted a similar problem for microprobe analyses of natural chloritoids and concluded that this is most probably due to inadequate correction of matrix effects. In order to avoid influence of the excess silicon on the calculated numbers of cations, these authors proposed to calculate the formulae of chloritoid on the basis of a fixed number of octahedral cations ($\text{Al} + \text{Fe} + \text{Mg} + \text{Mn} + \text{Ti} + \text{Ca} = 6$). Lodders *et al.* (1998) calculated the structural formulae of natural

Table 2. Composition of synthetic and natural Fe-Mg chloritoids in wt%. Cations per formula unit, calculated on the basis of 6 octahedral cations (1 σ : standard deviation).

MKM-	97-8	98-1	97-16	97-7	98-31	97-10	99-2	98-32	97-4
wt%									
SiO ₂	23.50 (45)	23.05(33)	22.89(12)	24.79(9)	24.11(59)	24.97(33)	25.48(23)	25.46(55)	25.08(25)
Al ₂ O ₃	38.33 (46)	37.64(80)	37.65(26)	39.47(18)	36.97(99)	40.55(51)	42.47 (12)	40.26(90)	40.43(42)
FeO	28.13(39)	27.38(54)	23.26(52)	21.75(56)	19.42(66)	18.03(38)	17.56(23)	16.59(66)	15.85(40)
MgO	0.00	0.00	2.14(39)	4.11(6)	3.72(14)	5.98(8)	6.5(12)	6.89(13)	7.91(14)
Σ	89.97	88.07	85.93	90.12	84.78	89.90	92.02	88.55	89.36
cations									
Si	2.05(4)	2.06(3)	2.06(1)	2.10(1)	2.17(1)	2.08(3)	2.05(3)	2.13(1)	2.07(3)
Al	3.95(2)	3.96(2)	4.00(2)	3.94(2)	3.98(2)	3.98(2)	4.04(2)	3.98(3)	3.93(3)
Fe ³⁺ ¹	0.05(2)	0.04(2)	0.00	0.06(1)	0.02(2)	0.02(2)	0.00(2)	0.02(3)	0.07(1)
Fe ²⁺	1.99(3)	2.00(4)	1.71(3)	1.48(3)	1.48(1)	1.25(4)	1.18(2)	1.14(2)	1.02(2)
Mg	0.00	0.00	0.29(1)	0.52(1)	0.51(1)	0.74(1)	0.78(1)	0.86(2)	0.97(2)
Σ	8.05	8.06	8.06	8.10	8.20	8.01	8.05	8.13	8.07
x _{Fe}	1.00	1.00	0.86	0.74	0.74	0.63	0.60	0.57	0.51
MKM-	98-4	98-28	97-6	98-40	98-38	98-43	RO1 ²	RO2 ³	CldT ⁴
wt%									
SiO ₂	25.80(38)	25.53(43)	26.61(17)	27.05(58)	26.85(80)	28.53(99)	24.65(18)	25.57(11)	24.20(33)
Al ₂ O ₃	41.53(68)	39.54(82)	43.00(78)	43.25(88)	42.86(83)	44.90(89)	39.43(46)	41.40(16)	39.35(52)
FeO	12.69(29)	12.39(48)	10.66(28)	4.79(29)	3.98(27)	0.00	18.58(62)	13.68(41)	25.02(24)
MgO	9.08(45)	9.29(36)	11.07(22)	14.71(40)	14.70(25)	17.58(80)	5.99(46)	9.32(24)	2.06(7)
Σ	89.31	91.35	91.35	89.79	88.40	91.00	90.00	90.38	91.01
cations									
Si	2.11(1)	2.16(2)	2.09(3)	2.11(2)	2.13(3)	2.16(3)	2.05(1)	2.06(1)	2.03(1)
Al	4.01(1)	3.94(1)	3.99(4)	3.98(1)	4.00(2)	4.01(2)	3.86(4)	3.94(1)	3.90(2)
Fe ³⁺ ¹	0.00(1)	0.06(1)	0.01(4)	0.02(1)	0.00	0.00	0.14(4)	0.06(1)	0.10(1)
Fe ²⁺	0.86(1)	0.81(2)	0.70(2)	0.30(2)	0.26(1)	0.00	1.18(8)	0.86(2)	1.66(1)
Mg	1.11(1)	1.19(3)	1.30(4)	1.71(1)	1.74(2)	1.99(2)	0.73(8)	1.12(3)	0.26(1)
Σ	8.11	8.17	8.10	8.11	8.13	8.16	8.05	8.06	7.97
x _{Fe}	0.44	0.41	0.35	0.15	0.13	0.00	0.59	0.43	0.86

¹ Fe³⁺ pfu = (4-Al pfu) ² in addition 1.30 wt% MnO ³ in addition 0.10 wt% MnO ⁴ in addition 0.38 wt% MnO

Table 3. Data collection and structure refinement data for some synthetic and natural chloritoids.

MKM-	97-8	98-1	97-16	98-31	97-10	99-2	97-4
space group	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$
reflections	5750	5750	5750	5750	5228	5750	5750
variables	56	59	61	59	59	78	57
$R_{(wp)est}$ %	2.9	1.8	3.1	2.6	2.9	2.5	2.5
$R_{(wp)}^0$ %	3.6	2.4	3.4	3.1	3.8	3.4	3.3
$R_{(p)}$ %	2.8	1.7	3.7	2.3	2.8	2.6	2.5
DWd ^a	1.2	1.0	1.5	1.3	1.1	1.0	1.0
χ^2 ^b	1.5	1.8	1.2	1.4	1.7	1.8	1.8
a (Å)	9.499(2)	9.504(3)	9.485(3)	9.478(2)	9.468(2)	9.467(3)	9.467(2)
b (Å)	5.485(2)	5.488(2)	5.477(2)	5.475(2)	5.468(1)	5.468(2)	5.466(1)
c (Å)	9.158(3)	9.164(6)	9.156(6)	9.152(3)	9.148(3)	9.148(3)	9.140(3)
α (°)	96.86(3)	96.89(3)	96.86(3)	96.82(2)	96.78(2)	96.77(3)	96.67(3)
β (°)	101.32(2)	101.33(3)	101.5(3)	101.43(2)	101.24(2)	101.39(2)	101.04(3)
γ (°)	90.00(2)	89.98(2)	90.02(3)	90.00(2)	90.00(1)	90.00(2)	90.0(1)
V_{cell} (Å ³)	464.3(3)	465.1(5)	462.6(3)	462.1(3)	461.2(2)	460.9(3)	460.9(2)
M1B-O(Å ³)	2.18(4)	2.18(3)	2.11(5)	2.12(3)	2.11(3)	2.11(3)	2.07(3)
x_{Fe}	1.0	1.0	0.86	0.74	0.63	0.60	0.51
cld (wt%)	100	100	88	100	93	92	100
st “							
sp “			6				
co “			6		7	8	
qtz “							
chl “							
ky “							

^a DWd: serial correlation after Durbin & Watson, see Post & Bish (1989)

chloritoids on the basis of 2 silicon atoms. However, if the SiO₂ values exceed the ideal value due to matrix effects, this method yields less than the cation total of 6 for the octahedral sites. Table 2 summarises the structural formulae of the synthetic and natural chloritoids calculated on a basis of 6 octahedral cations, *i.e.* according to Simon *et al.* (1997). Based on the results of Hanscom (1975, 1980) and Hälenius *et al.* (1981) the Fe³⁺ contents of the samples have been calculated according to $[Fe^{3+}] = 4 - [Al^{3+tot}]$. The microprobe analyses reveal that a small but variable amount of Fe³⁺ is incorporated in chloritoid. The incorporation of Fe³⁺ into the chloritoid structure, despite

IW buffering, is most probably caused by the high pressure of formation (Woodland & O'Neill, 1993; Vidal *et al.*, 1994).

X-ray diffraction

The triclinic and monoclinic polymorphs can easily be distinguished by X-ray diffraction. Halferdahl (1961) was the first to present the diffraction patterns of the two polymorphs. The natural chloritoids CldT and RO2 show the diffraction pattern of the monoclinic polymorph, while the natural sample RO1 and all the synthetic chloritoids show only the powder pattern of the tri-

Table 3. continued.

98-4	98-28	98-23	97-6	98-38	98-43	CldT	RO1	RO2
$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C\bar{1}$	$C2/c$	$C\bar{1}$	$C2/c$
5750	5750	5750	5750	5750	5750	5498	5848	5999
78	67	67	52	72	88	57	49	50
3.6	1.7	1.5	2.2	3.3	4.2	2.2	2.8	2.7
4.8	2.9	2.0	3.7	4.5	9.3	2.2	3.7	3.1
3.6	2.1	1.6	2.7	3.4	6.5	1.7	2.8	2.5
1.1	0.7	1.0	0.7	1.0	0.4	1.2	1.1	1.3
1.8	2.8	1.8	2.8	1.9	5.0	1.7	1.7	1.5
9.457(3)	9.455(2)	9.452(2)	9.451(2)	9.435(2)	9.429(2)	9.484(2)	9.481(2)	9.451(1)
5.463(2)	5.461(1)	5.456(2)	5.458(1)	5.448(1)	5.443(2)	5.486(1)	5.478(2)	5.4674(6)
9.147(3)	9.146(2)	9.132(3)	9.130(3)	9.122(3)	9.128(3)	18.180(6)	9.153(3)	18.159(3)
96.77(3)	96.72(2)	96.58(3)	96.66(3)	96.54(2)	96.54(3)	90.00	96.80(2)	90.00
101.30(3)	101.26(2)	100.93(3)	101.00(3)	100.80(2)	100.76(3)	101.75(2)	101.4(3)	101.4(1)
90.00(2)	90.02(1)	90.01(1)	90.00(2)	89.99(1)	90.01(1)	90.00	90.00(2)	90.00
460.1(2)	459.9(2)	459.2(2)	459.08(2)	457.5(2)	457.2(2)	926.10(5)	462.6(2)	919.7(2)
2.08(4)	-	2.06(4)	-	2.09(4)	-	2.18(3)	2.09(4)	2.13(2)
0.44	0.41	0.36	0.35	0.13	0.00	0.86	0.59	0.43
73	77	61	75	66 ^c	64 ^d	100	87	100
15	18	13	17	32	33			
		13						
9	2	3			1		13	
3		9	8					
	3							

^b $\chi^2 = (R(wp) / R(wp)_{est})^2$ ^c plus 2 wt% diasporite ^d plus traces of a not identified phase

clinic polymorph. According to the quantitative phase analyses using the Rietveld method, no monoclinic chloritoid was detected in the synthetic triclinic samples within the detection limit of X-ray diffraction (< 1 wt%). Details of the structure refinement of synthetic samples are given in Table 3 together with the lattice parameters, cell volumes of the unit cells, the refined mean M1B-O bond lengths and the results of the quantitative phase analyses. The Durbin-Watson d-statistics are relatively low, indicating serial correlations of the data points (Post & Bish, 1989). Fig. 3a-e show the lattice parameters *a*, *b* and *c*, the cell volumes and mean M1B-O distances of the syn-

thetic chloritoids of this study as a function of composition. The cell angles α , β and γ do not depend on composition, at least in a first approximation. The lattice parameters of the triclinic Mg end-member chloritoid are in good agreement with the data given by Chopin *et al.* (1992). There is a linear relationship between the cell edges as well as the cell volume and composition. Thus, the synthetic Fe-Mg chloritoid solid-solution series exhibits no excess volume of mixing. Linear least squares fits to the data revealed the following relations:

$$a [\text{\AA}] = 9.426 + 0.073 \cdot x_{\text{Fe}} \quad (r^2=0.99)$$

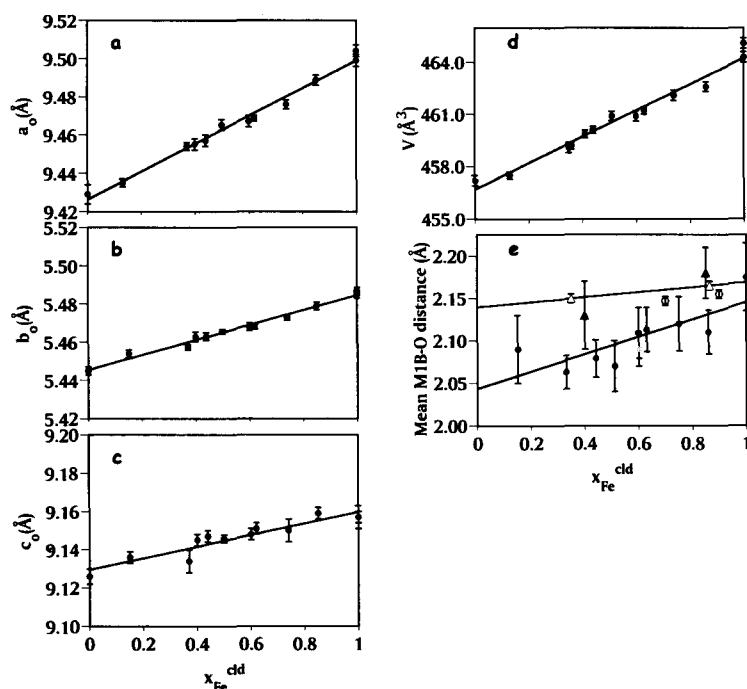


Fig. 3. (a–d) Lattice constants a , b , c and the unit-cell volume V , respectively, of synthetic chloritoid as a function of X_{Fe} . (e) Mean octahedral M1B–O bond distances in monoclinic chloritoid (triangles) and in triclinic chloritoids (circles). Open triangles: distances obtained on natural monoclinic chloritoids in single-crystal structure refinements (Hanscom, 1975; Ivaldi *et al.*, 1988); closed triangles: those obtained in this study on natural chloritoids in Rietveld refinements; open circles: distances obtained on natural triclinic chloritoids in single-crystal structure refinements (Hanscom, 1980; Koch-Müller *et al.*, in prep.); closed (dotted) circles: distances obtained on synthetic (natural) triclinic chloritoid in this study in Rietveld refinements.

$$\begin{aligned}
 b [\text{\AA}] &= 5.440 + 0.039 \cdot x_{\text{Fe}} \quad (r^2=0.98) \\
 c [\text{\AA}] &= 9.130 + 0.030 \cdot x_{\text{Fe}} \quad (r^2=0.88) \\
 V [\text{\AA}^3] &= 456.68 + 7.558 \cdot x_{\text{Fe}} \quad (r^2=0.97)
 \end{aligned}$$

The coefficients of parameters a and b are in excellent agreement with the relationships given by Chopin *et al.* (1992) for natural monoclinic chloritoids, whereas the parameter c and the cell volume is evidently halved in the triclinic polymorphs. Table 4 shows the refined fractional atomic coordinates of the synthetic, triclinic chloritoid MKM-97-4 in comparison to the refined fractional atomic coordinates of the monoclinic sample RO2 and, in brackets, the transformed triclinic coordinates of sample MKM-97-4. The sample MKM-97-4 was chosen because it has a similar composition to the monoclinic sample RO2. Nevertheless, there are significant differences between the monoclinic and transformed triclinic coordinates, especially in y , supporting

the results of Hanscom (1980) that the structures cannot be considered as polytypes. However, this result has yet to be verified by single-crystal structure refinements (Koch-Müller *et al.*, in prep.). The fractional atomic parameters obtained in the Rietveld refinements were used to calculate bond lengths in chloritoid. Fig. 3e shows a plot of the average M1B–O distance in triclinic synthetic and three triclinic natural chloritoids (RO1, this study; Hanscom, 1980 and Koch-Müller *et al.*, in prep.) as a function of composition together with the average M1B–O distances of four natural monoclinic chloritoids (CldT and RO2, this study; Hanscom, 1975; Ivaldi *et al.*, 1988;). If we consider only the distances obtained in the single-crystal structure refinements, which are definitely more accurate, it is clear that the M1B–O distances in triclinic chloritoids are smaller than in the monoclinic chloritoid, but follow the same trend as a function of composition. The average M1B–O dis-

Table 4. Fractional atomic coordinates for a synthetic triclinic chloritoid (MKM-97-4) and a natural monoclinic chloritoid (1 σ standard deviation), [transformed triclinic coordinates of MKM-97-4].

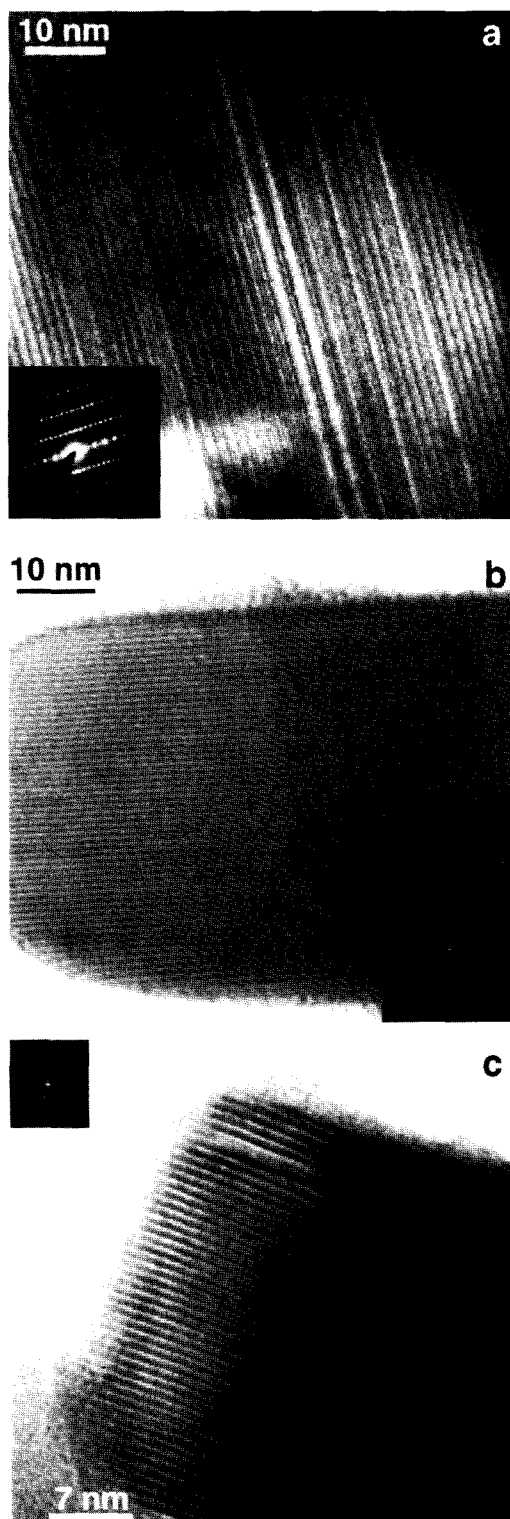
	MKM-97-4			RO2		
	triclinic, $C\bar{1}$, $x_{Fe} = 0.51$			monoclinic $C2/c$ $x_{Fe} = 0.43$		
	x	y	z	x	y	z
M1A	0.2500	0.2500	0.0000	0.2500	0.2500	0.0000
				[0.2500]	[0.2500]	[0.0000]
M2A	0.0000	0.5000	0.5000	0.0000	0.4261(38)	0.2500
				[0.0000]	[0.4025]	[0.2500]
M1B	0.0882(13)	0.7501(19)	0.0048(24)	0.0850(12)	0.7401(17)	0.0034(7)
				[0.0882]	[0.7501]	[0.0024]
M2B1	0.2500	0.2500	0.5000	0.2533(16)	0.6524(23)	0.2485(8)
				[0.2500]	[0.6526]	[0.2500]
M2B2	0.2500	0.7500	0.5000	-	-	-
T	0.4748(15)	0.4409(22)	0.3183(17)	0.4669(14)	0.4036(28)	0.1602(7)
				[0.4748]	[0.3788]	[0.1592]
O1A	0.1028(35)	0.4188(51)	0.0880(49)	0.1146(25)	0.3987(50)	0.0540(13)
				[0.1028]	[0.4016]	[0.0440]
O1B	0.2621(32)	0.9311(48)	0.0910(44)	0.2616(27)	0.9346(47)	0.0461(13)
				[0.2621]	[0.9133]	[0.0455]
O1C	0.4336(32)	0.4438(49)	0.1335(17)	0.4321(25)	0.4153(50)	0.0681(7)
				[0.4336]	[0.4178]	[0.0667]
O2A	0.3849(20)	0.2306(34)	0.3808(32)	0.3966(24)	0.1689(31)	0.1963(11)
				[0.3849]	[0.1563]	[0.1904]
O2B	0.3961(22)	0.6682(31)	0.4015(29)	0.3970(23)	0.6382(34)	0.1965(13)
				[0.3961]	[0.5899]	[0.2008]
O2C	0.1304(19)	1.0055(32)	0.4237(31)	0.1418(15)	0.8910(44)	0.1915(12)
				[0.1304]	[0.9229]	[0.2118]
O2D	0.1446(30)	0.4775(35)	0.3495(40)	0.1481(22)	0.4145(53)	0.1990(13)
				[0.1446]	[0.4093]	[0.1748]

tances obtained from Rietveld refinements of synthetic high-pressure chloritoids seem to decrease more strongly with substitution of Fe^{2+} by Mg than those of the monoclinic natural chloritoids (Fig. 3e).

High-resolution electron microscopy

X-ray diffraction revealed that the synthetic high-pressure chloritoids and the natural chloritoid RO1 are triclinic, space group $C\bar{1}$, whereas the natural samples CldT and RO2 are monoclinic. To check for the presence of monoclinic intergrowths in the triclinic crystals and *vice versa*, whose amount may be below the detection limit of X-ray diffraction, synthetic and natural chloritoids were investigated by transmission electron microscopy. The investigations were performed on the following samples: CLDT (pure natural Fe-Mg chloritoid), MKM-97-8 and MKM-98-1 (pure Fe end-member chloritoids), MKM-97-10 (synthetic

Fe-Mg chloritoids with corundum as impurity) and MKM-97-6 (synthetic Fe-Mg chloritoids with staurolite as impurity). The energy-filtered lattice fringe images were obtained with the electron beam perpendicular to the chloritoid (110)-plates. Thus, the fringes are one-dimensional only and can provide information concerning the $d_{(001)}$ spacings which are different in triclinic and monoclinic chloritoids. Such differences cannot be observed under ideal scattering conditions due to the systematic absence of reflections in the C-centred lattices type $C\bar{1}$ and $C2/c$. On the other hand, Jefferson & Thomas (1978) showed that, especially in thicker parts of the crystals, multiple scattering occurs which leads to otherwise symmetry-forbidden reflections. Thus, the triclinic and monoclinic forms can indeed be distinguished under these real scattering conditions with $d_{(001)}$ spacings of about 8.8 and 17.8 Å for the triclinic and monoclinic phases, respectively. Fig. 4a shows the lattice fringe image and the corresponding electron dif-



fraction pattern of the natural sample with a $d_{(001)}$ spacing of 17.8 Å and several lattice faults. Fig. 4b and c show lattice fringe images of the synthetic samples MKM-97-8 and MKM-97-10. These chloritoids are perfectly grown triclinic crystals with almost no lattice faults. All the high-pressure chloritoids show this perfect triclinic symmetry. It seems that pressure indeed promotes the formation of triclinic chloritoid.

Mössbauer spectroscopy

^{57}Fe -Mössbauer analyses of natural chloritoids have been performed by Tricker *et al.* (1978), Hålenius *et al.* (1981), De Grave *et al.* (1984) and Lodders *et al.* (1998). The Mössbauer spectra of the first three studies are very similar to each other and consist of two doublets. The very intense doublet (1), with an isomer shift (IS) of about 1.15 mm/s and a quadrupole splitting (QS) of about 2.45 mm/s at room temperature, was assigned to Fe^{2+} in octahedral coordination. The weak doublet (2), with an IS of about 0.30 mm/s and a QS of about 0.90 mm/s was assigned to Fe^{3+} in octahedral coordination (Table 5). Based on the ^{57}Fe Mössbauer parameters and the observed temperature dependence of these parameters Hålenius *et al.* (1981) assigned the Fe^{2+} doublet to the M1B octahedron and the Fe^{3+} doublet to the smaller M1A octahedron. Lodders *et al.* (1998) reported Mössbauer-spectra of chloritoids which occur as inclusions in pyrite cubes from Navajún, Spain. In one of four samples (NLS5) they obtained in the Mössbauer fit a higher IS value of 0.40 mm/s and a smaller QS value of 0.68 mm/s for the Fe^{3+} doublet than the authors mentioned above whereas those for the Fe^{2+} doublet are in good agreement (Table 5). Based on the Mössbauer fit and microprobe analyses (Al plus $\text{Fe}^{3+} = 4.4$ pfu instead of the ideal value of 4.0; $\Sigma \text{M}^{2+} = 1.6$ pfu instead of the ideal value of 2.0) they concluded that, in this sample, Fe^{3+} is incorporated in the M1A- and M1B-octrahedra. Therefore, they fitted two Fe^{3+} doublets, one for Fe^{3+} at M1A (about

← Fig. 4. (a) Lattice fringe image and electron diffraction pattern of the natural monoclinic sample CldT with the electron beam perpendicular to (110) showing a $d_{(001)}$ spacing of 17.8 Å and several lattice faults. (b and c) Lattice fringe images and electron diffraction pattern of the synthetic triclinic samples MKM-97-8 and MKM-97-10 showing a $d_{(001)}$ spacing of about 8.8 Å and almost no lattice faults.

Table 5. Room-temperature Mössbauer data for natural chloritoids reported in the literature and obtained in this study.

Author	Sample Nr.	Doublet 1				Doublet 2			
		IS (Fe ²⁺) mm/s	QS (Fe ²⁺) mm/s	Γ mm/s	Area % (Fe ²⁺)	IS (Fe ³⁺) mm/s	QS (Fe ³⁺) mm/s	Γ mm/s	Area % (Fe ³⁺)
Tricker <i>et al.</i> (1978)	A2091	1.15	2.49	0.28	90	0.29	0.83	0.32	10
Tricker <i>et al.</i> (1978)	A2092	1.15	2.43	0.30	85	0.32	0.87	0.33	15
Hålenius <i>et al.</i> (1981)	CTD 2	1.17	2.42	0.26	92.6	0.30	0.87	0.26	7.4
Hålenius <i>et al.</i> (1981)	CTD 1	1.16	2.41	0.26	94.9	0.31	0.90	0.26	5.1
De Grave <i>et al.</i> (1984)	Ottre 1 ^a	1.15	2.37	0.25	50-60	0.38 ^b	1.03 ^b	0.27 ^b	10
		1.14	2.52	0.27	40-30				
Lodders <i>et al.</i> (1998)	NLS0 ^c	1.15	2.44	-	94	0.25	0.98	-	6
Lodders <i>et al.</i> (1998)	NLS7 ^c	1.18	2.43	-	92	0.28	0.95	-	8
Lodders <i>et al.</i> (1998)	NLS5 ^c	1.16	2.45	-	80	0.40	0.68	-	20
Lodders <i>et al.</i> (1998)	NLS5 ^c	1.16	2.45	-	81	0.25	0.98	-	8.5
						0.50	0.63		10.5
this study	RO1	1.12	2.40	0.29	89.5	0.30	0.96	0.28	10.5
this study	RO1	1.12	2.40	0.06 ^e	88.5	0.29	0.98	0.10 ^e	11.5
VBF anal. ^d									
this study	RO2	1.12	2.41	0.29	94.0	0.29	1.04	0.28	6.0
this study	CldT	1.14	2.43	0.28	89.2	0.40	0.63	0.41	10.8
this study	CldT	1.15	2.42	0.05 ^e	90.3	0.39	0.65	0.36 ^e	9.7
VBF anal. ^d									
this study	CldT ^f	1.12	2.42	0.28	94	0.29	0.96	0.35	6

Note: IS, isomer shift; QS: quadrupole splitting, parameters relative to metallic Fe foil; Γ: full line width of half height.

^a The authors found that a fit with two doublets for Fe²⁺ in octahedral composition leads to smaller deviations between the experimental and calculated line shapes. However, finally they concluded that the decomposition into two ferrous doublets is an artifact due to thickness saturation effects. ^b Data obtained at 80 K. ^c Unfortunately, no data for the line widths for the doublets were given. ^d VBF analysis with Γ of the Lorentzian half width = 0.28 mm/s. ^e In the VBF analysis this is σ_A = Gaussian width of the component. ^f Treated with HCl before the measurement to remove impurities of hematite.

10 % of the total Fe content) with the Mössbauer parameters constrained to that of Fe³⁺ in M1A and one unconstrained for Fe³⁺ at M1B (about 8.5 % of the total Fe content) (Table 5).

In the present study, Mössbauer spectra were obtained on the natural chloritoid samples RO1, RO2 and CLDT, two synthetic Fe end-member chloritoids (MKM-97-8, MKM-98-9) and two synthetic Fe-Mg chloritoid samples (MKM-97-7, MKM-98-32). Fig. 5 (top) shows the observed and calculated Mössbauer-spectrum of the natural sample RO1. The Mössbauer spectra of the synthetic and natural chloritoids have been fitted with two doublets, one for octahedral Fe²⁺ and one for octahedral Fe³⁺. The standard deviations of the Mössbauer parameters IS, QS and Γ are estimated as ±0.01 mm/s (Fe²⁺ doublet) and ±0.02 mm/s (Fe³⁺ doublet). The Mössbauer parameters of sample RO1 and RO2 (Table 5) agree very well with the published data. In addition the relative

amount of Fe³⁺ agrees with the results of microprobe analysis (Table 2). This supports the location of Fe³⁺ at M1A. The Voigt-based analysis results in nearly the same Mössbauer parameters as the Lorentzian fit with almost no Gaussian components (Table 5).

The Mössbauer spectrum of sample CldT is shown in the middle part Fig. 5. The Mössbauer parameters for doublet 1 agree very well with the data mentioned above, while those of the Fe³⁺ doublet are in excellent agreement with the parameters given by Lodders *et al.* (1998) for the sample NLS5 with Fe³⁺ at M1A and M1B (Table 5). In addition, the relative amount of Fe³⁺ as determined by Mössbauer spectroscopy (11 % of Fe_{tot}) is higher than that calculated on the basis $Fe^{3+} = 4 - [Al^{3+ \text{ tot}} \text{ pfu}]$ (6 % of Fe_{tot}). This holds true in the Voigt-based analysis performed with two QSD sites for the sample CldT (Table 5). The Voigt-based analysis results in a higher Gaussian

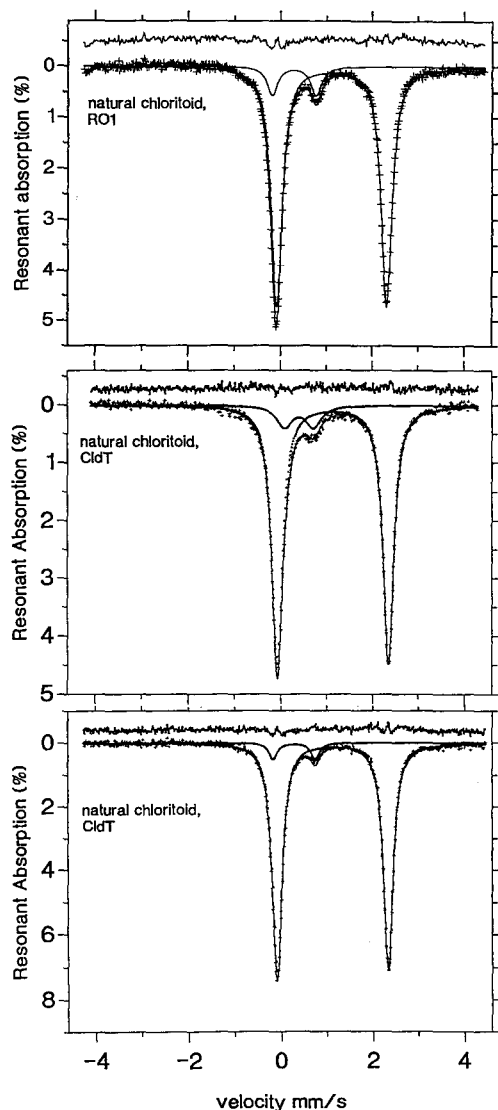


Fig. 5. Observed and resolved Mössbauer spectra of natural chloritoid, RO1 (top); natural chloritoid CldT containing impurities of hematite (middle), and natural chloritoid CldT after treatment in HCl (bottom).

component for the Fe^{3+} site than the Lorentzian fit, indicating either a higher atomic disorder, or Fe^{3+} -bearing impurities in the sample. Chloritoids originating from the same locality as sample CLDT are described by Halferdahl (1961) as containing small inclusions of hematite. Since hematite is soluble in HCl, we treated our sample

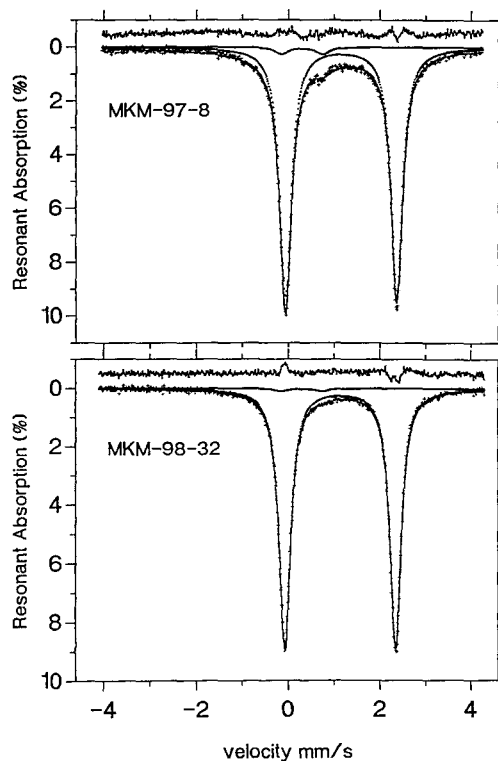


Fig. 6. Observed and resolved Mössbauer spectra of synthetic chloritoid, sample MKM-97-8, $x_{\text{Fe}} = 1.0$ (top) and sample MKM-98-32, $x_{\text{Fe}} = 0.57$ (bottom).

with this acid in order to remove the inclusions if present. Comparing the CldT spectrum in the middle part of Fig. 5 with a spectrum of the CldT sample treated in HCl (Fig. 5, bottom) revealed the existence of impurities – most probably hematite – in the untreated sample. The Mössbauer parameters of the Fe^{3+} doublet of the HCl-treated sample are in excellent agreement with those given for Fe^{3+} in M1A and the relative amount of Fe^{3+} as determined by Mössbauer spectroscopy agree with the microprobe analysis. Thus, the different Mössbauer parameters of the Fe^{3+} doublet and the high Fe^{3+} content are evidently caused by Fe^{3+} -bearing impurities, at least in our sample.

The two parts of Fig. 6 show the observed and calculated Mössbauer spectra of samples MKM-97-8 ($x_{\text{Fe}} = 1.0$) and MKM-98-32 ($x_{\text{Fe}} = 0.5$). As expected from the electron microprobe analyses, the spectra exhibit a strong Fe^{2+} component and a very weak component for Fe^{3+} . Therefore, the spectra can only be fitted to realistic values with

Table 6. Mössbauer parameters of the synthetic chloritoids.

Sample MKM-	Doublet 1				Doublet 2 ^a			
	IS (Fe ²⁺) mm/s	QS (Fe ²⁺) mm/s	Γ mm/ s	Area % (Fe ²⁺)	IS (Fe ³⁺) mm/s	QS (Fe ³⁺) mm/s	Γ mm/s	Area % (Fe ³⁺)
97-8	1.15	2.43	0.30	97.0	0.30	0.90	0.35	3.0
98-9	1.16	2.42	0.32	96.0	0.30	0.90	0.35	4.0
97-7	1.13	2.42	0.31	96.0	0.30	0.90	0.35	4.0
98-32	1.14	2.41	0.30	99.0	0.30	0.90	0.35	1.0

Note: IS, isomer shift; QS: quadrupole splitting, parameters relative to metallic Fe foil; Γ : full line width of half height. ^a Mössbauer parameters IS, QS and Γ fixed to the given values.

the IS and QS parameters of the Fe³⁺ components constrained. We constrained them to values for Fe³⁺ at M1A. Unconstrained fits results in a very broad doublet for the Fe³⁺ component with unrealistically high line widths. Table 6 summarizes the refined Mössbauer parameters of the synthetic materials. The IS and QS values for doublets 1 are comparable to those of the natural samples and, astonishingly, do not vary with composition, thus indicating that the Fe²⁺-bearing M1B octahedron indeed behaves rigidly within the chloritoid structures of the Fe-Mg solid solution series (see diffuse reflectance spectroscopy). The relative amount of Fe³⁺ in the synthetic samples is very low (1–4 % of the total Fe content) and is within the standard deviations, in good accordance with that estimated from electron microprobe analyses for Fe³⁺ at M1A supporting our fitting procedure. Due to the low intensity and strong peak overlap the uncertainty is relatively high and is estimated at ± 2 %.

Electronic absorption by diffuse reflectance spectroscopy

Published single-crystal spectra of chloritoids (Hålenius *et al.*, 1981) exhibit

- a weakly polarized absorption edge near 28000 cm⁻¹, decreasing in energy with increasing Fe³⁺ fraction;
- a strong broad band ($\Delta\epsilon_{1,2} \approx 5000$ cm⁻¹) centred at 16300 cm⁻¹ and strongly polarized along Y ($\angle a \approx 10^\circ$), with absorption coefficients parallel to the three principal vibration directions $\alpha_x < \alpha_y \gg \alpha_z$;
- two relatively narrow weak bands ($\Delta\epsilon_{1,2} \approx 2000$ cm⁻¹) at 11000 (ν_1) and 8000 cm⁻¹ (ν_2),

the first weakly polarized in the YZ plane, $\alpha_y > \alpha_z > \alpha_x$, the second strongly polarized along Z ($\angle c \approx 10^\circ$), $\alpha_x \approx \alpha_y \ll \alpha_z$;

(iv) several very weak narrow bands between 15000 and 25000 cm⁻¹, the most prominent of which occur at 24000, 22600 and at 20200 cm⁻¹.

Hålenius *et al.* (1981) assigned the broad band at (ii) to Fe²⁺ Fe³⁺ charge transfer. From the polarization behaviour, the authors concluded that Fe³⁺ is located in the L1 layer either at M1A or M1B. Further, from Mössbauer analysis, they concluded that Fe³⁺ is located at M1A. The small bands (iii) in the low-energy region are assigned by Hålenius *et al.* (1981) to spin-allowed crystal-field bands of Fe²⁺ in the M1B octahedron. The M1B octahedron is strongly distorted, site symmetry 1.

In connection with the present study, we looked for symmetry relations which might explain the polarization behaviour. The M1B octahedron can approximately be described as a tetragonal octahedron compressed along the O1AH-O1BH axis (Fig. 7a). Due to the strong distortion of the polyhedron, the ⁵T_{2g}-groundstate as well as the ⁵E_g excited state are split in the sequence for compressed octahedra (*D*_{4h} symmetry) as shown in Fig. 7b. Thus, three crystal-field band systems are to be expected, one of which is so low in energy (Fig. 7b) that it will give rise to a band in the infrared. Assuming *D*_{4h} symmetry, spectra should be polarized along the octahedral axes $\parallel z_o$ ($\angle a$ & X, Fig. 7a) and $\perp z_o$ ($\angle b$ & Y, and c & Z) but the pronounced polarization of ν_2 occurs parallel to the optical orientation Z. Similar problems occur with kosmochlore and viridine spectra (Abs-Wurmbach *et al.*, 1985; Abs-Wurmbach, 1987) which were solved assuming a point symmetry, being a supergroup to the true symmetry. Therefore, we tried to find a pseudosymmetry for

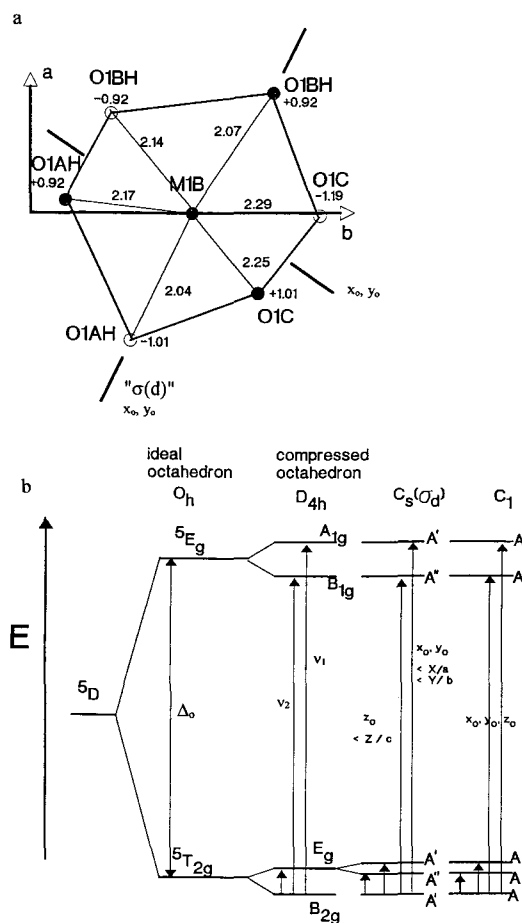


Fig. 7. (a) The M1B-octahedron in pseudosymmetry s_4 . (b) Schematic energy level schemes for Fe^{2+} in octahedra of descending symmetry from O_h to C_1 showing the splitting of the $^5T_{2g}$ groundstate and the ^5E_g excited state of the distorted site and the possible electronic transitions.

chloritoid, being a supergroup of the point symmetry C_1 . We may introduce

- a pseudo mirror plane within the compressed tetrahedral axis described above leading to " C_s " symmetry
 - a twofold rotation axis between the two oxygen ligands O1C being in cis-position, leading to " C_2 " symmetry
- or
- combine both symmetry elements leading to " C_{2h} " symmetry.

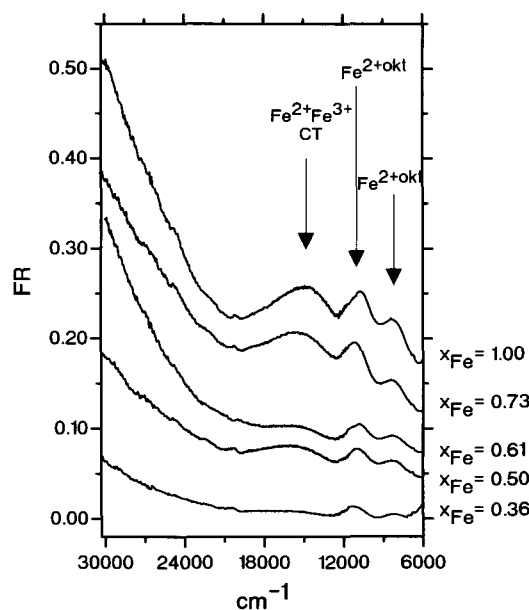


Fig. 8. Diffuse reflectance spectra of synthetic chloritoids. The quantity $FR (= f(R_\infty))$ is directly proportional to absorbance units.

The sequence of representations of energy levels at lower symmetry than D_{4h} was taken from the correlation tables of Wilson *et al.* (1955). A critical analysis of all these possibilities, while applying selection rules relevant for the different symmetries, leads to the conclusion that ii) and iii) are not in accordance with the observed polarization behaviour. But if we assume possibility i) with a pseudo vertical plane $\parallel z_0$ (now $\angle c$ & Z), the theoretical polarization behaviour of allowed electronic transitions is in accordance with the observed relations, taking for C_2 the energy level scheme connected with $C_2(\sigma_d)$ symmetry relations. This means that the symmetry plane, as seen for chloritoid in this pseudosymmetry, is situated between the ligands (σ_d = diagonal plane). The contributions of some absorption intensity of v_1 and v_2 transitions in the other optical polarization directions are due to the fact that optical and crystallographic orientations are not parallel to each other. It should be mentioned that, for the true point symmetry C_1 there are no symmetry-relevant selection rules. In this case, polarization behaviour must be explained by transition probabilities which might be quite different for the different octahedral orientations x_0, y_0, z_0 .

Table 7. Positions and widths of the charge transfer band (CTB) and the bands ν_1 and ν_2 .

sample MKM- x_{Fe}	CTB position (cm^{-1}) width (cm^{-1})	ν_1 position (cm^{-1}) width (cm^{-1})	ν_2 position (cm^{-1}) width (cm^{-1})	crystal-field splitting Δ_o (cm^{-1})	CFSE excess (J/mol)
97-8	14890	10650	8182	8966	0.00
1.00	5200	2000	2030		
98-9	14960	10600	8170	8935	0.00
1.00	4000	2600	2290		
98-16	15300	10740	8200	9020	-284
0.86	4000	1980	1880		
97-7	15010	10900	8200	9100	-530
0.74	5270	1900	1820		
98-31	15328	10900	8178	9089	-491
0.74	3500	2100	1950		
97-10	15630	10950	8233	9142	-578
0.63	2900	1800	1800		
99-2	15800	10820	8246	9083	-382
0.60	4240	1750	1490		
98-32	15330	10900	8190	9095	-394
0.57	3500	2100	2100		
97-4	15700	10870	8286	9128	-433
0.51	4800	1730	1980		
98-4	15750	10900	8246	9123	-363
0.44	5180	2400	1524		
98-28	15800	10900	8200	9100	-293
0.41	3100	2100	1530		
97-6	16000	11000	8190	9145	-326
0.35	4000	1630	1530		
98-38	16200	11000	8184	9142	-119
0.13	4000	1630	1530		
CldT	15040	10800	8150	9025	-303
0.85	3800	1900	1950		

Single-crystal spectra of the synthetic triclinic chloritoid, which are not included here, are very similar to those of Hålenius *et al.* (1981). However, the bands of the very thin chloritoid plates show extremely low intensities, especially in the more Mg-rich part of the solid-solution series.

Therefore, the absorption behaviour of the whole Fe-Mg solid-solution series could only be investigated by diffuse reflectance spectroscopy where a larger amount of material for each spectrum could be used. The additional phases corundum, hercynite, quartz, kyanite and staurolite observed in some samples show no absorption in the spectral range investigated, except for their absorption edges in the UV. The influence of small amounts of chlorite in two spectra can be neglected since it is very Mg-rich and the amount

does not exceed 9 wt%. The spectra of some of the synthetic chloritoids are shown in Fig. 8. There is a strong absorption edge due to ligand Fe^{3+} and Fe^{2+} charge transfer (Hålenius *et al.*, 1981). At 15000 cm^{-1} ($x_{\text{Fe}} = 1.0$) we observe a band due to $\text{Fe}^{2+}\text{Fe}^{3+}$ charge transfer (CT). The relative intensities of the charge transfer band of the different samples are in good accordance with the Fe^{3+} contents obtained by Mössbauer spectroscopy. Even in the most Mg-rich chloritoid shown in Fig. 8 ($x_{\text{Fe}} = 0.30$), a small amount of Fe^{3+} is detectable by the presence of the $\text{Fe}^{2+}\text{Fe}^{3+}$ CT band (Fig. 8). The crystal-field bands for the Fe end-member chloritoid are centered at 10650 and 8180 cm^{-1} . At least the crystal-field band at 10650 and the CT band shift slightly with increasing Mg content to higher energies in accordance with

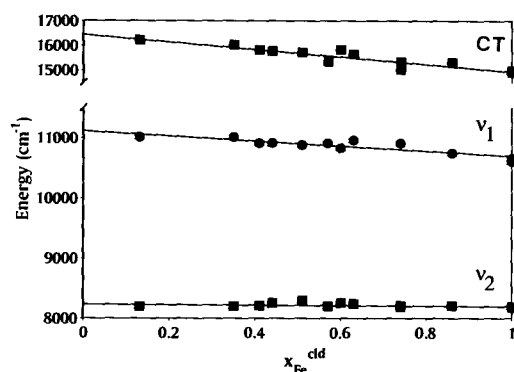


Fig. 9. Energy shift of the charge transfer band CT and the crystal field bands v_1 and v_2 of the synthetic chloritoids with composition.

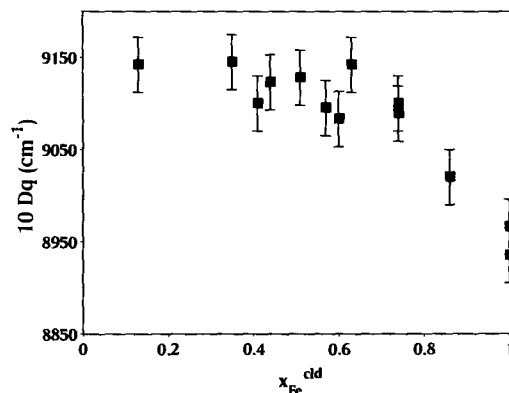


Fig. 10. Crystal-field splitting of Fe^{2+} in synthetic chloritoids as a function of composition.

shorter bond lengths in Mg-rich chloritoid (Fig. 9). The very weak band at 21000 cm^{-1} , which occurs in all the spectra shown in Fig. 8, is most probably due to spin-forbidden transitions in Fe^{2+} (Burns, 1993).

Table 7 summarizes the results of the band analyses for the charge transfer band (CTB), the crystal-field band at 11000 cm^{-1} (v_1) and the crystal-field band at *ca.* 8200 cm^{-1} (v_2). From the positions of the crystal-field bands, the crystal-field splitting Δ_o for Fe^{2+} in the M1B octahedron was calculated using the relation given for octahedra compressed along the tetrad axis (Burns, 1993).

$$\Delta_o = (v_1 - v_2)/2 + v_2 - 2/3 \delta_1 \quad (1)$$

where v_1 and δ_1 correspond to the energy differences between the lowest ground-state level and the excited state levels and to the energy differences between the energy levels of the split ground state, respectively (Fig. 7). Burns (1993) suggested a δ_1 value of 675 cm^{-1} , independent of composition. The crystal-field splitting $\Delta_{o,x}$ is plotted in Fig. 10 as a function of composition. It increases slightly with increasing Mg content. Using the R^{-5} proportionality between the octahedral crystal-field splitting of a $3d^N$ -ion, $10Dq$, and the mean distance between $3d^N$ -ion and the ligands, R , (Dunn *et al.*, 1965), the local mean cation-anion distance in the $3d^N$ -ion centred octahedra of a binary solid solution can be calculated from the equation

$$(\bar{R}_{3d^N-O})_x = (\bar{R}_{3d^N-O})_E [(10Dq_{3d^N})_E / (10Dq_{3d^N})_x] \quad (2)$$

Subscripts x and E designate the corresponding property in a binary solid solution with molar fraction x of the $3d^N$ -ion bearing end-member ($x_{\text{Fe}^{2+}}$) and in the end-member itself, respectively. $(\bar{R}_{3d^N-O})_E$ is the mean octahedral distance in the $3d^N$ -ion bearing end-member as obtained from X-ray diffraction methods of structure determination or refinement (*cf.* Burns, 1987; Langer, 1988; Langer *et al.*, 1997). It has been shown that local mean octahedral distances $(\bar{R}_{3d^N-O})_E$, as obtained by an evaluation of the crystal-field parameter $10Dq$, are larger or smaller than those from the crystal averaging diffraction methods (Langer, 1988; 1999), depending on whether the $3d^N$ -ion has larger or smaller radius, respectively, compared to the radius of the replaced spherical ion.

In order to check for such relationships in the present case of $(\text{Fe}_{1-x}^{2+}\text{Mg}_x)$ -chloritoids, the crystal-field splitting parameters $10Dq_{\text{Fe}^{2+},x}$ of Fe^{2+} in the (M1B) octahedra were extracted from the powder remission spectra of the solid solutions. Using these values, the spectroscopic $(\bar{R}_{3d^N-O})_E$ distances were calculated from eqn. (2). Due to the high uncertainties of the calculated bond lengths in the Rietveld refinements, the end-member distance $(\bar{R}_{3d^N-O})_E$ was extrapolated using the values given by Hanscom (1980) and Koch-Müller *et al.* (*in prep.*). The spectroscopic distance values obtained are plotted in Fig. 11 as a function of composition. The plot indicates that the Fe^{2+} -centred octahedra are compressible to the crystal-averaged size up to $x_{\text{Fe}^{2+}} = 0.8$ and then retain their size almost unchanged at lower $x_{\text{Fe}^{2+}}$ down to $x_{\text{Fe}^{2+}} = 0.1$. These deviations from crystal-averaged mean octahedral

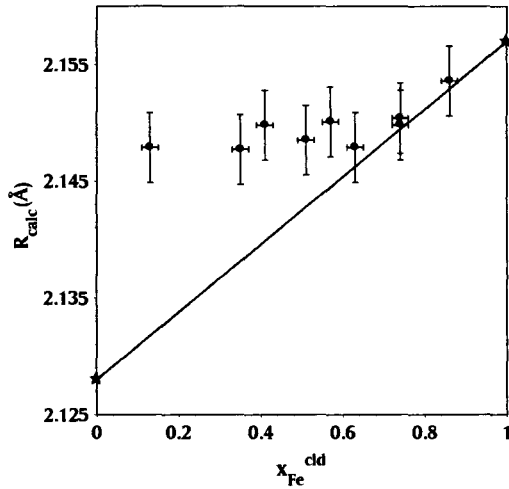


Fig. 11. Spectroscopic $(R_{3d^6-O})_x$ distances in the synthetic chloritoids as a function of composition. The solid line represents a linear extrapolation of the average M1B-O distances as obtained from X-ray diffraction (Hanscom, 1980; Koch-Müller *et al.*, in prep.).

distances as schematically shown by the linear interpolation in Fig. 11 between $x_{Fe2+} = 0.0$ and $x_{Fe2+} = 1.0$, and closely resemble the behaviour of local transition metal-oxygen distances in other binary solid solutions studied so far by single-crystal electronic spectroscopy (see discussion above). It is also in accordance with our results of Mössbauer spectroscopy.

Using equation 3a or 3b, the $CFSE^{excess}$ (excess crystal-field stabilization energy) for each solid solution can be calculated:

$$CFSE^{excess}(x_{Fe}) = x_{Fe} * (CFSE_{O,ss} - CFSE_{O,Fe-cld}) \text{ [J/mol]} \quad (3a)$$

or

$$CFSE^{excess}(x_{Fe}) = x_{Fe} * 0.4 * (\Delta_{O,Fe-cld} - \Delta_{O,ss}) * 11.966 \text{ [J/mol]} \quad (3b)$$

(Burns, 1993), with $\Delta_{O,Fe-cld}$, $\Delta_{O,ss}$ = crystal-field splitting energy in the Fe end-member and in the solid solution, respectively.

According to Burns (1993), solid solutions with positive or negative $CFSE^{excess}$ values behave in a thermodynamically non-ideal manner, since $CFSE^{excess}$ contributes to the enthalpy of mixing, ΔH^{excess} . Fig. 12 shows the $CFSE^{excess}$ for the synthetic chloritoids as a function of composition.

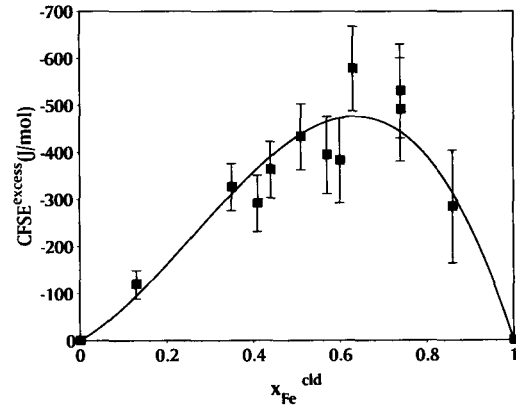


Fig. 12. The excess CFSE for synthetic Fe-Mg chloritoids as a function of composition. The solid line represents the best fit based on an asymmetric mixing model.

The data of Fig. 12 can be fitted to an asymmetrical mixing model for the solid solution series

$$CFSE^{excess} = x_{Fe} (1 - x_{Fe}) * (W_{G,Fe} + (W_{G,Mg} - W_{G,Fe}) * x_{Fe}) \quad (4)$$

where, $W_{G,Fe}$ and $W_{G,Mg}$ are the interaction parameters of the asymmetric model. The best fit resulted in the following parameters: $W_{G,Fe} = -525$ J/mol; $W_{G,Mg} = -2935$ J/mol.

The asymmetric deviation from ideality is negative with a maximum in the Fe-rich part of the system – indicating a gain in energy for the formation of Fe-rich chloritoids in respect to Mg-rich ones. However, since the spectra were obtained at ambient temperature and pressure, the gain in energy within the Fe-Mg solid solution may be different at the P and T of chloritoid formation. To transform the crystal-field splitting observed at ambient conditions to higher P and T, the compressibility and thermal expansion coefficients for the M1B octahedron of the chloritoid solid solutions are needed. Such data are only available for one Mg-rich chloritoid sample (Ivaldi *et al.*, 1988; Comodi *et al.*, 1992). According to these studies, the thermal expansion and compressibility coefficients for the M1B octahedron in magnesiochloritoid are close to the lowest values observed in other silicates. Assuming that these data are valid for the whole solid-solution series, one might expect that the pressure and temperature effect on Δ_o is negligible. Thus, independent on P and T Fe-

rich chloritoids are stabilized relative to Mg-rich compositions through a gain in CFSE and it is tempting to correlate this gain in energy with the rarity of magnesiochloritoid in nature. However, CFSE may only be one reason for the rarity of magnesiochloritoid in nature. Since Mg-rich chloritoids – in contrast to Fe-rich chloritoids – are only stable at high pressures, another even more important parameter which controls the formation of Mg-rich chloritoid is the rarity of high pressures during petrogenesis.

The non-ideal thermodynamic behaviour indicated by the existence of a $\text{CFSE}^{\text{excess}}$ term does not allow a prediction of the magnitude and direction of the deviation of the macroscopic mixing behaviour from ideality because $\text{CFSE}^{\text{excess}}$ of iron in the L1-layer is only one of several contributions to the bulk ΔH^{excess} . Contributions from lattice strain, from electrostatic interactions between the cations and anions, changes in the bonding characteristics *etc.* together all contribute to the macroscopic ΔH^{excess} . There are only few mineral examples where ΔH^{excess} and $\text{CFSE}^{\text{excess}}$ of a solid-solution series are known (see discussion in Ganguly & Saxena, 1987; Geiger & Rossman, 1994). In all these studies, $\text{CFSE}^{\text{excess}}$ shows the opposite direction of the deviation from ideality compared with the calorimetrically determined ΔH^{excess} term. More studies are needed to understand the systematics of these relations.

Conclusions

1) Fe-Mg chloritoids synthesized in the pressure range of 18 to 35 kbar crystallize in the triclinic space group *C1*. The triclinic crystals show almost no lattice faults and the Fe-Mg solid-solution series show no excess volume.

2) Mössbauer spectroscopy in combination with results of electron microprobe revealed a small amount of Fe^{3+} at M1A. Mössbauer parameters for Fe^{3+} at M1B as proposed by Lodders *et al.* (1998) were found in one natural sample, but this may be correlated with the presence of hematite impurities. The Mössbauer parameter IS and QS of the natural and synthetic chloritoids do not vary with composition, at least in the range of $x_{\text{Fe}} = 1.0$ to $x_{\text{Fe}} = 0.41$, indicating that the Fe^{2+} -bearing M1B octahedron behaves very rigidly within the Fe-Mg solid-solution series. This result is confirmed by results of diffuse reflectance spectroscopy.

3) Fe-Mg chloritoids show a small negative and asymmetric $\text{CFSE}^{\text{excess}}$, with a maximum in the Fe-rich part of the system. This gain of CFSE may be one reason for the rarity of magnesiochloritoid in nature and indicates non-ideal thermodynamic behaviour.

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