

Pressure-temperature stability and equation of state of staurolite: Implications for the water transport during cold slab subduction

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ABSTRACT

The stability and thermal equation of state (EoS) of synthetic staurolite were investigated under high pressure and temperature (P - T) conditions up to ~ 23 GPa and 850 K. *no* phase transition was observed within the experimental P - T range. The thermal EoS parameters, including the bulk modulus, pressure and temperature derivatives, and thermal expansion coefficient, were determined by fitting the pressure-volume-temperature data to high-temperature third-order Birch-Murnaghan EoS. Integrating the results of this study with those of previous studies led to an updated P - T phase diagram for staurolite. This diagram suggests that staurolite may have potential metastability extending to the depth of the Earth's mantle. The density and bulk sound velocity profiles along the Tonga slab geotherm indicate that staurolite could serve as an effective water carrier to sub-arc mantle depths. Notably, staurolite exhibits higher bulk sound velocities than most hydrous minerals do, implying that its presence in medium- to high-pressure metamorphic rocks may increase seismic velocities in corresponding lithologies.

1. Introduction

The transport of water into Earth's deep interior via hydrous minerals in subducting slabs represents a critical mechanism driving planetary evolution and geodynamic processes (Bang et al., 2025; Ishii et al., 2025; Xie et al., 2020; Zheng et al., 2016). Global subduction systems deliver approximately 6.7×10^{14} g/yr of water into the mantle through various hydrous minerals (Bang et al., 2025; Ohtani, 2015). Staurolite has been identified as a key hydrous mineral within the $\text{MgO} - \text{FeO} (\text{Fe}_2\text{O}_3) - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ (MFASH) system (Allen and Boettcher, 1983; Ma et al., 2025; Zanazzi et al., 2007). Moreover, its importance is further demonstrated by its occurrence as a secondary mineral in high-pressure metabasites and as inclusions in subduction-related diamonds (Abdel-Rahman, 1995; Allen and Boettcher, 1983; Borisova et al., 2022; Daniels et al., 1996; Peng and Mookherjee, 2020). Therefore, these collective findings underscore the significance of staurolite as a hydrous

phase in deep-water cycling.

Staurolite features a complex crystal structure with distinct cationic sites accommodating Al^{3+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, and Si^{4+} ions, whereas hydroxyl groups (OH^-) are predominantly located at H1 and H2 sites (Fig. 1). These hydroxyl groups play dual roles in both stabilizing the crystal framework and increasing the water storage capacity (Brighurst and Griffen, 1986). Although early studies classified staurolite as orthorhombic (space group $Ccmm$) (Náray-Szabó, 1929), modern crystallographic analyses reveal pseudo-orthorhombic symmetry with a monoclinic beta angle (β) deviating slightly from 90° (Comodi et al., 2002; Hawthorne et al., 1993a; Shan et al., 2007; Smith, 1968). The maintenance of $\beta = 90^\circ$ requires exceptionally stringent conditions (Hawthorne et al., 1993b); thus, classifying the structure of staurolite as monoclinic is more reasonable.

Despite its petrological importance, static compression and equation of state (EoS) studies of staurolite are very limited. To the best of our

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knowledge, the pressure–volume (P – V) EoS of staurolite has only been determined by Comodi et al. (2002), who carried out in situ high-pressure single-crystal X-ray diffraction (XRD) experiments on natural staurolite up to ~ 7.3 GPa and obtained the isothermal bulk modulus $K_0 = 180$ (2) GPa and its pressure derivative $K'_0 = 4.7$ (6). Additionally, the thermal expansion coefficient of staurolite has only been determined by Gibbons et al. (1981), who conducted powder XRD measurements of synthetic staurolite at a maximum temperature of 673 K and obtained a volumetric thermal expansion coefficient $\alpha_{V0} = 1.9 \times 10^{-5} \text{ K}^{-1}$. However, to date, the thermal EoS of staurolite under simultaneous high pressure and high temperature conditions has not been reported, which is necessary for modeling the density and bulk sound velocity profiles of staurolite within the deep Earth.

Within the MFASH system, the hydration sequence progresses from chlorite $\rightarrow$ amphibole $\rightarrow$ staurolite under evolving metamorphic conditions (Borisova et al., 2022; Gil Ibarguchi et al., 1991). Chlorite is dominant at 575 °C and 2 GPa, whereas the amphibole content peaks at 620 °C and 2.45 GPa (Borisova et al., 2022; Koch-Müller, 1997). Then, staurolite formation initiates at 625 °C and 2.56 GPa, reaches a maximum abundance at 630 °C and 2.6 GPa, and undergoes dehydration at 660 °C and 2.9 GPa (Borisova et al., 2022; Faryad and Hoinkes, 2006; Tsujimori and Liou, 2004). However, staurolite typically decomposes at shallow depths (~ 100 km) under normal geothermal gradients (Artemieva and Mooney, 2001; Pollack and Chapman, 1977; Zang et al., 2002). Staurolite could remain metastable under certain cold subduction conditions or in areas where the geothermal gradient is significantly lower than typical mantle conditions (Comodi et al., 2002; Daniels et al., 1996). Therefore, it is necessary to study the metastability of staurolite to better understand the dynamics of water transport into the Earth's deep interior.

In this study, we investigated the thermoelastic behavior and phase stability of staurolite under simultaneous high-temperature and high-pressure conditions via in situ synchrotron single-crystal XRD. We aim to: (1) determine the thermal EoS of staurolite, (2) constrain its P – T

stability field, and (3) model its density and bulk sound velocity along cold subduction slabs.

2. Sample and experiments

2.1. Sample

The staurolite sample was synthesized using via a DS6 $\times$ 1400 t multi-anvil press apparatus at 1.5 GPa and 740 °C for 96 h at the Institute of Geochemistry, Chinese Academy of Sciences. The starting materials used in the synthesis experiments were stoichiometric amounts of high purity ferric oxide (Fe_2O_3), aluminum oxide (Al_2O_3), silica (SiO_2), and deionized water. The synthetic methods used are similar to those used in our previous studies (Fan et al., 2019; Wu et al., 2024; Xu et al., 2018).

As shown in Table S1, the H_2O (or OH) content in the staurolite sample was not directly measured by EMPA because hydrogen cannot be detected by this technique. Instead, the structural formula was normalized on the basis of the stoichiometry of 22 oxygens per formula unit (O pfu), assuming that the anion site is occupied by O and OH with a total of 2 anions per formula unit. The proportion of OH was estimated by charge balance according to the total number of cations obtained from the EMPA data and the expected valence sum. This approach allows the calculation of the hydroxyl content indirectly from the deficit in total negative charge (O^{2-} vs. OH^-) required to balance the positive charge from cations.

In this study, the chemical composition of a staurolite sample was determined using an EPMA-1600 electron microprobe (Institute of Geochemistry, Chinese Academy of Sciences) with an accelerating voltage of 25 kV, a beam current of 10 nA, and a focused beam diameter of 10 μm . The elemental standards included garnet (Fe, Al, Si), corundum (Al), and olivine (Mg), and the data were corrected using a ZAF program. On the basis of the EMPA results, the empirical formula of the sample was normalized to 22 oxygen atoms, and the hydroxyl

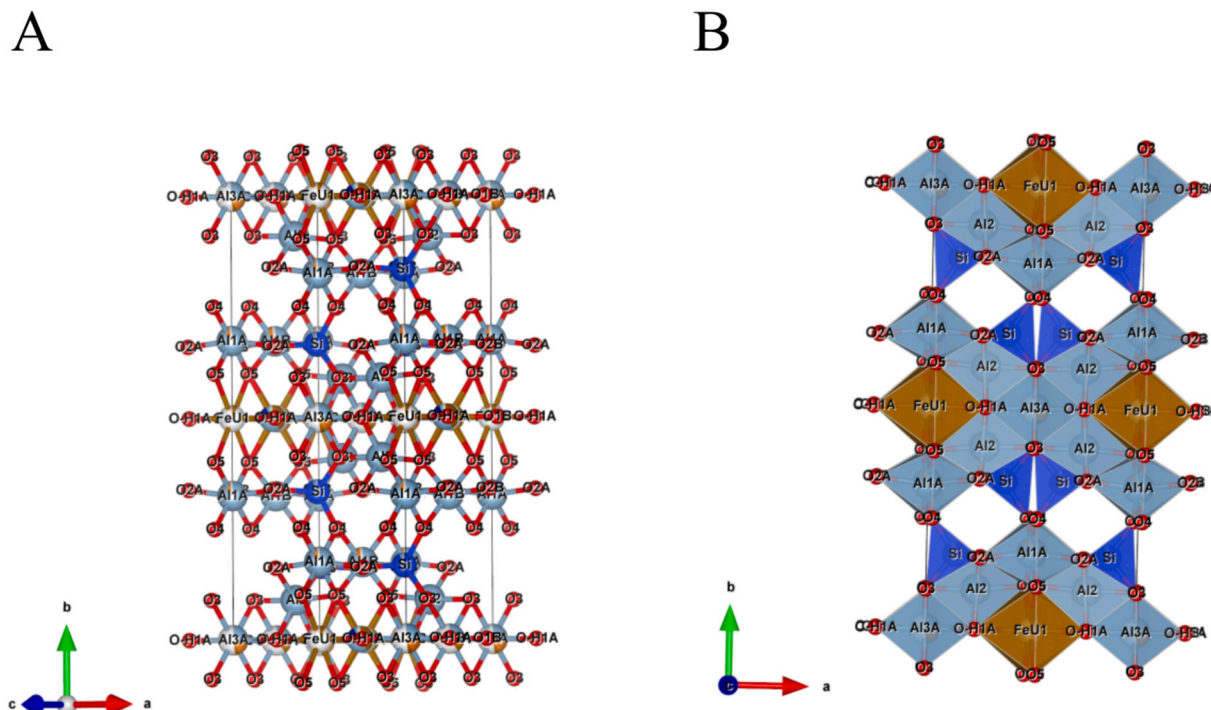


Fig. 1. Crystal structure of staurolite at ambient conditions with the style of ball-and-stick (A) and the style of polyhedron (B). Blue for silicon, light blue for aluminum, red for oxygen or hydroxide, and brown for iron. The crystal structure data are obtained from Bringhurst and Griffen (1986) and it is drawn by VESTA software (Bringhurst and Griffen, 1986; Momma and Izumi, 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

content was derived from the charge-balance calculation following the structural formula $[\text{Fe}_{1.85}\square_{0.15}] [\text{T2}, \text{M4}] [\text{Fe}_{0.55}\text{Al}_{8.45}] [\text{M1}, \text{M2}, \text{M3}] [\text{Al}_{0.14}\text{Si}_{3.86}] [\text{T1}]\text{O}_{22}[\text{O}_{0.55}, (\text{OH})_{1.45}]$.

2.2. Experiments

2.2.1. High-pressure and ambient-temperature single-crystal XRD experiments

High-pressure and ambient-temperature single-crystal XRD experiments were carried out by using a short symmetric diamond anvil cell (DAC) equipped with a pair of 500 μm culet-size diamond anvils. We used a WC seat (with an opening angle of approximately 80°) in our synchrotron single-crystal XRD experiments. The sample chamber was prepared from a rhenium gasket with a preindented thickness of ~ 60 μm and a 300 μm diameter hole in the center of the indented region. The staurolite sample, with a thickness of ~ 15 μm , was combined with gold powder, which was used as the pressure calibrant (Fei et al., 2007) as well as ruby, which was used as a pressure indicator for neon gas-loading. The XRD patterns of gold were collected at each pressure before and after sample data collection, and the average pressure values were used for EoS fitting. Neon gas was used as the pressure-transmitting medium by the gas-loading system at GeoSoilEnviroCARS, Advanced Photon Source, Argonne National Laboratory (Rivers et al., 2008).

In situ high-pressure and ambient-temperature synchrotron single-crystal XRD experiments were carried out at the 13-BM-C experimental station of the Advanced Photon Source, Argonne National Laboratory. The wavelength of the incident X-ray beam was 0.4340 $\text{\AA}$, and the beam size was 12×18 μm^2 . We used a MAR165 CCD detector to collect the diffraction images, and LaB₆ powder was used as the diffraction standard (Zhang et al., 2017). Wide and stepped φ exposures were collected for each single-crystal sample at each P - T point with a typical exposure time of 3 s/deg. The Bruker APEX3 software package was used to analyze the diffraction images, and the obtained unit-cell parameters and volumes of staurolite at high pressures are shown in Table S2.

2.2.2. High-pressure and High-temperature single-crystal XRD experiments

High-pressure and High-temperature single-crystal XRD experiments were carried out using a BX90-type external-heating diamond anvil cell (EHDAC) (Kantor et al., 2012), equipped with a pair of 500- μm culet-size diamond anvils. The sample chamber was prepared from a rhenium gasket with a pre-indented thickness of ~ 65 μm and an ~ 360 μm diameter hole in the center of the indented region. An $\sim 50 \times 55$ μm^2 fragment of single-crystal staurolite, together with gold powder and ruby was loaded into the sample chamber. The pressure was determined using the thermal EoS of gold (pressure marker) (Fei et al., 2007), we used the three strongest Au reflections—(111), (200), and (220)—to determine the unit-cell volume of gold. The pressure was then calculated by applying the gold equation of state to the measured unit-cell volume, and the mean value ($\pm 1\sigma$) is reported. The neon pressure medium was loaded into the sample chamber using the gas-loading system at GeoSoilEnviroCARS, Advanced Photon Source, Argonne National Laboratory (Rivers et al., 2008). A resistive heater was used to generate a maximum temperature of 850 K and the temperature was measured by a K-type thermocouple attached to one of the diamond anvils ~ 500 μm away from the diamond culet. To minimize the temperature instability for each heating run, each XRD pattern was collected after the experimental temperature was maintained for 600 s. The temperatures of the sample chamber were actively stabilized within ± 1 K by a temperature controller with a self-tuning function. Details of the experimental setup and cell assembly were described in our previous studies (Fan et al., 2010; Huang et al., 2020; Huang et al., 2021; Huang et al., 2023).

In situ high-pressure and high-temperature synchrotron single-crystal XRD experiments were also conducted at the 13-BM-C experimental station (Sutton et al., 2022; Zhang et al., 2017; Zhang et al., 2022) of the Advanced Photon Source, Argonne National Laboratory. A

MAR165 charge-coupled device (CCD) was used to collect diffraction patterns and the tilting and rotation of the detector relative to the incident X-ray beam were calibrated with LaB₆ powder as the XRD standard. The wavelength of the incident X-ray beam was 0.4340 $\text{\AA}$, and the beam size was focused to 12×18 μm^2 . Wide and stepped φ exposures were collected for each single-crystal sample at each P - T point with a typical exposure time of 2 s/deg. The φ -rotation axis was horizontal and perpendicular to the incident X-ray direction (Xu et al., 2022).

3. Results

The typical XRD patterns of synthetic staurolite at various pressures and temperatures are shown in Fig. S1. Our XRD results indicate that staurolite did not undergo a phase transition within the P - T range of this study. The refined unit-cell parameters and volumes of staurolite under various P - T conditions are shown in Tables S2 and S3, respectively. The normalized unit-cell parameters of staurolite are plotted as a function of pressure in Fig. 2 (A). Fig. 2 (B) shows the EoS curve derived from the fitting of the P - V data and compares it with the result reported by Comodi et al. (2002). Fig. 3 shows the pressure-volume-temperature (P - V - T) data fitted using the HT BM3-EoS at 300, 500, and 700 K.

First, we fitted the P - V data to derive the EoS parameters by using the room-temperature Birch-Murnaghan EoS. Then, we employed the high-temperature Birch-Murnaghan EoS approach to derive the thermal EoS parameters from the measured P - V - T data.

P - V equation of state for staurolite.

The P - V data (Table S2) were fitted using the third-order Birch-Murnaghan EoS as follows:

$$P = (3/2) K_{T0} \left[(V_{T0}/V)^{7/3} - (V_{T0}/V)^{5/3} \right] \times \left[1 + (3/4) (K'_{T0}-4) \left[(V_{T0}/V)^{2/3} - 1 \right] \right] \quad (1)$$

where V_0 , K_{T0} , and K'_{T0} are the zero-pressure and ambient temperature unit-cell volume, isothermal bulk modulus, and pressure derivative, respectively. Analyses of Eq. (1) by the *EoSFit-7c* program (Angel et al., 2014) with all parameters free yielded the following results: $K_0 = 171$ (3) GPa and $K'_0 = 5.4$ (5).

To evaluate the quality of our third-order Birch-Murnaghan EoS fitting, the relationship between the Eulerian definition of finite strain f_E ($f_E = [(V_0/V)^{2/3} - 1]/2$) and the “normalized stress” F_E ($F_E = P/3f_E (1 + 2f_E)^{5/2}$) is shown in Fig. S2 (Angel, 2000). The weighted linear fit of the data points yielded the intercept value of $F_E(0) = 174$ (4) GPa, which is consistent with the isothermal bulk modulus obtained by the third-order Birch-Murnaghan EoS ($K_0 = 171$ (3) GPa) within their uncertainties. Moreover, it is clear from Fig. S2 that the data points lie on an inclined straight line with a positive slope, indicating that K'_0 is greater than 4, which is consistent with $K'_0 = 5.4$ from the third-order Birch-Murnaghan EoS. Thus, the third-order Birch-Murnaghan EoS is a reasonable description of the P - V data in this study.

As shown in Fig. 2(A), the normalized unit-cell parameters (a/a_0 , b/b_0 , and c/c_0) of staurolite at room temperature are plotted as a function of pressure. By fitting the unit-cell parameters of staurolite at room temperature using a “linearized” third-order Birch-Murnaghan EoS with the *EoSFit-7c* program, we obtain $K_{a0} = 184.4$ (9) GPa and $K'_{a0} = 3.9$ (2), $K_{b0} = 139$ (7) GPa and $K'_{b0} = 11$ (2), and $K_{c0} = 180$ (1) GPa and $K'_{c0} = 3.9$ (2). The axial compressibility β_0 under ambient conditions has the following form (Angel et al., 2014):

$$\beta_0 = 1/K_0 \quad (2)$$

In analyses using Eq. (2), the axial compressibilities of the a -, b - and c -axes were $5.4 \times 10^{-3} \text{ GPa}^{-1}$, $7.2 \times 10^{-3} \text{ GPa}^{-1}$ and $5.6 \times 10^{-3} \text{ GPa}^{-1}$, respectively. The compressibility of the a - and c -axes are nearly identical, while the compressibility of the b -axis is 33 % and 29 % greater than those of the a - and c -axes, respectively, indicating that staurolite

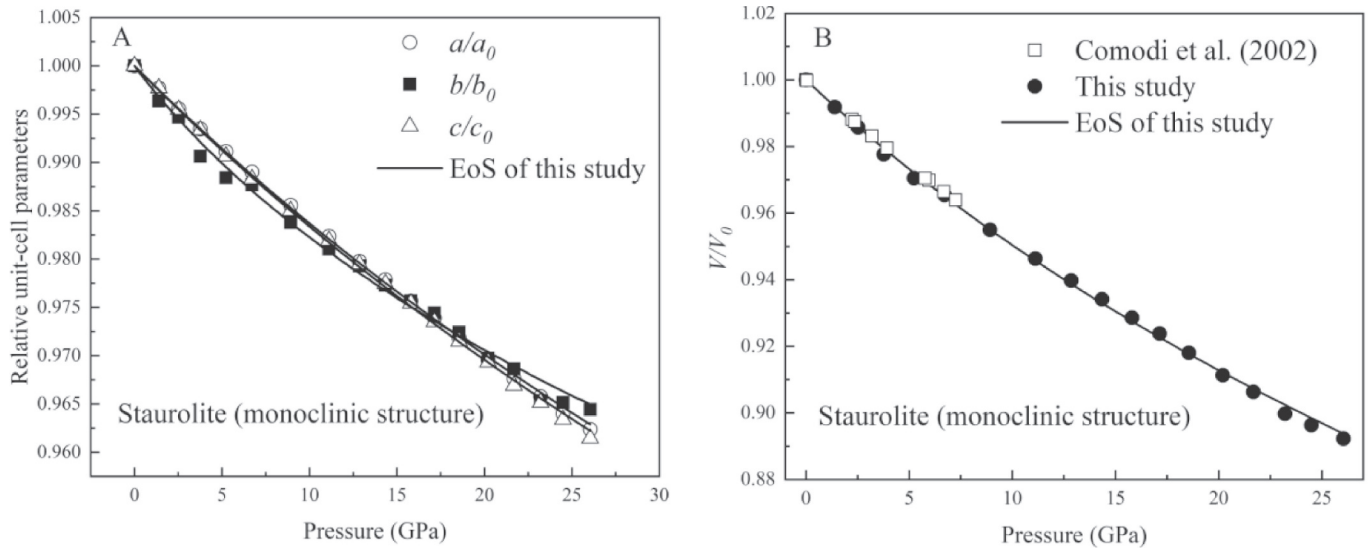


Fig. 2. Axial (A) and volumetric (B) compression of staurolite.

Note: In B, the black solid circle is the result of this study, and the hollow square is the experimental result of Comodi et al. (2002).

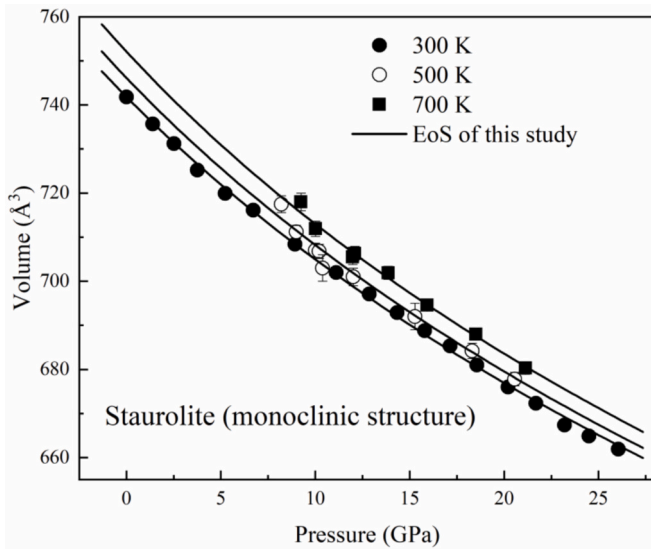


Fig. 3. Unit-cell volumes of staurolite as a function of pressure and temperature.

Note: Isothermal compression curves at various temperatures are represented by solid lines from the high-temperature BM EoS at 300, 500, and 700 K. The error bars of the data points are smaller than most of the symbols.

has axial compressive anisotropy.

3.1. P - V - T equation of state for staurolite

The P - V - T data (Table S3) were used to determine the thermal EoS parameters of staurolite up to ~ 22.5 GPa and 850 K. The high temperature third-order Birch-Murnaghan EoS was applied to our high P - T data as follows Eq. (1): In Eq. (1), the thermal dependences of the zero-pressure unit-cell volume V_{T0} and bulk modulus K_{T0} at different isotherms are expressed using the following equations:

$$V_{T0} = V_0 \exp \int_{300}^T \alpha_T dT \quad (3)$$

$$K_{T0} = K_0 + (\partial K_T / \partial T)_P \times (T - 300) \quad (4)$$

where V_0 , V_{T0} , and K_{T0} are the volume at zero pressure and room temperature, the volume at zero pressure and various temperatures, and its pressure derivative under ambient conditions, respectively. The temperature derivative of V_{T0} can be estimated as a function of the thermal expansion α_T (Eq. (3)). The thermal dependence of the bulk modulus K_{T0} is expressed by a linear function of temperature (Eq. (4)), assuming that the temperature derivative $(\partial K_T / \partial T)_P$ is constant in the temperature range studied.

Within the maximum P - T range of ~ 22.5 GPa and 850 K, no phase transition was observed in staurolite. Fitting the P - V - T data to the high-temperature third-order Birch-Murnaghan EoS yields the following results for staurolite: $K_0 = 171$ (5), $K'_0 = 5.3$ (8), $\alpha_{0V} = 1$ (1) $\times 10^{-5}$ K $^{-1}$, $\alpha_{1V} = 5$ (3) $\times 10^{-8}$ K $^{-2}$, and $(\partial K_T / \partial T)_P = -0.02$ (2) GPa/K. The obtained V_0 , K_0 , and K'_0 values are consistent with those from the P - V data fitting at 300 K within their uncertainties. The measured unit-cell volumes are plotted in Fig. 3 as a function of pressure together with the isotherms calculated using the thermal EoS parameters derived from the current fits, which show good agreement between the fitted curves and the measured P - V - T data.

3.2. P - T phase diagram of staurolite and its stability under high P - T conditions

The distribution and cycling of water in the Earth's interior substantially impact the geophysical, geochemical, and geodynamical properties of deep Earth (Hsieh et al., 2025; Zheng et al., 2016; Zheng and Hermann, 2014). Hydrous minerals play crucial roles in carrying and storing water in deep Earth (Horn and Skemer, 2025). The physical and chemical properties of subduction slabs are strongly related to the depth of water release from hydrous minerals (e.g., Zheng, 2019; Zheng et al., 2016; Zheng and Hermann, 2014). Additionally, the geothermal gradient strongly affects the depth at which hydrous minerals dehydrate in subducting slabs and thus affects water transport in the deep Earth.

Under normal and hot geothermal gradient conditions, many hydrous minerals in the shallow crust or upper mantle depth range decompose (Artemieva and Mooney, 2001; Frost, 2006; Lempert et al., 2020; Wang et al., 2025; Zang et al., 2002). However, the dehydration of hydrous minerals is likely to be restrained by low temperatures in cold subduction slabs, especially the super cold subduction slabs. Hydrous minerals survive at deep depths along cold subduction plates and carry large amounts of water into the middle and lower parts of the upper mantle (Chen et al., 2020; Thompson et al., 2020; Zhao and Ohtani,

2009; Zheng, 2019; Zheng et al., 2016). The release of water from hydrous minerals within subduction slabs to the deep Earth profoundly influences the geological processes of the deep Earth.

Fig. 4 illustrates the P - T stability field of staurolite (Comodi et al., 2002; Gibbons et al., 1981; Hoschek, 1969; Schmidt and Poli, 1998). Under normal geothermal gradient conditions (Artemieva and Mooney, 2001; Pollack and Chapman, 1977; Zang et al., 2002), staurolite decomposes into corundum and glass beyond a depth of approximately 100 km. However, under hot subduction conditions, staurolite breaks down into garnet at approximately 150 km depth. In contrast, under ultra-cold subduction conditions, such as the Tonga subduction zone, staurolite seems to maintain its structural stability and may persist in a metastable state down to the Earth's mantle depth.

4. Discussion

To date, only Comodi et al. (2002) have conducted single-crystal XRD studies on a natural staurolite at a maximum pressure of 7.3 GPa, using a methanol: ethanol = 4:1 pressure-transmitting medium, and obtained $K_0 = 180$ (2) GPa and $K'_0 = 4.7$ (6), where the obtained K_0 is $\sim 5\%$ higher than the obtained $K_0 = 171$ (3) GPa in this study. To further evaluate the negative correlation between K_0 and K'_0 and to assess the statistical significance of the difference between our results and previous measurements, we constructed the confidence ellipsoids for the fitted K_0 and K'_0 parameters based on the third-order Birch–Murnaghan equation of state (Fig. S3). The ellipsoids correspond to confidence levels of 68.3 %, 95.4 %, and 99.7 %, representing the 1σ , 2σ , and 3σ uncertainty domains, respectively. As shown in Fig. S3, a strong negative correlation

exists between the bulk modulus and its pressure derivative. To minimize the influence of this trade-off effect and enable a more direct comparison, we refitted the P - V data of Comodi et al. (2002) and this study with fixed $K'_0 = 4$, and obtained $K_0 = 182.5$ (3) GPa and $K_0 = 180$ (1) GPa, respectively. This means that the obtained K_0 of Comodi et al. (2002) is consistent with the obtained result of this study within their uncertainties.

The composition characteristics of staurolite from Comodi et al. (2002) ($\text{Fe}_{3.365}\text{Zn}_{0.025}\text{Li}_{0.114}\text{Co}_{0.009}\text{Mn}_{0.034}$) [T2, M4]($\text{Al}_2\text{Mg}_{0.307}$)[M3] ($\text{Al}_{15.491}\text{Fe}_{0.104}\text{Mg}_{0.394}\text{Cr}_{0.004}\text{Ti}_{0.07}$)[M1, M2, M3] ($\text{Si}_{7.534}\text{Al}_{0.466}$) [T1] O_{48}H_3) with the staurolite in this study ($[\text{Fe}_{1.85}\square_{0.15}]$ [T2, M4] $[\text{Fe}_{0.55}\text{Al}_{8.45}]$ [M1, M2, M3] $[\text{Al}_{0.14}\text{Si}_{3.86}]$ [T1] $\text{O}_{22}[\text{O}_{0.55}(\text{OH})_{1.45}]$), we found that in the staurolite described by Comodi et al. (2002), firstly, T1 site is predominantly occupied by Si (with minor Al), secondly, M1/M2 sites contain primarily Al with subordinate Fe, Mg, Cr, and Ti, thirdly, the M3 site hosts Al and Mg with vacancies, finally, T2/M4 sites are dominated by Fe with trace Zn, Li, Co, Mn, and vacancies. Notably, the Fe–O bond length (1.764 Å) is approximately 9 % longer than the Al–O bond length (1.622 Å) (Gibbons et al., 1981), indicating weaker bond strength in Fe^{2+} -O than in Al–O. The compressional behavior of staurolite is primarily controlled by the compression of its Al/Fe octahedral sites (Comodi et al., 2002). We calculated the Al/Fe ratio in both studies based on M1/M2/ M3 (Al-dominant) versus T2/M4 (Fe-dominant) site occupancies. The resulting Al/Fe ratios are 5.20 (Comodi et al., 2002) and 4.57 (this study), demonstrating marginally higher Al–O contents in the samples of Comodi et al. (2002). Furthermore, as illustrated in Fig. 2(B), the pressure-volume data from both studies exhibit near-overlapping trends, indicating similar compressional behavior. Moreover, when K'_0 is fixed to 4, the obtained K_0 of Comodi et al. (2002) ($K_0 = 182.5$ (3) GPa) is consistent with the obtained result of this study ($K_0 = 180$ (1) GPa) within their uncertainties, further supporting this similarity.

Gibbons et al. (1981) conducted a powder XRD study on staurolite with the composition $\text{Fe}_{4.15}(\pm 0.08)\text{Al}_{18.18}(\pm 0.18)\text{Si}_{7.28}(\pm 0.14)\text{O}_{48}\text{H}_4$ at a maximum temperature of 673 K, obtaining the axial thermal expansion coefficients: $\alpha_{0a}(300\text{K}) = 7.86 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_{0b}(300\text{K}) = 7.18 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\alpha_{0c}(300\text{K}) = 7.55 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. Since Gibbons et al. (1981) did not provide the volumetric thermal expansion coefficient of staurolite, we fitted their high-temperature data using Fei's thermal expansion equation to obtain $\alpha_{0V}(300\text{K}) = 1.9$ (1) $\times 10^{-5} \text{ K}^{-1}$. Converting the α_{0V} obtained in this study to the thermal expansion coefficient at 300 K yields $\alpha_{300\text{K}} = 2$ (1) $\times 10^{-5} \text{ K}^{-1}$, which is consistent with the thermal expansion coefficients obtained by Gibbons et al. (1981) within their uncertainties. However, in this study, we first obtained a $(\partial K/\partial T)_P = -0.02$ (2) GPa/K for staurolite under simultaneous high P - T conditions.

4.1. Implication

The updated P - T phase diagram of staurolite in this study indicates that staurolite can exist in a metastable state within cold subduction zones at depths reaching the Earth's mantle depth (Fig. 4). Additionally, the density profile of staurolite was modeled using its thermal EoS parameters (Table 1) and compared with those of other major hydrous minerals, including epidote, zoisite, lawsonite, diaspore, and antigorite, and the PREM model (Table S4). As shown in Fig. 5, the densities of all hydrous minerals increase gradually with depth from 50 km to 660 km along cold subduction slabs. The densities of staurolite are $\sim 7\%$, $\sim 9\%$, $\sim 10\%$, $\sim 18\%$, and $\sim 35\%$ higher than those of epidote, diaspore, zoisite, lawsonite, and antigorite, respectively. Additionally, the density of staurolite is $\sim 11\%$ and $\sim 3\%$ greater than that of the PREM model at depths of 50 km and 410 km, respectively. Thus, staurolite may facilitate subduction of the slab because of its high-density characteristics.

We calculated the staurolite, diaspore, lawsonite, epidote, zoisite, antigorite, garnet and omphacite bulk sound velocities at depths ranging from 200 km to 660 km using the reported thermal EoS parameters (Table S5) along the Tonga geotherm (Hacker et al., 2003; Hofmeister

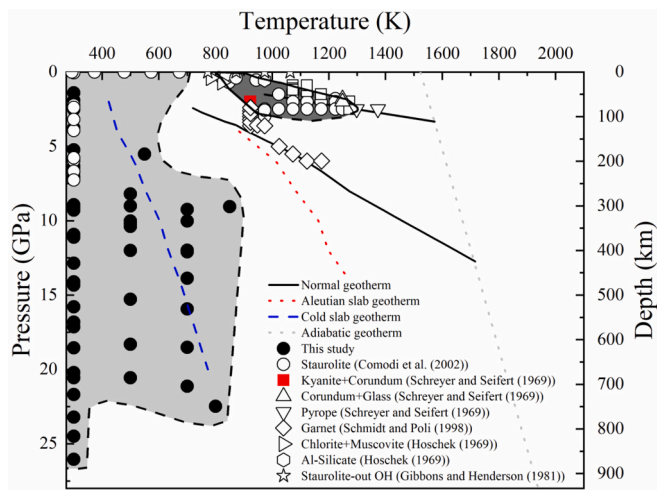


Fig. 4. P - T stability of staurolite.

Note: The black solid circles represent the data points of these experiments, and the white hollow circles represent the data points of previous studies (Comodi et al., 2002; Gibbons et al., 1981; Hoschek, 1969; Schmidt and Poli, 1998). The dark gray area represents the stability area of staurolite. The light gray area represents the metastable area of staurolite (Bowen and Tuttle, 1949; Philpotts and Ague, 2009; Spear, 1993). The red solid squares represent the stability of Kyanite + Corundum (K + C) (Schreyer and Seifert, 1969). The regular triangles represent the stability of Corundum + Glass (C + Gla). The inverted hollow triangles represent the stability of Pyrope (P). The hollow diamonds represent the stability of Garnet (G). Lateral hollow triangles represent the stability of Chlorite + Muscovite (Chl + M). The presence of regular hexagons reflects the stability of the Al-Silicate (Al-S). Hollow pentagonal hearts represent the stability of dehydroxylation of the staurolite (Sta-out OH). The blue dotted line represents the geothermal gradient of the Tonga plate and the red dotted line represents the geothermal gradient of the Aleutian plate (Bina and Navrotsky, 2000). The black lines represent the normal geotherm (Pollack and Chapman, 1977). The gray dotted line represents the adiabatic geotherm (Artemieva and Mooney, 2001; Zang et al., 2002). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Thermal equation of state parameters of staurolite.

Composition	Max <i>P</i> (GPa)	Max <i>T</i> (K)	Method	<i>K</i> ₀ (GPa)	<i>K'</i> ₀	<i>V</i> ₀ (Å ³)	Pressure medium	α_{0V} (10 ⁻⁵ K ⁻¹)	α_{1V} (10 ⁻⁸ K ⁻²)	($\partial K/\partial T$) _{<i>P</i>} (GPa/K)	Reference
Fe _{4.15} (±0.08)Al _{18.18} (±0.18)Si _{7.28} (±0.14)O ₄₈ H ₄	0.0001	673	Pd- XRD	—	—	—	—	1.9 (1)	—	—	Gibbons et al. (1981)
(Fe _{3.365} Zn _{0.025} Li _{0.114} Co _{0.009} Mn _{0.034}) (Al ₂ Mg _{0.307}) (Al _{15.491} Fe _{0.104} Mg _{0.394} Cr _{0.004} Ti _{0.07})(Si _{7.534} Al _{0.466})O ₄₈ H ₃	7.3	300	Sc-XRD	180 (2)	4.7 (6)	740.85 (7)	methanol: ethane = 4:1	—	—	—	Comodi et al. (2002)
[Fe _{1.85} □ _{0.15}] [T ₂ , M ₄] [Fe _{0.55} Al _{8.45}] [M ₁ , M ₂ , M ₃] [Al _{0.14} Si _{3.86}] [T ₁]O ₂₂ [O _{0.55} (OH) _{1.45}]	26.05	300	Sc-XRD	171 (3)	5.4 (5)	741.80 (3) *	Ne	—	—	—	This study
[Fe _{1.85} □ _{0.15}] [T ₂ , M ₄] [Fe _{0.55} Al _{8.45}] [M ₁ , M ₂ , M ₃] [Al _{0.14} Si _{3.86}] [T ₁]O ₂₂ [O _{0.55} (OH) _{1.45}]	22.5	700	Sc-XRD	171 (5)	5.3 (8)	741.80 (3) *	Ne	1 (1)	5 (3)	-0.02 (2)	This study

—, No data.

Pd-XRD, Powder-dispersive X-ray diffraction.

Sc-XRD, Single-crystal X-ray diffraction.

* ambient-condition unit-cell volume of staurolite has been directly measured.

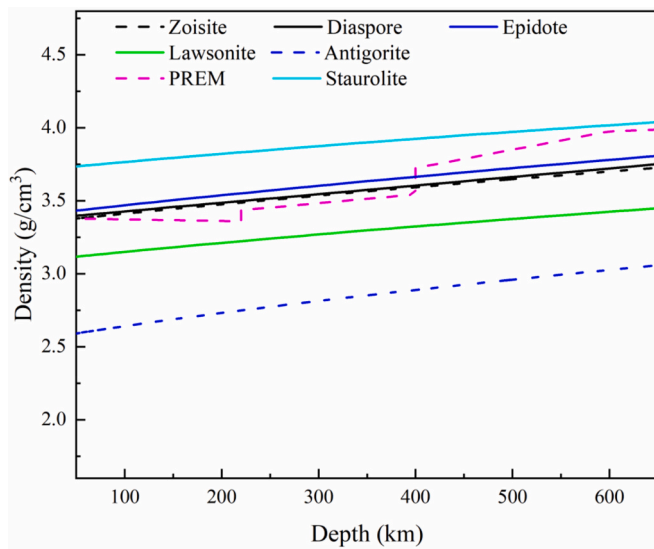


Fig. 5. Model density profiles of staurolite (this study) and other hydrous minerals (zoisite (Huang et al., 2023), lawsonite (Ballaran and Angel, 2003), antigorite (Yang et al., 2014), epidote (60 mol% epidote ferric end-member (Ca₂Al₂Fe³⁺Si₃O₁₂(OH)) (Huang, 2024) and diaspore (Huang et al., 2021)) to ~660 km along the Tonga slab geotherm, and compared with that of those PREM model (Dziewonski and Anderson, 1981).

and Mao, 2002; Huang, 2024; Huang et al., 2021; Huang et al., 2023; Suzuki and Anderson, 1983). Fig. 6 illustrates the comparison of the bulk sound velocities between staurolite and other major hydrous minerals (lawsonite, zoisite, epidote, and antigorite) and nominally anhydrous minerals (garnet and omphacite). At a depth of approximately 200 km, the bulk sound velocity of staurolite is not only ~5 %, ~7 %, ~13 %, and ~22 % higher than those of lawsonite, zoisite, epidote, and antigorite, respectively, but also ~7 % and ~11 % higher than those of garnet and omphacite, respectively. Thus, staurolite has a higher bulk sound velocity than most hydrous minerals and some upper mantle anhydrous minerals (e.g., garnet and omphacite) in cold subducting slabs, implying that its presence in medium- to high-pressure metamorphic rocks may increase seismic velocities in corresponding lithologies.

5. Conclusion

The *P*–*V* and *P*–*V*–*T* relationships and *P*–*T* stability of staurolite were

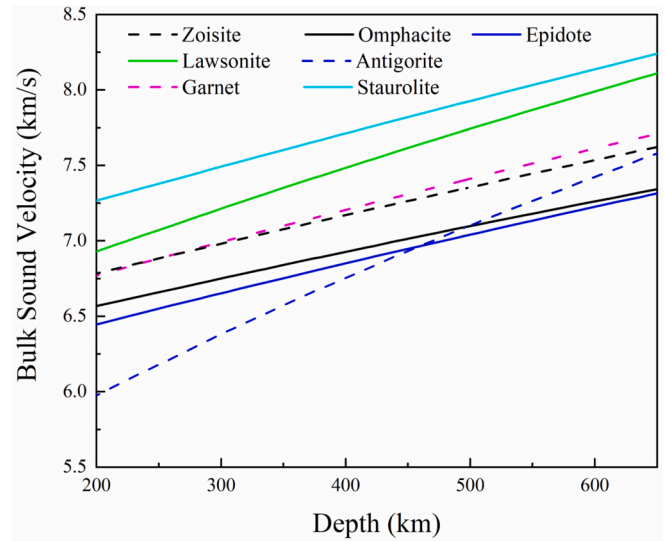


Fig. 6. Bulk sound velocities are plotted for staurolite (this study), epidote (60 mol% epidote ferric end-member (Ca₂Al₂Fe³⁺Si₃O₁₂(OH)) (Huang, 2024)), zoisite (Huang et al., 2023), antigorite (Yang et al., 2014), lawsonite (Ballaran and Angel, 2003; Grevel et al., 2000), garnet ((Mg_{0.144}Fe_{0.618}Ca_{0.219}Mn_{0.021})_{3.006}(Al_{0.947}Fe_{0.034}Si_{0.012})_{1.986}Si_{3.000}O₁₂) (Suzuki and Anderson, 1983; Xu et al., 2019)), omphacite (Nishihara et al., 2003).

investigated using a diamond anvil cell combined with synchrotron single-crystal XRD under maximum conditions of 850 K and ~23 GPa in this study. Our experimental results revealed that staurolite did not undergo any phase transition within the *P*–*T* range in this study. We fitted unit-cell volume and unit-cell parameter data with third-order Birch–Murnaghan EoS and the EoS parameters for staurolite were obtained: *K*₀ = 171 (3) GPa and *K'*₀ = 5.4 (5), *K*_{a0} = 184.4 (9) GPa and *K'*_{a0} = 3.9 (2), *K*_{b0} = 139 (7) GPa and *K'*_{b0} = 11 (2), *K*_{c0} = 180 (1) GPa and *K'*_{c0} = 3.9 (2). By fitting the *P*–*V*–*T* data using the high temperature third-order Birch–Murnaghan EoS, the thermal EoS parameters for staurolite were obtained: *K*₀ = 171 (5) GPa, *K'*₀ = 5.3 (8), α_{0V} = 1 (1) × 10⁻⁵ K⁻¹, α_{1V} = 5 (3) × 10⁻⁸ K⁻², ($\partial K/\partial T$)_{*P*} = -0.02 (2) GPa/K. These results differed from those of previous studies, and the possible reasons for these differences are discussed in this study. Combining the experimental results obtained in this study with those of previous studies, a *P*–*T* phase diagram for staurolite was further plotted. The density and bulk sound velocity along the Tonga slab geotherm were modeled. The *P*–*T* phase diagram and density profile of staurolite indicate that under

cold subduction conditions, staurolite can carry water down to mantle depth. Moreover, owing its high velocity, the presence of staurolite contributes to increasing the overall seismic wave velocity of subducting rocks. This characteristic may play an important role in plate subduction and the deep-water cycle of the Earth.

CRedit authorship contribution statement

Shijie Huang: Writing – original draft, Software, Methodology, Investigation, Funding acquisition, Data curation. **Jingui Xu:** Writing – review & editing, Methodology, Investigation. **Dongzhou Zhang:** Writing – review & editing. **Shanrong Zhang:** Writing – review & editing. **Yufeng Liu:** Writing – review & editing. **Yikui Liang:** Writing – review & editing. **Zimo Li:** Writing – review & editing. **Wenge Zhou:** Writing – review & editing, Conceptualization. **Dawei Fan:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

We confirm that there are no conflicts of interest associated with this submission, and that all authors have reviewed and approved the manuscript for publication. On behalf of my co-authors, I affirm that this is original work that has not been published before and is not currently under review elsewhere, either in whole or in part. All listed authors have contributed to and approved the final version of the manuscript. Finally, all the authors with no competing interests to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2025.108361>.

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