Structural effects of pressure on triclinic chlorite: A single-crystal study

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ABSTRACT

We present the results of a single-crystal X-ray diffraction structural study of chlorite in a diamond anvil cell up to 5.47 GPa. The sample is a clinochlore from Val Malenco, Italy, triclinic polytype IIb-4, S.G. Ct, with pseudomonoclinic metric and composition (Mg9.14Fe2+1.68)3(Si6.32Al1.02)O10(OH)16. Structural refinements were performed at several pressures with intensity data collected on a CCD diffractometer. Unit-cell parameters were accurately measured with the point-detector mounted on the same instrument.

The bulk modulus of chlorite fitting data to a third-order Birch-Murnaghan equation of state is $K_0 = 88(5)$ GPa with $K’ = 5(3)$. Results are in fair agreement with data based on powder neutron and synchrotron diffraction methods. The axial compressibility values were $\beta_{0a} = 3.4(2)$, $\beta_{0b} = 3.4(1)$, and $\beta_{0c} = 5.4(2) \times 10^{-1}$ GPa$^{-1}$. The metric of the lattice remains triclinic in the investigated pressure range. Axial anisotropy is strongly reduced with respect to the axial compressibilities observed in other phyllosilicates. Comparison of structural refinements at different pressures shows that the main structural deformations affect the interlayer region, where the hydrogen bonds are relevant to the structural properties of the phase. The mean decrease of the OH-O distances is about 10% from ambient pressure to ~5 GPa.

Compressibility data may be combined with those on thermal expansion to formulate an equation of state for chlorite. Taking into account the thermal expansion coefficient reported in literature for a chlorite with a composition quite similar to that of our sample, we can write the equation: $V = V_0 (1 – 1.14 \times 10^{-2} \Delta P + 2.316 \times 10^{-5} \Delta T)$, where $P$ is in GPa and $T$ in Celsius. Assuming an average rock density of 2.7 g/cm$^3$, this corresponds to an isochoric $P$-$T$ geothermal gradient of 18 °C/km.

Keywords: Chlorite, compressibility, equation of state, high pressure

INTRODUCTION

In the recent years, many authors have been interested in the stability range and decomposition of chlorite, because this mineral is among the hydrous phases having a role in the upper mantle mass transport and melting processes. Provided enough aluminum is present in descending material (such as the pelitic oceanic sediment), H$_2$O can be stored in hydrous minerals as lawsonite, staurolite, epidote, and chlorite (Poli and Schmidt 2002), other than in serpentine (Ulmer and Trommsdorff 1995). As a consequence, the breakdown of these phases will determine the actual dehydration of the slab. Chlorite contains around 13 wt% of water and also in a limited amount could strongly influence the slab buoyancy. There are few experimental studies on the stability conditions of chlorite. The most thermally stable chlorite composition is clinochlore, nominally Mg$_3$Al$_2$Si$_4$O$_{10}$(OH)$_6$, but many compositions show both Tschermak’s and Fe-Mg substitution.

Recently, petrological experiments (Fumagalli and Poli 2005) in the Na$_2$O-CaO-FeO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O (NCFMASH) found that the presence of Fe shifts the thermal stability of chlorite toward lower temperatures, as compared with phase equilibria in the simpler system MASH. Pawley (2003) has recently bracketed the reaction clinochlore + enstatite = forsterite + pyrope + H$_2$O up to 5 GPa. At $P/T$ higher than 4.8 GPa and 680 °C, an Al-bearing 10 Å phase was found to grow at the expense of chlorite (Fumagalli and Poli 2005), defining a new reaction leading to the disappearance of chlorite. As a consequence, the reaction involving chlorite and 10 Å phase should represent a critical step in the generation of fluids relevant for arc-magmatism.

Chlorite is a widespread family of di- and trioctahedral layer silicates. The trioctahedral chlorite structure can be described as formed by double layers of talc-type, negatively charged 2:1 layers, with ideal composition $(R^{2+},R^{3+})(Si_{4-x}Al_x)O_{10}(OH)_2$ separated by interlayer brucite-type octahedral layers [positively charged, with composition $(R^{2+},R^{3+})(OH)_2$] (Bailey 1988). The electrostatic interactions and a system of hydrogen bonding between T-O-T layer and O-interlayer contribute to the stability of the structure. Different T-O-T and O layer sequences are possible, creating a large number of different polytypes (Bailey 1988). The triclinic IIb-4 polytype, with symmetry $CT$, and the monoclinic IIb-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 and Bailey 1989; Joswig and Fuess 1990; Neutron diffraction: Joswig et al. 1980). The monoclinic structure was...

In view of chlorite being a major carrier of water in subducting slabs, it is important to know the stability field of this hydrous phase by studying its compressibility and pressure dependence of its crystal structure. Hazen and Finger (1978) based on only two data points at pressure carried out a pioneering single-crystal study on the behavior of chlorite up to 4 GPa, but the reliability of their results was hindered by the poor quality of the sample. To date, no other high-pressure single-crystal study has been reported, likely owing to the difficulty in finding suitable samples. Chlorite natural crystals are normally affected by stacking disorder and intergrowths, which make difficult to obtain reliable results. Welch and Marshall (2001) performed neutron high-pressure powder diffraction experiments on synthetic monoclinic clinochlore. Welch and Crichton (2002) determined the compressibility of synthetic IIb-clinochlore (metronically monoclinic) up to 8 GPa with synchrotron powder data. Kleppe et al. (2003) studied the effect of pressure on the hydrogen bonding system of chlorite with Raman spectroscopy up to 26.5 GPa.

On the basis of the abrupt change in the frequency of the OH range 5–25° and are reported in Table 2. The calculated density, assuming Z = 1, is $d_e = 2.70$ g/cm³. The crystal structure refinement was carried out with anisotropic displacement parameters using the SHELX-97 program (Sheldrick 1997), starting from the atomic coordinates of Joswig and Fuess (1990). Neutral atomic scattering factors and $\Delta f, \Delta f'$ coefficients from International Tables for Crystallography (Wilson and Prince 1999) were used. Full occupancy was assumed for all cation sites. The electronic density in the octahedral cation sites was accounted for by fitting the scattering factor curves of Mg and Fe with variable occupancy, and that of tetrahedral sites with the curves of Si and Al. The resulting sum of electrons in the cell was 157.2 and 109.3 e⁻ for octahedral and tetrahedral sites, in good agreement with data calculated on the basis of the chemical analysis (159.8 and 110.3 e⁻, respectively). The hydrogen atoms were localized in the difference electronic density map and included in the last cycles of refinement with equal isotropic atomic displacement factors and constraining the bond distance from the oxygen to 0.85 ± 0.05 Å. Their positions are reasonably close to those from neutron data refinement of Joswig et al. (1980). At the end of the refinement, no peak larger than 0.9 e/Å³ was present in the final difference Fourier synthesis. Table 3 lists the observed and calculated structure factors. The atomic coordinates are listed in Table 4.

**HIGH-PRESSURE EXPERIMENTS**

For the high-pressure crystal-structure refinements, a chlorite sample (sample 1) with a chip of Sm²⁺:BaFCl and a fragment of α-quartz, was mounted in a Meruel-Basset diamond anvil cell (DAC), equipped with type-I diamonds with 800-µm cuvet face diameter. The pressure chamber was a 380-µm diameter hole, made by spark erosion on a 250-µm thick steel Inconel 750X gasket pretrained to 180 µm. A methanol-ethanol mixture (4:1) was used as hydrostatic pressure-transmitting medium. The wavelength shift of the 6876 Å Sm³⁺ fluorescence line was measured

**EXPERIMENTAL METHODS**

A natural IIb-4 chlorite from Alpe Reguzzolo, Val Malenco (Italy), kindly supplied by the Mineralogy Museum of Florence University (no. 13087/626), was selected for high-pressure X-ray diffraction experiments. The samples are green platy crystals; their chemical composition was determined using an electron microprobe Cameca SX50 (IGG-section of Padova) by averaging seven spot analyses to obtain the formula:

$$\text{(Mg}_{0.88}\text{Fe}_{0.12}\text{Mn}_{0.03}\text{Ti}_{0.03}\text{Al}_{0.56}\text{Si}_{0.24}\text{Al}_{0.62}\text{O}_{10} (\text{OH})_{2}).$$

This composition corresponds to a clinochlore, following the terminology of Bayliss (1975).

For the refinement at room conditions, a triclinic crystal (0.12 $\times$ 0.08 $\times$ 0.01 mm in size) was mounted on a XCALIBUR (Oxford Diff.) diffractometer equipped with both CCD area and point detectors, operating at 50 kV and 40 mA, and using graphite monochromated Mo radiation ($\lambda, K = 0.7093$ Å). Diffraction data were first collected at room conditions with the area detector from the crystal in air. To maximize the reciprocal space coverage, a combination of $\omega$ and $\theta$ scans was used, with a step size of 0.4° and a time of 30 s/frame for a total of 1800 frames. Data were corrected for absorption with the program SADABS (Sheldrick 1996). Details of data collection and refinement are reported in Table 1. The unit-cell parameters were accurately measured by using the point detector and calculated by the least-squares fit of Bragg angles for about forty selected reflections in the θ range 5–25° and are reported in Table 2. The calculated density, assuming $Z = 1$, is $d_e = 2.70$ g/cm³. The crystal structure refinement was carried out with anisotropic displacement parameters using the SHELX-97 program (Sheldrick 1997), starting from the atomic coordinates of Joswig and Fuess (1990). Neutral atomic scattering factors and $\Delta f, \Delta f'$ coefficients from International Tables for Crystallography (Wilson and Prince 1999) were used. Full occupancy was assumed for all cation sites. The electronic density in the octahedral cation sites was accounted for by fitting the scattering factor curves of Mg and Fe with variable occupancy, and that of tetrahedral sites with the curves of Si and Al. The resulting sum of electrons in the cell was 157.2 and 109.3 e⁻ for octahedral and tetrahedral sites, in good agreement with data calculated on the basis of the chemical analysis (159.8 and 110.3 e⁻, respectively). The hydrogen atoms were localized in the difference electronic density map and included in the last cycles of refinement with equal isotropic atomic displacement factors and constraining the bond distance from the oxygen to 0.85 ± 0.05 Å. Their positions are reasonably close to those from neutron data refinement of Joswig et al. (1980). At the end of the refinement, no peak larger than 0.9 e/Å³ was present in the final difference Fourier synthesis. Table 3 lists the observed and calculated structure factors. The atomic coordinates are listed in Table 4.

**TABLE 1. Details of data collection and refinement at various pressures**

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$\theta$-range</th>
<th>No. measured reflections</th>
<th>No. independent reflections</th>
<th>$R_f, R_w$</th>
<th>$R_%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000*</td>
<td>3–35°</td>
<td>4592</td>
<td>2135</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>1.83</td>
<td>5.298(3)</td>
<td>9.183(4)</td>
<td>14.23(2)</td>
<td>90.22(7)</td>
<td>97.21(7)</td>
</tr>
<tr>
<td>2.62</td>
<td>5.307(4)</td>
<td>9.201(5)</td>
<td>14.28(2)</td>
<td>90.22(8)</td>
<td>97.14(8)</td>
</tr>
<tr>
<td>3.14</td>
<td>5.329(3)</td>
<td>9.222(4)</td>
<td>14.36(1)</td>
<td>90.30(6)</td>
<td>97.17(6)</td>
</tr>
<tr>
<td>3.55</td>
<td>5.352(3)</td>
<td>9.244(5)</td>
<td>14.41(1)</td>
<td>90.35(6)</td>
<td>97.20(6)</td>
</tr>
</tbody>
</table>

* Data collected with the sample in air.

**TABLE 2. Unit-cell parameters at different pressures**

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
<th>$V$(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>5.317(1)</td>
<td>9.214(1)</td>
<td>14.333(6)</td>
<td>90.1(3)</td>
<td>97.1(3)</td>
<td>89.97(2)</td>
<td>696.5(1)</td>
</tr>
<tr>
<td>1.65</td>
<td>5.303(07)</td>
<td>9.189(1)</td>
<td>14.270(5)</td>
<td>90.0(3)</td>
<td>97.2(3)</td>
<td>89.96(1)</td>
<td>689.2(2)</td>
</tr>
<tr>
<td>2.62</td>
<td>5.288(1)</td>
<td>9.164(1)</td>
<td>14.203(5)</td>
<td>90.0(3)</td>
<td>97.3(3)</td>
<td>89.95(1)</td>
<td>682.9(1)</td>
</tr>
<tr>
<td>3.24</td>
<td>5.277(1)</td>
<td>9.141(2)</td>
<td>14.163(5)</td>
<td>90.1(4)</td>
<td>97.2(4)</td>
<td>89.97(1)</td>
<td>677.8(1)</td>
</tr>
<tr>
<td>4.25</td>
<td>5.261(8)</td>
<td>9.114(1)</td>
<td>14.106(5)</td>
<td>90.2(3)</td>
<td>97.2(3)</td>
<td>89.97(1)</td>
<td>671.1(1)</td>
</tr>
<tr>
<td>4.85</td>
<td>5.252(3)</td>
<td>9.106(5)</td>
<td>14.113(1)</td>
<td>90.0(3)</td>
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<td>89.93(5)</td>
<td>669.3(5)</td>
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<tr>
<td>5.47</td>
<td>5.24(1)</td>
<td>9.112(6)</td>
<td>14.065(9)</td>
<td>90.0(3)</td>
<td>97.5(3)</td>
<td>89.92(2)</td>
<td>665.6(6)</td>
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* Data collected with the sample in air.
and 80 in the powder rings of the beryllium disks, the Sm2+:BaClF and quartz used as pressure positions with other phases present in the cell, namely the two diamonds, the severe signs of damage, with streaked re
crystal was recovered and examined in air at room conditions: the sample showed
were accurately measured with the point detector. Several re
detector, then corrected for absorption using Absorb V6.0 software (Angel 2004). Budzianowski and Katrusiak (2004). Intensity data were collected with the CCD
range 10–4–5.5 GPa. Higher pressure was hindered by failure of the gasket. The
for an approximate estimate of the pressure (Comodi and Zanazzi 1993); the quartz
were scattered and with large e.s.d. values, preventing reliable conclusions on the
Notes: For each atom values from top to bottom correspond to the refinements at 0.0001, 1.83, 3, 14, 4.25, and 4.85 GPa. The H positions are those from the refine-
ment in air. The occupancy of Mg against Fe in M sites in air refined to 0.905(2), 0.907(3), 0.936(3), and 0.938(3) Mg atoms for M1, M2, M3, and M4, respectively.
The occupancy of Si against Al in T sites refined to 0.654(4) and 0.652(4) for T1 and T2, respectively. Estimated standard deviations refer to the last digit.

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TABLE 4.—Continued

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq) iso (Å^2)</th>
</tr>
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<td>OH1</td>
<td>0.6913(3)</td>
<td>0.3335(1)</td>
<td>0.0734(8)</td>
<td>0.0098(2)</td>
</tr>
<tr>
<td>OH2</td>
<td>0.6905(9)</td>
<td>0.3331(5)</td>
<td>0.0771(1)</td>
<td>0.0061(1)</td>
</tr>
<tr>
<td>OH3</td>
<td>0.6921(9)</td>
<td>0.3331(6)</td>
<td>0.0781(1)</td>
<td>0.0053(3)</td>
</tr>
<tr>
<td>OH4</td>
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<td>0.3323(7)</td>
<td>0.0822(2)</td>
<td>0.0062(2)</td>
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<tr>
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<td>0.014(1)</td>
<td>0.0065(2)</td>
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<td>0.6971(3)</td>
<td>0.3430(8)</td>
<td>0.017(3)</td>
<td>0.0065(2)</td>
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</table>

Notes: For each atom values from top to bottom correspond to the refinements at 0.0001, 1.83, 3, 14, 4.25, and 4.85 GPa. The H positions are those from the refine-
ment in air. The occupancy of Mg against Fe in M sites in air refined to 0.905(2), 0.907(3), 0.936(3), and 0.938(3) Mg atoms for M1, M2, M3, and M4, respectively.
The occupancy of Si against Al in T sites refined to 0.654(4) and 0.652(4) for T1 and T2, respectively. Estimated standard deviations refer to the last digit.

RESULTS

Results of the refinement at room pressure

The structural results of the refinement are in very good agreement
with literature data. In particular, the partial ordering of

1 Deposit item AM-06-032, Table 3, observed and calculated structure factors. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
trivalent cations in the brucite-type layer with preference for the M4 site, as suggested for triclinic chlorites by Joswig and Fuess (1990) and Joswig et al. (1980). M4-O mean bond length is 2.021 Å, while M3-O is 2.041 Å, and M1-O and M2-O are 2.079 and 2.079 Å, respectively. The Si and Al in tetrahedra are disordered, T1-O and T2-O mean bond lengths being 1.650 Å, with equal Si/Al occupancy. The tetrahedral rotation angle $\phi$, defined as the difference between 120° and the $\Phi$ angles formed by the basal O-O edges of adjacent tetrahedra ($2\pi = \sum_{i=1}^{n} (120° - \Phi_i)/\Phi_i$; Weis et al. 1992), is 6.1°. The three OH groups of the brucite-type layer are involved as donors in H-bonds with the basal O atoms of the tetrahedral sheet. The O-O distances are 2.919, 2.918, and 2.908 Å, respectively for the OH2-O5, OH3-O4-O4 interactions. Table 5 lists bond distances and geometrical parameters.

**Compressibility**

The unit-cell parameters at various pressures are listed in Table 2 and shown in Figure 1. A third-order Birch-Murnaghan Equation of State (EoS) is the best approximation to describe the chlorine volume evolution with $P$, as suggested by plotting the “normalized stress” vs. the Eulerian strain (Jeanloz and Hansen 1991; Angel 2000, 2001) (Fig. 2). The refined EoS parameters are $V_0 = 701.8(1)$ Å$^3$, very close to the measured value (Table 2), $K_0 = 88(5)$ GPa and $K' = 5(3)$. Weighted $\chi^2$ is 4.4, maximum $\Delta P$ is 0.2 GPa. The value of bulk modulus obtained by fitting data with a 2nd-order EoS ($K'$ fixed to 4) is 89(3) GPa.

Compressibility data for chlorine in literature are quite scattered. Excluding the Hazen and Finger (1978) value (55 GPa) for the reasons already described, the bulk moduli determined from both natural and synthetic chlorite are $K_0 = 69(1)$ GPa (synthetic chamosite, EDS synchrotron data, Theye et al. 2003); 75.4(2.7) GPa (synthetic chinochlor, neutron powder-diffraction, Welch and Marshall 2001); 77.6(1.1) GPa (synthetic chinochlor, Grevel et al. 1997); 78.6(1.2) GPa (natural chinochlor, Theye et al. 2003); 81.0(5) GPa (synthetic chinochlor, synchrotron powder-diffraction data, Welch and Crichton 2002); 83.4(7) GPa for Mg-chlorite, 89.5(27) GPa for synthetic clinochlore, 84.1(18) GPa for Fe-chlorite (EDS synchrotron data, Pawley et al. 2002); 91.1(3.9) GPa (natural chamosite, Theye et al. 2003).

All these values were obtained for second order fits ($K' = 4$) and constraining the lattice to monoclinic symmetry, or occasionally to hexagonal symmetry (Theye et al. 2003). The data of Welch and Crichton (2002) and Pawley et al. (2002) show the better agreement with our data (difference less than 1.2%). Main differences between our data and those in literature may arise from the different methodologies employed, single-crystal vs. powder diffraction, and the nature of the samples. In any case, the value of bulk modulus of 47.2 GPa in the databases of Berman (1988) and Holland and Powell (1998) should be revised.

Chlorite is stiffer than other layer structures, when its bulk modulus is compared to those of other phyllosilicates such as talc (41.6 GPa, Pawley et al. 1995) and micas [54 GPa in phlogopite, Comodi et al. 2004; in the range 52–61 GPa in 2M1, muscovites, 58–62 GPa in 2M2, and 37 phengites, 66 GPa in paragonite, see Table 1 in Zanazzi and Pavese (2002) and references therein], or with brucite (47 GPa, Parise et al. 1994; 41 GPa, Catti et al. 1995; 44 GPa, Nagai et al. 2000).

**TABLE 5.** Values of bond distances (Å), polyhedral volumes (Å$^3$), and distortion parameters (following Robinson et al. 1971) at various pressures

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>0.001</th>
<th>1.83</th>
<th>3.14</th>
<th>4.25</th>
<th>4.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$b_0$</td>
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</tr>
<tr>
<td>$c_0$</td>
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<td></td>
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</tr>
<tr>
<td>$\beta_0$</td>
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<tr>
<td>$\Sigma$</td>
<td></td>
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<tr>
<td>$\Delta$</td>
<td></td>
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</tbody>
</table>

Notes: Estimated standard deviations refer to the last digit.

* is the angle variance (deg).† is the quadratic elongation.

The “axial moduli” were obtained by fitting a 2nd-order Birch-Murnaghan EoS for the $a$ and $b$ axes and a 3rd-order Birch-Murnaghan EoS for the $c$ axis, giving $a_0 = 5.332(1)$ Å, $K_0 = 99(2)$
GPAs: \( b_0 = 9.239(2) \) Å, \( K_0 = 97(2) \) GPAs; \( c_0 = 14.387(6) \) Å, \( K_0 = 62(7) \) GPAs, and \( K' = 5(3) \) values. The axial compressibility values (inverse of axial moduli divided by three), were \( \beta_{0a} = 3.4(2) \), \( \beta_{0b} = 3.4(1) \), and \( \beta_{0c} = 5.4(2) \times 10^{-3} \) GPa\(^{-1} \). The chlorite behavior is not unlike other phyllosilicates and micas, in that the \( c \) axis is most affected by pressure, due to the layered nature of these phases. Along the [0 0 1] direction chlorite is about 2 and 2.5 times less compressible than talc and phlogopite; micas shows the highest \( \beta_{0c} \) (13.3 \( \times 10^{-3} \) GPa\(^{-1} \), Comodi et al. 2004). However, chlorite has a greater compressibility in the \( a-b \) plane, with respect to other layer silicates; i.e., in phlogopite the axial compressibilities along \( a \) and \( b \) are 2.7 and 2.6 \( \times 10^{-3} \) GPa\(^{-1} \). Therefore the chlorite structure behaves anisotropically with pressure, but to a lesser extent than other layer silicates.

The lattice retains triclinic symmetry over the studied pressure range. The cell angle \( \gamma \) does not vary significantly, \( \alpha \) slightly decreases, whereas \( \beta \) slightly increases (Fig. 3). A similar behavior was observed in phlogopite (Comodi et al. 2004) and talc in experimental (Pawley et al. 1995) and theoretical (Stixrude 2002) studies.

**Figure 1.** Variations of unit-cell parameters of chlorite as a function of pressure. Solid curves represent the Birch-Murnaghan EoS best fit.

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**Structural evolution with \( P \)**

The stacking sequence of chlorite is characterized by 2:1 talc- and brucite-type layers, each contributing in a different way to the structural behavior at pressure. Table 5 lists the bond distances, as well as some geometrical parameters. We analyze how each chlorite polyhedron of the different layers is modified with increasing pressure. The octahedra of both talc- and brucite-type layers tilt and become more regular with pressure, as shown by the angle variance values (Robinson et al. 1971) reported in Table 5. Moreover, pressure dependence of the \( \psi \) angle (the angle between the body diagonal of the octahedron and the vertical, Bailey 1988), shows that the flattening of the octahedra decreases with \( P \) (Fig. 4), leading to a regularization and to an increase in the volume of the octahedron. As a consequence, a thickening along \( c^* \) and a reduction in the \( a-b \) plane of the octahedral sheet is achieved; the same mechanism was also observed in brucite (Parise et al. 1994; Nagai et al. 2000). On the contrary, tetrahedra distortion increases with \( P \) (Fig. 5), the tetrahedral thickness remains almost unchanged and the tetrahedral volumes slightly
decrease (Table 5). The tetrahedral distortion at high pressure could be also ascribed to the increased hydrogen bond strength between the OH of the brucite-type layer and the basal O of the tetrahedral sheet (Fig. 6).

On the whole, the polyhedral distortion with $P$ can explain the apparent anomalous result observed in the evolution of the volume of octahedra and tetrahedra: the volume slightly increases in the former and decreases in the latter, according to the general rule that regular polyhedra have the maximum volume with respect to any distorted polyhedra.

As in all layer silicates, to achieve dimensional matching of the relatively incompressible tetrahedral sheet with the more laterally compressible octahedral sheet, an increase of the ditrigonalization $\alpha$ of the six-member tetrahedral rings is required. In chlorite, $\alpha$ increases with pressure from 6.1 to 9.1° and this ditrigonalization reflects both the requirement for TOT misfit and the strengthening of OH-O hydrogen bonds, due to the thinning of the interlayer and the shortening of the O-O distances with $P$ (Figs. 6 and 7).

The interlayer region faces the talc-type to the brucite-type layer; here the hydrogen bonds formed between the layers affect the structural properties of the phase. In fact, in the studied pressure range the thickness of the brucite-type sheet increases by 11.5% whereas the T-O-T thickness increases by only 1.8%. On the contrary the interlayer is reduced of about 10%, and despite the increase in the thickness of brucite- and talc-type sheets, the greatest contraction of the structure is achieved normal to the sheets. Between 3.2 and 4.25 GPa the OH-O distance approaches the value of 2.7 Å, limit below which the O$_2$–O$_2$– are considered to be in contact (Brown 1976). Welch et al. (2004) suggested for clinochlore that this contact distance could be reached at about 8 GPa and after this pressure an anomalous structural behavior may occur. At 4.85 GPa however we found shorter O–O dis-
stances, in the range 2.66–2.58 Å (Fig. 6), without significant structure variations. When the 2.7 Å contact limit is reached, the main effect we find is the enhancement of the polyhedra distortion parameters, i.e., the tetrahedral angle variance (Fig. 5). Spectroscopic study by Kleppe et al. (2003) showed a strong discontinuity with a large increase in \( \frac{d\nu}{dP} \) for the OH mode of the brucite-type layer at 9–10 GPa. The high positive shifts of the O-H mode with \( P \) have been related by Hofmeister et al. (1999) to a H-H cation repulsion, which is a consequence of the decrease of the OH-O angle. Neutron diffraction data for clinochlore showed a considerable decrease in the OH-O angle from 170 to 155° (Welch and Marshall 2001), which is consistent with the in-plane movement of basal oxygen by an O-rotation of the tetrahedral ring (Fig. 7). The peculiar stiffer character of chlorite can be mainly ascribed to the narrower interlayer space due to non-superimposed cations across the interlayer. At high \( P \), the repulsive effects between OH and O caused by the interlayer shortening could explain the smaller compressibility along the \( c \) axis relative to other layer silicates, as well as the anisotropy in the cell deformation.

**DISCUSSION AND CONCLUSION**

To a first approximation, considering the structural effects of \( P \) and \( T \) to be approximately inversely related, we use our experimentally determined compressibility and thermal expansion from literature to define a \( P-V-T \) EoS. Pawley et al. (2002) suggested that the chemical substitutions in chlorite do not affect significantly the compressibility, in contrast to that observed for thermal behavior, which is strongly influenced by the Fe/Mg content (Symmes 1986). Nelson and Guggenheim (1993) obtained a thermal expansion coefficient for a chlorite having a composition quite similar to that of our sample. We combine this coefficient with our compressibility data to obtain the equation: \( V = V_0 (1 - 1.14 \times 10^{-2} \Delta P + 2.316 \times 10^{-5} \Delta T) \), where \( P \) is in GPa and \( T \) is in Celsius.

Using the EoS obtained in this study, we compute the thermal gradient for which the cell volume of chlorite is invariant. Assuming an average rock density of 2.7 g/cm\(^3\), the isochoric \( P-T \) path will correspond to a geothermal gradient of 18 °C/km, a value similar to that calculated for serpentine (20 °C/km, Mel-lini 2000). This gradient is compatible with a geotherm along an early subduction and slow convergence slab (Kincaid and Sacks 1997).

Since chlorite is involved in several phase-equilibrium reactions (i.e., with antigorite, amphibole, enstatite, 10 Å phase) an accurate evaluation of the bulk modulus is important in defining its behavior at HP. Its bulk modulus is higher than the other layer silicates, possibly because of the peculiar topology of the interlayer, where the OH-bonding system between the brucite- and talc-type layers makes the chlorite structure stiffer. The value of 88 GPa measured in this work is significantly different from the value 49.7 GPa reported in current databases (e.g., Holland and Powell 1998). The discussion of petrological phase equilibria is beyond the scope of this paper, but care should be taken when thermodynamic stability calculations are performed using current databases.

**ACKNOWLEDGMENTS**

This paper is dedicated to the memory of Charles V. Guidotti, a dear friend and colleague recently passed away. Charlie had a deep interest in merging petrology and crystal chemistry of phyllosilicates, trying to extend mineral properties at the atomic scale to the large scale events. The chlorite specimen was kindly supplied by G. Pratesi, Mineralogy Museum of the University of Florence. This research was

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