

Thermal behaviour of chlorite: an *in situ* single-crystal and powder diffraction study

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Abstract: The high-temperature behaviour of two natural chlorites has been studied by *in situ* X-ray diffraction: on a single-crystal of clinochlore, triclinic polytype I**b**-4, space group $C1$, with pseudomonoclinic metric and composition $(\text{Mg}_{9.14}\text{Fe}^{2+}_{1.02}\text{Fe}^{3+}_{0.01}\text{Mn}_{0.01}\text{Ti}_{0.01}\text{Al}_{1.76})_{\Sigma=11.95}(\text{Si}_{6.32}\text{Al}_{1.68})_{\Sigma=8}\text{O}_{20}(\text{OH})_{16}$; by powder diffraction for a chamosite with composition $(\text{Mg}_{3.52}\text{Fe}^{2+}_{4.33}\text{Fe}^{3+}_{1.15}\text{Al}_{2.85})_{\Sigma=11.85}(\text{Si}_{5.45}\text{Al}_{2.55})_{\Sigma=8}\text{O}_{20}(\text{OH})_{16}$ and same symmetry. Unit-cell parameters were measured for both samples up to 550 °C. Diffraction data for structural refinement of clinochlore were collected at 25, 301, 399 and 502 °C. Room temperature ^{57}Fe Mössbauer spectroscopy measurements were performed on the chamosite sample before and after heating, showing complete Fe oxidation above 500 °C. Mean thermal expansion coefficients of the two samples were: $\alpha_a = 1.05(3) \times 10^{-5}$, $\alpha_b = 1.02(3) \times 10^{-5}$, $\alpha_c = 0.99(5) \times 10^{-5}$ and $\alpha_V = 3.07(7) \times 10^{-5}/^\circ\text{C}$ for clinochlore and $\alpha_a = 2.47(25) \times 10^{-5}$, $\alpha_b = 0.93(5) \times 10^{-5}$, $\alpha_c = 0.93(12) \times 10^{-5}$ and $\alpha_V = 4.38(25) \times 10^{-5}/^\circ\text{C}$ for chamosite. These results confirm that the expansion of chlorite depends on the composition, but the dependence is not simply related to the Fe content, as suggested by previous studies.

The Si, Al tetrahedral volumes of clinochlore do not significantly change in the T range 25–550 °C. The expansion of M1, M2, M3 and M4 octahedra is 1.5, 1.9, 3.0 and 3.4 % respectively. The interlayer OH—O distances increase of about 1 %, the mean thermal expansion coefficient being $4.5 \times 10^{-6}/^\circ\text{C}$, indicating that the hydrogen bonds maintain their moderate strengths also at high temperature. The tetrahedral rotation angle α decreases from 6.38 to 3.34°.

A comparison with the modifications induced by pressure on the same sample of clinochlore confirms that the response of the structure to T and P is only approximately opposite. By combining the effects on cell volume, it is possible to formulate the following approximate equation of state: $V = V_0 (1 - 1.14 \times 10^{-2} \Delta P + 3.07 \times 10^{-5} \Delta T)$, where P is in GPa and T in °Celsius. The equation is valid for a triclinic polytype of chlorite having clinochlore composition.

Key-words: chlorite, expansion coefficients, equation of state, high-temperature crystal structure.

1. Introduction

Chlorite is a ubiquitous phase in low- to medium-grade metamorphism, and, among the hydrous phases that characterize the hydrated oceanic crust, has one of the highest water contents (~13 % H_2O by weight). This feature makes chlorite a key mineral in upper mantle mass transport and melting processes in subduction zones. The stability of this phase under high-pressure (HP), high-temperature (HT) conditions has relevant implications for these geological contexts and a better knowledge of the pressure and temperature dependence of its crystal structure may be used to constrain metamorphic reactions and deep water transport.

Stable-isotope signatures of chlorite and talc schists suggest that they formed by fluid-induced metasomatism of mafic, ultramafic and metasedimentary rocks during subduction (Spandler *et al.*, 2008). In this geodynamic setting the process of dehydration of these rocks occurs at

about 800 °C, significantly higher than in other lithologies, and at sub-arc depths. Such a process may be responsible for high trace elements and fluid transfer from the subduction slab to the overlying mantle wedge, where arc magmatism originates.

Experimental results (Fumagalli & Poli, 2005) have shown that the addition of Fe as well as Ca and Na in a simplified MASH system, to approach the natural bulk composition involved in subduction processes, strongly affects the phase equilibria and stabilities. In particular, the thermal stability of chlorite is shifted towards lower temperatures compared with the “pure” MASH system. Taking into account that chlorite contributes significantly to water budget in subduction zones, in the depth range relevant for arc magmatism, beyond the stability of amphiboles (Fumagalli & Poli, 2005), it is important to study the physical properties of chlorites with different iron contents.

The structure of trioctahedral chlorite consists of talc-type, negatively charged T—O—T 2:1 layers with

ideal composition $(R^{2+}, R^{3+})_3(Si_{4-x}Al_x)O_{10}(OH)_2$ alternating with positively charged brucite-type octahedral interlayer sheets with ideal composition $(R^{2+}, R^{3+})_3(OH)_6$ (Bailey, 1988). Electrostatic interactions and a system of hydrogen bonding between the T—O—T layer and the brucite-like sheet contribute to the stability of the structure. Different ways of positioning the T—O—T layer on the interlayer sheet create a large number of regular-stacking polytypes (Bailey, 1988). The triclinic *I1b*-4 polytype, with symmetry *C1*, and the monoclinic *I1b*-2 polytype, with symmetry *C2/m*, are the most abundant regular-stacking one-layer chlorites occurring in nature. The triclinic structure was refined and described by several authors (X-ray diffraction: Steinfink, 1958; Phillips *et al.*, 1980; Zheng & Bailey, 1989; Joswig & Fuess, 1990; Smyth *et al.*, 1997. Neutron diffraction: Joswig *et al.*, 1980). The monoclinic structure was described by Zheng & Bailey (1989), Rule & Bailey (1987) and Joswig & Fuess (1989).

While the compressibility and the crystal structure behaviour of clinocllore under pressure has been recently investigated (Welch & Marshall, 2001; Welch & Crichton, 2002; Kleppe *et al.*, 2003; Welch *et al.*, 2004; Zanazzi *et al.*, 2006, 2007), few experimental studies on chlorite behaviour at high temperature are known, due to the normally poor quality of chlorite crystals (Symmes, 1986; Nelson & Guggenheim, 1993; Pawley *et al.*, 2002). Up to now, the only single-crystal study is that of Nelson & Guggenheim (1993) on a chromian clinocllore.

The most thermally stable chlorite composition is clinocllore, nominally $Mg_5Al_2Si_3O_{10}(OH)_8$, but many compositions show both Tschermak's and Fe-Mg substitution. The different composition seems to have strong influence on thermal expansion. In contrast with other phyllosilicates, Nelson & Guggenheim (1993) found a nearly isotropic expansion of clinocllore. Symmes (1986) studied the thermal expansion of the unit-cell parameters of a clinocllore from Quebec and of an Fe-rich chlorite from Michigan, using powder diffraction data. He found significantly different expansion coefficients along the *c** axis for the two samples. Nelson & Guggenheim (1993) tried to relate this different behaviour to the Fe content of chlorite.

Here we describe the behaviour of two different chlorite compositions at high temperature, based on single-crystal and powder X-ray diffraction data. We used Mössbauer spectroscopy on the iron-richer sample to measure the iron oxidation that occurred during the high-temperature XRD experiments.

2. Materials and methods

2.1. Sample #1

Sample #1 is a clinocllore from Val Malenco, Italy, triclinic polytype *I1b*-4, S.G. *C1*, with pseudomonoclinic metric and composition $(Mg_{9.14}Fe^{2+}_{1.02}Fe^{3+}_{0.01}Mn_{0.01}$

$Ti_{0.01}Al_{1.76})_{\Sigma=11.95}(Si_{6.32}Al_{1.68})_{\Sigma=8}O_{20}(OH)_{16}$. It is the same specimen used to study the compressibility (Zanazzi *et al.*, 2006, 2007). The complete description of the sample and its crystal chemistry are reported in Zanazzi *et al.* (2006).

A crystal of sample #1, with dimensions $0.61 \times 0.55 \times 0.08$ mm, was fixed in a silica glass capillary with a ceramic cement (M-Bond GA-100 cement, M-M Division, Measurements Group Inc., Raleigh, North Carolina, USA) and mounted on a Philips PW1100 four-circle diffractometer equipped with the radiating microfurnace described in Comodi & Zanazzi (1993). The temperature of the heating device was calibrated according to the thermal expansion of a NaCl crystal (Pathak & Vasavada, 1970) and monitored with a Pt-Pt/Rh 13 % reference thermocouple near the sample. The precision of temperature measurements was better than 5 °C. Unit-cell parameters were measured at several temperatures up to 550 °C. At least 3 h were allowed for equilibration at each temperature, before each lattice parameters measurement. Cell parameters were determined by means of a least-squares procedure based on the Philips LAT routine over 35–50 reflections (2θ range 15–35°), accurately measured using graphite-monochromatized MoK α radiation. Due to dehydroxylation, the crystal showed clear symptoms of decay above 550 °C. Unit-cell parameters obtained at the different temperatures are listed in Table 1.

The XRD intensity data for structural refinement were collected at 25 °C (out of the microfurnace, up to $2\theta = 70^\circ$). The full sphere of reflections up to $2\theta = 40^\circ$ was measured at 301, 399 and 502 °C. Intensities were obtained by measuring step-scan profiles by the Lehman & Larsen (1974) method, corrected for absorption using the semi-empirical ψ -scan method of North *et al.* (1968), and then merged to have the set of unique reflections to be used in the structure refinement. Crystal-structure refinements were carried out in the *C1* space group by the SHELX-97 program (Sheldrick, 1997), starting from the atomic coordinates of Zanazzi *et al.* (2006). The refinement at 25 °C was performed with anisotropic displacement parameters. Neutral atomic scattering factors and $\Delta f'$, $\Delta f''$ coefficients from the International Tables for Crystallography (Wilson & Prince, 1999) were used. Full occupancy was assumed for all cation sites. The electronic density in these sites was accounted for by fitting the scattering factor curves of Mg and Fe for octahedral sites, and Si and Al for tetrahedral sites with variable occupancy. The resulting sum of electrons for the octahedral and tetrahedral sites in the cell was 156.2 and 109.1 e[−] respectively, in good agreement with data calculated on the basis of the chemical analysis (159.8 and 110.3 e[−]). In the last cycles of refinement the hydrogen positions found in a difference Fourier map were included and refined with the same isotropic thermal parameter and constraining the O—H bond length to 0.85 ± 0.05 Å. At the end of the refinement, no peak larger than $0.5 \text{ e}^-/\text{\AA}^3$ was present in the final difference Fourier synthesis.

Owing to the lower number of data due to the limits imposed by the microfurnace, the refinements at 301, 399

Table 1. Lattice parameters of samples #1 and #2 at different temperatures.

T (°C)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
Sample #1							
22	5.3303(4)	9.2332(4)	14.3938(13)	90.27(1)	97.26(1)	89.99(4)	702.72(6)
76	5.335(2)	9.234(1)	14.394(7)	90.31(2)	97.24(3)	89.96(1)	703.4(5)
122	5.334(1)	9.242(2)	14.413(6)	90.25(3)	97.25(2)	89.99(2)	704.8(5)
183	5.3396(3)	9.2477(4)	14.416(1)	90.28(1)	97.27(1)	89.98(1)	706.1(3)
251	5.3427(4)	9.2542(5)	14.427(2)	90.27(1)	97.27(1)	89.99(1)	707.6(3)
275	5.3442(4)	9.2572(5)	14.428(2)	90.28(1)	97.28(1)	89.99(1)	708.0(3)
301*	5.3454(6)	9.2584(5)	14.435(2)	90.29(1)	97.28(1)	90.00(1)	708.5(3)
349	5.3472(3)	9.2613(5)	14.436(1)	90.30(1)	97.29(1)	90.00(1)	709.1(3)
399*	5.3504(4)	9.2661(6)	14.447(2)	90.31(1)	97.29(1)	90.00(1)	710.5(3)
450	5.3533(5)	9.2700(6)	14.458(1)	90.32(1)	97.28(1)	90.01(1)	711.7(3)
502*	5.3568(5)	9.2778(7)	14.464(2)	90.30(1)	97.27(1)	90.00(1)	713.1(4)
555	5.3618(5)	9.2835(5)	14.465(2)	90.25(1)	97.24(1)	89.99(1)	714.3(4)
Sample #2							
25	5.345(1)	9.236(1)	14.276(2)	90.11(5)	97.51(5)	89.36(5)	698.7(8)
100	5.364(1)	9.245(1)	14.275(2)	90.27(5)	97.41(5)	89.66(5)	701.9(8)
150	5.367(1)	9.248(1)	14.276(2)	90.44(5)	97.43(5)	89.50(5)	702.1(8)
200	5.367(1)	9.250(1)	14.291(2)	90.38(5)	97.47(5)	89.48(5)	703.4(8)
250	5.377(1)	9.258(1)	14.292(2)	90.44(5)	97.39(5)	89.65(5)	705.5(8)
300	5.379(1)	9.262(1)	14.304(2)	90.51(5)	97.38(5)	89.57(5)	706.7(8)
350	5.389(1)	9.265(1)	14.311(2)	90.43(5)	97.37(5)	89.64(5)	708.6(8)
400	5.403(1)	9.267(1)	14.322(2)	90.36(5)	97.50(5)	89.41(5)	710.9(8)
450	5.407(1)	9.272(1)	14.341(2)	90.56(5)	97.54(5)	89.27(5)	712.7(8)
500	5.410(1)	9.270(1)	14.348(2)	90.57(5)	97.54(5)	89.27(5)	713.3(8)
25**	5.348(1)	9.234(1)	14.265(2)	90.58(5)	97.48(5)	89.01(5)	698.5(8)

*Data for refinement were collected at these T .

**after heating.

Table 2. Details of data collection and refinement for sample #1 at various temperatures.

T (°C)	25	301	399	502
Radiation (monoch. graphite)	MoK α	MoK α	MoK α	MoK α
θ -range	3–35°	3–20°	3–20°	3–20°
No. measured reflections	2738	1668	1905	1614
No. independent reflections	1626	372	383	383
Reflections with $I > 4\sigma(I)$	1483	368	364	375
No. refined parameters	156	56	56	56
R_{int} %	1.3	1.9	2.2	2.6
R_1 %	2.3	4.5	5.3	6.3

and 502 °C were carried out with isotropic atomic displacement parameters, and with site occupancies fixed to the values found at room conditions.

Details of data collection and refinement are listed in Table 2. A list of observed and calculated structure factors can be obtained from the authors. Atomic coordinates and displacement parameters are listed in Table 3.

2.2. Sample #2

Sample #2 is a chamosite from the Swiss Alps having the same symmetry as sample #1 and composition $(\text{Mg}_{3.52}\text{Fe}^{2+}_{4.33}\text{Fe}^{3+}_{1.15}\text{Al}_{2.85})_{\Sigma=11.85}(\text{Si}_{5.45}\text{Al}_{2.55})_{\Sigma=8}\text{O}_{20}(\text{OH})_{16}$. The

chemical composition is an average of five point analyses obtained by the SEM-EDS technique.

The HT powder diffraction measurements of sample #2 were carried out on the Philips “XPERT” diffractometer at the Dept. of Earth Sciences, University of Milan, equipped with a furnace (AHT PAP-1600). The shift of the sample for the thermal expansion of the sample holder was accounted for by moving the sample with a stepper motor. The temperature was read on a thermocouple placed about 20 mm from the sample. The chlorite was mixed with silicon powder as internal standard. The temperature was calibrated according to Dapiaggi *et al.* (2002). Data collections were performed at 25, 100, 150, 200, 250, 300, 350, 400, 450, 500 and again at 25 °C. Details of the experiment are listed in Table 4. Figure 1 shows the diffraction pattern at 400 °C. The Rietveld method was used to treat the HT powder diffraction patterns (Larson & Von Dreele, 2001) modelling background, peak-shape and preferred orientation by a Chebyshev polynomial expansion, a pseudo-Voigt profile function and the March-Dollase model (Dollase, 1986), respectively. The quality of the HT measurements did not allow an accurate refinement of the structure, and therefore the resulting atomic coordinates, displacement factors and occupancy factors are not discussed here. The unit-cell parameters were refined by the Le Bail method (Le Bail *et al.*, 1988).

Room temperature ^{57}Fe Mössbauer spectroscopy measurements of sample #2 before and after heating up

Table 3. Fractional atomic coordinates and thermal displacement factors U_{eq}/U_{iso} ($\text{\AA}^2$) of sample #1 at various temperatures.

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
T1	0.23159(10)	0.16805(6)	0.19168(4)	0.0076(1)
	0.2322(5)	0.1681(3)	0.1920(2)	0.019(1)
	0.2322(6)	0.1678(3)	0.1918(2)	0.021(2)
	0.2318(8)	0.1681(5)	0.1915(3)	0.024(2)
T2	0.73199(9)	0.00125(6)	0.19169(4)	0.0077(1)
	0.7322(5)	0.0020(3)	0.1918(2)	0.018(1)
	0.7324(6)	0.0019(3)	0.1917(2)	0.021(2)
	0.7325(8)	0.0024(4)	0.1916(3)	0.023(2)
M1	0	0	0	0.0079(2)
	0	0	0	0.015(2)
	0	0	0	0.018(2)
	0	0	0	0.021(2)
M2	0.00106(11)	0.33371(6)	−0.00003(4)	0.0089(2)
	0.0011(5)	0.3337(2)	0.0000(2)	0.016(1)
	0.0013(5)	0.3337(3)	0.0000(2)	0.019(2)
	0.0009(7)	0.3335(4)	−0.0002(3)	0.022(2)
M3	−0.00033(11)	0.16679(7)	0.49998(4)	0.0085(2)
	−0.0002(5)	0.1671(3)	0.5001(2)	0.023(1)
	−0.0003(5)	0.1670(3)	0.5000(2)	0.026(2)
	−0.0013(8)	0.1667(4)	0.5001(3)	0.035(2)
M4	0	½	½	0.0066(2)
	0	½	½	0.020(2)
	0	½	½	0.023(2)
	0	½	½	0.031(2)
O1	0.1928(2)	0.1675(2)	0.0768(1)	0.0099(3)
	0.1928(11)	0.1666(6)	0.0767(4)	0.016(2)
	0.1929(12)	0.1666(7)	0.0769(4)	0.020(2)
	0.1928(15)	0.1673(9)	0.0767(6)	0.019(3)
O2	0.6930(2)	0.0005(1)	0.0769(1)	0.0102(3)
	0.6925(11)	0.0013(6)	0.0769(4)	0.015(2)
	0.6926(12)	0.0008(7)	0.0770(5)	0.019(2)
	0.6927(16)	0.0018(9)	0.0770(6)	0.022(3)
O3	0.2133(3)	0.3350(2)	0.2329(1)	0.0163(3)
	0.2248(11)	0.3356(6)	0.2329(4)	0.028(2)
	0.2276(12)	0.3354(7)	0.2326(4)	0.032(3)
	0.2298(17)	0.3360(10)	0.2326(6)	0.041(3)
O4	0.5121(1)	0.1008(2)	0.2330 (1)	0.0168(3)
	0.5078(109)	0.0960(6)	0.2328(4)	0.023(2)
	0.5062(11)	0.0949(6)	0.2326(4)	0.027(2)
	0.5058(16)	0.0938 (9)	0.2321(2)	0.033(3)
O5	0.0121(3)	0.0687(2)	0.2330 (1)	0.0166(3)
	0.0078(11)	0.0740(6)	0.2326(4)	0.026(2)
	0.0062(12)	0.0761(7)	0.2325(4)	0.028(3)
	0.0066(16)	0.0778(9)	0.2324(6)	0.034(3)
OH1	0.6922(3)	0.3336(2)	0.0734(1)	0.0109(3)
	0.6916(11)	0.3340(6)	0.0741(4)	0.017(2)
	0.6915(12)	0.3334(7)	0.0744(5)	0.021(2)
	0.6912(16)	0.3343(9)	0.0741(6)	0.023(3)
OH2	0.1521(3)	−0.0006(2)	0.4304(1)	0.0152(3)
	0.1512(11)	−0.0008(6)	0.4300(4)	0.026(2)
	0.1510(13)	−0.0014(7)	0.4297(4)	0.027(2)
	0.1501(17)	−0.0012(10)	0.4292(7)	0.034(3)
OH3	0.1382(3)	0.3374(2)	0.4303(1)	0.0158(3)
	0.1370(11)	0.3370(6)	0.4297(5)	0.027(2)
	0.1374(13)	0.3364(7)	0.4297(5)	0.029(3)
	0.1363(18)	0.3370(10)	0.4294(7)	0.037(3)

Table 3. Continued.

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
OH4	0.6386(3)	0.1615(2)	0.4309(1)	0.0147(3)
	0.6361(11)	0.1615(6)	0.4301(4)	0.024(2)
	0.6365(13)	0.1619(7)	0.4301(5)	0.026(2)
	0.6360(17)	0.1620(10)	0.4295(7)	0.033(3)
H1	0.709(6)	0.335(4)	0.134(2)	0.037(5)
H2	0.132(7)	0.005(4)	0.375(2)	0.037(5)
H3	0.131(7)	0.338(4)	0.377(2)	0.037(5)
H4	0.620(7)	0.161(4)	0.375(2)	0.037(5)

Notes: For each atom, values from top to bottom correspond to the refinements at 25, 301, 399, 502 °C. The H positions are those from the refinement at 25 °C.

At 25 °C the occupancy of Mg against Fe refined to 0.913(2), 0.912(3), 0.940(3), 0.946(2) atoms for M1, M2, M3 and M4 respectively. The occupancy of Si against Al refined to 0.640(4) and 0.639(4) for T1 and T2 respectively.

Estimated standard deviations refer to the last digit.

Table 4. Details of powder data collection for sample #2.

Radiation (monoch. graphite)	CuK α
2 θ -range	5–110°
Step width	0.02°
Count time/step	5 s
Heating rate	25 °C/min
Refinement of lattice parameters	LeBail method, GSAS Larson & Von Dreele, 2001

to 500 °C were performed at the Dept. of Earth Sciences, University of Rome. About 15 mg of powder sample were grounded gently in an agate mortar with acetone and mixed with a powdered acrylic resin to avoid (or reduce) preferred orientations. The obtained absorber was within the limits for the thin absorber thickness described by Long *et al.* (1983). Data were collected at room temperature (294 K), using a conventional spectrometer system operated in constant acceleration mode with a ^{57}Co source of nominal strength of 25 mCi in rhodium matrix, and recorded in a multi-channel analyzer using 512 channels for the velocity range −4 to 4 mm/s. In order to have good statistics, more than 1 million counts per channel were collected. After velocity calibration against a spectrum of high-purity α -iron foil (25 μm thick), the raw data were folded to 256 channels. The spectrum was fitted using the Recoil 1.04 fitting program (Lagarec & Rancourt, 1988) and pure Lorentzian line shapes. Uncertainties were calculated using the covariance matrix and errors (2σ) were estimated to be no less than $\pm 3\%$ for both Fe^{2+} and Fe^{3+} absorption areas (Table 5).

3. Results and discussion

3.1. Thermal evolution of sample #1

Lattice parameters at different temperatures are reported in Table 1 and their variations with temperature are shown

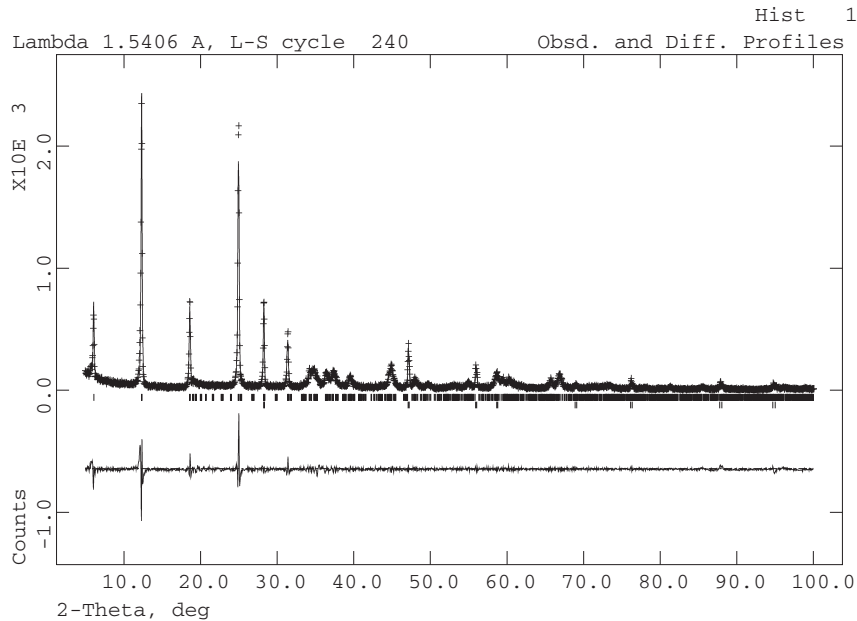


Fig. 1. Observed, calculated and residual diffraction pattern of sample #2 and silicon at 400 °C. Peak positions are marked by vertical bars.

Table 5. Mössbauer parameters of sample #2 measured at 294 K.

Sample #2	CS (mm/s)	QS (mm/s)	FWHM (mm/s)	Intensity (%)	Attribution
Before heating	1.13	2.71	0.26	48	Oct. Fe ²⁺
	1.12	2.48	0.22	23	Oct. Fe ²⁺
	1.04	2.18	0.26	8	Oct. Fe ²⁺
	0.31	0.68	0.47	15	Oct. Fe ³⁺
	0.44	1.21	0.32	6	Oct. Fe ³⁺
After heating	1.17	0.24	0.27	4	Oct. Fe ²⁺
	0.35	0.72	0.30	21	Oct. Fe ³⁺
	0.34	1.09	0.35	40	Oct. Fe ³⁺
	0.32	1.54	0.45	35	Oct. Fe ³⁺

Note: CS: centre shift (with respect to α -iron); QS: quadrupole splitting; FWHM: full width at half maximum; Oct. = octahedrally coordinated. Estimated uncertainties (2σ) are about 0.02 mm/s for CS, QS, FWHM, and no less than 3 % for intensity.

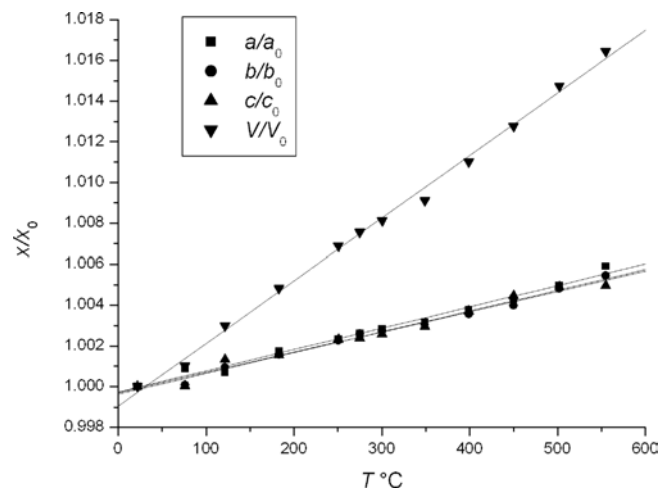


Fig. 2. Normalized lattice parameters of sample #1 at various temperatures.

in Fig. 2. The lattice angles do not show significant variations in the T range investigated.

Mean thermal expansion coefficients of the cell parameters calculated by the least-squares fitting of data measured at the different temperatures in the range 25–550 °C are: $\alpha_a = 1.05(3) \times 10^{-5}$, $\alpha_b = 1.02(3) \times 10^{-5}$, $\alpha_c = 0.99(5) \times 10^{-5}$ and $\alpha_V = 3.07(7) \times 10^{-5} / ^\circ\text{C}$, showing that the expansion is quite isotropic. These values are in fair agreement with those found by Nelson & Guggenheim (1993) for a magnesian-chromian chlorite ($\alpha_a = 0.787 \times 10^{-5}$, $\alpha_b = 0.806 \times 10^{-5}$, $\alpha_c = 0.729 \times 10^{-5}$ and $\alpha_V = 2.316 \times 10^{-5} / ^\circ\text{C}$) and by Symmes (1986) for a magnesian chlorite ($\alpha_a = 1.130 \times 10^{-5}$, $\alpha_b = 1.018 \times 10^{-5}$, $\alpha_c = 0.741 \times 10^{-5}$ and $\alpha_V = 2.935 \times 10^{-5} / ^\circ\text{C}$, as recalculated by Nelson & Guggenheim, 1993), and clinocllore by Pawley *et al.*

(2002) ($\alpha_a = 0.781 \times 10^{-5}$, $\alpha_b = 1.09 \times 10^{-5}$, $\alpha_c = 0.577 \times 10^{-5}$, and $\alpha_V = 2.5(6) \times 10^{-5} / ^\circ\text{C}$). In all cases the smallest expansion occurs along the c axis and, as observed by the previous authors, this is quite unexpected for a layer silicate. The comparison with thermal expansion measured on phlogopite by Tutti *et al.* (2000) and on a Ti-rich phlogopite by Venturi *et al.* (2008) suggests that the smaller thermal expansion of chlorite with respect to trioctahedral mica (the α_V is about one-half of that of phlogopite and $3/4$ of that of Ti-phlogopite) is due to the significantly smaller thermal expansion of the c parameter, whereas the α_a and α_b have about the same value as in other phyllosilicates.

Values of mean bond distances, polyhedral volumes, and distortion parameters at different temperatures are listed in Table 6. At room conditions the structure is in

Table 6. Values of bond distances (Å), polyhedral volumes (Å³), and distortion parameters (following Robinson *et al.*, 1971) of sample #1 at various temperatures.

<i>T</i> (°C)	25	301	399	502
T1—O1	1.640(2)	1.650(7)	1.647(8)	1.648(10)
—O3	1.656(2)	1.660(7)	1.659(7)	1.664(10)
—O4	1.659(2)	1.658(6)	1.655(7)	1.662(10)
—O5	1.657(2)	1.651(7)	1.648(7)	1.641(10)
<T1—O>	1.653	1.655	1.652	1.654
<i>V</i> _{T1}	2.32(1)	2.32(3)	2.31(3)	2.32(4)
σ ² _{T1} *	2.46	1.97	2.05	2.14
λ _{T1} **	1.001	1.000	1.000	1.000
T2—O2	1.640(2)	1.645(7)	1.644(8)	1.643(10)
—O4	1.654(2)	1.649(6)	1.653(7)	1.647(10)
—O5	1.656(2)	1.655(7)	1.657(7)	1.664(10)
—O3	1.656(2)	1.655(7)	1.657(7)	1.658(10)
<T2—O>	1.652	1.651	1.653	1.653
<i>V</i> _{T2}	2.31(1)	2.31(3)	2.31(3)	2.32(4)
σ ² _{T2} *	2.51	2.31	2.16	2.07
λ _{T2} **	1.001	1.001	1.000	1.000
Tetr. rot. α†	6.4(1)	4.2(2)	3.8(2)	3.3(2)
T sheet thickness	2.229(2)	2.233(6)	2.230(6)	2.231(7)
M1—OH1 × 2	2.066(1)	2.072(6)	2.080(7)	2.074(9)
—O1 × 2	2.090(1)	2.088(6)	2.091(7)	2.097(9)
—O2 × 2	2.088(1)	2.097(6)	2.099(7)	2.101(9)
<M1—O>	2.081	2.086	2.090	2.091
<i>V</i> _{M1}	11.84(2)	11.93(3)	12.00(3)	12.02(4)
ψ _{M1} ‡	58.7	58.6	58.6	58.6
σ ² _{M1} *	32.91	31.13	30.30	31.11
λ _{M1} **	1.010	1.009	1.009	1.009
M2—OH1	2.066(2)	2.078(6)	2.078(7)	2.081(9)
—OH1	2.068(2)	2.081(6)	2.087(7)	2.088(9)
—O2	2.083(2)	2.088(6)	2.092(7)	2.091(9)
—O2	2.089(2)	2.093(6)	2.095(7)	2.105(9)
—O1	2.084(2)	2.088(6)	2.091(7)	2.091(9)
—O1	2.086(2)	2.097(6)	2.101(7)	2.098(9)
<M2—O>	2.079	2.088	2.091	2.092
<i>V</i> _{M2}	11.81(2)	11.96(3)	12.02(3)	12.04(4)
ψ _{M2} ‡	58.7	58.6	58.6	58.6
σ ² _{M2} *	32.57	31.72	30.67	31.43
λ _{M2} **	1.010	1.010	1.009	1.009
O sheet thickness	2.162(3)	2.173(7)	2.181(7)	2.179(8)
M3—OH4	2.053(2)	2.057(7)	2.058(8)	2.065(10)
—OH4	2.054(2)	2.075(7)	2.073(8)	2.083(10)
—OH3	2.058(2)	2.061(7)	2.061(8)	2.069(10)
—OH3	2.061(1)	2.073(7)	2.075(8)	2.082(10)
—OH2	2.057(2)	2.065(7)	2.064(8)	2.068(10)
—OH2	2.060(1)	2.070(7)	2.076(8)	2.077(10)
<M3—O>	2.057	2.067	2.068	2.074
<i>V</i> _{M3}	11.15(2)	11.35(3)	11.37(3)	11.49(4)
ψ _{M3} ‡	58.7	61.0	60.9	60.8
σ ² _{M3} *	83.87	79.01	77.51	74.07
λ _{M3} **	1.027	1.025	1.025	1.023
M4—OH2 × 2	1.993(2)	2.005(6)	2.010(7)	2.019(9)
—OH4 × 2	1.990(2)	1.996(6)	2.002(7)	2.009(9)
—OH3 × 2	1.994(2)	2.004(6)	2.011(7)	2.009(9)
<M4—O>	1.992	2.002	2.007	2.012
<i>V</i> _{M4}	10.26(2)	10.43(3)	10.51(3)	10.61(4)
ψ _{M4} ‡	60.1	59.9	59.9	59.8
σ ² _{M4} *	58.95	54.58	55.04	51.47
λ _{M4} **	1.018	1.017	1.017	1.016
O sheet thickness	1.985(3)	2.007(7)	2.011(7)	2.027(8)
OH2—O5	2.919(2)	2.941(7)	2.949(7)	2.950(7)
OH3—O3	2.920(2)	2.937(7)	2.947(7)	2.952(7)

Table 6. Continued.

<i>T</i> (°C)	25	301	399	502
OH4—O4	2.894(2)	2.904(7)	2.914(7)	2.919(7)
TOT ... O	2.821(3)	2.823(7)	2.827(7)	2.827(8)
thickness				
TOT thickness	6.620(3)	6.639(7)	6.641(7)	6.641(7)

Notes: Estimated standard deviations refer to the last digit.

*σ² is the angle variance (deg²).

**λ is the quadratic elongation.

†α is the tetrahedral rotation angle (deg); see text for definition.

‡ψ is the octahedral flattening angle (deg).

excellent agreement with that determined on a different crystal selected for the HP study from the same specimen. A detailed description of the structure is reported in Zanazzi *et al.* (2006).

The comparison with the refinements at higher *T* shows that the Si, Al tetrahedral volumes do not significantly change in the *T* range 25–500 °C. Tetrahedral sheet thickness remains almost unchanged (from 2.229(2) Å to 2.231(7) Å). The expansion of M1, M2, M3 and M4 octahedra is 1.5, 1.9, 3.0 and 3.4 % respectively. The M1, M2 octahedral thickness increases from 2.162(3) to 2.179(8) Å; that of M3, M4 layer from 1.985(3) to 2.027(8) Å.

Owing to the different expansion of tetrahedral and octahedral sheets in the 2:1 layer, a decrease of the ditrigonality is necessary to facilitate dimensional matching between the sheets. As a consequence the tetrahedral rotation angle α (Hazen & Burnham, 1973) decreases from 6.38 to 3.34°.

The interlayer OH—O distances increase of about 1 %, the mean thermal expansion coefficient being 4.5×10^{-6} °C, indicating that the hydrogen bonds maintain their moderate strengths also at high temperature. In spite of the increase of the OH—O bonds, the TOT—O thickness increases only from 2.821(2) to 2.827(8) Å, suggesting that the expansion is accompanied by a general distortion of the structure, changing the layer misfit.

All these structural modifications are in quite good agreement with those previously determined for clinocllore (Nelson & Guggenheim, 1993). In particular the increase of the dimensions of M4 site (where trivalent cations are preferentially located) with *T* is confirmed, as well as the increased distortion of M3 site. As suggested by Nelson & Guggenheim (1993), these effects and the crystal chemical behaviour of trivalent cations in the structure yield a rationale on the oxidation mechanism of Fe²⁺ that would be quite independent from the oxidizing conditions of the environment.

As shown by Mössbauer spectroscopy on sample #2 (see later), we cannot exclude that iron oxidation also occurred in the clinocllore sample; the low Fe content in this sample (1.02 a.f.u.) makes the effect of redox processes less important.

3.2. Thermal evolution of sample #2

The lattice parameters at various T are shown in Table 1 and Fig. 3. The thermal expansion coefficients calculated in the range 25–400°C (to avoid the effects of Fe oxidation after heating highlighted by Mössbauer spectroscopy) are: $\alpha_a = 2.47(25) \times 10^{-5}$, $\alpha_b = 0.93(5) \times 10^{-5}$, $\alpha_c = 0.93(12) \times 10^{-5}$ and $\alpha_V = 4.38(25) \times 10^{-5}/^\circ\text{C}$. These values are quite different from those measured for clinocllore. In particular sample #2 is more expandible than clinocllore, and shows a stronger anisotropy, with the larger expansion along the a axis. This is in contrast with that observed by Symmes (1986) on a Fe-rich chlorite, where maximum expansion was along the c axis.

The Mössbauer absorption spectrum of sample #2, both before and after heating, is typical of paramagnetic materials with different degrees of oxidation. For the first spectrum (before heating) two fitting models were tried. The first trial was done following Smyth *et al.* (1997), using three quadrupole doublets: two quadrupole doublets with centre shift (CS) values about 1.1 mm/s and quadrupole splitting (QS) values of 2.4 and 2.7 mm/s, which were assigned to Fe^{2+} ; the third doublet with CS of 0.3 mm/s and QS of 0.8 mm/s, which was assigned to Fe^{3+} . However, the fit between observed and calculated spectra was not very satisfying ($\chi^2 = 4.1$), so that a model with five quadrupole doublets was tried: three doublets with CS values about 1.1 mm/s and QS values of 2.2, 2.5, 2.7 mm/s, assigned to Fe^{2+} octahedrally coordinated, and two with CS about 0.3–0.4 mm/s and QS of 0.7 and 1.2 mm/s, assigned to Fe^{3+} octahedrally coordinated (Table 5). The accordance between observed and calculated spectra was better than before ($\chi^2 = 3.2$) and this model was finally chosen. Notably, in both cases Fe^{3+} proportions were quantified at 21 % Fe_{tot} from direct area measurement ($\text{Fe}^{3+}_{\text{raw}}$), and became 18 % Fe_{tot} when adjusting for the temperature-dependent, recoil-free fraction ($\text{Fe}^{3+}_{\text{corr}}$) as suggested by De Grave & Van Alboom (1991) and Eeckhout &

De Grave (2003). The second spectrum (after heating) was satisfactorily reproduced ($\chi^2 = 1.4$) with four quadrupole doublets: one doublet with CS of 1.2 mm/s and QS of 0.24 mm/s, which was assigned to Fe^{2+} octahedrally coordinated; three doublets with CS about 0.3 mm/s and QS of 0.8, 1.1 and 1.5 mm/s, which were assigned to Fe^{3+} octahedrally coordinated. The Fe^{3+} proportions were quantified at 96 % Fe_{tot} from direct area measurement ($\text{Fe}^{3+}_{\text{raw}}$), and became 95 % Fe_{tot} when adjusting for the temperature-dependent, recoil-free fraction ($\text{Fe}^{3+}_{\text{corr}}$). The Mössbauer spectra are shown in Fig. 4.

The evolution of Mössbauer spectra with temperature is obviously related to the almost complete oxidation of Fe^{2+} to Fe^{3+} . In addition to Fe^{3+} quantification, Mössbauer doublets contain also information about short-range order around Fe nuclei. In particular, variations in the chemical/structural environment (*i.e.*, electric field gradient) surrounding the Fe nuclei are recorded in the QS values. This was clearly showed for tourmaline (Andreozzi *et al.*,

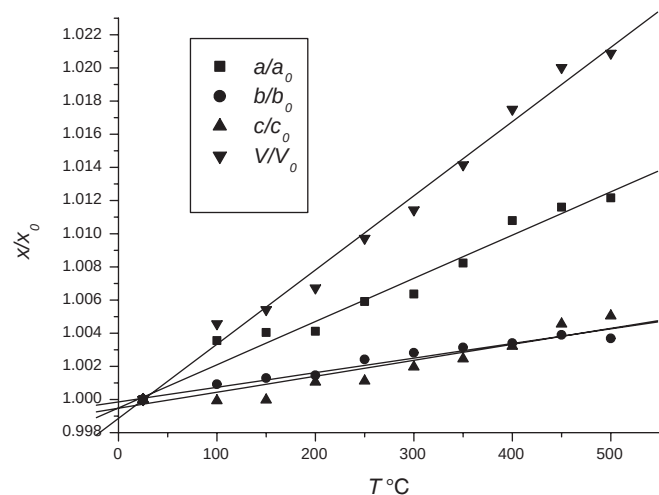


Fig. 3. Normalized lattice parameters of sample #2 at various temperatures.

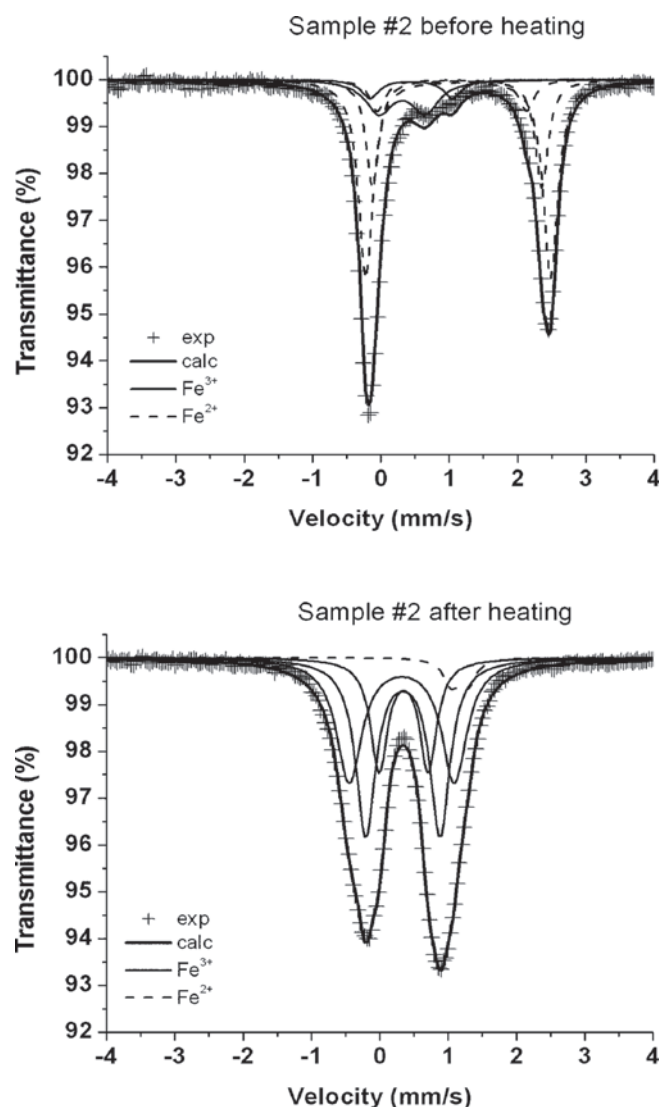


Fig. 4. Mössbauer spectra of sample #2 before and after heating.

2008), and could be tentatively applied here for our chlorite. In this light, the increase of QS values observed for Fe^{3+} suggests an increase of local disorder in the next-nearest neighbourhood, that is in the surrounding octahedra, whereas the decrease of QS to values close to zero observed for Fe^{2+} suggests a decrease of such disorder around the few Fe^{2+} nuclei remained.

3.3. Sample #1 vs. Sample #2

The comparison of the evolution with temperature of lattice parameters of the two chlorite samples shows that the increase of temperature acts on the cell dimensions as the substitution of a small ion, such as magnesium, by an ion with a larger ionic radius, such as iron. In particular we observed that the a/c ratio, at room condition, is 0.3703 for sample #1 and 0.3744 for sample #2. With increasing temperature the a/c ratio slightly increases in both samples due to the slightly higher thermal expansion of the a parameter with respect to the c parameter.

3.4. High-temperature vs. high-pressure behaviour

A comparison with the modifications induced by pressure on the same chlorite sample (Zanazzi *et al.*, 2006, 2007) confirms that the response of the structure to T and P is only approximately opposite. In fact the structural deformation induced by pressure affects mainly the interlayer region related to the increase of hydrogen bond lengths, which determine the anisotropy in the compressibility of lattice parameters. On the other hand the thermal expansion is almost the same for all lattice parameters.

Moreover, looking more in detail to the evolution of the four M polyhedra with P and T , we observed that whereas M1 and M2 are the most compressible polyhedra (Zanazzi *et al.*, 2007) these polyhedra remain almost unchanged with temperature increase while M3 and M4 are the most expandable polyhedra.

This behaviour is a quite common feature in minerals: taking into account polyhedra with about the same chemical content, large polyhedra are more compressible with respect to smaller polyhedra (*e.g.*, M1 and M2 with respect M3 and M4) but with temperature increase, the larger polyhedra have a smaller thermal expansion with respect to the smaller ones. This effect is likely related to the asymmetry of potential energy curve.

However, chlorite is one of the few minerals for which complete single-crystal X-ray diffraction data at high P and high T are available on the same sample. These data allow determination of the evolution of the cell volume under different P - T conditions. In particular by combining the effects of T and P , it is possible to formulate the following approximate equation of state $V = V_0 (1 - 1.14 \times 10^{-2} \Delta P(\text{GPa}) + 3.07 \times 10^{-5} \Delta T(^{\circ}\text{C}))$. The equation is valid for the triclinic polytype of clinocllore.

4. Conclusions

The above results show the high influence of composition on thermal behaviour of chlorite. However, the crystal-chemical mechanism that constrains the behaviour at HT is not yet well understood, and seems to be more complex than simply related to the Fe content, according to the Nelson & Guggenheim (1993) hypothesis. It is well known from the literature that the HT-dependent Fe oxidation itself may be accompanied by loss of hydrogen and/or cation vacancies. A thorough comprehension of such mechanism needs other parameters, such as local order-disorder and structural vacancies, to be taken into account. Therefore, further work on compositionally different samples is required to unravel the role of the various factors on chlorite thermal expansion.

Acknowledgements: We thank Drs. Dapiaggi and Gatta of Milan University for the HT powder diffraction data. Formal reviews by Joseph R. Smyth and Marcello Mellini improved the manuscript and are gratefully acknowledged. This work was funded by M.I.U.R., P.R.I.N. 2006 project “Studi sperimentali su materiali geologici alle alte pressioni e temperature”, grant to P.F.Z.

References

- Andreozzi, G.B., Bosi, F., Longo, M. (2008): Linking Mössbauer and structural parameters in elbaite-schorl-dravite tourmalines. *Am. Mineral.*, **93**, 658–666.
- Bailey, S.W. (1988): Chlorites: structures and crystal chemistry. in “Hydrous Phyllosilicates (Exclusive of Micas)”, S.W. Bailey, ed. *Rev. Mineral.*, **19**, 347–403. Mineralogical Society of America and Geochemical Society, Washington, U.S.A.
- Comodi, P. & Zanazzi, P.F. (1993): Structural study of ellenbergerite. Part I: effects of high temperature. *Eur. J. Mineral.*, **5**, 819–829.
- Dapiaggi, M., Artioli, G., Petras, L. (2002): A newly developed high temperature chamber for *in-situ* X-ray diffraction: setup and calibration procedures. *Rigaku J.*, **19**, 35–41.
- De Grave, E. & Van Alboom, A. (1991): Evaluation of ferrous and ferric Mössbauer fractions. *Phys. Chem. Minerals*, **18**, 337–342.
- Dollase, W.A. (1986): Correction of intensities for preferred orientation in powder diffractometry: application of the March model. *J. Appl. Crystallogr.*, **19**, 267–272.
- Eeckhout, S.G. & De Grave, E. (2003): Evaluation of ferrous and ferric Mössbauer fractions. Part II. *Phys. Chem. Minerals*, **30**, 142–146.
- Fumagalli, P. & Poli, S. (2005): Experimentally determined phase relations in hydrous peridotites to 6.5 GPa and their consequences on the dynamics of subduction zones. *J. Petrol.*, **46**, 3, 555–578.
- Hazen, R.M. & Burnham, C.W. (1973): The crystal structure of one layer phlogopite and annite. *Am. Mineral.*, **58**, 889–900.
- Joswig, W. & Fuess, H. (1989): Neutron diffraction study of a one-layer monoclinic chlorite. *Clays Clay Miner.*, **37**, 511–514.

- , — (1990): Refinement of a one-layer triclinic chlorite. *Clays Clay Miner.*, **38**, 216–218.
- Joswig, W., Fuess, H., Rothbauer, R., Takeuchi, Y., Mason, S.A. (1980): A neutron diffraction study of a one-layer triclinic chlorite (penninite). *Am. Mineral.*, **65**, 349–352.
- Kleppe, A.K., Jephcoat, A.P., Welch, M.D. (2003): The effect of pressure upon hydrogen bonding in chlorite: a Raman spectroscopic study of clinocllore to 26.5 GPa. *Am. Mineral.*, **88**, 567–573.
- Lagarec, K. & Rancourt, D.G. (1998): RECOIL. Mössbauer spectral analysis software for Windows, version 1.0. Department of Physics, University of Ottawa, Canada.
- Larson, A.C. & Von Dreele, R.B. (2001): GSAS: general structure analysis system. Report LAUR 86–748, Los Alamos National Laboratory, New Mexico, USA.
- Le Bail, A., Duroy, H., Fourquet, J.L. (1988): Ab-initio structure determination of LiSbWO_6 by X-ray powder diffraction. *Math. Res. Bull.*, **23**, 447–452.
- Lehman, M.S. & Larsen, F.K. (1974): A method for location of the peaks in step-scan-measured Bragg reflexions. *Acta Crystallogr.*, **A30**, 580–584.
- Long, G.J., Cranshaw, T.E., Longworth, G. (1983): The ideal Mössbauer effect absorber thickness. *Mössbauer Effect Ref. Data J.*, **6**, 42–49.
- Nelson, D.O. & Guggenheim, S. (1993): Inferred limitations to the oxidation of Fe in chlorite: a high-temperature single-crystal X-ray study. *Am. Mineral.*, **78**, 1197–1207.
- North, A.C.T., Phillips, D.C., Mathews, F.S. (1968): A semiempirical method of absorption correction. *Acta Crystallogr.*, **A24**, 351–359.
- Pathak, P.D. & Vasavada, N.G. (1970): Thermal expansion of NaCl, KCl and CsBr by X-ray diffraction and the law of corresponding states. *Acta Crystallogr.*, **A26**, 655–658.
- Pawley, A.R., Clark, S.M., Chinnery, N.J. (2002): Equation of state measurements of chlorite, pyrophyllite, and talc. *Am. Mineral.*, **87**, 1172–1182.
- Phillips, T.L., Loveless, J.K., Bailey, S.W. (1980): Cr^{3+} coordination in chlorites: a structural study of ten chromian chlorites. *Am. Mineral.*, **65**, 112–122.
- Robinson, K., Gibbs, G.V., Ribbe, P.H. (1971): Quadratic elongation, a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 191–193.
- Rule, A.C. & Bailey, S.W. (1987): Refinement of the crystal structure of a monoclinic ferroan clinocllore. *Clays Clay Miner.*, **35**, 129–138.
- Sheldrick, G.M. (1997): SHELX-97. Programs for crystal structure determination and refinement. Institut für Anorganische Chemie, University of Göttingen, Germany.
- Smyth, J.R., Darby Dyar, M., May, M.M., Bricker, O.P., Acker, J.G. (1997): Crystal structure refinement and Mossbauer spectroscopy of an ordered, triclinic clinocllore. *Clays Clay Miner.*, **45**, 544–550.
- Spandler, C., Hermann, J., Faure, K., Mavrogenes, J.A., Arculus, R.J. (2008): The importance of talc and chlorite ‘hybrid’ rocks for volatile recycling through subduction zones; evidence from the high-pressure subduction mélange of New Caledonia. *Contrib. Mineral. Petrol.*, **155**, 181–198.
- Steinfink, H. (1958): The crystal structure of chlorite. II. A triclinic polymorph. *Acta Crystallogr.*, **11**, 195–198.
- Symmes, G.H. (1986): The thermal expansion of natural muscovite, paragonite, margarite, pyrophyllite, phlogopite and two chlorites: the significance of high T/P volume studies on calculated phase equilibria. B.A. thesis, Amherst College, Amherst, Massachusetts.
- Tutti, F., Dubrovinsky, L.S., Nygren, M. (2000): High temperature study and thermal expansion of phlogopite. *Phys. Chem. Minerals*, **27**, 599–603.
- Ventrucci, G., Zema, M., Scordari, F., Pedrazzi, G. (2008): Thermal behavior of a Ti-rich phlogopite from Mt. Vulture (Potenza, Italy): an in situ X-ray single-crystal diffraction study. *Am. Mineral.*, **93**, 632–648.
- Welch, M.D. & Crichton, W.A. (2002): Compressibility of clinocllore to 8 GPa at 298 K and a comparison with micas. *Eur. J. Mineral.*, **14**, 561–565.
- Welch, M.D. & Marshall, W.G. (2001): High-pressure behavior of clinocllore. *Am. Mineral.*, **86**, 1380–1386.
- Welch, M.D., Kleppe, A.K., Jephcoat, A.P. (2004): Novel high-pressure behavior in chlorite: a synchrotron XRD study of clinocllore to 27 GPa. *Am. Mineral.*, **89**, 1337–1340.
- Wilson, A.J.C. & Prince, E., eds. (1999): International tables for X-ray crystallography, volume C: mathematical, physical and chemical tables, 2nd edn. Kluwer Academic, Dordrecht, NL.
- Zanazzi, P.F., Montagnoli, M., Nazzareni, S., Comodi, P. (2006): Structural effects of pressure on triclinic chlorite: a single-crystal study. *Am. Mineral.*, **91**, 1871–1878.
- , —, — (2007): Structural effects of pressure on monoclinic chlorite: a single-crystal study. *Am. Mineral.*, **92**, 655–661.
- Zheng, H. & Bailey, S.W. (1989): Structures of intergrown triclinic and monoclinic IIB chlorites from Kenya. *Clays Clay Miner.*, **37**, 308–316.

Received 25 November 2008

Modified version received 19 December 2008

Accepted 30 January 2009