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Thermal equations of state of dioctahedral micas on the join muscovite–paragonite

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Abstract Powder diffraction measurements at simultaneous high pressure and temperature on samples of 2M1 polytype of muscovite (Ms) and paragonite (Pg) were performed at the beamline ID30 of ESRF (Grenoble), using the Paris-Edinburgh cell. The bulk moduli of Ms, calculated from the least-squares fitting of V – P data on each isotherm using a second-order Birch–Murnaghan EoS, were: 57.0(6), 55.1(7), 51.1(7) and 48.9(5) GPa on the isotherms at 298, 573, 723 and 873 K, respectively. The value of $(\partial K_T/\partial T)_P$ was $-0.0146(2)$ GPa K⁻¹. The thermal expansion coefficient α varied from $35.7(3) \times 10^{-6}$ K⁻¹ at P ambient to $20.1(3) \times 10^{-6}$ K⁻¹ at $P = 4$ GPa [$(\partial\alpha/\partial P)_T = -3.9(1) \times 10^{-6}$ GPa⁻¹ K⁻¹]. The corresponding values for Pg on the isotherms at 298, 723 and 823 K were: bulk moduli 59.9(5), 55.7(6) and 53.8(7) GPa, $(\partial K_T/\partial T)_P = -0.0109(1)$ GPa K⁻¹. The thermal expansion coefficient α varied from $44.1(2) \times 10^{-6}$ K⁻¹ at P ambient to $32.5(2) \times 10^{-6}$ K⁻¹ at $P = 4$ GPa [$(\partial\alpha/\partial P)_T = -2.9(1) \times 10^{-6}$ GPa⁻¹ K⁻¹]. Thermoelastic coefficients showed that Pg is stiffer than Ms; Ms softens more rapidly than Pg upon heating; thermal expansion is greater and its variation with pressure is smaller in Pg than in Ms.

Keywords Muscovite · Paragonite · Compressibility · Thermal expansion · Synchrotron powder diffraction

Introduction

“White” dioctahedral micas play a crucial role in most petrologic processes, in both magmatic and metamorphic environments. Understanding their thermoelastic behaviour is important to provide a reliable basis for interpretation and prediction of phase equilibria, as these minerals are used as geothermometers and geobarometers. Nonetheless, only few studies by in situ high-pressure and high-temperature experiments on muscovite, paragonite and phengites are available in literature. The only P – V – T equation of state (EoS) is referred to be on phengite-3T (Pavese et al. 1999).

As a first approximation, the rock-forming white micas can be described as crystalline solutions among the three end members muscovite, paragonite and margarite. The present study concerns the join muscovite–paragonite. The ideal chemical formula of muscovite (Ms) is $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$. Paragonite (Pg), ideally $\text{NaAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, is the Na analogue of Ms. Between these two end members there is a partial solid solution with a slightly asymmetric unmixing solvus. Many attempts have been performed to use the partitioning of Na and K between coexisting Ms and Pg as a geothermometer (Guidotti and Sassi 1976). Difficulties arise from using solvus curves that are not accurate enough to model the thermodynamic properties of these two micas. Inasmuch as the exact shape of the solvus and how it changes in function of pressure and temperature are not well known, thermometric estimates are often inconsistent. The molar volumes of the terms along the Ms–Pg join and how they change with pressure and temperature must be exactly known before a more accurate phase diagram can be drawn. Recent studies by Comodi and Zanazzi (1995, 1997) contributed to the knowledge of the molar volumes of muscovite and paragonite-2M1 polytypes and of their variation with P through compressibility measurements on single crystals in a diamond-anvil cell at room temperature. These data, together with thermal expansion coefficients

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measured at room pressure for Ms (Symmes 1986; Guggenheim et al. 1987; Catti et al. 1989) and Pg (Comodi and Zanazzi 2000) allowed a definition of an approximate P - V - T equation of state for K- and Na-dioctahedral micas. However, these are only an indication of volumetric behaviour at the boundaries of the P - T conditions achieved in rocks in the Earth's crust. To determine more accurately the behaviour of Pg-Ms micas it is essential to verify if there are any "non-linear effects" when both P and T are high.

If the effects of P and T on the volumetric properties of Ms-Pg micas were precisely known for the full range of P - T conditions of geologic interest, it would be possible to accurately calculate effects on the Pg-Ms solvus. Relatively small changes in excess molar volume could have significant effects on solvus limb positions, particularly in the 600 to 700 °C range.

The aim of this study is the determination of the molar volume behaviour of muscovite and paragonite at simultaneous high P and T .

Experimental method

Muscovite and paragonite samples were kindly supplied by Professor C. Guidotti. Ms (equivalent to sample 7-8/7/63 in Evans and Guidotti 1966) came from Western Maine (USA). Its composition, very near to the ideal one, is $K_{1.79}Na_{0.16}Al_{3.63}Ti_{0.08}Fe_{0.15}^{3+}Mg_{0.17}Al_{1.94}Si_{6.06}O_{20}(OH)_2$ (Evans and Guidotti 1966). Approximately 10 mg of $2M_1$ Ms and Pg were accurately selected under microscope and ground under acetone. The same preparation procedure was followed for Pg, which came from a jadeitite from the Motagua Fault Zone, Guatemala (American Museum of Natural History, catalogue number AMNH104213; equivalent to sample MVJ84-9C described by Harlow 1994) and has the composition $Na_{1.84}K_{0.10}Ca_{0.03}Al_{3.95}Ti_{0.01}Fe_{0.15}^{3+}Mg_{0.04}Al_{2.05}Si_{5.95}O_{20}(OH)_2$ (C.V. Guidotti, personal communication).

The Ms and Pg powders were mixed with NaCl in proportion 3:1 by weight. The diffraction measurements were performed in the angle-dispersive mode at the beamline ID30 of the European Synchrotron European Facility (ESRF, Grenoble). High pressure and high temperature were achieved by means of a large-volume Paris-Edinburgh cell. The cell assembly used has been described in detail elsewhere (Besson et al. 1992; Mezouar et al. 1996; Le Godec et al. 2000). The heating was obtained by a graphite-element resistance. Temperature was monitored by a CrAl thermocouple placed at the centre of the microfurnace (uncertainty up to ± 3 K). The data were recorded by an MAR3450 imaging plate (IP, 100- μ m pixel resolution). The beam was monochromated by an Si(111) crystal, obtaining a $\lambda = 0.2647$ Å, and focused into a 0.1×0.1 -mm² spot on the sample. Exposure times were about 50 s. Measurements were carried out along the isotherms 298, 573, 723 and 873 K for Ms, and 298, 423, 723, 823 K for Pg. The temperatures of the highest isotherms were chosen to avoid dehydroxylation processes, which become relevant in Ms above 900 K (Guggenheim et al. 1987; Mazzucato et al. 1999) and in Pg above 850 K (Comodi and Zanazzi 2000). Pressure was increased in steps of 0.5–0.7 GPa in the range 0–6 GPa and was calibrated by the EoS of NaCl (Birch 1986) using lattice parameters determined from X-ray diffraction profiles for each P - T point. The uncertainty in pressure was estimated to be less than 0.1 GPa.

For each isotherm an individual sample was prepared, packing the powder into a boron nitride (h-BN) can of 1 mm diameter and 2 mm length. The container was inserted in the graphite microfurnace, and the assembly was placed into a boron-epoxy gasket between the tungsten carbide anvils. For each data point, a time of about 20 min was allowed to reach the equilibrium; data

recording and readout took about 5 min for each diffraction pattern.

The diffraction rings collected on the IP were integrated in the part not shadowed by the WC anvils and converted into standard 2θ patterns using FIT2D program (Hammersley 1995; Hammersley et al. 1996) and then analyzed by means of the multiphase profile-fitting technique using the GSAS software package (Larson and Von Dreele 2001). An example of the diffraction image and the corresponding experimental and calculated powder diffraction pattern is shown in Fig. 1. The unit-cell parameters of Ms, Pg, NaCl and h-BN were refined by the Le Bail method (Le Bail et al. 1988). The background curve was fitted with a Chebyshev polynomial with 20 coefficients. The pseudo-Voigt profile function proposed by Thomson et al. (1987) was used to fit the experimental pattern. For Ms and Pg the asymmetry correction according to Finger et al. (1994) and the preferred orientation correction along the diffraction vector [001], using the formulation of Dollase-March (Dollase 1986) were applied. To account for the observed broadening of diffraction effects with $k \neq 3n$, due to the presence of stacking faults frequent in micas (Nespolo and Ferraris 2001), two Lorentzian coefficients for the anisotropic broadening were refined to better fit the Bragg peaks for the two different classes of reflections ($k = 3n$ and $k \neq 3n$).

Results and discussion

The lattice parameter data for Ms obtained at pressures up to 5 GPa on the isotherms 298, 573, 723 and 873 K are shown in Table 1. Cell-volume data are plotted in Fig. 2. The same data for paragonite along the isotherms 298, 423, 723 and 823 K are reported in Table 2 and Fig. 3. Only few points were measured on the isotherm at 423 K, because of the breaking of the thermocouple, which made it impossible to obtain a reliable value for compressibility of paragonite at this temperature.

Volume-pressure data of Ms and Pg at 298 K were fitted with the Birch-Murnaghan EoS.

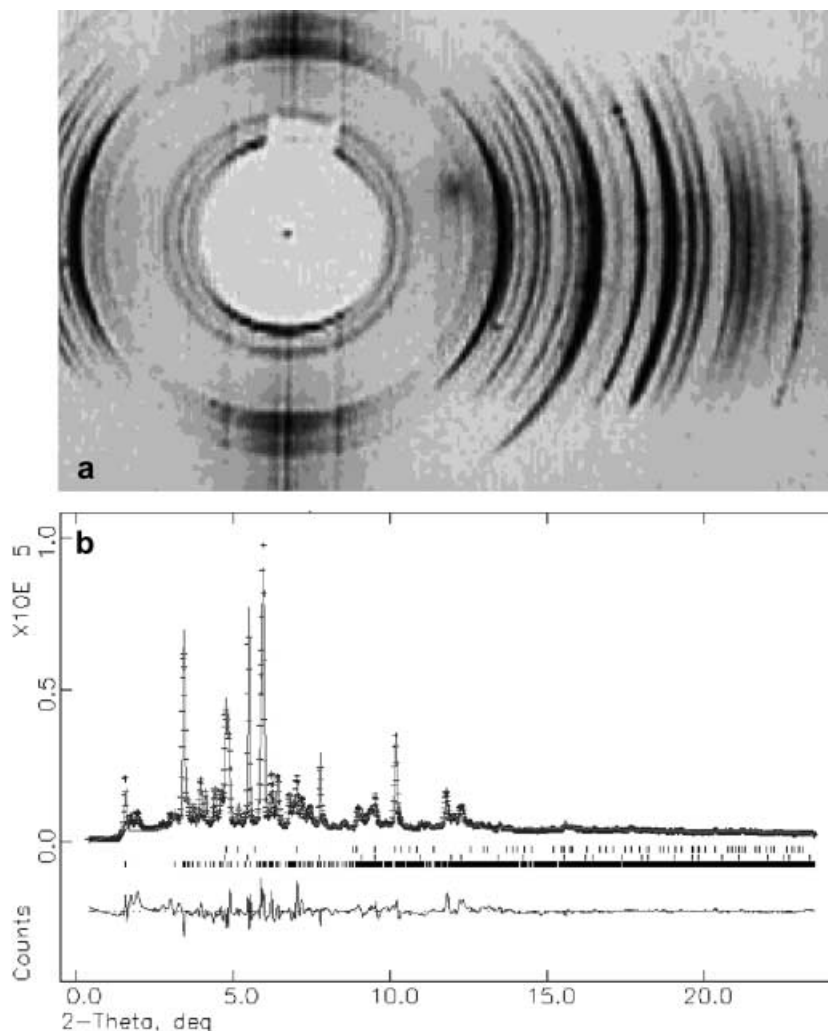
A plot of the "normalized stress" defined as $F_E = P/[3f_E(1 + 2f_E)^{5/2}]$ versus the finite strain $f_E = [(V_0/V)^{2/3} - 1]/2$ obtained from the P - V data is linear (Fig. 4a, b) for both micas, and shows that a second-order truncation of the EoS could describe the measured data adequately (Angel 2000).

The F_E/f_E plots of Fig. 4 show that a second-order EoS is reliable to fit data also at higher T . Therefore, fixing $K' = 4$, we obtained the cell volumes V_0 and $V_0(T)$ and the bulk moduli K_0 and $K_0(T)$ listed in Table 3.

Muscovite

The bulk modulus of Ms at 298 K, 57.0(6) GPa, can be compared with the reported values in literature, which are quite scattered. These values are 58.2 GPa (Vaughan and Guggenheim 1986, by Brillouin spectroscopy); 52.0 GPa ($K' = 3.2$; Sekine et al. 1991, by shock wave); 56.0 GPa (K' fixed at 4; Catti et al. 1994, by static compression neutron powder diffraction); 61.4 GPa ($K' = 6.9$; Faust and Knittle 1994, by static compression powder diffraction); 56.0 GPa (Comodi and Zanazzi 1995, by

Fig. 1 a The diffraction pattern of muscovite at 873 K and 3.6 GPa on the image plate, and **b** the converted intensity vs. 2-theta plot, with the experimental (*crosses*), calculated (*solid line*) and difference pattern. The peak positions of h-BN (*upper bars*), NaCl (*intermediate bars*) and muscovite (*lower bars*) are reported



static compression single-crystal diffraction; K_0 calculated as the inverse of the compressibility coefficient); 57.0 GPa ($K' = 9.2$; phengite $2M_1$; Smyth et al. 2000, by single-crystal diffraction). The differences can be ascribed to the different methods used in experiments and calculations and the different composition of the samples. It is known that a phengitic component can increase the stiffness of mica for the higher tetrahedral silicon contents (Smyth et al. 2000), as well the Na content (Comodi and Zanazzi 1995, 1997).

The bulk moduli on the isotherms at 573, 723 and 873 K were, respectively, 55.1(7), 51.1(7) and 48.9(5) GPa (Table 3; Fig. 5). Therefore the first derivative of K_0 versus temperature, dK_0/dT , is $-0.0146(2)$ GPa K^{-1} and $(\partial\beta_T/\partial T)_P$ is $5.1(9) \times 10^{-6}$ GPa $^{-1}$ K^{-1} .

The thermal expansion coefficient α of Ms, measured between 298 and 873 K, varied from $3.57(3) \times 10^{-5}$ K^{-1} at P ambient to $2.01(3) \times 10^{-5}$ K^{-1} at $P = 4$ GPa [$(\partial\alpha/\partial P)_T = -3.9(1) \times 10^{-6}$ GPa $^{-1}$ K^{-1}]. The value of α at ambient P is in good agreement with that found by Guggenheim et al. (1987) (3.54×10^{-5} K^{-1}) and is slightly smaller than those of Catti et al. (1989) (4.2×10^{-5} K^{-1}) and Symmes (1986) (4.7×10^{-5} K^{-1}).

Paragonite

The bulk modulus of Pg at 298 K is 59.9(5) GPa, at variance with the value 54.6(4) GPa (recalculated by fixing $K' = 4$ from P - V data of Comodi and Zanazzi 1997).

The values of $K_0(T)$ measured at 723 and 823 K were 55.7(6) and 53.8(7) GPa, respectively (Table 3 and Fig. 5). dK_0/dT is $-0.0109(1)$ GPa K^{-1} and $(\partial\beta_T/\partial T)_P$ is $3.4(5) \times 10^{-6}$ GPa $^{-1}$ K^{-1} .

The thermal expansion coefficient α measured between 298 and 823 K varied from $4.41(2) \times 10^{-5}$ K^{-1} at P ambient to $3.25(2) \times 10^{-5}$ K^{-1} at $P = 4$ GPa [$(\partial\alpha/\partial P)_T = -2.9(1) \times 10^{-6}$ GPa $^{-1}$ K^{-1}]. The value of α found for Pg at ambient P by the single-crystal method (Comodi and Zanazzi 2000) is 5.9×10^{-5} K^{-1} ; Symmes (1986) reported $\alpha = 4.9 \times 10^{-5}$ K^{-1} by powder diffraction.

These results are on the whole quite significant, even if it must taken into account the experimental difficulties of HP-HT study on micas, and care must be used in interpreting data. As pointed out by Pavese et al. (1999), the possible causes of error lie in the layer nature of these silicates, yielding preferred orientation especially

Table 1 Lattice parameters and cell volume values (\AA^3) as a function of pressure (GPa) and temperature (K) for muscovite. The V_0 value on each isotherm is calculated from the second-order BM EoS, since the instrumental setting did not allow diffraction data collection at room pressure

P (GPa)	T (K)	a (\AA)	b (\AA)	c (\AA)	β ($^\circ$)	V (\AA^3)
0.0	298(3)	–	–	–	–	933.0(1)
0.7(1)	298(3)	5.210(1)	8.961(1)	19.811(3)	95.12(1)	921.2(2)
1.4(1)	298(3)	5.185(2)	8.952(1)	19.654(3)	95.30(1)	908.4(3)
2.1(1)	298(3)	5.172(1)	8.946(2)	19.582(3)	95.47(2)	901.9(2)
2.9(1)	298(3)	5.157(2)	8.938(1)	19.462(4)	95.63(1)	892.8(3)
3.3(1)	298(3)	5.140(2)	8.929(2)	19.377(3)	95.82(2)	884.7(3)
3.7(1)	298(3)	5.131(1)	8.928(3)	19.348(5)	96.03(1)	881.4(3)
4.0(1)	298(3)	5.127(2)	8.926(2)	19.317(4)	96.18(2)	878.9(4)
4.3(1)	298(3)	5.110(2)	8.918(3)	19.255(5)	96.15(3)	872.4(3)
4.6(1)	298(3)	5.105(3)	8.916(3)	19.186(5)	96.25(3)	868.0(4)
0.0	573(3)	–	–	–	–	938.0(2)
0.8(1)	573(3)	5.198(1)	9.030(2)	19.742(2)	95.63(2)	922.2(2)
1.5(1)	573(3)	5.192(1)	9.022(1)	19.601(4)	95.66(1)	913.7(3)
1.9(1)	573(3)	5.188(2)	9.011(1)	19.506(3)	95.69(2)	907.4(2)
2.4(1)	573(3)	5.181(1)	8.994(2)	19.445(3)	95.72(1)	901.6(3)
2.9(1)	573(3)	5.165(3)	8.987(2)	19.397(5)	95.73(3)	895.9(3)
3.2(1)	573(3)	5.160(1)	8.970(3)	19.288(4)	95.76(3)	888.2(4)
3.5(1)	573(3)	5.158(2)	8.964(3)	19.271(5)	95.77(2)	886.5(3)
3.8(1)	573(3)	5.153(3)	8.956(2)	19.244(6)	95.77(2)	883.6(4)
4.0(1)	573(3)	5.148(3)	8.951(3)	19.187(6)	95.80(3)	879.6(4)
0.0	723(3)	–	–	–	–	944.1(3)
0.2(1)	723(3)	5.215(1)	9.052(1)	20.049(3)	95.71(2)	941.7(3)
0.9(1)	723(3)	5.201(1)	9.033(1)	19.838(3)	95.73(1)	927.4(3)
1.7(1)	723(3)	5.188(1)	9.021(2)	19.708(5)	95.78(2)	917.7(4)
2.3(1)	723(3)	5.171(2)	9.011(1)	19.573(4)	95.83(2)	907.3(3)
2.8(1)	723(3)	5.116(3)	8.999(3)	19.433(4)	95.88(3)	897.6(4)
3.4(1)	723(3)	5.154(2)	8.991(3)	19.341(5)	95.97(2)	891.4(4)
3.8(1)	723(3)	5.145(3)	8.976(2)	19.251(5)	96.16(3)	883.9(5)
4.1(1)	723(3)	5.139(3)	8.970(4)	19.222(6)	96.14(4)	881.0(4)
4.8(1)	723(3)	5.133(4)	8.960(4)	19.028(5)	96.38(3)	869.7(5)
0.0	873(3)	–	–	–	–	952.5(2)
0.6(1)	873(3)	5.225(1)	9.038(2)	20.043(4)	95.69(1)	941.9(3)
1.2(1)	873(3)	5.212(1)	9.019(1)	19.886(5)	95.71(1)	930.1(3)
1.5(1)	873(3)	5.210(2)	9.014(2)	19.843(4)	95.73(2)	927.2(4)
2.0(1)	873(3)	5.199(2)	9.006(2)	19.783(4)	95.76(1)	921.6(3)
2.5(1)	873(3)	5.186(2)	8.994(2)	19.669(5)	95.81(2)	912.7(3)
2.8(1)	873(3)	5.178(3)	8.986(3)	19.613(5)	95.85(2)	907.8(4)
3.2(1)	873(3)	5.169(2)	8.979(2)	19.499(5)	95.97(3)	900.1(4)
3.6(1)	873(3)	5.161(2)	8.965(3)	19.364(6)	96.02(2)	891.0(5)
3.9(1)	873(3)	5.154(3)	8.968(4)	19.283(5)	96.07(3)	886.3(3)
4.2(1)	873(3)	5.152(4)	8.959(4)	19.272(6)	96.12(2)	884.5(5)
4.4(1)	873(3)	5.148(4)	8.949(3)	19.240(7)	96.13(4)	881.3(5)
4.6(1)	873(3)	5.140(4)	8.940(5)	19.192(7)	96.15(4)	876.8(6)

when P increases. The quality of data is degraded by the large volume of the cell. The full profile of diffraction is complicated by several diffracting phases belonging to the chamber elements and to the pressure-transmitting medium and calibrant. This makes the process of profile fitting more difficult. The pressure values have been derived from the internal calibrant with known EoS, and are affected by nominal uncertainties of about 0.1 GPa. Deviating stress and thermal and pressure gradients might be present across the cell. Non-hydrostatic conditions in the pressure cell when studying powder samples could be a significant source of error in lattice-parameter determination (Fei and Wang 2000). Therefore, the quality of data obtainable from HP–HT experiments is not excellent, and the esd of cell volumes is high, reflected in the high esd of bulk moduli and other coefficients.

The only study on mica under simultaneous HP–HT with a methodology similar to that used in the present

work is that on phengite-3T (Pavese et al. 1999). These authors found thermoelastic properties roughly similar to those found for Ms and Pg in the present study. They reported the bulk modulus in the range 58–51 GPa, depending on the EoS used in calculations; the value is quite similar to that found for Ms. The dK_0/dT value is $-0.031 \text{ GPa K}^{-1}$, which is smaller than the value found here for Ms and Pg. The bulk thermal expansion is $3.0 \times 10^{-5} \text{ K}^{-1}$, slightly smaller than the value found for Ms and significantly smaller than the value of Pg.

Conclusions

On the basis of P – V – T data measured for muscovite and paragonite samples by powder diffraction on the ID30 beam line at ESRF synchrotron source (Grenoble), in spite of the difficulties of the experiment, we obtained

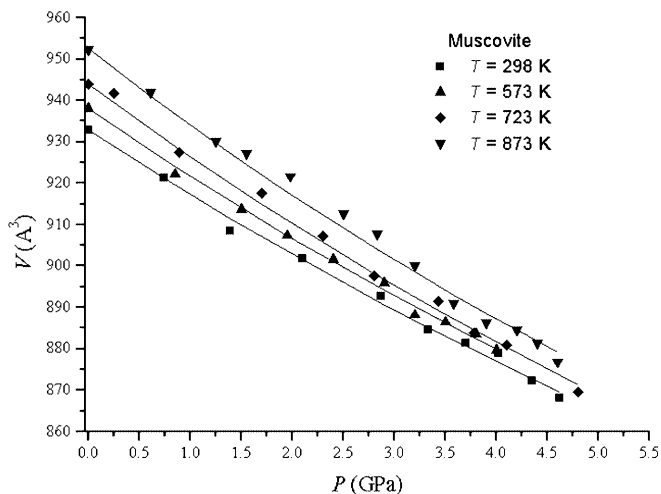


Fig. 2 Variation in cell volume (\AA^3) of muscovite as a function of pressure (GPa) on the isotherms at 298, 573, 723 and 873 K. The *solid line* represents the fitting to the second-order Birch-Murnaghan EoS on each isotherm

Table 2 Lattice parameters and cell volume values (\AA^3) as a function of pressure (GPa) and temperature (K) for paragonite. The V_0 value on each isotherm is calculated from the second-order BM EoS, since the instrumental setting did not allow diffraction data collection at room pressure

P (GPa)	T (K)	a (\AA)	b (\AA)	c (\AA)	β ($^\circ$)	V (\AA^3)
0.0	298(3)	—	—	—	—	885.4(1)
0.7(1)	298(3)	5.124(1)	8.869(1)	19.346(3)	94.56(1)	876.4(2)
1.4(1)	298(3)	5.111(1)	8.836(2)	19.249(2)	94.60(1)	866.5(2)
1.9(1)	298(3)	5.099(2)	8.821(1)	19.201(3)	94.63(2)	860.8(3)
2.4(1)	298(3)	5.094(1)	8.806(2)	19.143(3)	94.65(1)	855.9(2)
2.7(1)	298(3)	5.092(1)	8.781(2)	19.089(4)	94.68(1)	850.7(3)
3.0(1)	298(3)	5.086(1)	8.777(1)	19.063(3)	94.69(2)	848.1(3)
3.5(1)	298(3)	5.078(2)	8.748(2)	18.981(4)	94.74(2)	840.3(4)
3.8(1)	298(3)	5.070(2)	8.746(2)	18.944(5)	94.79(1)	837.0(3)
4.0(1)	298(3)	5.067(1)	8.744(2)	18.926(4)	94.82(2)	835.6(4)
4.3(1)	298(3)	5.060(2)	8.730(3)	18.864(5)	94.88(2)	830.3(4)
4.4(1)	298(3)	5.058(2)	8.729(2)	18.852(5)	94.89(3)	829.3(4)
4.7(1)	298(3)	5.051(3)	8.722(2)	18.826(4)	94.94(2)	826.3(5)
4.8(1)	298(3)	5.050(2)	8.717(3)	18.814(5)	94.97(3)	825.1(4)
5.0(1)	298(3)	5.041(3)	8.701(3)	18.781(6)	95.02(3)	820.4(5)
0.0	423(3)	—	—	—	—	890.9(2)
0.1(1)	423(3)	5.141(1)	8.927(2)	19.430(3)	94.29(1)	889.2(2)
0.8(1)	423(3)	5.136(2)	8.885(1)	19.347(3)	94.37(2)	880.3(2)
1.3(1)	423(3)	5.133(1)	8.860(2)	19.279(3)	94.41(2)	874.2(3)
0.0	723(3)	—	—	—	—	899.4(2)
0.5(1)	723(3)	5.152(1)	8.951(1)	19.419(3)	94.06(2)	893.3(3)
1.5(1)	723(3)	5.134(2)	8.892(1)	19.219(3)	94.29(1)	874.9(2)
2.0(1)	723(3)	5.130(1)	8.872(1)	19.141(2)	94.40(2)	868.6(3)
2.3(1)	723(3)	5.122(2)	8.861(2)	19.098(4)	94.42(2)	864.2(3)
2.7(1)	723(3)	5.112(2)	8.852(1)	19.065(4)	94.48(3)	860.1(4)
3.0(1)	723(3)	5.109(2)	8.844(2)	19.043(3)	94.50(2)	857.8(3)
3.3(1)	723(3)	5.101(1)	8.827(2)	19.017(4)	94.55(3)	853.6(4)
3.6(1)	723(3)	5.094(2)	8.815(1)	18.971(3)	94.56(2)	849.2(4)
3.9(1)	723(3)	5.088(3)	8.806(3)	18.918(4)	94.60(3)	844.9(5)
4.2(1)	723(3)	5.082(2)	8.797(2)	18.872(5)	94.59(2)	841.0(4)
4.4(1)	723(3)	5.078(3)	8.793(3)	18.831(6)	94.67(3)	838.0(6)
0.0	823(3)	—	—	—	—	906.0(3)
0.8(1)	823(3)	5.152(1)	8.937(1)	19.427(3)	94.01(3)	892.3(4)
2.0(1)	823(3)	5.133(2)	8.894(2)	19.214(4)	94.27(4)	874.7(3)
2.3(1)	823(3)	5.129(1)	8.876(2)	19.147(3)	94.41(4)	869.1(4)
2.7(1)	823(3)	5.120(2)	8.866(1)	19.104(4)	94.42(3)	864.6(4)
3.1(1)	823(3)	5.113(2)	8.860(3)	19.040(5)	94.48(3)	859.9(5)
3.7(1)	823(3)	5.104(2)	8.852(2)	18.929(4)	94.67(4)	852.4(6)
4.0(1)	823(3)	5.102(3)	8.844(3)	18.907(5)	94.93(4)	850.0(4)
4.4(1)	823(3)	5.093(3)	8.833(3)	18.835(7)	95.20(5)	843.8(6)

thermoelastic parameters that allow the following conclusions:

1. Results confirm that Pg is stiffer than Ms, in agreement with the results from single-crystal studies at ambient T by Comodi and Zanazzi (1995, 1997). Taking into account the structure of dioctahedral mica, the smaller compressibility observed as Na content increases has been explained by stronger repulsion of the basal oxygen sheets on both sides of the interlayer ions, which are nearer in Pg than in Ms.
2. Furthermore, Ms softens more rapidly than Pg upon heating.
3. Thermal expansion coefficient is greater in Pg than in Ms and its variation with P is smaller in Pg than in Ms.

On the basis of thermoelastic parameters, it is possible to write an equation of state of the type:

$$V(P, T) = V_0(1 + \alpha\Delta T)(1 - \beta P)$$

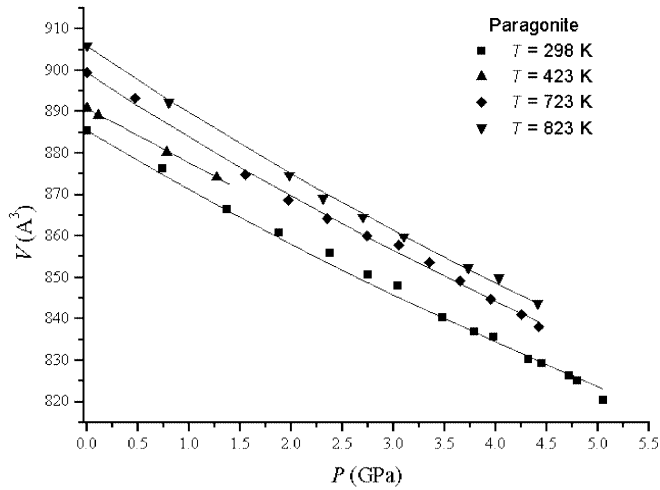


Fig. 3 Variation of cell volume (\AA^3) of paragonite as a function of pressure (GPa) on the isotherms at 298, 423, 723 and 823 K. The solid line represents the fitting to the second-order Birch-Murnaghan EoS on each isotherm

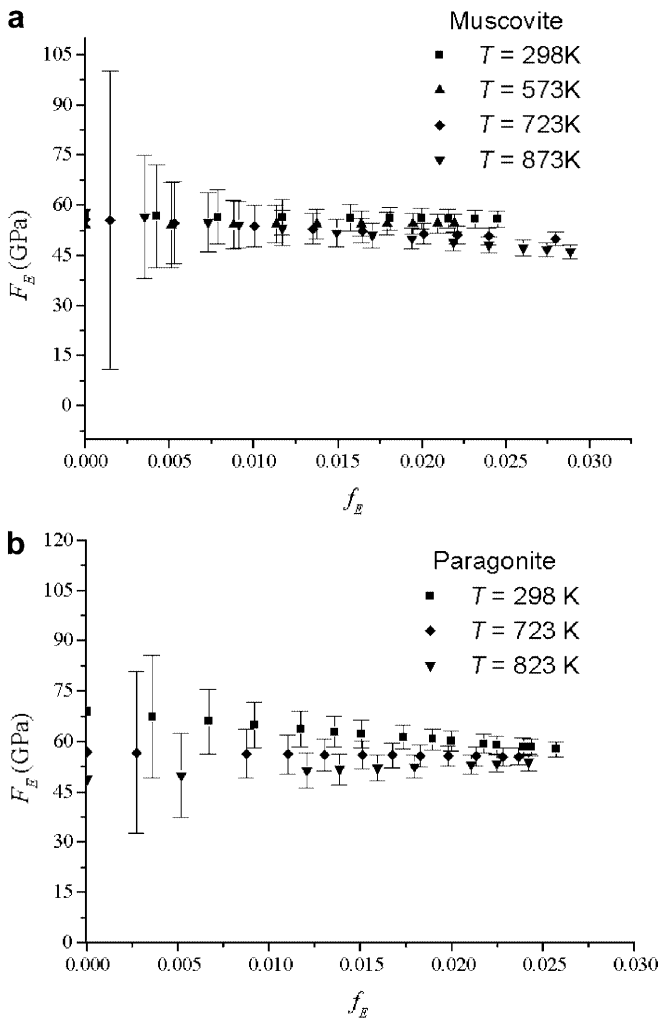


Fig. 4a, b Plot of the “normalized stress”, defined as $F_E = P/[3f_E(1+2f_E)^{5/2}]$, versus the finite strain $f_E = [(V_0/V)^{2/3}-1]/2$ in muscovite (a) and paragonite (b) on the different isotherms. The esds were calculated according to Heinz and Jeanloz (1984)

Table 3 Bulk moduli (GPa) at room pressure as a function of temperature (K) for muscovite and paragonite

Muscovite	Paragonite
$T = 298 \text{ K } K_0 = 57.0(6) \text{ GPa}$	$T = 298 \text{ K } K_0 = 59.9(5) \text{ GPa}$
$T = 573 \text{ K } K_0 = 55.1(7) \text{ GPa}$	$T = 723 \text{ K } K_0 = 55.7(6) \text{ GPa}$
$T = 723 \text{ K } K_0 = 51.1(7) \text{ GPa}$	$T = 823 \text{ K } K_0 = 53.8(7) \text{ GPa}$
$T = 873 \text{ K } K_0 = 48.9(5) \text{ GPa}$	

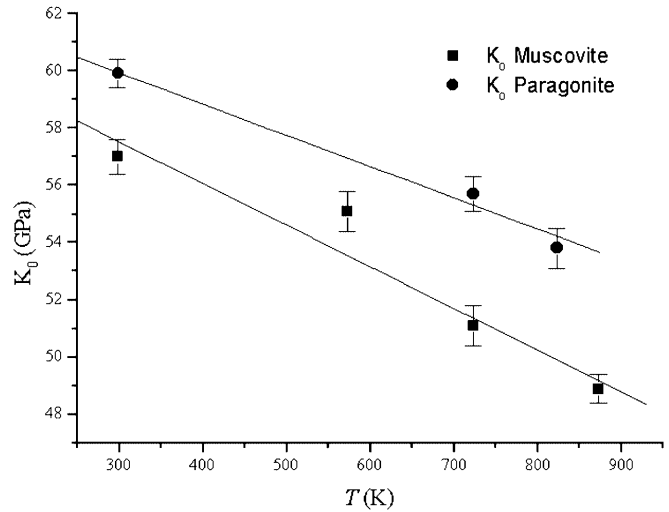


Fig. 5 Bulk moduli (GPa) at room pressure of muscovite on the isotherms at 298, 573, 723 and 873 K, and of paragonite at 298, 723 and 823

where V_0 is the molar volume at 298 K and room pressure, P is the pressure in GPa and ΔT is $T(\text{K}) - 298$. Since $\alpha = \alpha_0 + (\partial\alpha/\partial P)_T P$ and $\beta = \beta_0 - (\partial\beta/\partial T)_P \Delta T$, we obtain:

$$V(P, T) = V_0[1 + \alpha_0\Delta T - \beta_0 P + (\partial\alpha/\partial P)_T P\Delta T - (\partial\beta/\partial T)_P P\Delta T] .$$

Taking into account the values of α , β (K_0^{-1}), $(\partial\alpha/\partial P)_T$ and $(\partial\beta/\partial T)_P$ from the experiment (note the validity of the fundamental thermodynamic relationship $(\partial\alpha/\partial P)_T = -(\partial\beta/\partial T)_P$ in the limits of esd), we obtain for Ms and Pg:

$$\begin{aligned} Ms \ V(P, T) = & V_0[1 + 3.57(3) \times 10^{-5} \Delta T - 0.0175(2)P \\ & - 3.9(1) \times 10^{-6} P\Delta T - 5.1(9) \times 10^{-6} P\Delta T] \end{aligned}$$

$$\begin{aligned} Pg \ V(P, T) = & V_0[1 + 4.41(2) \times 10^{-5} \Delta T - 0.0166(2)P \\ & - 2.9(1) \times 10^{-6} P\Delta T - 3.4(5) \times 10^{-6} P\Delta T] . \end{aligned}$$

This is a significant datum concerning the shape of the Ms–Pg solvus at high P and T and its petrologic implications. Since Pg is less compressible than Ms, and this especially at high T , an increase of P and T affects the Na limb of the solvus with respect to the K side of the Ms–Pg join to a lesser extent, in agreement with chem-

ical data for natural Pg–Ms pairs from various paragneisses (Guidotti et al. 1994).

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