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The crystal structures and compressibilities of layer minerals at high pressure. II. Phlogopite and chlorite

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Abstract

Unit-cell dimensions of natural phlogopite from Franklin, New Jersey, have been determined at 1 atm and at 18, 35, and 47 kbar. The structure of phlogopite has been refined (wR = 14.7 percent) from three-dimensional X-ray diffraction data collected at 35 kbar, and is compared with previously published room-condition and high-temperature crystal-structure data. The change in unit-cell dimensions of monoclinic phlogopite between 1 atm and 47 kbar may be represented by a prolate spheroid, where compressibility perpendicular to the silicate layers is approximately five times the value within the layers. Mean metal–oxygen bond distances at 1 atm and 35 kbar, respectively, are 2.97 and 2.80A for inner K–O, 3.31 and 3.23A for outer K–O, 1.65 and 1.65A for (Si,Al)–O, 2.06 and 2.07A for M1–(O,F), and 2.06 and 2.03A for *M*2–(O,F). The weaker K–O bonds compress more than the average Mg–(O,F) bonds, which compress more than the (Si,Al)–O bonds.

Unit-cell dimensions of a natural II*b* type chlorite were measured at 1 atm and at 22 and 40 kbar. The strain ellipsoid of compression is a prolate spheroid with axial ratio 3:1 and maximum compression direction perpendicular to the layers. The large anisotropies in mica and chlorite compression are due to the difference in bonding within the 2:1 layers versus the bonding between these layers.

Introduction

Layer minerals have extremely anisotropic bonding characteristics that strongly affect the physical properties of these compounds (Hazen and Finger, 1978). A knowledge of anisotropies in physical properties is important in characterizing these minerals and may lead to a greater understanding of their interatomic forces. The objectives of this investigation, therefore, are to determine the pressure response of the structure of a trioctahedral mica and a chlorite and to relate this anisotropic response to the differences in bonding within and between 2:1 layers.

Experimental

Phlogopite

A crystal (100 × 80 × 35 μm) of phlogopite from Franklin, New Jersey, with the composition $(K_{0.76}Na_{0.16}Ba_{0.05}\square_{0.03})(Mg_{2.98}Fe_{0.01}Ti_{0.01})(Al_{1.05}Si_{2.95})O_{10}(F_{1.3}OH_{0.7})$, was selected from material described by Hazen and Burnham (1973). Unit-cell dimensions of this monoclinic *C*2/*m* mica were determined at 1 atm from least-squares refinement of twelve diffraction maxima positions on an automated four-circle Picker diffractometer using the method of Tichý (1970). Unit-cell dimensions are identical within experimental uncertainty (Table 1) to those determined by Hazen and Burnham (1973).

The crystal of phlogopite was mounted in a miniature diamond-anvil high-pressure cell (Merrill and Bassett, 1974), with an Inconel, type 750X (International Nickel Company, Inc.) gasket and 1:1 glycerin:water as the hydrostatic pressure medium. Procedures for centering the crystal, measuring unit-cell dimensions, correcting for diamond-cell X-ray absorption, and collecting X-ray diffraction intensities with an automated four-circle diffractometer are described by Finger and King (1978). Unit-cell dimensions were measured at 18, 35, and 47 (all ±1) kbar; pressure was calibrated using the shift in the R_1 fluorescence line of 10 μm ruby crystals in the cell. All accessible reflections from 0.1 to 0.7 sin θ/λ were collected, including 866 reflections of which 175 were nonequivalent observed ($I > 2\sigma$).[1] Intensities were

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[1] Tabulated observed and calculated structure factors are available from the authors on request.

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Table 1. Unit-cell dimensions of phlogopite and chlorite at several pressures

P (kbar)	a (A)	b (A)	c (A)	β (°)	Vol (A^3)
Phlogopite					
1 atm	5.3078(4)*	9.1901(5)	10.155(1)	100.08(1)	487.7(2)
18(1)	5.281(2)	9.141(2)	9.940(16)	100.01(8)	472.6(8)
35(1)	5.260(1)	9.100(1)	9.791(9)	100.68(4)	460.5(5)
47(1)	5.247(3)	9.072(3)	9.614(18)	100.75(9)	449.6(8)
Chlorite					
1 atm	5.366(2)	9.298(1)	14.205(7)	97.5(4)	702.6(4)
22(1)	5.313(8)	9.219(6)	13.9(1)	97.7(6)	675(6)
40(1)	5.28(1)	9.16(1)	13.6(1)	98.0(1.0)	652(10)

**Parenthesized figures represent esd's of least units cited.*

corrected for absorption by the pressure cell and by the specimen, and refinement was attained using program RFINE (Finger and Prince, 1975). Neutral scattering factors of Cromer and Mann (1968) and the anomalous scattering coefficients of Cromer and Liberman (1970) were used.

The peak-to-background intensities for phlogopite were low owing to the relatively low scattering power of the mineral, the small size of the crystal, the high absorption and general scattering of X-rays by the beryllium and diamond components of the pressure cell, and the diffuseness of observed diffraction maxima (presumably due to slight bends and edge defects common to single crystals of layer minerals). Furthermore, no reflections (*hkl*) with $|l| > 5$ could be collected because of the geometrical restrictions of the diamond cell (Finger and King, 1978). The high-pressure structure refinement is, consequently, of poor quality, with R = 15.3 percent (weighted R = 14.7 percent). A difference Fourier map, however, shows no major features.

Table 2. Electron microprobe analysis of Black Mountain chlorite*

Oxide	Wt. %	Number of ions**	
SiO_2	22.6	Si	4.92
TiO_2	0.06	Ti	0.01
Al_2O_3	23.4	Al	6.02
FeO†	33.9	Fe	6.18
MnO	0.16	Mn	0.03
MgO	8.69	Mg	2.84
CaO	0.04	Ca	0.01
Na_2O	0.00	Na	0.00
K_2O	0.00	K	0.00
H_2O††	11.2		

**Analysis of 20 points on two grains by Douglas Rumble III, Geophysical Laboratory.*

***Calculated on the basis of 20 cations.*

†Mössbauer spectroscopy of this chlorite by David Virgo, Geophysical Laboratory, suggests that greater than 95% iron is present as Fe^{2+}.

††Water content calculated by difference.

Chlorite

Specimens of chlorite from Black Mountain, Moosilauke Quadrangle, New Hampshire, were kindly provided by Dr. Douglas Rumble III. The composition of this material is $(Mg_{2.84}Fe_{6.18}Al_{2.94})(Al_{3.08}Si_{4.92})O_{20}(OH)_{16}$, as determined by electron microprobe analysis (Table 2). Unit-cell parameters, given in Table 1, were determined at 1 atm, 22 kbar, and 40 kbar; the chlorite is monoclinic, *C2/m*, and is a II*b* polytype, as described by Brown and Bailey (1962).

Results

Phlogopite

Unit-cell dimensions of phlogopite at four pressures appear in Table 1. The strain ellipsoid of compression (Ohashi and Burnham, 1973) obtained from the difference between unit cells at room pressure and 47 kbar is a prolate spheroid with the maximum compression direction perpendicular to the layers and a 5:1 axial compression ratio. The bulk modulus of phlogopite is 585 ± 20 kbar, which is significantly smaller than the 1 to 2 Mbar bulk moduli typical of most other silicates (Clark, 1966).

Atomic coordinates and selected interatomic dis-

Table 3. Atomic fractional coordinates and isotropic temperature factors of phlogopite at 35 kbar

Atom	*x*	*y*	*z*	*B*
T	0.573(4)*	0.1663(8)	0.212(5)	1.0(2)
M(1)	0	1/2	1/2	0.2(3)
M(2)	0	0.8316(14)	1/2	0.3(2)
K	0	0	0	1.2(3)
O(1)	0.821(4)	0.225(3)	0.156(5)	1.3†
O(2)	0.498(5)	0	0.156(5)	1.3†
O(3)	0.649(5)	0.166(2)	0.393(6)	0.6†
(F,OH)	0.124(6)	0	0.393(6)	0.8†

**Parenthesized figures represent esd's of least units cited.*
†Parameter fixed in refinement.

tances for phlogopite at 35 kbar are listed in Tables 3 and 4. Although errors of bond distances are large (± 1 percent), significant changes are observed with respect to the room-pressure structure (Hazen and Burnham, 1973). The greatest changes are associated with the interlayer potassium site; mean inner and outer K–O distances are, respectively, 2.969(1) and 3.312(2)A at room pressure, and 2.80(3) and 3.23(3)A at 35 kbar. The inner K–O bonds compress approximately 6 percent from 1 atm to 35 kbar, indicating an interlayer polyhedron bulk modulus of only 200 ± 30 kbar. This potassium site is the most compressible polyhedron yet observed in oxygen-based compounds.

The mean *M*(1)–(O,F) distance increases slightly, by less than half a standard deviation, whereas the *M*(2)–(O,F) site decreases from 2.063(1)A at 1 atm to 2.03(4)A at 35 kbar. The mean Mg–(O,F) distance of the two octahedra in phlogopite, therefore, decreases by less than one standard deviation, from 2.064(1)A at room pressure to 2.04(4)A at 35 kbar. The calculated magnesium octahedral bulk modulus is approximately 1200 ± 2000 kbar, which is consistent with previous experimental values (Hazen and Prewitt, 1977). Note, however, that the error associated with this calculated bulk modulus is greater than the bulk modulus itself, owing to the large high-pressure bond distance errors.

Within experimental error, no change is observed in the mean tetrahedral (Si,Al)–O distance between 1 atm and 35 kbar. Because the mean magnesium–oxygen distance decreases by only one standard deviation, it is not possible to determine from bond-distance data alone whether the silicon tetrahedron is less compressible than the mean magnesium octahedron. However, evidence that the tetrahedral bulk modulus is significantly greater than the octahedral bulk moduli is provided by the tetrahedral rotation angle, α. This angle changes from 7.5(1)° at 1 atm to 9.3(8)° at 35 kbar. The increase in α with pressure is a consequence of the greater compressibility of the octahedral layer compared with the tetrahedral layer (Hazen, 1977).

Chlorite

Unit-cell dimensions of chlorite at three pressures are listed in Table 1. Natural chlorites commonly have numerous crystal defects, including bends and stacking faults, that give rise to diffuse reflections. Errors in calculation of c and β unit-cell parameters consequently are large. It is, however, evident from data in Table 1 that chlorite and mica compression are similar. The chlorite strain ellipsoid of compression is a prolate spheroid with maximum compression perpendicular to the silicate layers and axial compression ratio of 3:1. The bulk modulus of this chlorite is 550 ± 100 kbar, which is similar to that observed for phlogopite.

Discussion

Comparison of high-pressure and high-temperature mica structures

Takeda and Morosin (1975) determined the crystal structure of a synthetic fluorphlogopite at 750°C. Changes of the phlogopite structure on compression are similar to those on cooling. The strain ellipsoid of compression, or of cooling, is a prolate spheroid with axial ratio 5:1 and the long axis perpendicular to the mica layers. The interlayer potassium site shows the greatest volume reduction, the magnesium octahedra have lesser volume decreases, and the tetrahedral site changes little. In both cases the tetrahedral rotation angle increases as the size of the octahedra decreases with respect to the tetrahedra. Thus, the trioctahedral

Table 4. Selected interatomic distances in phlogopite at 35 kbar

Bond		Distance (A)	Bond		Distance (A)
T-O(1)		1.60(2)*	M(2)-O(3)	[2]	1.94(5)
T-O(1)		1.67(2)	M(2)-O(3)	[2]	2.11(4)
T-O(2)		1.64(2)	M(2)-(F,OH)	[2]	1.98(4)
T-O(3)		1.68(8)	mean M(2)-(O,F)		2.03
mean T-O		1.65			
			K-O(1)	[4]	2.82(3)
T-T	[2]†	3.04(1)	K-O(2)	[2]	2.78(3)
T-T		3.04(1)	mean inner K-O		2.80
mean T-T		3.04			
			K-O(1)	[4]	3.22(3)
			K-O(2)	[2]	3.26(3)
M(1)-O(3)	[4]	2.11(4)	mean outer K-O		3.23
M(1)-(F,OH)	[2]	1.98(4)			
mean M(1)-(O,F)		2.07	Δ(K-O)		0.43

**Parenthesized figures represent esd's of least units cited.*
†Bracketed figures represent bond multiplicities.

mica phlogopite illustrates the "inverse relationship" (Hazen and Prewitt, 1977) between structural changes with temperature and pressure.

Bonding anisotropy in layer silicates

The anisotropic compressibilities of phlogopite and chlorite are a consequence of the weakness of interlayer K–O and Van der Waals and hydrogen bonds, respectively, relative to the shorter divalent, trivalent, and tetravalent cation–anion bonds within the talc-like and brucite-like layers. Compression within the layers (a and b axes) is restricted by the strength of the octahedral and tetrahedral sheets. The interlayer distances, on the other hand, are characterized by weaker bonds; therefore the c axes of mica and chlorite have large compressibilities.

The relative contributions of interlayer and intralayer volume changes to bulk compression of phlogopite may be calculated from the average z atomic fractional coordinates of O(1) and O(2). The intralayer volume is $(1 - 2z)\cdot a\cdot b\cdot c\cdot \sin\beta$, and the interlayer volume is $2z\cdot a\cdot b\cdot c\cdot \sin\beta$. At room pressure, intralayer and interlayer volumes are 324 and 164A^3, respectively; at 35 kbar they are 317 and 144A^3. The bulk modulus of the intralayer volume is 1600 ± 400 kbar, which is comparable to bulk moduli in garnets, olivines, pyroxenes, and other dense oxygen-based compounds (Clark, 1966). The interlayer bulk modulus, on the other hand, is less than 300 kbar. Seventy-five percent of the volume change of phlogopite with pressure is due to compression of this interlayer volume.

Conclusions

Previous studies on layer compounds (Takeda and Morosin, 1975; Hazen and Finger, 1978) and the present investigation on mica and chlorite have demonstrated that the extremely anisotropic physical properties of some layer minerals are a result of bonding differences. The anisotropic structural response of minerals such as micas and chlorites to pressure and temperature will influence the physical properties of rocks that contain layer minerals. Geological implications of this anisotropic behavior will be considered in a subsequent paper.

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