

Pressure-induced phase transitions in rhodonite and related chain silicates

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ABSTRACT

Rhodonite (MnSiO_3) is a pyroxenoid with a single-chain silicate structure related to pyroxenes. In this study, we investigated the structural evolution of synthetic rhodonite up to 35.0(1) GPa using in situ synchrotron single-crystal X-ray diffraction. The results indicate that rhodonite retains its triclinic structure ($P\bar{1}$) throughout the pressure range; however, it undergoes an isosymmetric second-order phase transition at 10.9(1) GPa, driven primarily by an increase in Mn coordination number. Contrary to earlier findings on amorphization, rhodonite retains its crystallinity up to 35.0(1) GPa. Moreover, this study also reviews the high-pressure phase transitions in orthopyroxenes, clinopyroxenes, and pyroxenoids, with a particular focus on mechanisms and characteristics of the structural phase transitions. Through comparative analysis, we have identified both commonalities and differences among these chain silicates. Specifically, we have further highlighted the crucial roles played by the rotations of tetrahedra, increases in coordination numbers, and the interplay between these factors in governing their phase transitions. These findings not only enhance our understanding of pyroxenoid structural evolution at high pressure but also provide valuable insights into chain silicate stability in the deep Earth.

Keywords: Pyroxenoids, pyroxenes, chain silicates, phase transitions, high pressure

INTRODUCTION

Pyroxenes and pyroxenoids, both chain silicate minerals, are distinct from each other in terms of the repeat unit of their tetrahedral chains and the resulting structural complexities (Nesse 2002). Due to the abundance of pyroxenes in the Earth's crust and mantle, numerous studies have reported their phase transitions at high pressures. These results provide a fundamental basis for modeling the structure and physical properties of pyroxenes in the deep Earth (e.g., Hugh-Jones et al. 1994; Arlt et al. 1998; Serghiou et al. 2000; Lin et al. 2005; Zhang et al. 2013a; Hu et al. 2017; Pakhomova et al. 2017; Xu et al. 2018; Lazarz et al. 2019; Li et al. 2024).

In contrast, research on the high-pressure stability and phase transitions of pyroxenoids remains relatively limited. Existing high-pressure studies on pyroxenoids have primarily focused on the phase transitions of wollastonite and related minerals. For instance, wollastonite undergoes a phase transition to a triclinic structure above 8.5 GPa and exhibits two $P\bar{1} \rightarrow P\bar{1}$ transitions at high pressures. The first one is a first-order phase transition, while the second may be classified as a second-order transition (Milani et al. 2021). Similarly, CaSiO_3 -walsstromite

follows a phase transition sequence of $P\bar{1} \rightarrow C2/m \rightarrow P2_1/c$ upon compression, where the first transition is first-order, and the second exhibits characteristics of a second-order transition (Milani et al. 2021).

The high-pressure behavior of the two pyroxenoids, pyroxmangite and rhodonite (Fig. 1), has received little attention. Zanazzi et al. (2008) reported that pyroxmangite does not experience any phase transition up to 5.6 GPa. Based on Raman spectroscopy data, Serghiou et al. (2004) suggested that rhodonite may undergo amorphization at ~ 33 GPa; however, this conclusion lacks direct crystallographic evidence. Therefore, further high-pressure crystallographic studies are required to verify whether rhodonite undergoes phase transitions or amorphization at high pressures.

Despite the extensive prior research on the high-pressure phase transitions of pyroxenes and the existing investigations into the high-pressure behavior of pyroxenoids, a systematic synthesis and comparison of high-pressure phase transitions between pyroxenes (orthopyroxenes and clinopyroxenes) and pyroxenoids is currently lacking. Such a comparative analysis would be valuable in elucidating the similarities and differences in the high-pressure phase transition behavior of orthopyroxenes, clinopyroxenes, and pyroxenoids.

In this study, we employ high-pressure synchrotron single-crystal X-ray diffraction (SCXRD) to obtain more reliable structural information on rhodonite, a pyroxenoid, at pressures up to 35.0(1) GPa. The results allow us to analyze its compression

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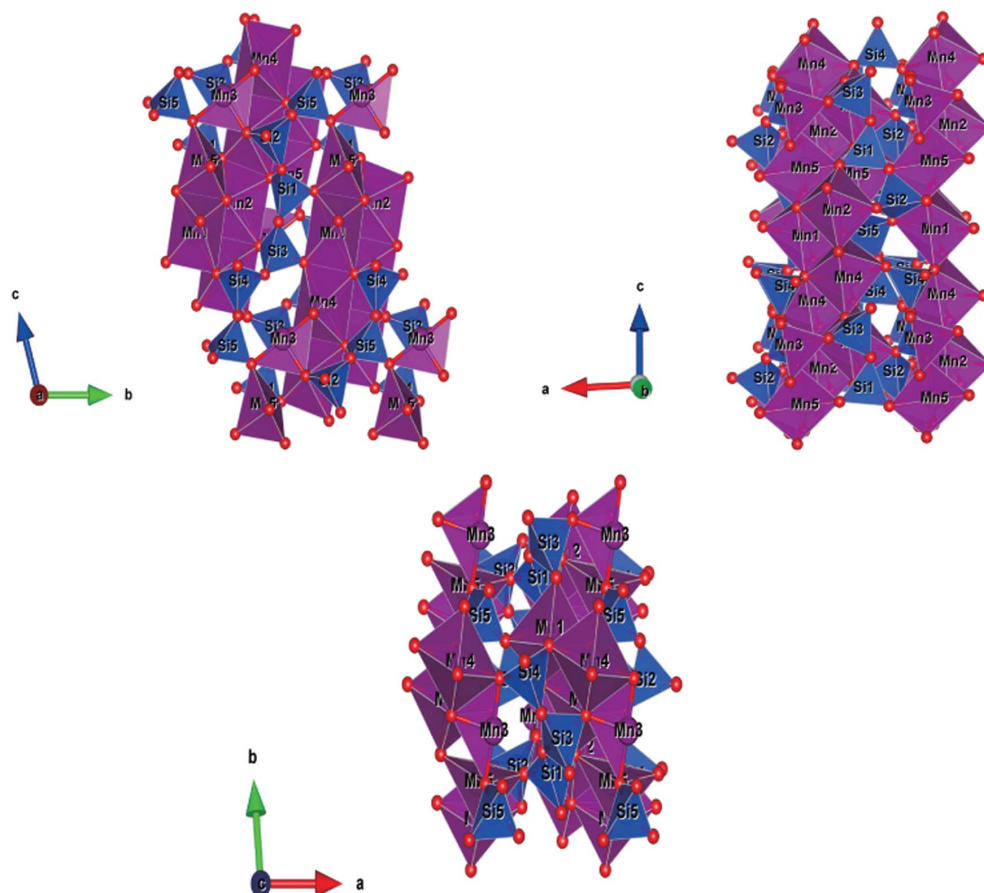


FIGURE 1. Crystal structure of rhodonite at ambient pressure along the *a*-, *b*-, and *c*-axis. Red balls represent oxygen. The numbers indicate different Mn and Si sites. (Color online.)

behavior, phase stability, and structural transitions. In addition, this study further reviews the phase transitions in orthopyroxenes, clinopyroxenes, and pyroxenoids. We place particular emphasis on the characteristics and mechanisms of these transitions, alongside a comparative discussion of their respective commonalities and distinctions.

EXPERIMENTAL METHODS

Synthesis of Rhodonite

The end-member rhodonite crystals were synthesized using a multi-anvil pressure apparatus (DS6*1400t) at the Institute of Geochemistry, Chinese Academy of Sciences. The reactants consisted of a stoichiometric mixture of high-purity MnO and SiO₂ (≥99.9%, Aladdin Company), which were sealed in a copper capsule along with 1 wt% ultrapure water. In the high-pressure–high-temperature synthesis, the sample assembly was similar to that described by Xu et al. (2018). The sample assembly was first compressed to 1.6 GPa in 30 min, then heated to 1273 K in 60 min. After a duration of 8 h, the sample chamber was quenched from high temperature to room temperature in a few seconds, and the decompression to ambient pressure (AP) was completed in half an hour. The rhodonite crystals (~100 μm) were then extracted from the product (Fig. 2a).

A scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDS) was used to analyze the chemical composition of the gold-coated sample. The operational parameters included a 15 kV accelerating voltage, 3.2–6.8 nA beam current, and a 10.4 mm working distance. The EDS results (Fig. 2b) reveal that the synthetic crystals are primarily composed of Mn, Si, and O, with only trace amounts of Al and Cu present as impurities. In combination with the subsequent

single-crystal diffraction analysis (Table 1), the synthetic crystals are identified as rhodonite with a composition close to MnSiO₃.

High-Pressure SCXRD

A selected single crystal was initially mounted onto a polymer micromesh sample holder for ambient SCXRD to ensure the crystal diffraction quality for subsequent high-pressure SCXRD experiments. For the high-pressure experiments, the crystal was pressurized using a diamond-anvil cell (DAC) with diamond culets of diameter 300 μm. A rhenium gasket with an initial thickness of 250 μm was indented to ~50 μm using the diamond anvils. A laser perforator was then used to create a sample chamber with a diameter of 180 μm in the indentation area of the rhenium gasket. A rhodonite crystal and a ruby sphere were placed together into the sample chamber. Neon was subsequently loaded to serve as the pressure-transmitting medium using the GSECARS gas-loading system (Rivers et al. 2008). The pressure was calibrated by measuring ruby fluorescence (Mao et al. 1986; Shen et al. 2020). The pressure was measured before and after data collection, and the average value was reported (Table 1).

In situ high-pressure synchrotron SCXRD experiments were conducted at the GSECARS (Sutton et al. 2022) 13-BM-C beamline (Xu et al. 2022a) of the Advanced Photon Source (APS), Argonne National Laboratory. SCXRD images were collected using a PILATUS 1M detector mounted on a six-circle diffractometer. The incident X-ray wavelength was 0.4340 Å, with a beam size of 12 × 18 μm. The detector tilt, rotation, and sample-to-detector distance were calibrated using LaB₆ powder as a reference (Zhang et al. 2017, 2022). The Φ -axis rotation step size was set to 0.5°, with a measurement exposure time of 1%.

During the experiments, SCXRD data were collected at 17 distinct pressure points, ranging from ambient pressure up to 35.0(1) GPa. The experimental data were reduced using the APEX 4.0 software suite. Crystal structure refinements were performed using the SHELX software package (Sheldrick 2008), facilitated

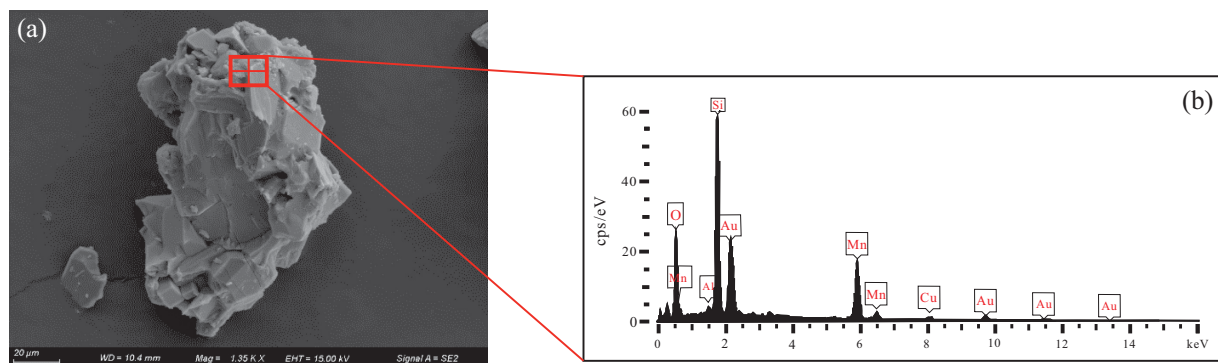


FIGURE 2. Backscattered electron (BSE) image (a) and energy-dispersive X-ray spectroscopy (EDS) spectrum of rhodonite (b). (Color online.)

TABLE 1. Unit-cell parameters and volume of rhodonite at different pressures

P (GPa)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
0.0001	6.702(1)	7.618(1)	11.854(1)	105.62(1)	92.41(1)	94.39(2)	579.9(1)
2.3(1)	6.653(1)	7.572(1)	11.767(1)	105.57(1)	92.36(1)	94.31(2)	568.2(2)
3.3(2)	6.635(1)	7.552(1)	11.730(1)	105.52(1)	92.32(1)	94.27(2)	563.6(2)
4.5(1)	6.614(1)	7.527(1)	11.686(1)	105.47(1)	92.27(1)	94.22(1)	558.1(1)
5.8(1)	6.589(1)	7.501(1)	11.641(1)	105.43(1)	92.23(1)	94.19(1)	552.1(1)
7.1(1)	6.571(1)	7.478(1)	11.600(1)	105.37(1)	92.19(1)	94.13(1)	547.2(1)
8.3(1)	6.553(1)	7.455(1)	11.560(1)	105.34(1)	92.17(1)	94.06(1)	542.3(1)
9.5(1)	6.535(1)	7.436(1)	11.525(1)	105.30(1)	92.14(1)	94.01(1)	538.0(1)
10.9(1)	6.521(1)	7.416(1)	11.485(1)	105.28(1)	92.18(1)	93.83(2)	533.6(1)
13.1(1)	6.488(1)	7.378(1)	11.415(1)	105.17(1)	92.16(1)	93.68(2)	525.4(1)
15.0(1)	6.458(1)	7.348(1)	11.361(1)	105.07(1)	92.14(1)	93.56(2)	518.8(1)
17.0(1)	6.427(1)	7.312(1)	11.303(1)	104.89(1)	92.11(1)	93.48(3)	511.6(2)
20.2(1)	6.396(1)	7.268(1)	11.219(1)	104.69(1)	92.16(1)	93.19(3)	502.9(2)
24.3(1)	6.356(2)	7.210(2)	11.110(2)	104.44(2)	92.43(2)	92.52(3)	491.8(3)
28.5(1)	6.327(2)	7.133(2)	10.994(2)	104.32(2)	93.21(2)	91.72(3)	479.5(3)
32.7(1)	6.302(5)	7.084(3)	10.914(4)	104.46(4)	94.30(4)	90.68(7)	470.2(5)
35.0(1)	6.270(5)	7.046(4)	10.856(4)	104.29(4)	94.74(4)	90.60(7)	463.0(5)

Note: Numbers in parentheses represent standard deviations to the last significant digit.

by the Olex 2 user interface (Dolomanov et al. 2009). Interatomic distances and polyhedral parameters were calculated using the VESTA software (Momma and Izumi 2011). Structure refinement was performed only for data up to 20.2 (1) GPa, as the quality of the data collected at higher pressures was insufficient for reliable structural refinement.

RESULTS

Equation of State

Table 1 summarizes the unit-cell parameters and volume of rhodonite from ambient pressure to 35.0(1) GPa. At ambient pressure, SCXRD analysis indicates that the rhodonite sample belongs to the triclinic system, space group $P\bar{1}$, with unit-cell parameters and volume given as: $a = 6.702(1)$ Å; $b = 7.618(1)$ Å; $c = 11.854(1)$ Å; $\alpha = 105.62(1)^\circ$; $\beta = 92.41(1)^\circ$; $\gamma = 94.39(2)^\circ$; $V = 579.89(13)$ Å³. As pressure increases, the unit-cell parameters a , b , and c show a clear decreasing trend, from 6.702(1), 7.618(1), and 11.854(1) Å at ambient pressure to 6.270(5), 7.046(4), and 10.856(4) Å at 35.0(1) GPa, respectively. The unit-cell parameters and volume exhibit a consistent decreasing trend with increasing pressure (Figs. 3a and 3c). In contrast, the angles α , β , and γ demonstrate significant anisotropy with increasing pressure. Before 10.9(1) GPa, all cell parameters show a declining trend. After 10.9(1) GPa, the trend in α remains relatively unchanged, while the decreasing trend in β significantly slows down, eventually increasing from 92.11(1)° at 17.0(1) GPa to 94.74(4)° at

35.0(1) GPa. The decreasing trend in γ becomes more pronounced, reaching 90.60(7)° at 35.0(1) GPa (Fig. 3b).

To further analyze the influence of pressure on the unit-cell volume, the equation of state (EoS) parameters for rhodonite were obtained through fitting the whole range pressure-volume data to the third-order Birch-Murnaghan Eos (III-BM-EoS) using the EosFit7-GUI software (Angel et al. 2014). The obtained EoS parameters are $V_0 = 579.8(2)$ Å³, $K_0 = 114(1)$ GPa, and $K'_0 = 3.0(1)$, where V_0 , K_0 , and K'_0 represent the zero-pressure volume, isothermal bulk modulus, and its pressure derivative, respectively.

The quality of the EoS fitting was assessed using the volume Eulerian finite strain $\{f_E = [(V_0/V)^{2/3} - 1]/2\}$ vs. “normalized stress” $\{F_E = P/[3f_E(2f_E + 1)^{5/2}]\}$ (Angel 2000). As shown in Figure 3d, a noticeable discontinuity is observed between 10.9(1) and 13.1(1) GPa, indicating that only piecewise fitting of the 0–10.9(1) GPa and the ranges of 10.9(1)–35.0(1) GPa can accurately describe the data. Therefore, a III-BM-EoS was used to fit the 0–10.9(1) and 10.9(1)–35.0(1) GPa data ranges separately. The fitting results for the pressure range from 0 to 10.9(1) GPa are as follows: $V_0 = 579.9(1)$ Å³, $K_0 = 107(3)$ GPa, and $K'_0 = 4.7(7)$. For the pressure range of 10.9(1)–35.0(1) GPa, the fitting results are: $V_0 = 579.9(1)$ Å³, $K_0 = 116(2)$ GPa, and $K'_0 = 2.9(1)$.

Additionally, the unit-cell axial compressibilities were determined to be 0.002971, 0.002792, and 0.003287 GPa^{−1} for the

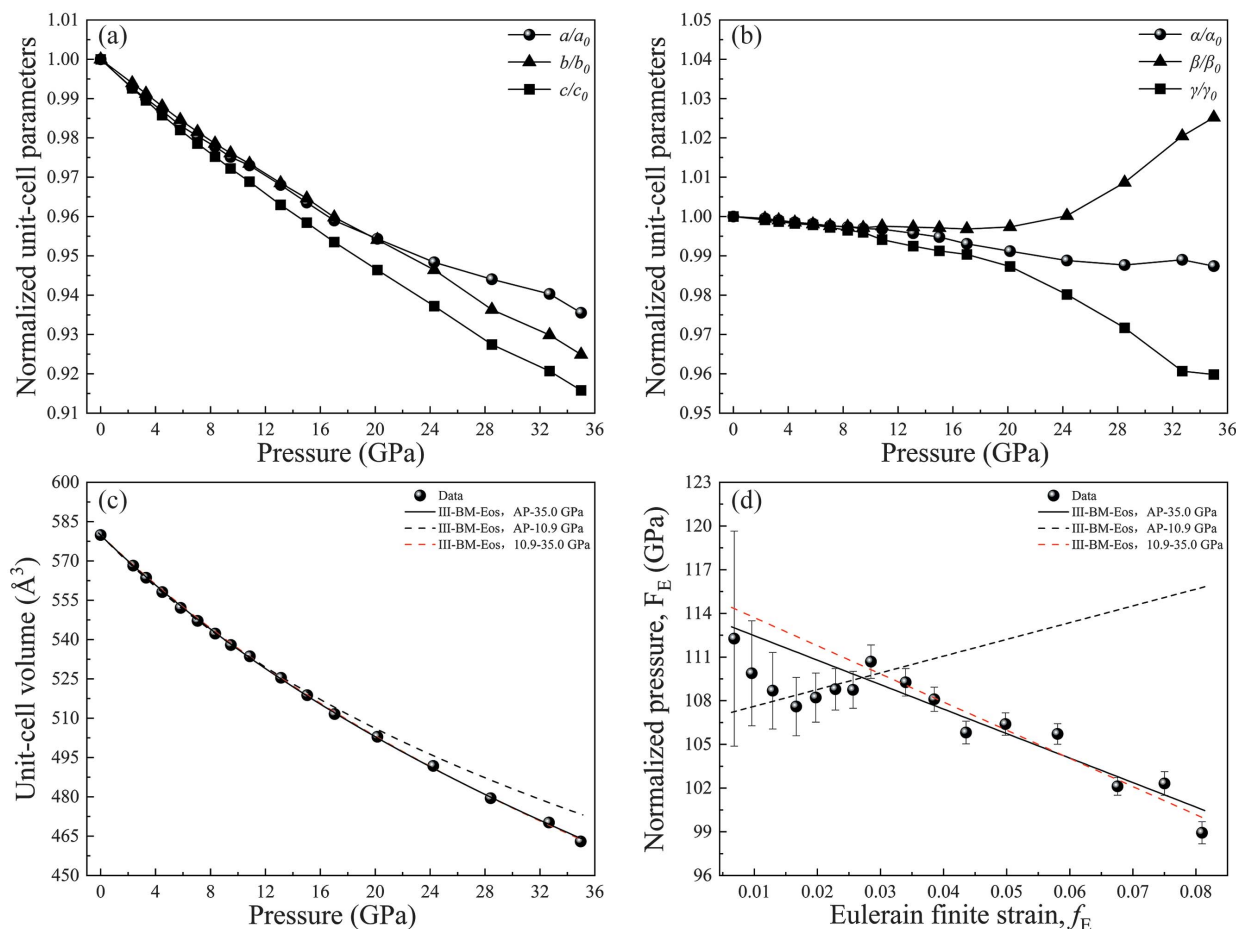


FIGURE 3. Unit-cell parameters (a, b) and volume (c) as a function of pressure, along with Eulerian strain-Normalized pressure (f_E - F_E) plot (d). In (c–d), the solid black line represents the results of fitting the data from ambient pressure (AP) to 35.0(1) GPa to a III-BM-EoS. The dashed black line indicates the III-BM-EoS fit of the data from ambient pressure to 10.9(1) GPa, while the dashed red line represents the III-BM-EoS fit of the data from 10.9 to 35.0 GPa. (Color online.)

a -, b -, and c -axes, respectively. The results highlight pronounced anisotropic compression, with the c -axis being the most compressible.

Polyhedral Compression

In the rhodonite structure, there are five distinct positions for Mn, each typically having a coordination number of 6; additionally, there are also five positions for Si, each with a coordination number of 4. The Mn-O polyhedra are linked by bridging oxygens to $[\text{Si}_5\text{O}_{15}]$ single chains extending along the $[101]$ direction. The structure of rhodonite at ambient pressure is illustrated in Figure 1. With increasing pressure, the Mn-O and Si-O polyhedra display distinct compression behaviors.

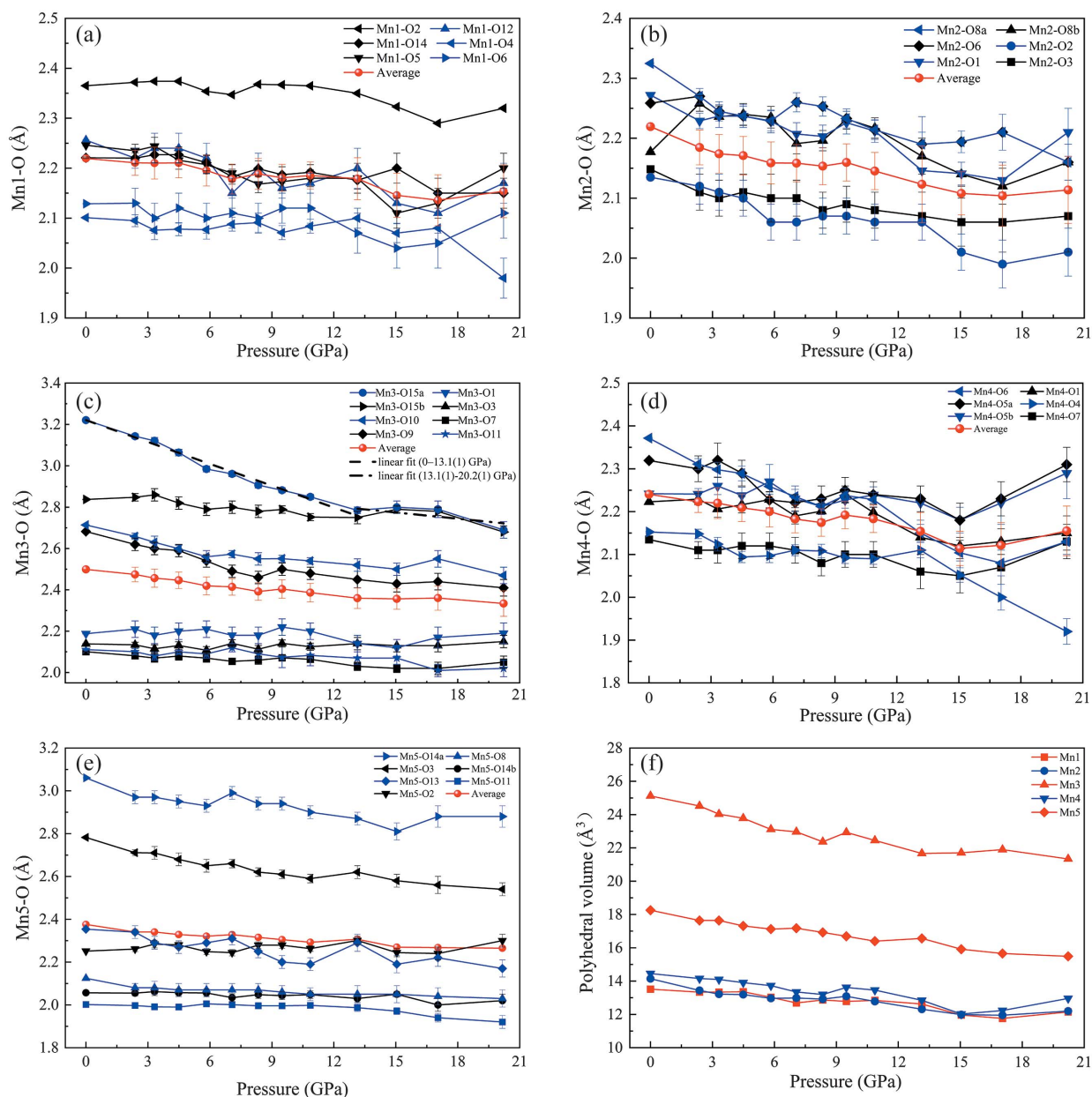
Table 2 provides detailed information on the structural refinement of rhodonite under various pressures. Based on the structural refinement details and crystal structure analysis, rhodonite maintains the $P\bar{1}$ space group throughout the entire pressure range. At ambient pressure, Mn1, Mn2, and Mn4 atoms are surrounded by six O atoms, with average Mn-O distances ($d_{\text{Mn-O}}$) of 2.219(1), 2.219(1), and 2.241(1) Å, respectively. In contrast, Mn3 and Mn5 atoms are surrounded by eight and seven O atoms, with

average Mn-O distances of 2.499(2) and 2.376(2) Å, respectively. The volumes of the polyhedra Mn1O_6 , Mn2O_6 , and Mn4O_6 are 13.52, 14.14, and 14.45 Å³, respectively, while the volumes of the polyhedra Mn3O_8 and Mn5O_7 are larger, measuring 25.12 and 18.26 Å³, respectively (Online Materials¹ Table S1). On the other hand, under ambient pressure, the average Si-O distances of the five SiO_4 tetrahedra (Si1O_4 , Si2O_4 , Si3O_4 , Si4O_4 , and Si5O_4) are 1.629(1), 1.630(1), 1.627(1), 1.621(1), and 1.620(1) Å, and the tetrahedral volumes are 2.21, 2.19, 2.20, 2.17, and 2.15 Å³, respectively (Online Materials¹ Table S2).

As pressure increases, the interatomic distances and polyhedral volumes of the MnO_{6-8} and SiO_4 polyhedra exhibit distinct compressional behaviors (Figs. 4 and 5). Specifically, for the Mn1O_6 , Mn2O_6 , and Mn4O_6 octahedra, most Mn-O distances, except for $d_{\text{Mn4-O5}}$, decrease irregularly with increasing pressure, reducing by 0.78–10.78% from ambient pressure to 20.2(1) GPa. In contrast, the variation of $d_{\text{Mn4-O5}}$ does not follow a clear overall trend. Below ~15.0(1) GPa, it fluctuates irregularly between 2.2 and 2.3 Å. Above 15.0(1) GPa, however, it increases from 2.180(30) to 2.290(60) Å at 20.2(1) GPa, corresponding to a total increase of 5.05%. For the Mn5O_7 polyhedron, at ambient

TABLE 2. Structural refinement details of rhodonite at different pressures

P (GPa)	0.0001	2.3(1)	3.3(2)	4.5(1)	5.8(1)	7.1(1)	8.3(1)
R _{int} (%)	5.37	3.79	3.21	3.85	4.04	3.35	3.23
R ₁ (%)	3.17	4.62	4.46	4.60	4.77	4.86	4.83
wR ₂ (all reflections, %)	8.89	10.86	12.21	12.96	12.99	14.77	13.59
Goodness of fit	1.052	1.050	1.104	1.086	1.075	1.096	1.089
No. of total reflections	11926	1226	1237	1220	1203	1184	1174
No. of reflections [Fo > 4sig(Fo)]	4034	534	554	547	537	554	541
P (GPa)	9.5(1)	10.9(1)	13.1(1)	15.0(1)	17.0(1)	20.2(1)	
R _{int} (%)	3.44	3.30	3.59	4.09	4.05	4.91	
R ₁ (%)	5.44	5.29	5.64	6.12	8.35	8.61	
wR ₂ (all reflections, %)	16.09	14.91	15.98	16.95	22.05	22.57	
Goodness of fit	1.049	1.083	1.092	1.051	0.985	0.976	
No. of total reflections	1156	1154	1130	1102	1094	1076	
No. of reflections [Fo > 4sig(Fo)]	507	496	487	449	416	381	

**FIGURE 4.** Mn-O interatomic distances (a–e) and Mn-O polyhedral volumes (f) as a function of pressure. (Color online.)

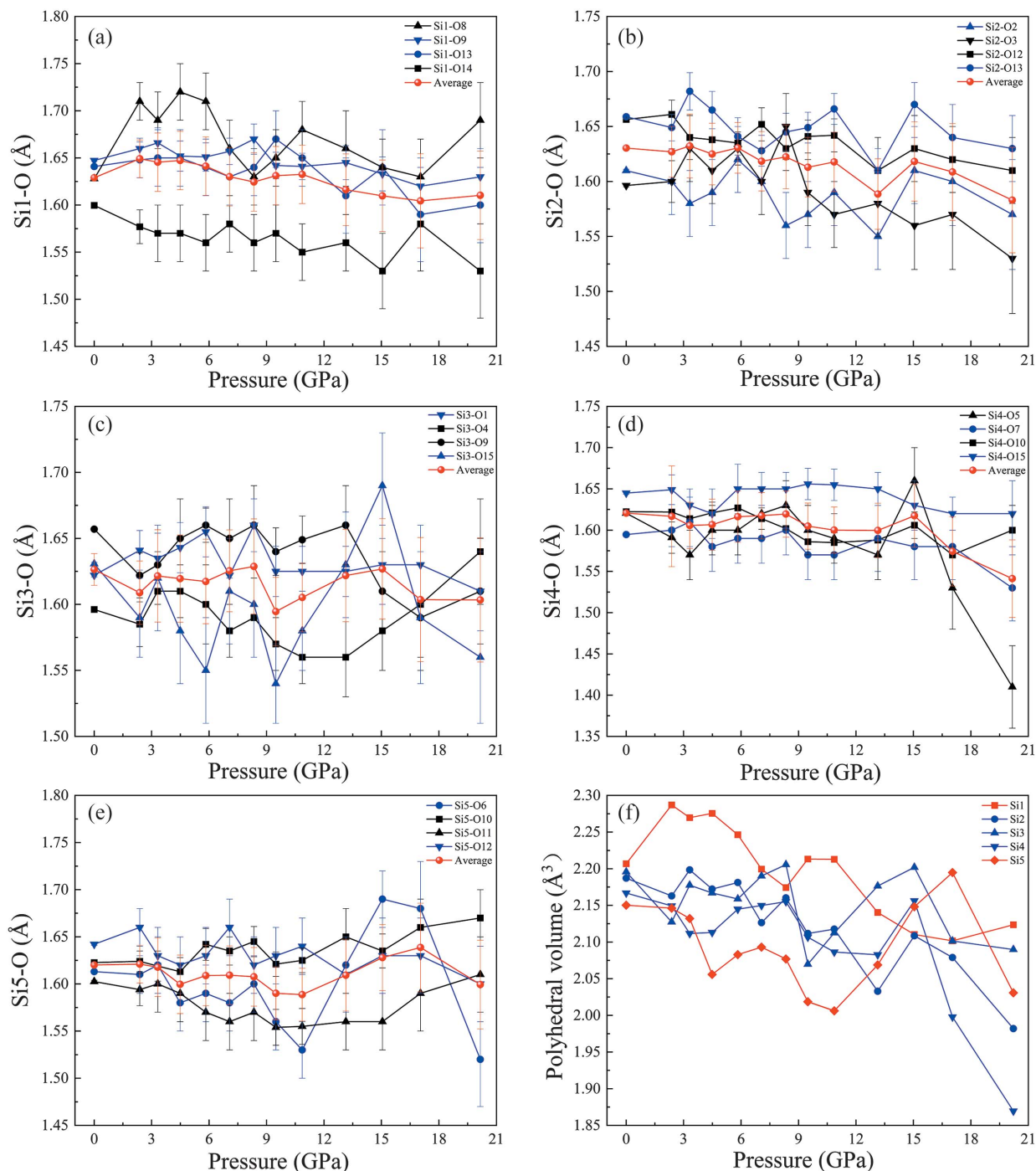


FIGURE 5. Si-O interatomic distances (a–e) and polyhedral volumes (f) at various pressures. (Color online.)

pressure, $d_{\text{Mn5-O14a}}$ [3.061(1) Å] is the longest, while $d_{\text{Mn5-O11}}$ [2.002(1) Å] is the shortest. With increasing pressure, all $d_{\text{Mn5-O}}$, except for $d_{\text{Mn5-O2}}$, show irregular decreases, reducing by 1.80–8.70% from ambient pressure to 20.2(1) GPa. In contrast, $d_{\text{Mn5-O2}}$ fluctuates irregularly between 2.25 and 2.30 Å from ambient pressure to 20.2(1) GPa. In the Mn3O_8 polyhedron, there are seven close oxygen atoms and one distant O atom (O15a). At ambient pressure, $d_{\text{Mn3-O15a}}$ [3.221(1) Å] is the longest, while

$d_{\text{Mn3-O7}}$ [2.101(1) Å] is the shortest. As pressure increases, $d_{\text{Mn3-O7}}$, $d_{\text{Mn3-O9}}$, $d_{\text{Mn3-O10}}$, $d_{\text{Mn3-O11}}$, and $d_{\text{Mn3-O15b}}$ show irregular decreases, reducing by 2.43–10.14% from ambient pressure to 20.2(1) GPa. Notably, $d_{\text{Mn3-O15a}}$ decreases significantly, from 3.221(1) Å at ambient pressure to 2.690(40) Å at 20.2(1) GPa, resulting in a reduction of 16.49%. Specifically, $d_{\text{Mn3-O15a}}$ decreases from 3.221(1) Å at ambient pressure to 2.785(16) Å at 13.1(1) GPa, corresponding to a reduction of 13.54%. A linear

fitting of the data yields a contraction rate of 0.035(1) Å/GPa. Between 13.1(1) to 20.2(1) GPa, $d_{\text{Mn3-O15a}}$ further decreases to 2.690(40) Å, representing an additional reduction of 4.57%, with a linear contraction rate of 0.010(6) Å/GPa. Meanwhile, $d_{\text{Mn3-O1}}$ and $d_{\text{Mn3-O3}}$ exhibit slight expansions of 0.09% and 0.51%, respectively, as pressure increases.

For MnO_6 , MnO_8 , and MnO_7 polyhedra, the volume decreases with increasing pressure. From ambient pressure to 20.2(1) GPa, the volume changes for the Mn1O_6 and Mn4O_6 polyhedra are relatively small, decreasing by 10.14% and 10.31%, respectively, while the volume of the Mn2O_6 polyhedron decreases by 13.77%. In contrast, the Mn3O_8 and Mn5O_7 polyhedra have larger volumes, and their volumes decrease by 15.05% and 15.16% from ambient pressure to 20.2(1) GPa, indicating higher compressibility.

For the SiO_4 tetrahedra, the interatomic distances and polyhedral volumes do not exhibit significant regularity with increasing pressure. Specifically, for Si1O_4 , the interatomic distances $d_{\text{Si1-O9}}$, $d_{\text{Si1-O13}}$, and $d_{\text{Si1-O14}}$ decrease by 1.03%, 2.50%, and 4.38%, respectively, as pressure increases. Notably, $d_{\text{Si1-O8}}$ increases from 1.628(1) Å at ambient pressure to 1.690(40) Å at 20.2(1) GPa, an increase of 3.81%, with a change from 1.628(1) Å at ambient pressure to 1.710(30) Å at 5.8(1) GPa, an increase of 5.04%. From 5.8(1) to 8.3(1) GPa, it decreases from 1.710(30) to 1.630(30) Å, a reduction of 4.68%, before increasing again to 1.690(40) Å at 20.2(1) GPa, which corresponds to an increase of 3.69%. For Si2O_4 , most Si-O interatomic distances decrease with increasing pressure, showing reductions of 1.75% to 4.14%. In Si3O_4 , most Si-O distances exhibit a downward trend except for $d_{\text{Si3-O4}}$, which decreases by 0.74% to 4.35%. The distance $d_{\text{Si3-O4}}$ increases from 1.596(1) Å at ambient pressure to 1.640(40) Å at 20.2(1) GPa, an increase of 2.76%. Notably, $d_{\text{Si3-O15}}$ decreases from 1.631(1) Å at ambient pressure to 1.540(30) Å at 9.5(1) GPa, then increases to 1.690(40) Å at 15.0(1) GPa, before rapidly dropping to 1.560(50) Å at 20.2(1) GPa (Fig. 5c). For Si4O_4 , with increasing pressure, most $d_{\text{Si4-O}}$ distances show a decreasing trend, where $d_{\text{Si4-O10}}$, $d_{\text{Si4-O15}}$, and $d_{\text{Si4-O7}}$ decrease by 1.42% to 4.08%, while $d_{\text{Si4-O5}}$ decreases by 13.02%. Notably, $d_{\text{Si4-O5}}$ decreased from 1.621(1) Å at ambient pressure to 1.570(30) Å at 13.1(1) GPa, followed by a rapid increase to 1.660(40) Å at 15.0(1) GPa. As pressure continued to rise, the distance decreased from 1.660(40) to 1.410(50) Å at 20.2(1) GPa (Fig. 5d). In Si5O_4 , $d_{\text{Si5-O12}}$ and $d_{\text{Si5-O6}}$ decreased by 2.56% and 5.77%, respectively, while $d_{\text{Si5-O11}}$ and $d_{\text{Si5-O10}}$ increased by 0.44% and 2.90%. Notably, $d_{\text{Si5-O6}}$ decreased from 1.613(1) Å at ambient pressure to 1.530(30) Å at 10.9(1) GPa, followed by a rapid increase to 1.690(30) Å at 15.0(1) GPa. As pressure continued to rise, the $d_{\text{Si5-O6}}$ distance decreased from 1.690(30) to 1.520(50) Å at 20.2(1) GPa (Fig. 5e).

For SiO_4 volume, from ambient pressure to 20.2(1) GPa, Si1O_4 , Si3O_4 , and Si5O_4 exhibit relatively low compressibility, decreasing by 3.76%, 4.83%, and 5.53%, respectively. In contrast, Si2O_4 and Si4O_4 demonstrate higher compressibility, declining by 9.37% and 13.79%, respectively. Notably, except for Si1O_4 , the volumes of the other SiO_4 show a trend of increasing and then decreasing after 13.1(1) GPa.

DISCUSSION

Pressure-Induced Isosymmetric Second-Order Phase Transition in Rhodonite

The f_E - F_E plot of the unit-cell volume (Fig. 3d) exhibits a significant discontinuity at 10.9(1) GPa, indicating a change in the compression mechanism of rhodonite at this pressure. Notably, it is associated with a marked discontinuity in the bulk modulus (Online Materials¹ Fig. S1). The bulk modulus increases rapidly with pressure below 10.9(1) GPa, displaying a linear relationship, while above 10.9(1) GPa, it shows a different linear growth pattern. Furthermore, between 10.9(1) and 35.0(1) GPa, the rate of increase of the bulk modulus is lower than that observed at pressures below 10.9(1) GPa. However, this change in the compression mechanism does not lead to a discontinuity in the unit-cell volume (Fig. 3c) or alter the crystal symmetry. Therefore, this phenomenon indicates that rhodonite undergoes an isosymmetric second-order phase transition at 10.9(1) GPa.

Isosymmetric phase transitions refer to those transitions where there is no change in symmetry during the process. These transitions stand in sharp contrast to other types of phase transitions, which are typically accompanied by changes in symmetry (Christy 1995). Based on the thermodynamic characteristics and structural changes during the transition, isosymmetric phase transitions can be first- or second-order. The causes of isosymmetric phase transitions have been summarized by Zhong et al. (2025), including: (1) increase in coordination number (Xu et al. 2017a; Zhong et al. 2025); (2) charge transfer (Yokokura et al. 2015; Clarke et al. 2020); (3) tilting and rotation of SiO_4 tetrahedra (Dove et al. 1995); (4) layer shift (Jin et al. 2024); and (5) spin crossover transition (Li et al. 2023). Among these, the isosymmetric second-order phase transitions triggered by coordination number increase have been observed in aegirine (Xu et al. 2017a) and cerite (Zhong et al. 2025). In these two minerals, the coordination number increases in Na^+ and REE^{3+} under high pressures, triggering the phase transitions.

In this study, the isosymmetric second-order phase transition observed between 10.9(1) and 13.1(1) GPa is primarily attributed to a pressure-induced increase in the coordination number of Mn3. Specifically, the Mn3-O15a interatomic distance decreases significantly from 3.221(1) Å at ambient conditions to 2.850(12) Å at 13.1(1) GPa, representing an 11.52% reduction (Fig. 4c; Online Materials¹ Table S1c). Beyond this pressure, however, the rate of distance contraction slows markedly, with only a 3.4% decrease between 13.1(1) and 20.2(1) GPa. This nonlinear behavior implies that a stable Mn3-O15a bond is formed within the 10.9(1)–13.1(1) GPa range, altering the local coordination environment and marking a transition in the compression mechanism. Notably, this structural transformation appears unique to the Mn3 polyhedron and is not evident in other coordination polyhedra within the rhodonite structure.

Further support for this coordination-driven transition is provided by the evolution of polyhedral volumes. Among the Mn-centered units, the Mn3O_8 polyhedron exhibits the highest compressibility, with a total volume reduction of 15.05% from ambient pressure to 20.2(1) GPa. Interestingly, a notable decrease in compressibility occurs beyond 13.1(1) GPa, coinciding with

the stabilization of the Mn3-O15a bond, which reinforces the interpretation of a coordination-induced phase transition.

We note that two Si-O bond lengths exhibit irregular pressure-dependent behavior near the phase transition pressure. Specifically, $d_{\text{Si3-O15}}$ and $d_{\text{Si5-O6}}$ display a non-monotonic trend, characterized by an initial contraction up to ~10 GPa, followed by a slight expansion (Figs. 5c and 5e). These variations likely result from local distortions accommodating the reconfiguration of the surrounding Mn-O network. Moreover, pressure-dependent changes in the Si-O-Si bond angles (Fig. 6) and the morphology

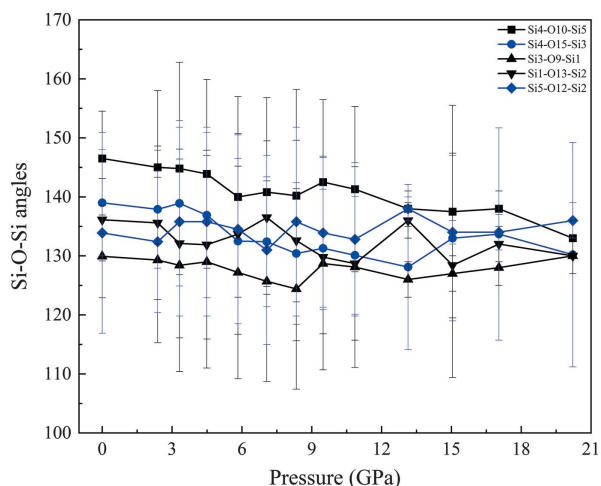


FIGURE 6. Evolution of Si-O-Si angles as a function of pressure. (Color online.)

of the SiO₄ tetrahedral chain (Fig. 7) do not show any significant anomalies near the phase transition pressure. This suggests that rotations of SiO₄ tetrahedra may not play a prominent role in the phase transition. Therefore, these findings indicate that the isosymmetric phase transition in rhodonite is primarily driven by the formation of a new Mn-O bond and the associated increase in Mn3 coordination, which are coupled with polyhedral volume changes and subtle, localized adjustments in the silicate framework.

Comparisons of the Phase Transitions in Pyroxenes and Pyroxenoids

A Review of Previous Studies

Pyroxene is an important rock-forming mineral in the Earth's crust and the second most abundant mineral in the upper mantle, following olivine. Based on their symmetry, pyroxene can be divided into orthopyroxene and clinopyroxene subgroups (Duffy and Vaughan 1988). Natural orthopyroxenes occur as solid solutions between enstatite (En; MgSiO₃) and ferrosilite (Fs; FeSiO₃), although in some cases other components such as Ca and Al are also important. The clinopyroxene subgroup, on the other hand, includes variations such as the Ca-rich (e.g., diopside and hedenbergite), Na-rich (e.g., aegirine, jadeite, kosmochlor), clinoenstatite and clinoferrosillite, solid solutions between Ca- and Na-rich (e.g., omphacite) and augite. Less commonly occurring clinopyroxenes include spodumene, pigeonite, kanoite, and jervisite. Moreover, under specific geological conditions and chemical compositions, chain silicates that are structurally more complex than pyroxenes, known as pyroxenoids (space group $P\bar{1}$), may also form.

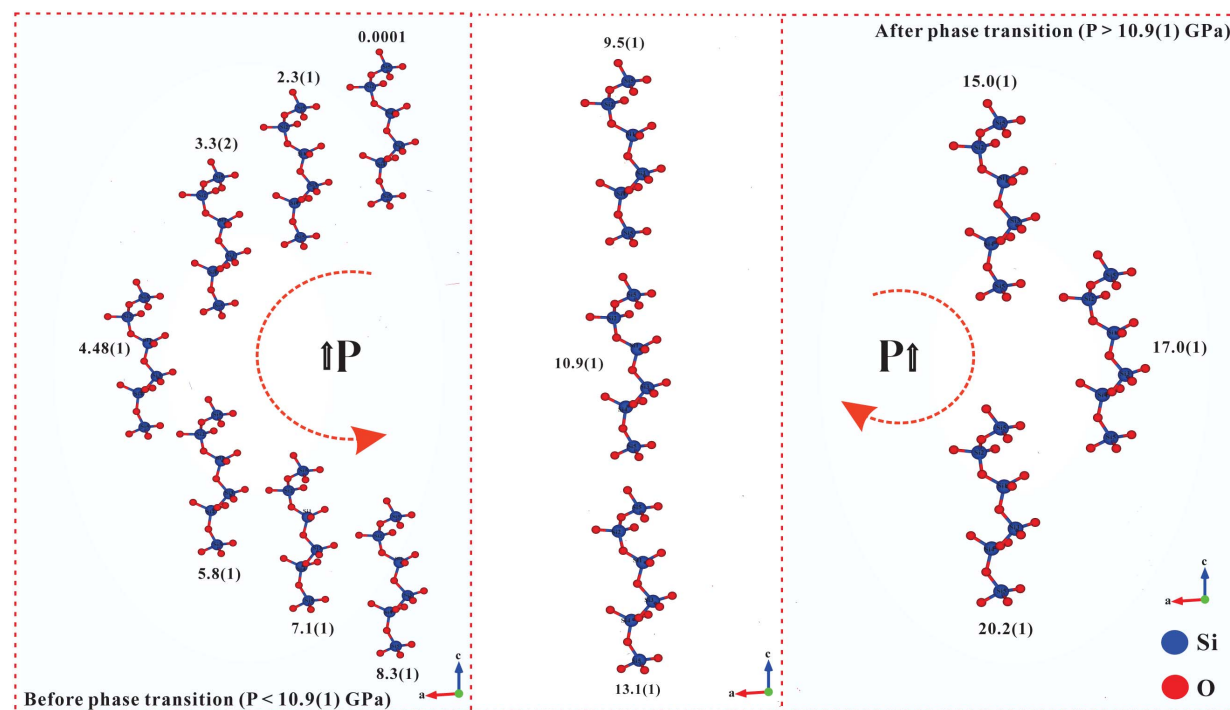


FIGURE 7. Structural evolution of Si-O tetrahedral chains in rhodonite with increasing pressure, shown at consistent orientation to highlight pressure-induced distortion and rotation of the tetrahedra. The numbers in the figure indicate the corresponding pressure values (GPa). (Color online.)

Numerous studies have documented the high-pressure behavior of orthopyroxene (Table 3), encompassing end-member orthopyroxenes (En and Fs), En-Fs solid solutions, and orthopyroxenes containing Ca, Al, Ni, and trace amounts of water (Serghiou et al. 2000; Lin et al. 2005; Zhang et al. 2012, 2013a, 2013b, 2016; Dera et al. 2013; Finkelstein et al. 2015; Xu et al. 2018, 2020, 2022b, 2024). Orthopyroxenes exhibit a diverse array of phase transitions. The high-pressure phases of orthopyroxenes (the initial phase is α -opx with *Pbca* space group) vary with composition [see Xu et al. (2020, 2022b) for a detailed discussion]. Upon compression, β -opx (*P2₁/c* space group) emerges as the first high-pressure phase for both end-member compositions and En-Fs solid solutions, as well as for those containing other metals such as Al, Ca, Ni, and trace amounts of water. For end-member enstatite, the second high-pressure phase is either β -popx (*P2₁ca*) (Serghiou et al. 2000) or α -popx (*P2₁ca*) (Li et al. 2024). For the end-member ferrosilite, the second high-pressure phase is γ -opx (*Pbca*) (Xu et al. 2020). In the case of En₉₀Fs₁₀, the second high-pressure phase is identified as α -popx (Finkelstein et al. 2015). Conversely, for En-Fs solid solutions with compositions ranging from En = 0 to 70, the second high-pressure phase is

γ -opx (*Pbca*) (Dera et al. 2013; Xu et al. 2020). For Ni-bearing enstatite, the second high-pressure phase is β -opxII (*P2₁/c*) (Xu et al. 2018). The third high-pressure phase of orthopyroxene is β -popx, which has been confirmed by SCXRD for En₉₀Fs₁₀ (Finkelstein et al. 2015) and Ni-En₃₁Fs₆₅ (Xu et al. 2024). Notably, the incorporation of Ca and Al primarily shifts the pressure at which phase transitions occur without altering the structural characteristics of the high-pressure phases (Zhang et al. 2013b; Xu et al. 2022b). Furthermore, trace amounts of water do not significantly affect the high-pressure structures or the transition pressures (Xu et al. 2018, 2020).

Similar to orthopyroxene, the high-pressure behaviors of the clinopyroxene group have been extensively investigated (Table 4). Under ambient pressure, clinoferrrosilite, clinoenstatite, kanoite, and pigeonite share the *P2₁/c* space group; however, at high pressure, they undergo first-order phase transitions to structures with a *C2/c* space group (HP-*C2/c*) (Hugh-Jones et al. 1994; Arlt et al. 1998; Nestola et al. 2004; Lazarz et al. 2019). With further increases in pressure, clinoferrrosilite and clinoenstatite transition to structures with a *P2₁/c* space group (HP-*P2₁/c*) (Pakhomova et al. 2017; Lazarz et al. 2019). Conversely, diopside and

TABLE 3. Phase transitions of orthopyroxenes under high pressure

Orthopyroxene	Phase transition	Transition pressure (GPa)	Maximum pressure (GPa)	References
En	<i>Pbca</i> → <i>P2₁/c</i>	11.2	70	Serghiou et al. (2000)
	<i>P2₁/c</i> → <i>P2₁ca</i>	39.0		
En	<i>Pbca</i> → <i>P2₁/c</i>	10.5	22	Lin et al. (2005)
En	<i>Pbca</i> → <i>P2₁/c</i>	13.3	18	Zhang et al. (2013b)
En	<i>Pbca</i> → <i>P2₁/c</i>	12.9	34.3	Xu et al. (2018)
En	<i>Pbca</i> → <i>P2₁/c</i>	13.5	34	Li et al. (2024)
	<i>P2₁/c</i> → <i>P2₁ca</i>	29		
En ₉₄ Fs ₆	<i>Pbca</i> → <i>P2₁/c</i>	13.5	29.8	Xu et al. (2018)
	<i>P2₁/c</i> → <i>P2₁/c</i>	29.8		
En ₉₁ Fs ₉	<i>Pbca</i> → <i>P2₁/c</i>	12.9	34	Li et al. (2024)
	<i>P2₁/c</i> → <i>Pbca</i>	30		
En ₉₀ Fs ₁₀	<i>Pbca</i> → <i>P2₁/c</i>	12.4	18	Zhang et al. (2013b)
En ₉₀ Fs ₁₀	<i>Pbca</i> → <i>P2₁/c</i>	12.4	48.5	Finkelstein et al. (2015)
	<i>P2₁/c</i> → <i>P2₁ca</i>	28.4		
	<i>P2₁ca</i> → <i>P2₁ca</i>	38.6		
En ₈₇ Fs ₁₃	<i>Pbca</i> → <i>P2₁/c</i>	11.2	19.1	Zhang et al. (2013a)
En ₈₆ Fs ₁₁	<i>Pbca</i> → <i>P2₁/c</i>	15	34	Li et al. (2024)
	<i>P2₁/c</i> → <i>Pbca</i>	30		
En ₈₄ Fs ₈ MgTs ₆ Wo ₂	<i>Pbca</i> → <i>P2₁/c</i>	13.5	14.5	Zhang et al. (2012)
En ₇₉ Fs ₉ MgTs ₁₀ Wo ₂	<i>Pbca</i> → <i>P2₁/c</i>	16.0	34.8	Xu et al. (2022b)
	<i>P2₁/c</i> → <i>Pbca</i>	28.0		
En ₇₆ Fs ₉ Di ₄ MgTs ₁₁	<i>Pbca</i> → <i>P2₁/c</i>	16.0	18	Zhang et al. (2013b)
En ₇₄ Fs ₂₁	<i>Pbca</i> → <i>P2₁/c</i>	15	34	Li et al. (2024)
	<i>P2₁/c</i> → <i>Pbca</i>	30		
En ₇₀ Fs ₃₀	<i>Pbca</i> → <i>P2₁/c</i>	13.3	25.1	Xu et al. (2020)
	<i>P2₁/c</i> → <i>Pbca</i>	25.1		
En ₆₈ Fs ₈ MgTs ₂₄	<i>Pbca</i> → <i>P2₁/c</i>	14.4	35.1	Xu et al. (2022b)
En ₆₇ Fs ₂₃ MgTs ₁₀	<i>Pbca</i> → <i>P2₁/c</i>	14.2	32.6	Xu et al. (2022b)
	<i>P2₁/c</i> → <i>Pbca</i>	31.2		
En ₅₅ Fs ₄₅	<i>Pbca</i> → <i>P2₁/c</i>	12.4	26.2	Xu et al. (2020)
	<i>P2₁/c</i> → <i>Pbca</i>	20.8		
En ₄₄ Fs ₅₆	<i>Pbca</i> → <i>P2₁/c</i>	12.9	32.2	Xu et al. (2020)
	<i>P2₁/c</i> → <i>Pbca</i>	18.2		
Ni-En ₃₁ Fs ₆₅	<i>Pbca</i> → <i>P2₁/c</i>	12.1	33.8	Xu et al. (2024)
	<i>P2₁/c</i> → <i>Pbca</i>	15.6		
	<i>Pbca</i> → <i>P2₁ca</i>	33.8		
En ₁₄ Fs ₈₂ MgTs ₂	<i>Pbca</i> → <i>P2₁/c</i>	10.6	32.3	Dera et al. (2013)
	<i>P2₁/c</i> → <i>Pbca</i>	12.7		
Fs	<i>Pbca</i> → <i>P2₁/c</i>	6.3	30.7	Xu et al. (2020)
	<i>P2₁/c</i> → <i>Pbca</i>	12.5		

Notes: The phase transitions occurring in orthopyroxenes in the table are all first-order transitions. En = enstatite (MgSiO₃); Fs = ferrosilite (Fe₂Si₂O₆); MgTs = Mg-tschemakite (MgAl₂SiO₆); Wo = wollastonite (CaSiO₃); Di = diopside (CaMgSi₂O₆); *Pbca* → *P2₁/c* (α -opx → β -opx); *P2₁/c* → *P2₁/c* (β -opx → β -opx II); *P2₁/c* → *Pbca* (β -opx → γ -opx); *P2₁/c* → *P2₁ca* (β -opx → α -popx); *P2₁/c* → *P2₁ca* (β -opx → β -popx); *Pbca* → *P2₁ca* (γ -opx → β -popx); *P2₁ca* → *P2₁ca* (α -popx → β -popx).

spodumene, which possess a $C2/c$ space group at ambient pressure, transform to structures with a $P2_1/c$ space group (HP- $P2_1/c$) under high pressure (Arlt and Angel 2000; Chopelas and Serghiou 2002; Plonka et al. 2012). While augite, jadeite, jervisite, kosmochlor, omphacite, and hedenbergite share the same $C2/c$ space group as diopside, they either undergo unknown phase transitions at high pressure or exhibit no phase transitions within the experimental pressure range (Table 4) (Zhang et al. 1999, 2016; Posner et al. 2014; Barzowska et al. 2017; Xu et al. 2017b). Protopyroxene ($Pbcn$) undergoes a first-order phase transition during compression, transforming to the $P2_1cn$ structure (Yang et al. 1999). Additionally, Xu et al. (2017a) found that aegirine ($C2/c$ space group) experiences an isosymmetric second-order phase transition at ~ 24 GPa (Table 4).

In comparison to pyroxenes, research on the high-pressure behavior of pyroxenoids is relatively limited and primarily focuses on wollastonite and its derivative minerals (Table 5). At ambient pressure, wollastonite, CaSiO_3 -wollastonite, CaGeO_3 -wollastonite, pyroxmangite, and rhodonite all belong to the $P\bar{1}$ space group (Nagai and Yamanaka 1997; Serghiou et al. 2004; Zanazzi et al. 2008; Milani et al. 2021). However, these minerals exhibit distinct phase transition behaviors under high-pressure conditions. Wollastonite undergoes two phase transitions while maintaining structures within the $P\bar{1}$ space group. CaSiO_3 -wollastonite initially transitions to the $C2/m$ space group and subsequently reverts to the $P2_1/c$ space group as pressure increases further. It is noteworthy that the first phase

transition of wollastonite and CaSiO_3 -wollastonite is first-order, while the second phase transition is second-order (Fig. 8d). However, it cannot be confirmed that the phase transition occurring in wollastonite is necessarily a second-order transition (Milani et al. 2021). High-pressure Raman spectroscopic data indicate that CaGeO_3 -wollastonite first transitions to a rhodonite-like structure and subsequently to a perovskite structure (Nagai and Yamanaka 1997). Pyroxmangite does not undergo any phase transitions within 5.6 GPa (Zanazzi et al. 2008).

Serghiou et al. (2004) reported that rhodonite experiences amorphization at 33 GPa, based on high-pressure Raman spectroscopic data. However, in this study, we found that rhodonite ($P\bar{1}$ space group) undergoes an isosymmetric second-order phase transition under high pressure, driven by increases in the coordination number of Mn (Fig. 8c). Furthermore, the crystal structure of rhodonite retains its integrity up to 35.0(1) GPa without exhibiting any characteristics of amorphization, as indicated by SCXRD data. The observed amorphization of rhodonite in the study by Serghiou et al. (2004) is likely attributed to the non-hydrostatic conditions generated by the Ar pressure medium. In contrast, according to the high-pressure Raman spectroscopic data by Lin and Shen (2016), Pseudowollastonite (CSP), which belongs to the $C2/c$ space group at ambient pressure, first transitions to CSP-II and subsequently undergoes amorphization as pressure increases further. Wollastonite-2M (CSW), with a $P2_1/a$ space group at ambient pressure, undergoes three phase transitions: first transitioning to CSW-Ha, then to

TABLE 4. Phase transitions of clinopyroxenes under high pressure

Clinopyroxenes	Phase transition	Transition pressure (GPa)	Maximum pressure (GPa)	Reference(s)
Aegirine	$C2/c \rightarrow C2/c$	24	60	Xu et al. (2017a)
Augite	No phase transition		27	Xu et al. (2017b)
Clinoferrosilite	$P2_1/c \rightarrow C2/c$	1.5	45	Hugh-Jones (1994); Pakhomova et al. (2017)
	$C2/c \rightarrow P2_1/c$	30–36		
Clinoenstatite	$P2_1/c \rightarrow C2/c$	6	50.2	Lazarz et al. (2019)
	$C2/c \rightarrow P2_1/c$	45		
Diopside	$C2/c \rightarrow P2_1/c$	56	71	Chopelas and Serghiou (2002); Plonka et al. (2012)
Hedenbergite	$C2/c \rightarrow \text{Unknown}$	53	68	
	$\text{Unknown} \rightarrow \text{Unknown}$	68		Zhang et al. (1999)
Jadeite	No phase transition		30	Posner et al. (2014)
Jervisite	$C2/c \rightarrow \text{Unknown}$	10–12	30	Barzowska (2017)
Kanoite	$P2_1/c \rightarrow C2/c$	5.1	5.2	Arlt et al. (1998)
Kosmochlor	No phase transition		40.2	Posner et al. (2014)
Omphacite	No phase transition		47	Zhang et al. (2016)
Protopyroxene	$Pbcn \rightarrow P2_1cn$	2.03–2.5	10.4	Yang et al. (1999)
Pigeonite	$P2_1/c \rightarrow C2/c$	5.1	6.5	Nestola et al. (2004)
Spodumene	$C2/c \rightarrow P2_1/c$	3.2	8.84	Arlt and Angel (2000)

TABLE 5. Phase transitions of pyroxenoids under high pressure

Pyroxenoids	Space group	Transition pressure (GPa)	Maximum pressure (GPa)	Reference
CaGeO_3 -wollastonite	$P\bar{1} \rightarrow \text{Unknown}$	6	27	Nagai and Yamanaka (1997)
	$\text{Unknown} \rightarrow \text{Unknown}$	15		
CaSiO_3 -wollastonite	$P\bar{1} \rightarrow C2/m$	8.5	20	Milani et al. (2021)
	$C2/m \rightarrow P2_1/c$	12–13		
Wollastonite	$P\bar{1} \rightarrow P\bar{1}$	8.2	22	Milani et al. (2021)
	$P\bar{1} \rightarrow P\bar{1}$	19.2		
Pseudowollastonite	$C2/c \rightarrow \text{Unknown}$	10	35.4	Lin and Shen (2016)
	$\text{Unknown} \rightarrow \text{Unknown}$	22–23		
Wollastonite-2M	$P2_1/a \rightarrow \text{Unknown}$	8.5	35.4	Lin and Shen (2016)
	$\text{Unknown} \rightarrow \text{Unknown}$	19		
	$\text{Unknown} \rightarrow \text{amorphization}$	26		
Pyroxmangite	No phase transition		5.6	Zanazzi et al. (2008)
Rhodonite	$P\bar{1} \rightarrow \text{amorphization}$	33	33	Serghiou et al. (2004)
Rhodonite	$P\bar{1} \rightarrow P\bar{1}$	10.9	35.0	This study

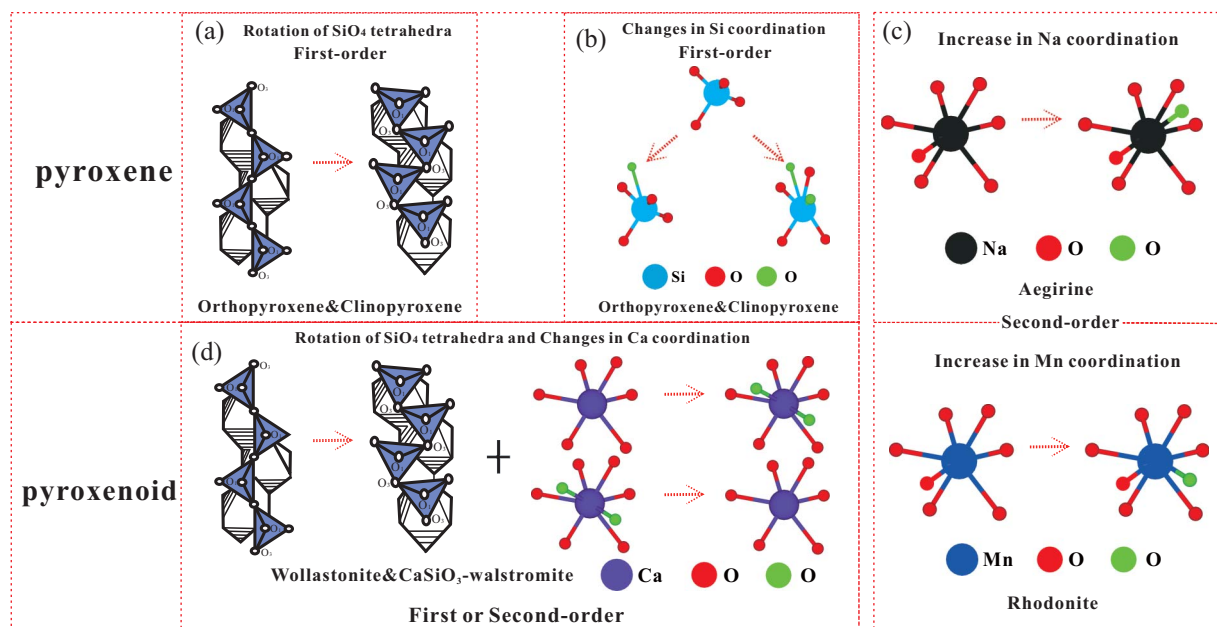


FIGURE 8. A summary of pressure-induced phase transitions in chain silicates (pyroxene and pyroxenoid), highlighting various mechanisms. (a) Type-I involves rotation of SiO₄ tetrahedra; (b) type-II is characterized by an increase in the Si coordination number; (c) type-III involves an increase in the coordination number of Mn or Na; (d) type-IV combines the rotation of SiO₄ tetrahedra with changes (increases/decreases) in the Ca coordination number. Type-I and type-II are first-order, type-III is second-order, and type-IV can be either first- or second-order. (Color online.)

CSW-Hb, and ultimately undergoing amorphization, similar to rhodonite and CSP.

Comparisons of the Phase Transition Mechanisms

The fundamental building units of orthopyroxene, clinopyroxene, and pyroxenoid are all SiO₄ tetrahedra, which form single-chain silicates through corner-sharing. Due to their similar structures, these three mineral groups exhibit analogous mechanisms for high-pressure phase transitions, including those driven by the rotation of SiO₄ tetrahedra (Fig. 8a). This mechanism is one of the primary causes of phase transitions in orthopyroxene and clinopyroxene (Hugh-Jones et al. 1994; Arlt et al. 1998; Yang et al. 1999; Arlt and Angel 2000; Nestola et al. 2004; Zhang et al. 2012; Dera et al. 2013; Pakhomova et al. 2017; Xu et al. 2018, 2020; Lazarz et al. 2019). In orthopyroxene and clinopyroxene, phase transitions can also be triggered by changes in the coordination number of Si in addition to the rotation of SiO₄ tetrahedra (Fig. 8b) (Hugh-Jones et al. 1994; Serghiou et al. 2000; Chopelas and Serghiou 2002; Finkelstein et al. 2015; Lazarz et al. 2019; Li et al. 2024; Xu et al. 2024). However, for pyroxenoids (Table 5), phase transitions driven by changes in the coordination number of Si have not yet been reported. In contrast, pyroxenoids often experience phase transitions driven by the rotation of SiO₄ tetrahedra that are accompanied by changes in cation coordination (Fig. 8d) (Milani et al. 2021). Moreover, in clinopyroxene and pyroxenoid, phase transitions can be induced not only by tetrahedral rotation and changes in Si coordination but also by an increase in the coordination number of metal cations. The phase transitions in aegirine (Xu et al. 2017a) and rhodonite are two examples (Fig. 8c).

Isosymmetric phase transitions are commonly observed in mineral physics studies. However, most of the phase transitions identified in orthopyroxene are not isosymmetric (Table 5), with isosymmetric transitions occurring only in En₉₀Fs₁₀ (α-popx (*P*₂₁*ca*) → β-popx (*P*₂₁*ca*) transition (Finkelstein et al. 2015) and Ni-En₉₄ (β-opx (*P*₂₁*c*) → β-opx II (*P*₂₁*c*) (Xu et al. 2018). Similar to orthopyroxene, most phase transitions in clinopyroxene are also not isosymmetric, with an isosymmetric phase transition observed only in aegirine (Xu et al. 2017a) (Table 3). In pyroxenoids (Table 5), studies have reported isosymmetric phase transitions in wollastonite (Milani et al. 2021) and rhodonite (this study). However, no evidence of isosymmetric phase transitions has been found in other pyroxenoids.

In orthopyroxene and clinopyroxene, phase transitions are predominantly first-order, and the transition mechanisms primarily involve the rotation of SiO₄ tetrahedra and an increase in the Si coordination number. The rotation of tetrahedra occurs because the compressibility of SiO₄ tetrahedra is significantly lower than that of octahedra. As pressure increases, the tetrahedra rotate to accommodate the compression of the octahedra, leading to a rearrangement of the structure. This process triggers a volume collapse, thus a first-order phase transition (Hugh-Jones et al. 1994; Arlt et al. 1998; Nestola et al. 2004; Zhang et al. 2012; Dera et al. 2013; Pakhomova et al. 2017; Lazarz et al. 2019; Xu et al. 2020). Additionally, first-order phase transitions resulting from increases in Si coordination are attributed to the low compressibility of Si-O bonds. An increase in coordination necessitates a redistribution of internal space within the crystal structure, resulting in a significant volume drop. Experimental results indicate that phase transition in pyroxenes induced by changes in Si coordination are accompanied by a substantial

decrease in volume (Finkelstein et al. 2015; Pakhomova et al. 2017; Lazarz et al. 2019; Xu et al. 2024).

Unlike the tetrahedral-rotation-type phase transitions in pyroxenes, the phase transitions in wollastonite and CaSiO_3 -wollastonite are characterized by changes (increase and decrease) in the coordination number of Ca, in addition to tetrahedral rotation (Milani et al. 2021). Consequently, in certain cases, such as the transitions from wollastonite-II to wollastonite-III and from CaSiO_3 -wollastonite-II to CaSiO_3 -wollastonite-III, the volume reduction associated with tetrahedral rotation can be offset by the corresponding increase or decrease in the coordination number of Ca. Therefore, these phase transitions are classified as second-order. In contrast, when the alteration in the coordination number of Ca is insufficient to compensate for the volume decrease caused by tetrahedral rotations, the transitions are classified as first-order, as observed in the transitions from wollastonite-I to wollastonite-II and from CaSiO_3 -wollastonite-I to CaSiO_3 -wollastonite-II.

Currently, no second-order phase transitions have been reported in orthopyroxene. In contrast, a second-order phase transition is observed only in aegirine, resulting from an increase in the coordination number of Na (Xu et al. 2017a). Compared to orthopyroxene and clinopyroxene, second-order phase transitions are more common in pyroxenoids. In addition to the transitions from wollastonite-II to wollastonite-III and from CaSiO_3 -wollastonite-II to CaSiO_3 -wollastonite-III, this study identifies a second-order phase transition in rhodonite. This transition is very similar to that observed in cerite (Zhong et al. 2025).

The second-order phase transition in rhodonite is primarily attributed to two factors: first, as pressure increases, only the coordination number of Mn3 atom increases, while the coordination numbers of other Mn atoms remains unchanged; second, as pressure increases, the Mn3-O15 bond length significantly decreases (Fig. 4c), whereas the Si3-O15 and Si5-O6 bond lengths increase near the transition pressure (Figs. 5c and 5e). Thus, the volume reduction resulting from the increase in the coordination number of Mn3 can be buffered by the increase in the Si-O bond lengths, leading to rhodonite exhibiting characteristics of a second-order phase transition.

IMPLICATIONS

This study provides insights into the behavior of single-chain silicates under high-pressure conditions. Orthopyroxene undergoes a series of first-order phase transitions, typically involving structural transformations from $Pbca$ (α -opx) to $P2_1/c$ (β -opx), then to $Pbca$ (γ -opx) or $P2_1ca$ (α -popx), and finally to β -popx. The mechanisms governing these transitions primarily include SiO_4 tetrahedral rotations and an increase in silicon coordination number. Similarly, the phase transition mechanisms of clinopyroxene mainly involve tetrahedral rotations and an increase in silicon coordination number. However, a second-order phase transition induced by changes in the coordination number of Na ions has also been observed.

In contrast, pyroxenoids, including rhodonite, exhibit both first- and second-order phase transitions. Unlike orthopyroxene and clinopyroxene, pyroxenoids maintain a triclinic structure ($P\bar{1}$ space group) at high pressures. In the case of rhodonite, an

isosymmetric second-order phase transition occurs at 10.9(1) GPa, driven by an increase in Mn coordination. Wollastonite and CaSiO_3 -wollastonite also undergo a combination of first- and second-order transitions, as a result of the interplay of SiO_4 tetrahedral rotations and cation coordination changes.

The fundamental similarities in phase transition mechanisms across these single-chain silicates lie in the importance of SiO_4 tetrahedral rotations, which facilitate structural rearrangements under compression. However, a key distinction arises in the role of coordination number changes. While orthopyroxene and clinopyroxene predominantly undergo transitions driven by increases in Si coordination, pyroxenoids, including rhodonite, exhibit transitions governed by changes in metal cation coordination, such as Mn and Ca. Moreover, second-order transitions are notably more common in pyroxenoids than in pyroxenes, likely due to the cation coordination adjustments counterbalancing the volume drop induced by tetrahedral distortions. These findings highlight the diversity of phase transition mechanisms among chain silicates, emphasizing the distinct compression behaviors of pyroxenes and pyroxenoids. Understanding these structural transformations is essential for constraining the stability and evolution of single-chain silicates in deep Earth environments. However, the phase transition mechanisms of pyroxenoids at high temperatures, particularly those of rhodonite, remain poorly understood, representing a key area for future investigation.

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