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M. Koch-Müller · V. Kahlenberg · C. Schmidt
R. Wirth

Location of OH groups and oxidation processes in triclinic chloritoid

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Abstract Triclinic Fe^{2+} and Fe^{3+} -chloritoid end members, as well as Fe^{2+} - Fe^{3+} -chloritoid solid solutions were synthesized in order to determine the location of the OH groups in the structure and to investigate the possibility of Fe^{3+} incorporation on the M1B site and the corresponding oxidation mechanism. The samples were analyzed using transmission electron microscopy, electron energy-loss and ^{57}Fe Mössbauer spectroscopy, polarized single-crystal, KBr powder and in situ high-pressure infrared spectroscopy. The structure of a natural triclinic chloritoid was refined by single-crystal X-ray diffraction in order to locate the proton-accepting oxygens in the triclinic structure. The results of valence bond calculations, polarized single-crystal and in situ high-pressure IR spectroscopy revealed that the orientations of the OH dipoles are the same as those in monoclinic chloritoid. The annealing experiments in air show that the incorporation of Fe^{3+} on M1B increases with temperature. After 3 h at 530 °C all Fe^{2+} was oxidized to Fe^{3+} without decomposition of the structure. This also holds true for a heating duration of 24 h. The incorporation of Fe^{3+} at M1B sites is coupled with a dehydration process starting at about 350 °C during which the H1A protons leave first.

Key words Fe-Chloritoid · OH groups · Dehydration · Oxidation · Spectroscopy

Introduction

Chloritoid is a rock-forming mineral found in Al-rich metapelitic rocks. It forms a complete Fe-Mg solid solution series $[(\text{Fe}_x\text{Mg}_{1-x})_2(\text{Al}_y\text{Fe}_{1-y}^{3+})\text{Al}_3\text{O}_2[\text{SiO}_4]_2(\text{OH})_4]$ with minor substitution of Al by Fe^{3+} . It occurs in at least two modifications: a triclinic 1Tc form (SG $\bar{C}1$) and a monoclinic 2M₂ one (SG C2/c). The crystal structure of monoclinic chloritoid was investigated by Brindley and Harrison (1952), Harrison and Brindley (1957), Hanscom (1975) and Ivaldi et al. (1988). Atomic coordinates for the hydrogen positions are given only in Hanscom (1975), who refined the structure to R-values of 0.041. The monoclinic structure consists of alternating L1 and L2 octahedral layers perpendicular to [0 0 1] with two of each layer type in the unit cell. L1 consists of edge-sharing M1A and M1B octahedra and L2 of M2A and M2B octahedra. According to Hanscom (1975) and Hålenius et al. (1981), the octahedral sites M2A and M2B are fully occupied by Al, the divalent cations Fe^{2+} and Mg are located on M1B, while Fe^{3+} and the remaining Al occupy the M1A octahedron. The two octahedral layers are linked by isolated SiO_4 tetrahedra and hydrogen atoms. Hanscom (1975) located two different hydrogen positions in the structure in difference synthesis electron maps computed during the final stage of his refinement: the H1A hydrogen is bonded to O1A and forms a strong hydrogen bridge to O2D in the adjacent octahedral layer with an O···O distance of 2.666 Å. The H1B hydrogen forms a strong O1B-H1B dipole which points to the center of a triangle of oxygens (O2A, O2B, O2C) in the adjacent octahedral layer with an average O···O distance of about 2.9 Å. The only refinement of the triclinic structure is that by Hanscom (1980), which yielded an R value of 0.080. Better results were hindered by poor crystallinity and very likely a large degree of stacking disorder. Hanscom (1980)

M. Koch-Müller (✉)
Technische Universität Berlin,
Institut für Angewandte Geowissenschaften I, BH1,
Ernst-Reuter-Platz 1, 10587 Berlin, Germany

V. Kahlenberg
Universität Bremen, FB Geowissenschaften,
Kristallographie, Klagenfurter Str., 28359 Bremen

C. Schmidt · R. Wirth
GeoForschungsZentrum Potsdam, Telegrafenberg,
Projektbereich 4.1, 14473 Potsdam, Germany

Present address:
M. Koch-Müller
Geophysical Laboratory CHiPR,
Carnegie Institution of Washington,
5251 Broad Branch Road, N.W.,
Washington, DC 20015-1305, USA
e-mail: monika.koch-muller@gl.ciw.edu
Tel.: +1-202-686-2410 ext. 2443; Fax: +1-202-686-2419

claims that the triclinic chloritoid is very similar to the monoclinic modification. It contains only one of each octahedral layer type and the reduction in symmetry from monoclinic to triclinic is mainly caused by displacements of the Al-bearing sites in the L2 layer. Based on the similarity of both structures, Hanscom (1980) assumed that the interlayer hydrogen bonding in triclinic chloritoid is the same as that in the monoclinic structure. However, this has not been proven.

Lodders et al. (1998) investigated a highly oxidized Fe-rich chloritoid and suggested that, in this chloritoid, Fe^{3+} occupies sites usually occupied by Fe^{2+} . If this is correct, a calculation of the Fe^{3+} content based on electron microprobe analyses using the formula $[\text{Fe}^{3+}] = 4 - [\text{Al}^{\text{tot}}]$ can result in incorrect Fe^{3+} estimates. This will dramatically affect geothermometric calculations (e.g., Vidal et al. 1999). If Fe^{3+} substitutes for Fe^{2+} at M1B, an additional mechanism is needed to achieve charge compensation. As in most $\text{Fe}^{2+}\text{Fe}^{3+}$ -bearing OH-containing minerals, the oxidation may be accompanied through a loss of hydrogen: $(\text{Fe}^{2+} + \text{OH}^-)^{\text{clid}} + 1/2 \text{O}_2 \Rightarrow (\text{Fe}^{3+} + \text{O}^{2-})^{\text{clid}} + 1/2 \text{H}_2\text{O}$. An anhydrous chloritoid with a crystal structure slightly different from that of chloritoid was synthesized by Bachmann (1956) by heating a natural chloritoid in air to temperatures to 800 °C. On the other hand, Ivaldi et al. (1988) reported an Mg-rich chloritoid ($x_{\text{Fe}} = 0.35$) which lost both types of protons simultaneously at about 700 °C with a sudden breakdown of the structure at about 750 °C.

The aim of this study is to locate the OH groups in triclinic chloritoid as well as to investigate experimentally the possibility of Fe^{3+} incorporation on M1B sites in triclinic chloritoids and the mechanism of the oxidation process.

Experimental methods

Syntheses

Fe^{2+} -chloritoid end member was synthesized at the Technische Universität Berlin in a piston-cylinder apparatus at 2.0–2.5 Gpa and about 600 °C using rock-salt assemblies. We used stoichiometric mixtures of synthetic FeO (prepared from a stoichiometric mixture of Fe and Fe_2O_3 in evacuated quartz-glass ampules), amorphous SiO_2 (aerosil 200, Degussa, heated at 1000 °C for 48 h) and $\gamma\text{-Al}_2\text{O}_3$ (reacted from 99.95% Al foil from Merck) as starting materials and added water in excess. Run durations were 48 h. The runs were buffered at oxygen fugacities defined by the iron/wüstite buffer (IW). For a detailed description of the experimental setup see Koch-Müller et al. (2000).

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 and 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-defined natural minerals were used as standards: andalusite, wollastonite (Si), andalusite,

K-feldspar (Al), olivine (Mg), spessartine (Mn) and hematite, metallic iron (Fe). Table 1 presents the compositions of the chloritoids investigated in this study.

Single-crystal X-ray structure refinement

Bond valence sum calculations were undertaken to assign the proton-accepting oxygen atoms in triclinic chloritoid. The bond distances required for these calculations were determined by single-crystal X-ray structure refinements of a natural triclinic chloritoid from Kuçadasi, Turkey. A platy crystal (sample RO1-b) was selected for the structural investigations. Diffraction intensities were obtained on a Nonius Kappa CCD four-circle diffractometer (see Table 2). The data reduction included Lorentz and polarization corrections as well as an analytical absorption correction based on eight indexed faces of the crystal using the program PLATON (Spek 1999). Structure refinements were started using the atomic coordinates for the triclinic chloritoid given by Hanscom (1980). However, the positions were transformed from $\text{C}\bar{1}$ to the primitive unit cell. The refinements were performed with the program SHELXL-93 (Sheldrick 1993). Both X-ray scattering factors for the different cations in their respective valence state, as well as real and imaginary anomalous dispersion coefficients, were taken from the International Tables for X-ray Crystallography (Ibers and Hamilton 1974). The values for O^{2-} were taken from Hovestreydt (1983). The following refinement strategy was applied: initially, a composition corresponding to the microprobe analysis was assumed, where the divalent cations Fe^{2+} , Mg^{2+} , as well as Mn^{2+} occupy the M1B site and Fe^{3+} and Al^{3+} the M1A position. The positions M2A, M2B1, and M2B2 were considered to be occupied exclusively by Al^{3+} . Due to the similar scattering factor curves of Fe^{2+} and Mn^{2+} , no differentiation was made between these two cations. No constraints on the bulk chemistry were applied. However, a full occupancy of all sites was assumed. After ten cycles the refinement of both isotropic temperature factors and site occupancies converged at 0.099. During the next stage of the least-squares calculations, anisotropic displacement parameters were introduced. Bond valence sums were then calculated using the final refined atomic coordinates and the parameters given by Brown and Altermatt (1985).

Polarized single-crystal infrared spectroscopy

Polarized infrared spectra were measured at the Technische Universität Berlin using a Bruker IFS66 FTIR microscope spectro-

Table 1 Composition of synthetic and natural chloritoid in wt%. Cations per formula unit, calculated on the basis of six octahedral cations (1 σ : standard deviation)

MKM-	97-8	98-1	CldT	RO1-b	99-3 ^b
wt%					
SiO_2	23.50(45)	23.05(33)	24.20(33)	25.00(19)	26.29(64)
Al_2O_3	38.33(46)	37.64(80)	39.35(52)	39.56(35)	43.13(59)
FeO	28.13(39)	27.38(54)	25.02(24)	21.88(99)	30.57
MnO	—	—	0.38(10)	1.04(8)	—
MgO	0.00	0.00	2.06(7)	4.40(65)	—
Σ	89.97	88.07	91.01	91.88	99.99
Cations					
Si	2.05(4)	2.06(3)	2.03(1)	2.07(1)	2.06(3)
Al	3.95(2)	3.96(2)	3.90(2)	3.87(2)	3.99(4)
$\text{Fe}^{3+ \text{ a}}$	0.05(2)	0.04(2)	0.10(1)	0.13(1)	2.01(4)
Fe^{2+}	1.99(3)	2.00(4)	1.66(1)	1.38(8)	—
Mn	—	—	0.02(1)	0.07(1)	—
Mg	0.00	0.00	0.26(1)	0.54(8)	—
Σ	8.05	8.06	7.97	8.07	8.07
x_{Fe}	1.00	1.00	0.86	0.69	—

^a Fe^{3+} pfu = (4-Al pfu)

^b AEM analyses. Notice that the Σ of the oxide has been set to 100%

Table 2 Experimental details of the X-ray data collection and refinement parameters for the triclinic chloritoid

A Crystal-cell data	
a (Å)	5.4744(5)
b (Å)	5.4766(6)
c (Å)	9.1505(10)
α (°)	83.53(5)
β (°)	76.68(5)
γ (°)	60.06(6)
V (Å ³)	231.33
Space group	$P\bar{1}$
Z	1
Unit cell content	[(Fe, Mn) _{1.40} Mg _{0.60}](Al _{3.84} Fe _{0.16})Si ₂ O ₁₀ (OH) ₄
D _{calc} (g cm ⁻³)	3.52
μ (cm ⁻¹)	33.3
B Intensity measurement	
Crystal shape	Fragment of a plate
Crystal dimensions	0.100 × 0.50 × 0.50 mm ³
Diffractometer	Nonius Kappa-CCD
Monochromator	Graphite
θ range	2.2°–30.1°
Rotation axis and width	$\phi/2^\circ$
Reflection range	h ≤ 7; k ≤ 7; l ≤ 12
Measured reflections ^a	2032
Unique reflections	1351
Unique reflections [I > 2 σ (I)]	1116
Max/min transmission	0.844/0.761
C Refinement of the structure	
Parameters used in the refinement	0.084, 0.0991
R1 [F ₀ > 4 σ (F ₀)], R1 (all reflections)	
wR2 (all reflections)	0.1866
Weighting parameter a, b	0.12, 3.50
Goodness of fit	1.11
R1 = $\Sigma F_o - F_c / \Sigma F_o $	wR2 = $[\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o)^2)]^{0.5}$
w = $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	P = $[2F_c^2 + \max(F_o^2, 0)]/3$

^a R_{eq} is not given, because in space group $P\bar{1}$ no information concerning the internal consistency of the single-crystal data set can be derived from this parameter

meter equipped with a Global light source, a KBr beamsplitter, a KRS5 polarizer and an MTC detector. The settings for the spectrometer were 1 cm⁻¹ and 128 averaged scans. The spectra were collected on idiomorphic chloritoid (0 0 1) plates of synthetic Fe-chloritoid end member (MKM-97-8). The thickness of the crystal plates is estimated at 1–5 μ m. To determine the direction of the OH dipoles within the (0 0 1) plane the angular relations between the *a*-axis and the electric vector of the polarized radiation was changed from 0° to 350° and the absorbance of the ν_{OH} bands was measured every 10°. The baseline for each spectrum was assumed to be linear and interpolated between the background near 3700 cm⁻¹ and that near 2700 cm⁻¹.

High-pressure infrared spectroscopy

In situ high-pressure powder FTIR spectra were recorded at the GeoForschungsZentrum, Potsdam, to determine the response of the monoclinic and triclinic crystal structures to pressure. The pressure was exerted on the samples using a diamond-anvil cell similar to that designed by Bassett et al. (1993). The cell was modified to facilitate FTIR spectroscopy, i.e., to achieve a reasonable signal-to-noise ratio. The opening angle was increased to 60°, type I diamond anvils were substituted with type II diamonds, which have a lower N content and are more transparent to IR light, and the glass windows at the top and the bottom of the cell were removed. Powders of triclinic (monoclinic) chloritoid, several small ruby grains, and poly-chlorotrifluorethylene, which served as the pressure medium (e.g., Langer 1990), were placed in the sample chamber of the cell. As triclinic sample we used a synthetic Fe²⁺-chloritoid end member (MKM-98-1) and as monoclinic polymorph a natural sample from Üstüaçiksarinç, Turkey (CldT). The pressure was determined from

the energy shift of the R₁ ruby fluorescence line relative to its energy at ambient conditions (Piermarini et al. 1975). The energy shifts were measured using a Dilor XY Raman microprobe equipped with an argon laser which provided the 514.53-nm excitation line. We observed that the poly-chlorotrifluorethylene used in this study crystallized at pressures between 1.0 and 1.5 GPa. Therefore, two to six different ruby grains in the sample chamber were measured to check for changes in the hydrostatic pressure. Significant line broadening and a larger scatter of the measured R₁ fluorescence bands of the individual ruby grains occurred above the crystallization pressure. In that case, the error in pressure was estimated from the range of the calculated values which were usually within $\pm 10\%$ of the average pressure. All spectra were taken at room temperature. Wavenumber offsets were corrected by measuring the wavenumber of a ruby standard at ambient pressure and temperature immediately before obtaining a spectrum at elevated pressures. After determining the pressure, an IR spectrum of the chloritoid sample in the range of 4000 to 2000 cm⁻¹ was obtained using a Bruker IFS66v microscope spectrometer. The measuring conditions were the same as before, except that the recorded spectra were unpolarized. The sample chamber pressures were checked after the IR measurements to verify that no significant decrease in pressure had occurred. The pressure in the cell was then increased and the procedure described above was repeated.

Oxidation processes

Several of the previously synthesized Fe²⁺-chloritoid end member samples were used to study the oxidation processes. These samples were heated in air for 0.5 to 24 h and then quenched. Table 3 summarizes the experimental conditions.

Table 3 Experimental conditions of the heating experiments

Sample MKM-	Temperature (°C)	Run duration (h)
99-13	350	0.5
99-14	400	0.8
99-11	450	2.0
99-12	450	3.0
99-3	530	24.0
99-4	530	3.0

Transmission electron microscopy

Unheated and heated chloritoids were investigated by high-resolution electron microscopy at the GeoForschungsZentrum, Potsdam, using a Philips CM200 TEM with a twin lens configuration at 200 kV. The electron microscope is equipped with an EDAX X-ray analyzer with ultrathin window.

A Gatan imaging filter GIF allows energy-filtered imaging and electron energy-loss spectroscopy (EELS). All high-resolution images are energy-filtered (zero-loss) using a 5-eV window. Analytical electron microscopy (AEM) was carried out on the heated samples in transmission mode with a spot size of 55 nm. The spectra were corrected for absorption and fluorescence applying the EDAX software package. The specimen thickness necessary for absorption correction was determined by electron energy-loss spectroscopy (EELS) using the total intensity of the electrons reaching the EEL spectrometer and the intensity of the zero-loss peak (Egerton 1996). EDX analyses were quantified using the ratio technique of Cliff and Lorimer (1975): $c_a/c_{Si} = k_{a, Si} * (I_a/I_{Si})$. The $k_{a, Si}$ factors k_{FeSi} , k_{AlSi} , k_{MnSi} and k_{MgSi} were determined from synthetic and natural chloritoid standard materials which have been measured by electron microprobe (Koch-Müller and Wirth, in prep.).

Electron energy-loss spectroscopy

EELS was used to determine the oxidation state of iron. Fe-L₂, L₃ edges can be used to discriminate between Fe³⁺ and Fe²⁺. The Fe L₃ - edge maximum of Fe²⁺ minerals is located at 707.8 eV and that of Fe³⁺ at 709.5 eV (Garvie and Craven 1994; Garvie et al. 1994; van Aken et al. 1998a, b). The energy resolution in the EELS measurement was 1 eV and the spectra were recorded with an energy dispersion of 0.3 eV pixel⁻¹ or 0.1 eV pixel⁻¹. The spectra were acquired in the diffraction mode, camera length 50 mm, spectrometer aperture 2 mm, convergence angle 1.5 mrad, collection angle 12 mrad.

Table 4 Atomic positions in fractional co-ordinates and equivalent isotropic displacement parameters (Å² × 10³)

	Atoms per unit cell	x	y	z	U(eq)
M1A(Al/Fe)	0.844(16)/0.156(16)	0.0000	0.0000	0.0000	9(1)
M2A	1	0.0000	0.5000	0.5000	4(1)
M1B(Fe/Mg)	1.402(24)/0.598(24)	0.3304(3)	-0.6622(2)	-0.0012(1)	9(1)
M2B1	1	0.0000	0.0000	0.5000	4(1)
M2B2	1	0.5000	0.5000	0.5000	5(1)
T	2	0.4272(4)	-0.0001(4)	-0.3127(2)	5(1)
O1A	2	0.0284(11)	-0.3046	-0.1065(6)	12(1)
O1B	2	0.7234(12)	-0.6954(12)	-0.1012	13(1)
O1C	2	0.3529(11)	0.0013(10)	-0.1280(6)	9(1)
O2A	2	0.1263(10)	0.1619(10)	-0.3760(5)	5(1)
O2B	2	0.6151(10)	-0.3252(9)	-0.3756(5)	4(1)
O2C	2	0.6142(10)	-0.8373(9)	-0.3747(5)	4(1)
O2D	2	0.1300(10)	-0.3325(10)	-0.4042(6)	5(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectra were measured on heated and unheated samples to check for the presence of Fe³⁺. The experiments were conducted at the Technische Universität, Berlin, using a Mössbauer spectrometer (driving unit and MCA from Halder Electronic, Germany) equipped with a source of ⁵⁷Co in Pd. The velocity scale and isomer shift were calibrated against natural iron (α-Fe foil). The modified program MBF (Nagel 1990) was used to resolve peaks using Lorentzian functions. Details of the Mössbauer measurements were described by Koch-Müller et al. (2000).

KBr-powder spectroscopy

KBr powder infrared spectroscopy was used to study the dehydration process. 0.7 to 1.3 mg of ground synthetic chloritoid were mixed with 450 mg KBr and pressed to disks of 13 mm diameter. The powders and KBr were dried at 120 °C before and after the mixing to eliminate adsorbed water. The infrared spectra were recorded using an IFS66v FTIR spectrometer. Evacuated sample chamber and a DTGS detector were used for the measurements. The operating conditions for the spectrometer were 1 cm⁻¹ resolution and 128 averaged scans.

Results and discussion

Location of OH groups

Single-crystal X-ray structure refinement

Table 2 lists the details of the structure refinement. The final R for 109 parameters and 1116 independent observed reflections is 0.084. The resulting structural formula for the triclinic chloritoid is: [(Fe,Mn)_{1.40}Mg_{0.60}](Al_{3.84}Fe_{0.16})Si₂O₁₀(OH)₄. This is in good agreement with electron microprobe analyses performed on the crystal (RO1-b) after the X-ray studies (see Table 1). The refined atomic coordinates and isotropic displacement factors, as well as selected interatomic distances and angles, are given in Tables 4 and 5. Bond valence sums calculated from the parameters given by Brown and Altermatt (1985) indicate that all anion positions except O1A and O1B are oxygen atoms having bond valence sums of about 2 vu. The sum of bond valences

Table 5 Selected bond distances (Å) and bond angles (°)

M1A-O1B	1.926(6) × 2	M2A-O2D	1.799(5) × 2
O1A	1.948(6) × 2	O2B	1.944(4) × 2
O1C	2.018(5) × 2	O2A	1.950(5) × 2
Mean	1.964	Mean	1.898
M1B-O1B	2.059(6)	M2B1-O2D	1.796(5) × 2
O1A	2.070(5)	O2A	1.937(5) × 2
O1B	2.124(6)	O2C	1.950(5) × 2
O1A	2.138(5)	Mean	1.894
O1C	2.224(5)		
O1C	2.256(5)		
Mean	2.145		
T-O2B	1.640(5)	M2B2-O2D	1.795(5) × 2
O2C	1.641(5)	O2B	1.947(5) × 2
O2A	1.644(5)	O2C	1.954(5) × 2
O1C	1.645(5)	Mean	1.899
Mean	1.643		
O2B-T-O2C	109.0(2)		
O2B-T-O2A	109.1(2)		
O2C-T-O2A	109.1(2)		
O2B-T-O1C	110.0(2)		
O2C-T-O1C	110.0(3)		
O2A-T-O1C	109.6(3)		
Mean	109.5		

for O1A and O1B from one M1A and two M1B sites are 1.187 and 1.237 vu, respectively. Thus, as in monoclinic chloritoid, both the O1A site and the O1B site correspond to hydroxyl groups in the triclinic chloritoid. A full list of anisotropic displacement parameters as well as observed and calculated structure factors can be obtained from the authors upon request.

Polarized single-crystal infrared spectroscopy

KBr powder spectra of monoclinic chloritoid were described by Franolet (1978) and Chopin et al. (1992). A spectrum of a triclinic chloritoid was given by De Grave et al. (1984). The spectra of monoclinic and triclinic chloritoid are very similar in the range of the OH stretching vibrations (4000–1500 cm⁻¹). Two intense bands and one band of very low intensity can be distinguished: the intense band at 3500 cm⁻¹ was assigned by De Grave et al. (1984) to stretching vibrations of the strong O1B-H1B dipole and the intense band at 3000 cm⁻¹ to stretching vibrations of the relatively weak O1A-H1A dipole with the strong hydrogen bridge. The weak band at 2150 cm⁻¹ was explained as a first overtone of the bending $\delta_{\text{O(1A)-H(1A)}}$ at 1100 cm⁻¹. Figure 1 shows the polarized single-crystal spectra of the synthetic triclinic chloritoid (MKM-97-8) obtained on a (0 0 1)-plate with $E//a$ and $E//b$ in the energy range of 4000 to 2500 cm⁻¹. The sample is an Fe²⁺-chloritoid end member with about 5 wt% Fe³⁺ at M1A (Table 1). As described by De Grave et al. (1984) for a natural, Fe-rich chloritoid, the spectrum consists of two intense bands, one at 3500 cm⁻¹ and one at 3000 cm⁻¹. However, both OH-stretching bands exhibit a more or less pronounced shoulder at the high-energetic side of each band. The band and the shoulder most probably represent stretch-

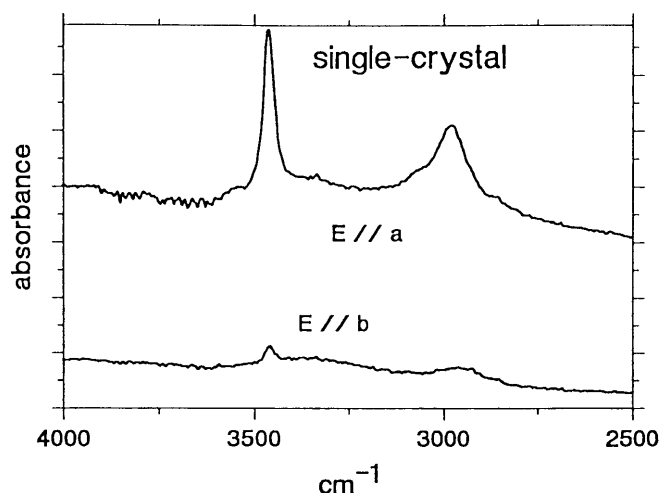


Fig. 1 Polarized single-crystal spectra obtained on a synthetic (0 0 1)-chloritoid plate with $E//a$ and $E//b$

ing vibrations of OH groups located in different chemical environments: both O1A-H1A and O1B-H1B are coordinated by two Fe²⁺ (M1B) and one Al or Fe³⁺ (M1A). The intense bands are clearly due to vibrations of OH groups coordinated by [Fe²⁺_{M1B} Fe²⁺_{M1B} Al^{M1A}]. The shoulders at the high energetic sides must be related to substitution of Al by Fe³⁺ at M1A [Fe²⁺_{M1B} Fe²⁺_{M1B} Fe³⁺_{M1A}], since this is the only substitution which occurs in the Fe²⁺ end members. In addition, a comparison of IR powder spectra obtained on natural Fe-rich chloritoids and synthetic Mg-rich chloritoids (relatively high and very low Fe³⁺ at M1A, respectively, see Koch-Müller et al. 2000) seems to confirm the assignment. However, the assignment is in contradiction to the fact that the energy of an OH band is anticorrelated with the electronegativities of the cations bonded to the hydroxyl ions. In the case of the [Fe²⁺_{M1B} Fe²⁺_{M1B} M³⁺_{M1A}] configuration, the electronegativity increases with the substitution of Al by Fe³⁺ from 1.56 to 1.60. Thus, the shoulders should be observed at energies lower than the main bands. Further investigations are necessary to clear the nature of the shoulders. All four OH-stretching vibrations show the same polarization behavior, displaying the strongest intensity with $E//a$ and decreasing to nearly zero intensity with $E//b$. From the directions of the OH dipole vectors in monoclinic chloritoid (Hanscom 1975) one expects two OH bands, both with the highest intensity with $E//a$ and the lowest intensity with $E//b$, as observed in the spectra of the triclinic chloritoid. This shows that the directions of the OH dipoles in the (0 0 1) planes of the triclinic chloritoid are similar to those of monoclinic chloritoid.

High-pressure infrared spectroscopy

Due to the perfect {0 0 1} cleavage of chloritoid, it is impossible to obtain single-crystal infrared spectra on crystal plates parallel to c to check the orientation of the

OH dipoles in this direction. Therefore, we used an indirect method to gain insight into the orientation of the dipoles, i.e., we compared the response of triclinic and monoclinic chloritoid to pressure using a diamond-anvil cell in combination with an IR-microscope spectrometer. Chloritoid has its greatest compressibility parallel to c (Comodi et al. 1992). Therefore, energy changes of the O1B-H1B- and O1A-H1A-stretching vibrations as a function of pressure are expected to be high and indicative for a certain structural environment. In this study, the wavenumbers of the hydroxyl vibrations were determined as a function of pressure at ambient temperature on synthetic triclinic Fe^{2+} -chloritoid (MKM-98-1) and on one natural Fe-rich sample of monoclinic chloritoid (CldT). Figure 2 compares the spectrum of a triclinic Fe^{2+} -chloritoid end member obtained at a pressure of 2.8 GPa to that obtained at ambient conditions. As for sample MKM-97-8, the spectra consists of 2 intense bands ($[\text{Fe}^{2+}\text{M1B} \text{ Fe}^{2+}\text{M1B} \text{ Al}^{\text{M1A}}]$) with shoulders at the high energetic side. The band and shoulder caused by the O1A-H1A dipole shift with increasing pressure towards lower energies while those assigned to the O1B-H1B dipole and to the first overtone of the bending vibration shift in the opposite direction. The wavenumbers of the stretching bands show an approximately linear pressure dependence (Fig. 3). High-pressure spectra obtained in this study on the natural monoclinic sample display the same behavior. This is an additional indication that the orientations of the OH dipoles in monoclinic and triclinic chloritoids are similar. The H1A-O1A and H1B-O1B dipoles and their hydrogen bondings to oxygens in the adjacent layer are shown in more detail in Fig. 4. The H1A-O1A dipole builds a nearly linear O1A-H1A...O2D bond. The O1A...O2D distance decreases with pressure. Thus, the corresponding OH band is shifted to lower energy. Comodi et al. (1992) determined in a single-crystal X-ray diffraction study using a diamond-anvil cell that the O1A...O2D distance changes from 2.653(2) Å at 0.0001 GPa to

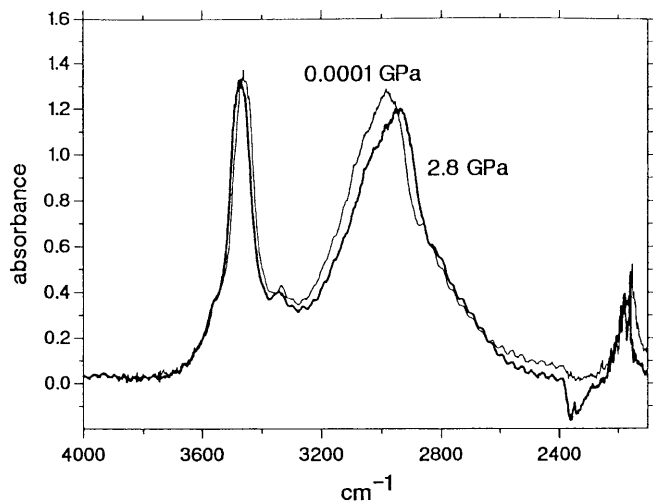


Fig. 2 Infrared spectra of synthetic Fe^{2+} -chloritoid taken at ambient conditions and 2.8 GPa in a diamond-anvil cell

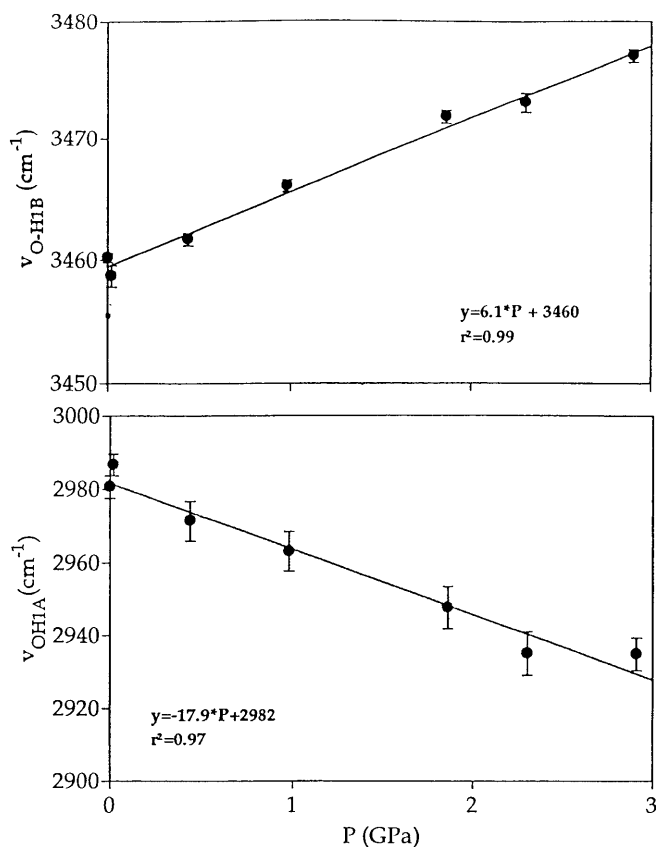


Fig. 3 Energies of the O1B-H1B- and O1A-H1A-stretching vibrations of the intense bands ($[\text{Fe}^{2+}\text{M1B} \text{ Fe}^{2+}\text{M1B} \text{ Al}^{\text{M1A}}]$) of Fe^{2+} -chloritoid as a function of pressure

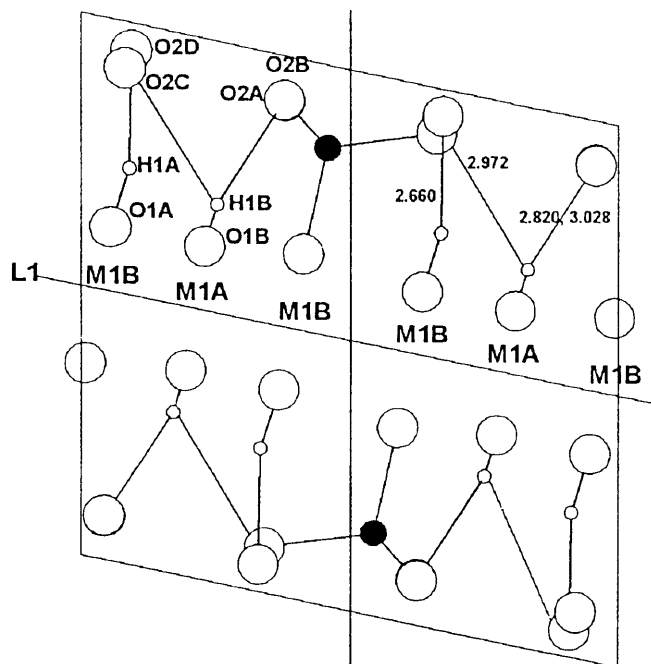


Fig. 4 A part of the chloritoid structure showing the coordination of the OH dipoles and the hydrogen bridge bondings

2.578(15) Å at 3.4 GPa. The O1B-H1B dipole points into a triangle formed by O2C, O2A, and O2B. The average O···O distance is about 2.9 Å. All three oxygens show a charge deficiency. The distances between O1B and each of the oxygens in the triangle decrease with pressure by about 0.6% (Comodi et al. 1992). However, due to the strong bending of the O1B-H1B···O configuration, the decrease in the O···O distance increases the bending angle, which leads to a weakening of the hydrogen bridge bonding H1B···O. Thus, the corresponding OH band shifts to higher energy. This is in agreement with findings of Hofmeister et al. (1999), who pointed out that the energy of stretching vibrations depends not only on the OH···O bond length but also on the bond angle. The observed shift in the energy of the $\delta_{\text{O(1A)}-\text{H(1A)}}$ band to higher wavenumbers with increasing pressure corresponds to the expected behavior of bending vibrations (Langer 1990).

Oxidation processes

X-ray diffraction diagrams of the heated samples exhibit the diffraction pattern of triclinic chloritoid. However, the peaks are broad, which prevents an accurate Rietveld analysis of the heated samples. The heating may have produced strong distortions in the chloritoid structure.

Transmission electron microscopy

Energy-filtered lattice fringe images were obtained with the electron beam perpendicular to (1 1 0)-plates of unheated and heated chloritoid samples. The fringes are one-dimensional only and can provide information about the $d_{(001)}$ spacings. Figure 5 shows the lattice fringe image and the corresponding electron diffraction pattern (upper part of Fig. 5, right) obtained on a (1 1 0) plate of the heated sample MKM-99-3. This sample shows a triclinic symmetry like the unheated Fe^{2+} -chloritoid samples (Koch-Müller et al. 2000). However, the $d_{(001)}$ -spacing is with 9.4 Å about 4% larger than that of the unheated sample. A comparable increase in the c lattice constant was observed by Bachmann (1956) for a natural sample heated to 930 °C and was explained by a rearrangement of the oxygen framework and the loss of hydrogen bonding. The composition of our heated chloritoid was obtained using analytical electron microscopy. A calculation of the formula based on six octahedral cations yielded a nearly ideal composition which consists of two Fe^{3+} , four Al, and two Si atoms pfu (Table 1).

Electron energy-loss spectroscopy

Figure 6 shows the superposition of the EEL spectra of the Fe^{2+} -chloritoid end member and of the heated

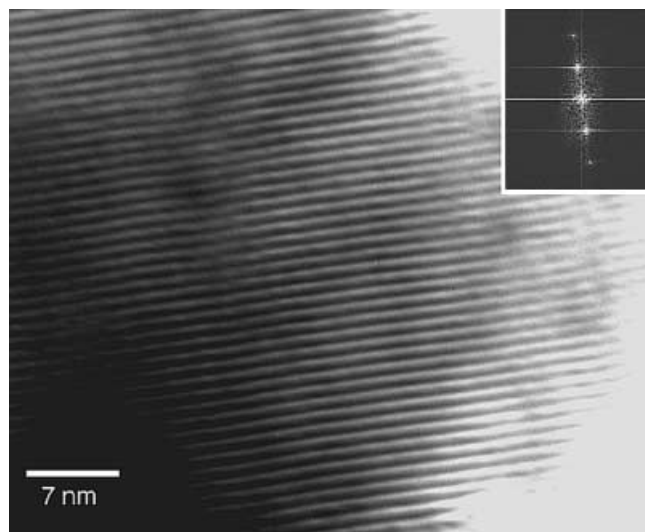


Fig. 5 Lattice fringe image and electron diffraction pattern of a Fe^{3+} -chloritoid end member (MKM-99-3) taken on (1 1 0) cleavage plates

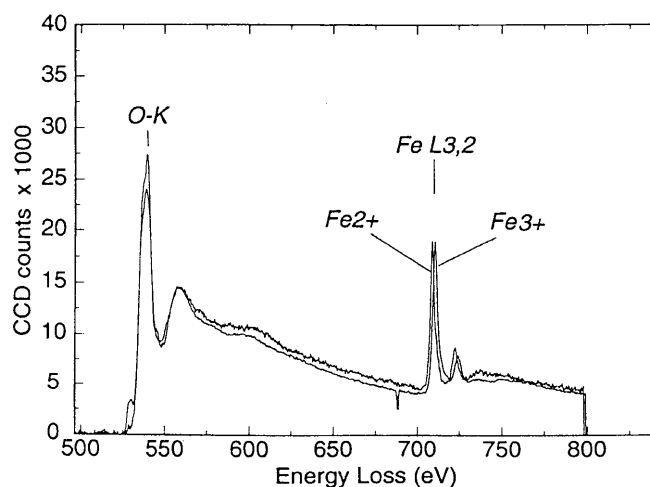


Fig. 6 Electron energy loss spectra of Fe^{2+} - and Fe^{3+} -chloritoid end member

sample MKM-99-3 including the oxygen K edge and the Fe $L_{3,2}$ edge. Both the L_3 and L_2 edges of Fe in the EEL spectrum of the heated sample are shifted to a higher energy loss in comparison to those of the unheated sample. The prepeak at lower energies of the oxygen K edge is due to Fe^{3+} (van Aken et al. 1998b). This indicates that all Fe^{2+} is oxidized to Fe^{3+} in the heated sample.

Mössbauer spectroscopy

Figure 7 (top) shows the Mössbauer spectrum of the synthetic Fe^{2+} -chloritoid end member MKM-97-8. The spectrum was fitted with two doublets: one for Fe^{2+} at M1B with $IS = 1.15 \text{ mm s}^{-1}$, $QS = 2.42 \text{ mm s}^{-1}$, and

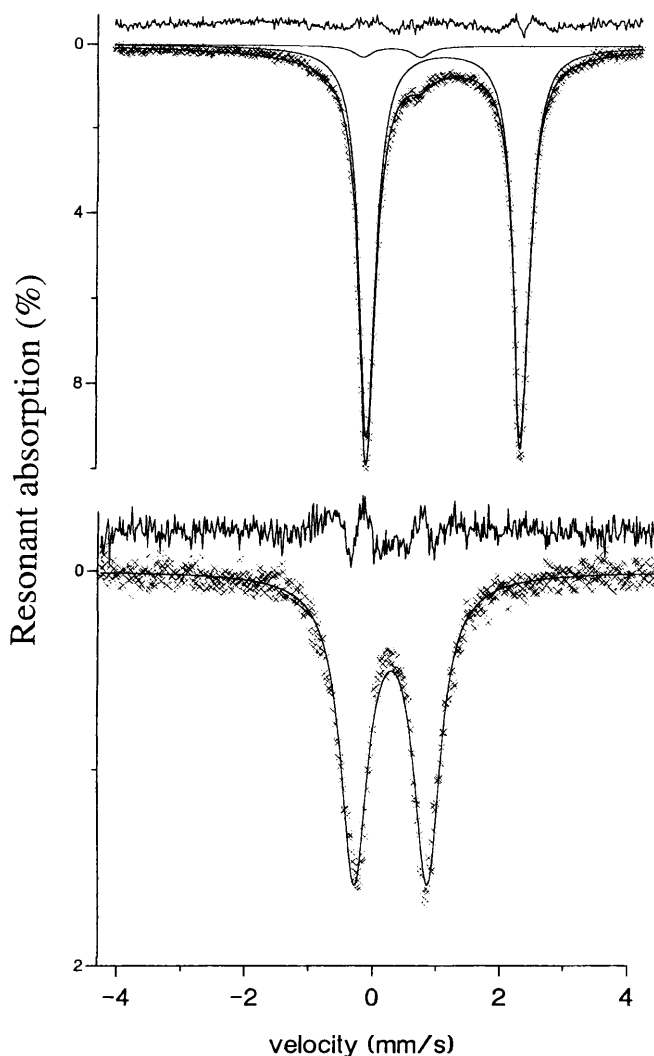


Fig. 7 Mössbauer spectra of chloritoids taken at room temperature. *Top* Synthetic Fe^{2+} -chloritoid; *bottom* sample MKM-99-3, annealed at 530 °C in air for 24 h

$\Gamma = 0.30 \text{ mm s}^{-1}$ and the other for Fe^{3+} at M1A with $IS = 0.30 \text{ mm s}^{-1}$, $QS = 0.90 \text{ mm s}^{-1}$, and $\Gamma = 0.30 \text{ mm s}^{-1}$. The amount of Fe^{3+} in the synthetic Fe^{2+} -chloritoid end member is about 3% of the total Fe content and is within the standard deviations, in good accordance with that estimated from electron microprobe analyses for Fe^{3+} at M1A (Table 1). However, sample heating in air increases the Fe^{3+} content dramatically. After 24 h of annealing at 530 °C, all Fe^{2+} was oxidized to Fe^{3+} , as indicated by one broad doublet in the Mössbauer spectrum with $IS = 0.29 \text{ mm s}^{-1}$, $QS = 1.14 \text{ mm s}^{-1}$, and $\Gamma = 0.51 \text{ mm s}^{-1}$ (Fig. 7, bottom). Since the chemical analysis corresponds to four Al-bearing and two Fe^{3+} -bearing sites pfu, we assigned the doublet to Fe^{3+} at M1B. The Mössbauer parameters of this $\text{Fe}^{3+[\text{M1B}]}$ -bearing chloritoid are quite different from those proposed by Lodders et al. (1998) for Fe^{3+} at M1B ($IS = 0.40 \text{ mm s}^{-1}$; $QS = 0.68 \text{ mm s}^{-1}$) (see discussion in Koch-Müller et al. 2000). The large half

width of the doublet is most likely due to the strong distortion of the chloritoid structure during heating leading to different geometric arrangements of the ligand atoms around Fe^{3+} .

KBr powder spectroscopy

Figure 8 shows a sequence of KBr-powder IR spectra of Fe-chloritoid end members which were heated at different temperatures for 0.5–24 h. The area ratios of the OH bands ($\text{area}_{\text{H1B}}/\text{area}_{\text{H1A}}$) increases strongly due to the loss of H1A protons during heating. Only a very broad band at about 3490 cm^{-1} due to H1B protons is observed in the sample heated to 530 °C, indicating that almost all H1A protons had left the structure. This holds true even for a heating duration of 24 h. The fact that the H1A protons leave the structure first is consistent with the weaker O1A-H1A dipole in comparison with the strong O1B-H1B dipole. The spectra confirm the assignment of De Grave et al. (1984) of the band at 2150 cm^{-1} [bending $\delta_{\text{O(1A)}-\text{H(1A)}}$ vibrations] since with increasing heating temperature the intensity of this band also decreases.

Thus, heating of a Fe^{2+} -chloritoid in air to 530 °C results in a partly dehydrated Fe^{3+} -chloritoid end member with the formula $\text{Fe}_2^{3+} \text{Al}_4\text{Si}_2\text{O}_{12}(\text{OH})_2$. The relatively high QS parameter for Fe^{3+} at M1B in the partly dehydrated sample is in agreement with the more symmetric coordination of the M1B octahedron after heating: in an unheated chloritoid, the M1B cation is coordinated by four hydroxyl groups, two O1A-H1A, and two O1B-H1B, and by two oxygen atoms in a *cis* configuration, whereas the partial dehydration process results in a more symmetric charge distribution around M1B with two O1B-H1B groups and four oxygens in a *trans* configuration. Further heating to 800 °C causes complete dehydration and structural rearrangement of the oxygen framework, giving the formula $\text{Fe}_2^{3+} \text{Al}_4\text{Si}_2\text{O}_{13}$ (Bachmann 1956).

Literature data concerning the dehydration reaction in chloritoid vary greatly in their results: Bachmann (1956) conducted thermal gravimetric analysis of natural Fe-rich chloritoids and X-ray analyses of the heated products. These gravimetric thermal analyses show one reaction starting at about 360 °C which has a maximum at 550 °C. This was interpreted as a combination of dehydration and oxidation of Fe^{2+} to Fe^{3+} . Franolet (1978) used thermal differential and thermal gravimetric analysis to study the dehydration behavior of an Mn $^{2+}$ -rich chloritoid which had the composition $(\text{Mn}_{0.88}\text{Fe}_{0.55}^{2+} \text{Mg}_{0.54})(\text{Al}_{3.93}\text{Fe}_{0.07}^{3+})(\text{Si}_{1.97})\text{O}_{10}(\text{OH})_4$. He observed a continuous reaction which started at about 670 °C and displayed a maximum at 770 °C. Heating of the sample in air at 500 °C for 2 h resulted in no changes. Ivaldi et al. (1988) conducted single-crystal structure refinements on an Mg-rich chloritoid in the temperature range of 25 to 700 °C. This crystal showed a simultaneous loss of protons followed by a sudden

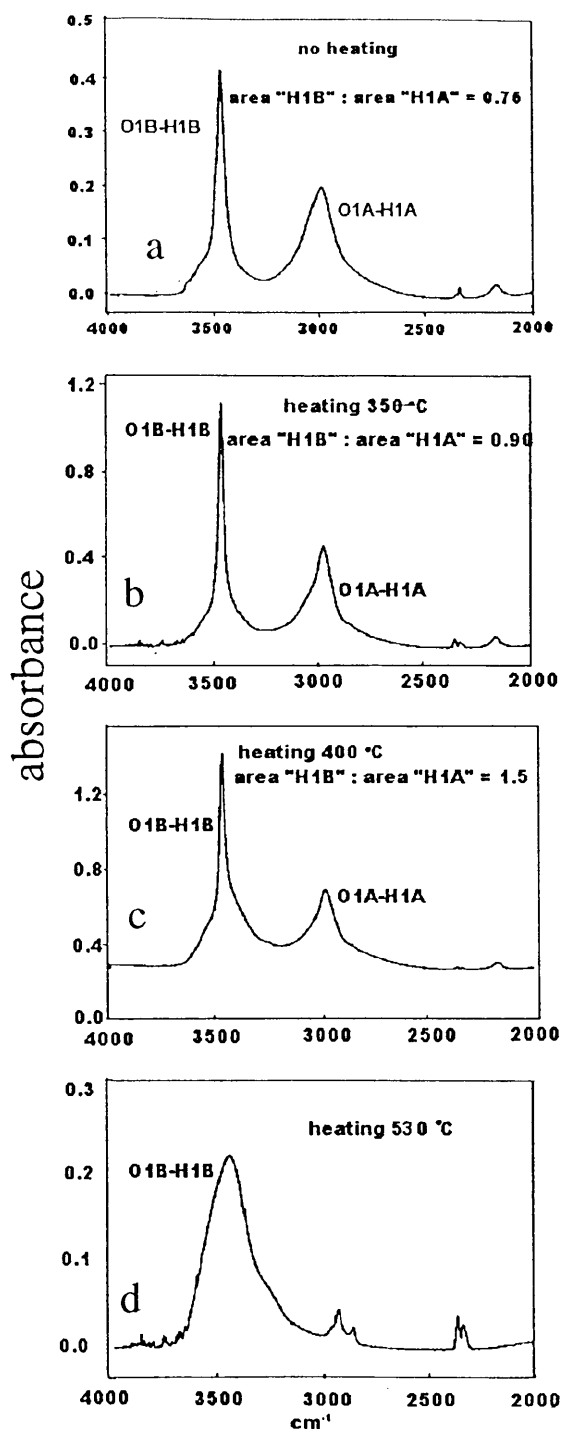


Fig. 8a–d Infrared spectra of chloritoids taken at room temperature. **a** Synthetic Fe^{2+} -chloritoid; **b–d** Quenched products of the heating experiments. The band at 2150 cm^{-1} is due to the first overtone of the O1A-H1A-bending vibrations and those around 2350 cm^{-1} are due to stretching vibrations of atmospheric CO_2

breakdown of the structure at around $750\text{ }^\circ\text{C}$, in both air and N_2 . Van der Plas et al. (1958) used thermal differential and thermal gravimetric analysis to study Fe-rich samples with an unusually high Na content reported as $(\text{Fe}_{1.4}^{2+}\text{Mg}_{0.16}\text{Na}_{0.33})(\text{Al}_{3.77}\text{Fe}_{0.37}^{3+})\text{Si}_{1.96}$.

They observed an endothermic reaction at about $770\text{ }^\circ\text{C}$, which they assigned to a simultaneous loss of the OH groups. Puga (1970) described two endothermic events (650 and $765\text{ }^\circ\text{C}$) for an Mg-rich sample and a single peak at $766\text{ }^\circ\text{C}$ for Fe-rich chloritoid.

The results of our study are in good agreement with those of Bachmann (1956). However, they differ from the results of dehydration experiments reported by van der Plas et al. (1958) and Puga (1970) for Fe-rich chloritoids. Either the oxidation of Fe^{2+} to Fe^{3+} was prevented in their experiments or the dehydration was delayed because of the relatively fast heating rates used in their experiments. The results of Fransolet (1978) and Ivaldi et al. (1988) may differ from our data due to the low Fe^{2+} content in their samples.

Conclusions

- Polarized single-crystal and in situ high-pressure IR spectroscopy reveals that the structural arrangement of the O1A-H1A and O1B-H1B dipole in triclinic chloritoid is similar to that in monoclinic chloritoid.
- Fe^{3+} incorporation on M1B in chloritoid is coupled with a dehydration mechanism.
- This mechanism occurs only if the sample is heated in air. The H1A protons are the first protons which leave with increasing temperature.
- The Mössbauer parameters of this $\text{Fe}^{3+}[\text{M1B}]$ -bearing chloritoid ($IS = 0.3\text{ mm s}^{-1}$; $QS = 1.1\text{ mm s}^{-1}$) are quite different from those proposed by Lodders et al. (1998) (see discussion in Koch-Müller et al. 2000).
- “Normal” metamorphic chloritoid should contain Fe^{3+} exclusively at M1A.

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