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XRD Investigation of a Natural Oligoclase at Pressure Up to 27 GPa

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Abstract The volume compressibility of natural oligoclase ($Na_{0.86}K_{0.02}Ca_{0.12}Mg_{0.01}(Fe_{0.01}Al_{1.12}Si_{2.87}O_8))$ was investigated by in situ powder synchrotron X-ray diffraction (XRD) methods at pressure up to 27 GPa，and the equations of state (EoS) of the oligoclase were obtained. The experimental data indicate that the oligoclase specimen underwent triclinic to monoclinic phase transition ($P\bar{1}$ to C2) at about 3.5 GPa and a further phase transition from C2 to C2/m in monoclinic symmetry at about 10 GPa with increasing pressure. The bulk modulus of the triclinic phase was calculated to be $K_0=73.8$ GPa，and those of monoclinic phases with C2 symmetry and C2/m symmetry to be $K_{(C2)}=124$ GPa and $K_{(C2/m)}=272$ GPa，respectively. The stiffness of the T-O-T angle，the strength of the M-O bond and bending of Si-O-Al angle are as a function of the chemical compositions of feldspars. The substitution of mingled ions for main ions in the crystal structure of the oligoclase modified T-O-T angle and the strength of the M-O bonds，resulting in variation of high pressure behavior of the oligoclase. Unit cell compression of triclinic phase oligoclase is obviously anisotropic. The results indicate that oligoclase may probably contribute to the deep recycle of alkali and alkaline-earth elements in the cool subduction zone.

Keywords Compressibility；Bulk modulus；Natural oligoclase；XRD；High pressure

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Introduction

Feldspar minerals are a main component of the crust，which may be carried into the mantle by the cool slab in the subduction zone where temperature is not high enough to decompose feldspar[1-2]. Additionally，mineral physics studies provide basic information on physical，chemical，thermodynamic and transport properties of constituents of the Earth's interior[3]. Therefore，the behavior of feldspar at high pressure has been investigated by both experiments[3-9] and theoretical simulation[10-11].

The volumetric behavior and elastic bulk and shear moduli of minerals as well as their derivatives are the critical parameters in extrapolating laboratory results to mantle conditions[3, 12-13]. The parameters as a function of pressure and temperature can be investigated using the technique of in situ measurements at high pressure and high temperature (HPT)[14-16]. For example，the measurements of elastic wave velocities and conductivity of rocks at HPT can interpret formation and evolution of the discontinuous zones in the Earth[17-18] and structure of lithosphere[19]. Moreover，the

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studies of phase transitions of minerals in the Earth's mantle indicated that the shift of phase boundaries has significant implications for the topography of the 410 and 660 km seismic discontinuities[3, 13].

The crystal structure and phase transition of feldspar minerals have been extensively studied[9, 20-22]. Structurally, feldspar minerals consist of a framework of AlO_4 and SiO_4 tetrahedra that are linked by shared oxygen atoms. Upon cooling, different Al-Si ordering schemes develop to avoid the energetically unfavorable Al-O-Al linking[16, 23]. The first principle investigations at high pressure indicated that the tetragonal hollandite structure of KAlSi3O8 (space group $I4/m$) can be degenerated to a monoclinic symmetry with two of the eight Si atoms replaced by two Al atoms[11]. The experiments for stability and compressibility of feldspars at high pressure indicate that anorthite (An) and albite (Ab) are stable in the crust and uppermost mantle (pressures <2 GPa), and sanidine is stable to at least 4 GPa[24], and that hollandite II phase $KAlSi_3O_8$ may be a potential host mineral of potassium in the Earth's lower mantle[25].

Chemical composition is one of the most important factors that control the structure and property of feldspars[26-27]. Feldspar minerals are stoichiometrically represented as compounds of three end-members: $KAlSi_3O_8$ (K-feldspar), $NaAlSi_3O_8$ (Ab) and $CaAl_2Si_2O_8$ (An). Plagioclase is solid solution of Ab and An. However, the chemical compositions of natural feldspars are very complex, containing many kinds of cations and anions, which can cause evident variation of physical-chemical properties of the minerals. For instance, the bulk moduli of plagioclase series are function of An content[28]; and the determinative chart of cell parameters (α, β and γ) of plagioclase shows that the parameters approximate linearly increase with increasing An content of plagioclase[7]. The measurements of high-resolution transmission electron microscopy indicated that structural fluctuations occurred in both An with lower Al-Si ordering and Na-bearing plagioclase, and that the magnitudes of the fluctuations decreased with increase of Na content[16]. Moreover, Downs et al.[29] suggested that An-rich plagioclase had an EoS characterized by $K'=\mathrm{d}K/\mathrm{d}P<4$, but Ab was reported to have $K'>4$. The determinations of the EoS of oligoclase ($An_{20}Ab_{76}Or_3$ to $An_{89}Ab_{11}$) revealed that the calculated values of bulk modulus increased with the increase of pressure and no phase transition was found up to 8.23 GPa[8]. The cell parameters of plagioclase are function of concentrations of metal ions[30].

The compressibility of the three end-member feldspars was determined to 5 GPa by single crystal XRD techniques, and a reversible phase transition of An at pressure between 2.55 and 2.95 GPa was observed[24, 31]. Ab-rich plagioclase has a $C\bar{1}$ symmetry, and calcic plagioclase has $I1$ and $P\bar{1}$ symmetries[32]. The investigation of structure and EoS of low Ab ($NaAlSi_3O_8$) using high-pressure single-crystal XRD indicated that the low Ab remained triclinic in space group up to 9.43 GPa although the evolution of the unit-cell parameters and volume exhibit some unusual features at pressures above 4 GPa[33]. However, it was reported that An under hydrostatic pressure underwent $P\bar{1}-I\bar{1}$ phase transformation at 2.6 GPa and a reversible polymorphic transition from $I\bar{1}$ polymorph to a phase of higher symmetry at 10 GPa[34]. High-pressure amorphization of An has been observed under static pressures in a diamond anvil cell (DAC), characterized by a significant reduction in the intensity of Bragg reflections at pressures between 10 and 14 GPa, and complete X-ray amorphous between 14 and 20 GPa[35], and complete Raman spectrum amorphous at 16 GPa[34].

Physical and chemical data of three end members of feldspars and chemically simple oligoclase ($Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8$) are easily found in the literature[5-6, 8, 24, 32, 36]. However, cell parameters and elastic property of natural oligoclase with complex chemical compositions are rarely reported. Effect of composition of plagioclase on the cell parameters is still poorly understood. Therefore, this paper aims at investigating the effect of chemical composition on the cell parameters and compressive behavior of the natural oligoclase with complex components.

1　Sample and methods

1.1　Sample

The oligoclase sample was separated from a coarse grained granite sample, collected from a huge granitic vein occurring in a large granodiorite body in Fangshan, Beinjing Municipality, China[37]. The granite is approximately composed of 55% oligoclase, 25% microcline, 3% perthite, 15% quartz, and small amount of mica and magnetite. The chemical compositions of the oligoclase sample, measured with the electron-probe microanalyzer, were presented with the mean values of components at 10 sites of the oligoclase crystal (Table 1). The measured data have an error less than 0.01%. The oligoclase contains more cations of Mg^{2+}, Fe^{2+}, Mn^{2+}, Ti^{4+} and Cr^{6+} than an oligoclase ($Na_{0.84}Ca_{0.16}Al_{1.16}Si_{2.84}O_8$) reported by Phillips et al.[6]. The calculation indicated that all Al^{3+} and Fe^{3+} could combine within tetrahedral structure and Mn^{2+} and Mg^{2+} occupy the same kind of positions (M) as Ca^{2+} in the crystal. The chemical formula of the oligoclase was calculated to be $Na_{0.86}K_{0.02}Ca_{0.12}Mg_{0.01}(Fe_{0.01}Al_{1.12}Si_{2.87}O_8)$.

Table 1 Chemical compositions of the oligoclase (Wt%)

SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	FeO	MnO	TiO_2	Cr_2O_3	P_2O_5	H_2O	Total
65.16	21.47	2.59	9.94	0.35	0.12	0.14	0.01	0.01	0.01	nd	nd	99.20

Note: Compositions were measured with a JXA-8800 Electronic Probe Microanalyzer at Institute of Geophysics and Geology, Chinese Academy of Science. nd- not determined. Nd: not determined.

The micro-Raman spectroscopic measurements of the oligoclase sample at ambient condition indicated that it is characterized by the more intensive peaks of 288, 480 and 516 cm^{-1} and others of 335, 374, 411 and 458 cm^{-1}[38]. The X-ray pattern of the oligoclase is characterized by intensive peaks of the planes of (1 −1 1), (−2 −3 1), (0 4 1), (−1 −5 1), (−3 −3 1), (−2 0 4), (3 4 0), (1 −5 3), and (−3 7 4) (Fig. 1), which fits very well to the triclinic model of oligoclase[6]. The structure of the oligoclase was identified to be triclinic with space group of $P\overline{1}$. The unit cell parameters under the ambient condition were measured to be $a = 8.157\,0(15)$ Å, $b = 12.919\,6(44)$ Å, and $c = 8.409\,4(22)$ Å; $\alpha = 95.869(23)°$, $\beta = 122.399(21)°$, and $\gamma = 86.721(30)°$; and $V_0 = 744.34(20)$ Å^3.

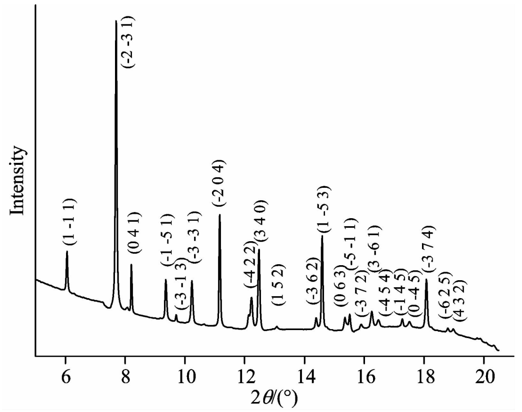

Fig. 1 X-ray pattern of the oligoclase taken under the ambient condition, the Miller indices for each peak marked in the figure were identified by PowderCell 2.3

1.2 Method

The oligoclase crystal was first washed with alcohol in an ultrasonic bath, then ground into powder with grain diameter of less than about 10 μm. The powder was loaded in a Mao-Bell piston-type of DAC[14] with a 4∶1 mixture of methanol and ethanol as the pressure-transmitting medium, which can ensure hydrostatic pressure up to about 10 GPa and quasi-hydrostatic pressure at pressure over 10 GPa[34, 39]. A piece of 200 μm thick rhenium plate was employed as the gasket, on which a hole of 150 μm in diameter was made for loading the sample and ruby chips. Ruby chips loaded in the cell were as the pressure gauge, and the measured pressures have the uncertainty limits of ±6%[40].

The angle dispersive X-ray diffraction (ADXRD) of the oligoclase were in situ measured on line using the synchrotron radiation beam line of X17C in the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory at room temperature and pressures up to 27 GPa. The beam size was 24 μm×20 μm. The calibration file is CeO_2_std250_1. The beam line parameters were as following: the sizes of both horizontal and vertical pixels were 64.396 00 μm; the distance between the sample and the detector (Fuji image plate) was 260.9387 mm, the rotation angle of the tilting plate was 84.939 04°, and angle of the detector tilt at the plane was 0.484 335°.

The X-ray diffraction data of the oligoclase were progressed by the software of Refine 2 and PowderCell 2.3[41], which gave the XRD pattern.

2 Results

All peaks in the XRD patterns of the oligoclase at room-temperature soften and broaden with increasing pressure, and the peaks of 2θ values larger than 12 finally merge into the broad bands at pressure above 2 GPa. At pressures above 10 GPa, however, the widths of the diffraction peaks broaden significantly with increasing pressure. Simultaneously, some new peaks occur at higher pressure, which is related to phase transition. The width evolution of the significant peaks as a function of pressure can be attributed to solidification of the pressure-transmitting medium, which resulted in change from

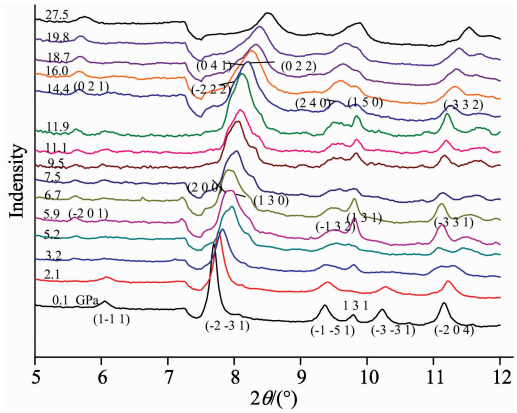

Fig. 2 Angle-dispersive X-ray diffraction patterns of the oligoclase at room-temperature for selected pressures, the pressure for each curve is marked at the left end of the line, and the numbers in bracket are the miller indices for the peaks

hydrostatic pressure to quasi-hydrostatic pressure in the sample chamber. The amorphization of the crystal also enforced the broadening of the XRD peaks when pressure was larger than 20 GPa (Fig. 2).

The unit cell parameters varied in the different ways with increasing pressure (Table 2; Fig. 3). The value of *a* increased sharply from 3.3 to 4.0 GPa, but the *c* value decreased and the *b* value changed little. At the same time, the values of γ and α became 90°, and the β value decreased. After pressure approaching about 10 GPa, values of *a* and *b* decreased slightly, but the *c* value showed no change. The variations of unit cell parameters indicate the phase transition of the oligoclase.

Table 2 Cell parameters of the oligocalse at different pressures and room temperature

P/GPa	a/Å	b/Å	c/Å	α/(°)	β/(°)	γ/(°)	V_0/Å^3
0.000 1	8.157 0(15)	12.919 6(44)	8.409 4(22)	95.869(23)	122.399(21)	86.721(30)	744.34(20)
0.1	8.139(12)	12.906(24)	8.383(16)	95.72(14)	122.13(16)	86.88(14)	742.0(13)
0.9	8.137 3(33)	12.921(10)	8.301 4(37)	95.71(12)	122.078(57)	86.743(57)	735.39(47)
2.1	8.013(10)	12.920(26)	8.293(36)	95.20(36)	121.16(16)	87.06(16)	727.6(47)
2.9	8.115(23)	12.960(83)	8.233(27)	94.00(98)	120.94(44)	87.76(43)	723.9(34)
3.3	8.040(27)	12.958(79)	8.250(28)	95.7(10)	122.16(37)	86.40(47)	716.7(25)
4.0	8.551(13)	12.953(19)	7.217(12)	90.0	116.76(34)	90.0	713.6(27)
4.4	8.550(18)	12.951(28)	7.210(15)	90.0	116.75(47)	90.0	713.43(36)
4.7	8.630(37)	12.900(12)	7.153(62)	90.0	116.77(45)	90.0	711.3(66)
5.2	8.594(26)	13.001(90)	7.032(44)	90.0	116.14(32)	90.0	705.3(48)
5.9	8.571(18)	12.969(86)	7.012(41)	90.0	115.94(31)	90.0	700.9(45)
6.7	8.526(41)	12.952(32)	7.049(44)	90.0	116.63(31)	90.0	696.0(37)
7.5	8.502(19)	12.912(25)	7.068(26)	90.0	116.69(25)	90.0	693.3(28)
8.3	8.528(12)	12.912(18)	6.996(19)	90.0	116.58(14)	90.0	688.9(16)
9.5	8.5274(58)	12.908(13)	6.9922(89)	90.0	116.850(78)	90.0	686.69(84)
9.9	8.456(42)	12.945(37)	6.934(37)	90.0	116.06(42)	90.0	681.9(46)
11.1	8.502(29)	12.834(43)	7.010(27)	90.0	117.29(30)	90.0	679.8(30)
11.9	8.491(24)	12.824(35)	6.994(21)	90.0	117.14(23)	90.0	677.8(23)
14.4	8.459(15)	12.802(22)	6.962(13)	90.0	116.75(15)	90.0	673.2(15)
16.0	8.438(24)	12.746(33)	6.956(11)	90.0	116.79(21)	90.0	667.8(24)
18.7	8.423(36)	12.736(45)	6.911(40)	90.0	116.79(39)	90.0	661.9(37)
19.8	8.348(46)	12.730(32)	6.958(41)	90.0	117.28(34)	90.0	657.2(34)
27.5	8.335(26)	13.16(11)	6.456(53)	90.0	114.65(33)	90.0	643.8(64)

The numbers in the brackets stand for errors.

3 Discussion

3.1 Phase transition

The XRD data revealed that oligoclase underwent at least two stages of phase transitions with increasing pressure from ambient to 27.5 GPa. First, triclinic to monoclinic ($P\bar{1}-C2$) transition was found at pressure of about 3.3 GPa. The phase transition was characterized by disappearing the (1 −1 1), (−3 −1 3) and (−3 −3 1) peaks, splitting the (−2 −3 1) and (−2 0 4) peaks, and occurrence of the (−2 0 1), (2 0 0), (1 3 0), (−1 3 2), (1 3 1) and (−3 3 1) peaks (Fig. 2), and sharply changing values of the unit cell parameters, *a*, *c*, γ and α (Table 2; Fig. 3). The pressure of this phase transition is concordant to the result that the micro-Raman spectroscopic measurements revealed the phase transition of the oligoclase at pressure of 3.5 GPa[38]. This phase transition was completely finished at about 6.0 GPa in our experiment. Such wide pressure range of the phase transition may be attributed to that energy needed in phase transition is compensated by the mechanical energy of loading in the DAC system. Therefore, this phase transition could be the first-order transition, as anorthite phase transition[24, 34, 42], and displacement transition because of obvious variations of the unit cell parameters. The high pressure behavior of the oligoclase can be considered to be similar to that of anorthite because oligoclase is structurally similar to anorthite, but different form albite[6]. It was reported that anorthite underwent triclinic to monoclinic transformation at 2.6 GPa[32, 42]. The XRD measurements of strontium feldspar ($Ca_{0.2}Sr_{0.8}Al_2Si_2O_8$) single crystal indicated that the first order transition was from triclinic to monoclinic at about 4.3 GPa, and unit cell parameters were as a function of pressure to 7.7 GPa at room temperature[43].

The values of cell parameter *a* of triclinic phase oligoclase is smaller than those of *c*. Values of *a* and *c* decreased obviously with the increase of pressure, but those of *b* varied slightly. For the monoclinic phase, however, values of *a* of the oligoclase became larger than those of *c*; and *a*, *b* and *c* show a decrease tendency with the increase of pressure (Fig. 3). The variations of the unit cell parameters of the oligoclase with pressure appear to be correlated with the change of Si-O-Al bond angles within the structure[33] and movements from the T_2 sites into T_1 sites producing large, quantitatively predictable changes in *b* and *c*[44]. The isochemical variations in the unit cell parameters are related to Al/Si distribution among the non-equivalent tetrahedral (*T*) sites of the feldspar framework[45]. Additionally, the unit cell parameters of $Ca_{1-x}Sr_xAl_2Si_2O_8$ were measured as a function of Ca^{2+} concentration[46].

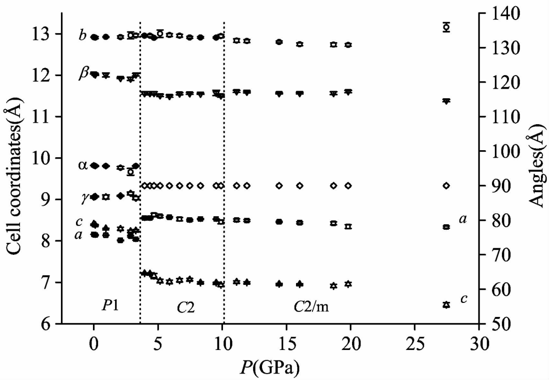

Fig. 3 Variations of unit cell parameter lengths with pressure. The vertical errors bars with the symbols indicate most errors are smaller than the symbol size. The vertical dot lines indicate the pressures of phase transitions

Secondly, *C*2—*C*2/*m* transition in monoclinic symmetry at about 10.0 GPa can be identified by disappearing right-shoulder of the (1 3 0) peak, splitting the (2 0 0) and (−3 3 1) peaks and occurrence of the (0 2 1), (−2 2 2), (0 4 1), (0 2 2), (2 4 0), (1 5 0) and (−3 3 2) peaks (Fig. 2). The refinement of the unit cell parameters of the oligoclase well fitted the model of C2/m symmetry when pressure above 9.9 GPa, which may indicate a displacement phase transition. The reversible polymorphic transition of anorthite into a phase of higher symmetry at 10 GPa was also reported[34]. The Raman spectra for anorthite at room temperature indicated that the reversible displace phase transition occurred at 10 GPa[42]. In addition, Sr-feldspar phase transition as *I*2/*c*→*P*2$_1$/*c* symmetry change at about 7.3 GPa was also observed[47]. Unfortunately, the decompression measurement was not performed in our experiment.

It is noted that the pattern of the peaks at pressure of 27.5 GPa shows difference from those at pressure less than 20.0 GPa and the peaks are severely broadened (Fig. 2), which may be attributed to pressure caused amorphization and displacement.

3.2 Effect of chemical composition on phase transition

The chemical compositions of feldspar minerals control both the structure and behavior of feldspars. The calculated unit cell volume of the experimental oligoclase is 744.34 Å^3, which is larger than those of $NaAl_2Si_2O_8$ albite (664.78 Å^3)[24, 36], oligoclases of $An_{16}Or_2Ab_{82}$ (666.59 Å^3) and $An_{28}Or_2Ab_{70}$ (668.4 Å^3)[6]; but less than that of $Na_{0.80}Ca_{0.20}Al_{1.2}Si_{2.8}O_8$ oligoclase (791.3 Å^3)[6]. Such difference of the unit cell volumes may be caused by different concentrations of larger-radius cations in the plagioclases, and Al/Fe contents at the tetrahedral sites and the linkage factor that are the dominant factors influencing T-O bond lengths[48]. The cell volume can be enlarged by substitution of larger radius Ca^{2+} and K^+ for smaller radius Na^+ on octahedral sites in the feldspars, which is compensated by a simultaneous substitution of Al^{3+} and/or Fe^{3+} for Si^{4+} on the tetrahedral sites. Reasonably, different kinds of cations occupying the M position have different coordination. For example, M=K or Rb, the coordination number is usually chosen as nine; for M=Li, the coordination appears to be five; but M=Na, the coordination appears to be seven or nine depend on the framework[29]. The fitted unit cell volume of feldspars indicated that the unit cell volumes of plagioclases under ambient condition increase with increasing An component[6, 8, 30, 36, 49] and those of alkali-feldspars increased with increasing K^+ component[45, 50]. The coupled substitution of (Al+P) for (Si+Si) in sodium aluminum phosphorus feldspars (KAl_2PSiO_8 and $NaAl_2PSiO_8$) with P changed the feldspar framework, resulting in the increase in cell volume of about 1.4%[51]. As mentioned by Viswanathan and Kielhorn[27], the physical properties and structures of all feldspar mixed crystals depend upon the order/disorder of the (Si, Al) atoms and the composition and structure of the end members involved.

Additionally, differences in chemical compositions of the feldspar can change the pressure of phase transition. The experimental oligoclase (Table 1) contains more kinds of ions than the feldspars cited here. The different minor ions, such as Mg^{2+}, Fe^{3+}, Mn^{2+}, Ti^{4+}, Cr^{3+}, Sr^{2+} and P^{5+}, substitute for the main ions (Al^{3+}, Si^{4+}, Ca^{2+}, Na^+ and K^+) in the crystal structure can result in deformation of crystal structure. Consequently, high pressure behavior of the oligoclase may be changed. In the ordered Na-K feldspar series[5, 50] and K-Rb feldspar series[49], the cell parameters are as a function of average alkali cation radius, and the cell volume increases with increasing average radius of alkali cations and K and Rb contents. Discontinuities in unit cell geometry found within the plagioclase series may be attributed to the ordering patterns of Si, Al, and Na, Ca at certain favorable compositions[30]. The number of calcium atoms, to which oxygen atoms are bonded, significantly influences the individual T-O distance in anorthite[52], and plagioclases of different Mole percentage of An have different structural phases[30]. This is the reason why feldspars behave in the different ways at high pressure.

3.3 Compressibility of oligoclase

The isothermal bulk modulus K_0 and its first derivative K'_0 of the oligoclase were derived by least-square fitting the experimental volume-pressure data to the third-order Birch-Murnaghan equation of state[53]

$$P=\frac{3}{2}K_0\left[\left(\frac{V_0}{V}\right)^{7/3}-\left(\frac{V_0}{V}\right)^{5/3}\right]\cdot$$
$$\left\{1-\frac{3}{4}\left(4-\frac{3}{4}(4-K'_0)\right)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\}$$

where K_0 is the isothermal bulk modulus at zero pressure, K'_0 is the first derivative of K_0, V_0 is the volume at zero pressure, and V is the volume at high pressure. The bulk moduli of the oligoclase in three phases (space group symmetry: $P\overline{1}$, $C2$ and $C2/m$) were calculated to be $K_0=73.8$ GPa ($K'=10.98$), $K_{(C2)}=124$ GPa ($K'=1.05$) and $K_{(C2/m)}=272$ GPa ($K'=0.625$), respectively. The ambient bulk modulus (K_0) of the oligoclase is comparable with the reported values (55～85 GPa) of plagioclase moduli[54].

The calculated bulk moduli of the oligoclase are as a function of pressure. The bulk modulus increases by about 36% from triclinic symmetry to monoclinic symmetry, and about 97% from C2 to C2/m in monoclinic symmetry. Correspondingly, the calculated unit cell volume decrease by 1.2% from triclinic to monoclinic symmetry, and by 2.7% from C2 to C2/m symmetry. Those can be attributed to the larger radius cations (Table 1) substitution for Na^+. As reported by Angel[8, 54], both isothermal bulk modulus (K_T) and adiabatic bulk modulus (K_S) of feldspars increased with increasing An component. Plagioclase feldspars are far less compressible than alkali feldspars, and the isothermal bulk modulus increases by about 40% from albite to anorthite[55]. Feldspar bulk moduli may be controlled by the stiffness of the T—O—T angles and the strength of the M-O bonds[29, 54]. The compression may be accomplished through the bending of Si-O-Al angles, which squeezes together the chains of four-member rings that run parallel to (001) and are separated by zigzag channels containing Na, K, Ca and Mg atoms[29]. In addition, the simulating results of $KAlSi_3O_8$ at high pressure indicated that $(Si,Al)O_6$ octahedron is much less compressible than the KO_8 polyhedron (the K_0 values of AlO_6, SiO_6 and KO_8 were 246, 302 and 193 GPa, respctively[11].

Variations of the cell parameter lengths with pressure indicate that compressive behavior of the oligoclase is anisotropic, i. e. it is more compressible along the *c* axis than the *a* and *b* axes (Fig. 3). Similarly, the anisotropic compressional behaviors of plagioclases[24] and coesite that is structurally similar to feldspar[56] have been observed. The structural changes accompanying with compression can be attributed to the rotation of the Si_2 tetrahedron. Anisotropy of compression of feldspars has been attributed to the channels that are occupied by the extra-framework cations such as Na, K, Ca etc. and parallel to (001) plane within the structure. Approximately 60% of the volume compression in all feldspar structures and coesite is accommodated by compression along the (100) plane normal, perpendicular to these channels[54, 56].

The cell volume (V) of the oligoclase varied with increasing pressure (P) (Fig. 4). For pressure ranging from 0 to 3.0 GPa, the EoS ($V=744.2(3)-8.9(5)P$) of the triclinic phase oligoclasewas yielded by least-square fitting of cell volume and pressure data ($n=6$) with a correlation coefficient $R=0.9997$. At $3.0<P<10$ GPa, the EoS becomes $V=736(1)-5.3(2)P$ by fitting of cell-volume and pressure data ($n=11$) with $R=0.9999$; and at $10<P<22$ GPa, $V=706(2)-2.4(2)P$ ($n=8$, $R=0.9994$). Similarly, the EoS of anorthite at $1<P<10$ GPa was given to be $V=669.81-6.17P$ ($n=8$, $R=0.99104$)[8]. The EoS of oligoclase of triclinic symmetry has the largest slop of −8.31 corresponding to the small bulk modulus value of 73.8 GPa, indicating the highest compressibility of the triclinic phase oligoclase. The slops of the equations decrease from the lower pressure phase to the high pressure one, indicating the decrease of compressibility of the oligoclase. The decomposition of the oligoclase sample did not occurred under the experimental condition, indicating that oligoclase may carry alkali and alkaline-earth elements into the mantle by the cool subducted slab under the condition of lower geothermal gradient, as reported by Hirao et al.[25].

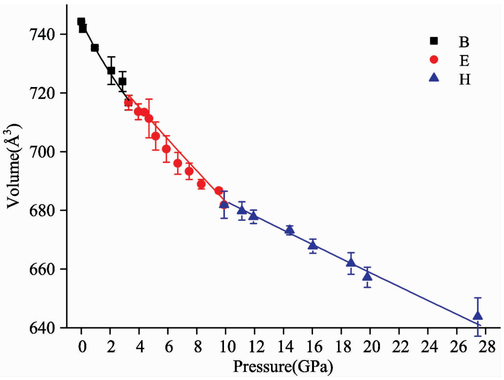

Fig. 4 The plot of unit cell volume versus pressure. The vertical bars present the errors of unit cell volume, and solid lines are calculated EoS of the oligoclases in three phases

4 Conclusion

The in situ powder synchrotron XRD reveals volume compressibility of the natural oligoclase at room temperature and pressures up to 27 GPa. The bulk moduli of oligoclase in three phases were determined to be $K_0=73.8$ GPa, $K_{(C2)}=124$ GPa and $K_{(C2/m)}=272$ GPa, respectively. Unit cell compressions of the triclinic phase oligoclase are obviously anisotropic, and the softest direction likely is approximately perpendicular to (100) plane. The equations of state of three phases of the oligoclase were obtained.

It is determined that the oligoclase underwent two phase transitions at pressures of about 3 GPa and 10 GPa. Bulk modulus increase by about 36% from triclinic to monoclinic symmetry, and about 97% from C2 to C2/m in monoclinic symmetry. The oligoclase bulk moduli may be controlled by the stiffness of the T-O-T angles and the strength of the M-O bonds. Furthermore, the T-O-T angles and the strength of the M-O bonds are as a function of the chemical compositions of feldspar minerals. The substitutions of different minor ions, such as Mg^{2+}, Fe3+, Mn^{2+}, Ti^{4+}, Cr^{3+}, Sr^{2+} and P^{5+} for the main ions (Al^{3+}, Si^{4+}, Ca^{2+}, Na^+ and K^+) in the oligoclase crystal resulted in deformation of the crystal structure. Consequently, high pressure behavior of the oligoclase was changed. The stability of the oligoclase at high pressure indicated that oligoclase may act as a carrier of alkali and alkaline-earth elements into the mantle in the cool subduction zone. Feldspar minerals may play an important role in the evolution of crust and mantle and element recycling.

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压力高达 27 GPa 下天然奥长石的 XRD 分析

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摘　要　在室温高达 27 GPa 压力下对天然奥长石（$Na_{0.86}K_{0.02}Ca_{0.12}Mg_{0.01}(Fe_{0.01}Al_{1.12}Si_{2.87}O_8))$粉晶进行了原位同步辐射 X 光衍射(XRD)测量，获得了样品的状态方程。实验数据表明随着压力增大奥长石样品在大约 3.5 GPa 发生了三斜向单斜的相变($P\bar{1}\rightarrow C2$)和在大约 10.0 GPa 发生了单斜对称相变($C2\rightarrow C2/m$)。样品三个相的体模量计算值分别为 $K_0=73.8$ GPa ($K'=10.98$)，$K_{(C2)}=124$ GPa ($K'=1.05$) 和 $K_{(C2/m)}=272$ GPa ($K'=0.625$)。样品的元素组成影响其 T—O—T 键角的刚度、M—O 键的强度和 Si—O—Al 键角的弯曲，从而导致奥长石样品在高压行为的特殊变化。三斜相的奥长石晶胞压缩性具明显的各向异性。实验结果表明在冷俯冲带奥长石可能是碱金属和碱土金属深循环的载体。

关键词

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