



# Thermodynamic Properties of Fe-Bearing Wadsleyite and Determination of the Olivine-Wadsleyite Phase Transition Boundary in $(\text{Mg,Fe})_2\text{SiO}_4$ System

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The self-consistent molar volumes, elastic properties and thermodynamic properties of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  wadsleyite have been determined over a wide temperature and pressure range based on an iterative numerical approach and experimental data from the literature. The obtained molar volumes, adiabatic bulk modulus, and shear modulus generally agree with the available experimental and theoretical results. The thermodynamic properties of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  were also reinvestigated. Comparisons on thermodynamic properties show that the thermal expansions, heat capacities, and entropies of both  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  exhibit negative and nonlinear behavior with increasing pressure. Besides, the pressure plays a more important role in thermodynamic properties of the  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  than that of the  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$ . Using the Clausius-Clapeyron equation combined with molar volumes and entropies of both compositions, the phase transition boundary of Fe-bearing olivine and wadsleyite is estimated. The calculated transition pressure shows a nonlinear relationship with increasing temperature, and the value is generally lower than the previous studies on Fe-free olivine and wadsleyite at the same temperature. On the basis of our phase relation, the temperature at the 410 km discontinuity is estimated as  $1795 \pm 70$  K under anhydrous conditions. The results not only confirm the feasibility of the Clausius-Clapeyron equation in obtaining the solid-solid phase transition, but also suggest that the existence of Fe might decrease the transition pressure of olivine-wadsleyite, which would consequently cause a higher temperature at the 410 km discontinuity.

**Keywords:** Fe-bearing wadsleyite, entropy, Clausius-Clapeyron equation, phase transition boundary, 410 km discontinuity

## INTRODUCTION

Olivine ( $\alpha$ -phase) and its high-pressure polymorphs (i.e., wadsleyite and ringwoodite) dominate the Earth's upper mantle and mantle transition zone (Ringwood, 1962). Since it has been widely accepted that the Earth's mantle is peridotitic, the seismic wave discontinuities in the Earth's mantle are usually considered to be related to the high-pressure transformations of olivine (Ringwood and Major, 1970). Furthermore, the existence of the 410 and 520 km discontinuities are attributed to the olivine-wadsleyite ( $\beta$ -phase) and wadsleyite-ringwoodite ( $\gamma$ -phase) transformations, respectively. Previous studies reported that temperatures at these seismic wave discontinuities can be estimated by comparing the depth of the seismic wave discontinuities with the phase transition pressures of mantle minerals (Ito and Katsura, 1989). In turn, it indicates that an accurate phase transition boundary of olivine-wadsleyite is necessary to constrain the temperature at the 410 km discontinuity.

Although it has been demonstrated that there is non-negligible Fe (~10 mol%) in natural olivine (Bina and Wood, 1987), most studies on the phase transition boundary of olivine-wadsleyite are still limited in  $\text{Mg}_2\text{SiO}_4$  system (Morishima et al., 1994; Jacobs et al., 2006; Akaogi et al., 2007; Ottonello et al., 2008; Holland and Powell, 2011; Dorogokupets et al., 2015). To date, the transition pressures in  $(\text{Mg,Fe})_2\text{SiO}_4$  system have been only determined at several temperatures (Katsura and Ito, 1989; Chen et al., 2002; Katsura et al., 2004), and the effect of Fe on the olivine-wadsleyite phase transition boundary in a continuous  $P$ - $T$  range remains unclear.

The determination of the phase transition boundary is usually based on the phase equilibrium, which requires the volumes and thermodynamic properties of coexisting phases at high-temperatures and high-pressures (HT-HP). The molar volume and thermodynamic properties, including thermal expansion and heat capacity, of San Carlos olivine ( $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ ) at HT-HP were reported via an iterative numerical approach in Su et al. (2018). Pioneering investigations on Fe-bearing wadsleyite ( $\beta$ - $(\text{Mg,Fe})_2\text{SiO}_4$ ) has shown the effect of Fe on the elastic properties (Li and Liebermann, 2000; Liu et al., 2009) and electrical conductivities (Dai and Karato, 2009; Yoshino et al., 2012). At the same time, few works have been devoted to the thermodynamic properties of Fe-bearing wadsleyite at HT-HP.

This study aims to determine the thermodynamic properties of Fe-bearing wadsleyite at HT-HP, and apply them to investigate the effect of Fe on the olivine-wadsleyite phase transition boundary. We refined our calculation procedure and derived the self-consistent molar volume, elastic moduli, thermal expansion, heat capacity, and entropy of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  based on existing experimental measurements. We also reanalyzed our early investigations on  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ , and compared the effect of pressure on the thermodynamic properties of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ . Then, we determined the phase transition boundary of olivine-wadsleyite in  $(\text{Mg,Fe})_2\text{SiO}_4$  system using the obtained molar volumes and entropies of two compositions at HT-HP combined with Clausius-Clapeyron equation. Finally, by

comparing the depth of the discontinuity with the transition pressure, we estimated the temperature at the 410 km discontinuity.

## METHODS

### Calculation Procedure

The approach used in this study is described in our recent studies (Su et al., 2018; Su et al., 2022), and the fundamental procedure is described below. The uncertainties of the derived parameters at different  $P$ - $T$  conditions are estimated from the experimental measuring error propagations using Taylor series expansion.

The thermal expansion ( $\alpha$ ) at constant pressure is related to volume ( $V$ ) as:

$$\alpha(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right) \quad (1)$$

And the integration of Eq. 1 yields:

$$V(T) = V_0 \exp \left[ \int_{T_0}^T \alpha(T) dT \right] \quad (2)$$

where  $V_0$  represents the volume at ambient condition. The isothermal derivative of volume with respect to pressure can be written as:

$$\left( \frac{\partial V}{\partial P} \right)_T = -V^2 \left( \frac{1}{v_\phi^2} + \frac{T\alpha^2}{C_p} \right) \quad (3)$$

where  $C_p$  stands for the heat capacity,  $v_\phi$  refers to the bulk sound velocity (Bina and Silver, 1990). The bulk sound velocity is related to the specific volume and adiabatic bulk modulus ( $K_S$ ) by  $v_\phi = (VK_S)^{1/2}$ , which can be calculated from the  $P$ - wave velocity ( $v_p$ ) and  $S$ - wave velocity ( $v_s$ ) by Eq. 4.

$$v_\phi = \left( v_p^2 - \frac{4}{3} v_s^2 \right)^{\frac{1}{2}} \quad (4)$$

Meanwhile, the isothermal derivative of the heat capacity with respect to pressure can be evaluated by Eq. 5.

$$\left( \frac{\partial C_p}{\partial P} \right)_T = -VT \left[ \alpha^2 + \left( \frac{\partial \alpha}{\partial T} \right)_P \right] \quad (5)$$

To start the calculation, first, we use the experimental determined volume at high-temperature and ambient pressure conditions to obtain the thermal expansion at ambient pressure. With the obtained thermal expansion and heat capacity as a function of temperature at ambient pressure, the approximate volume at an arbitrary reference pressure could be estimated using Eq. 3. Then resulting volume at this reference pressure can be used to update the value of thermal expansion and heat capacity at the same pressure with Eqs 1, 5, respectively. Hence, iteration of this loop leads to converged volume, thermal expansion, and heat capacity as a function of temperature and pressure based on the experimental elastic wave velocity at HT-HP.

**TABLE 1** | Fitting coefficients and their uncertainties of Eq. 10 to calculate the *P*- and *S*- wave velocities of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> at HT-HPs.

	$v_0$	$v_1$	$v_2$	$v_3$	$v_4$	$v_5$
$v_P$	9,350 (8)	80.8 (25)	-0.42 (2)	-1.97 (19)	$-5.59 (377) \times 10^{-5}$	0.016 (3)
$v_S$	5,465 (9)	25.7 (28)	-0.36 (3)	-0.60 (22)	$-8.09 (429) \times 10^{-5}$	0.016 (3)

With the determined volume as well as the elastic wave velocity at HT-HP, the adiabatic bulk modulus ( $K_S$ ) and shear modulus ( $G$ ) can be obtained using Eqs 6, 7, respectively.

$$K_S = \frac{1}{V} \left( v_P^2 - \frac{4}{3} v_S^2 \right) \quad (6)$$

$$G = \frac{1}{V} v_S^2 \quad (7)$$

Furthermore, since the temperature and pressure dependences of entropy ( $S$ ) are related to the heat capacity and thermal expansion via Eqs 8, 9, respectively (Johari, 2021), the entropy at HTHP can be also derived with the entropy measured at ambient conditions.

$$S(P_0, T) = S(P_0, T_0) - \int_{T_0}^T \left( \frac{C_P}{T} \right) dT \quad (8)$$

$$S(P, T_0) = S(P_0, T_0) - \int_{P_0}^P \alpha V dP \quad (9)$$

## Thermoelastic Data of Fe-Bearing Wadsleyite

### Elastic Wave Velocity at High-Temperature and High-Pressure Conditions

Previous studies have measured the elastic wave velocity of Fe-bearing wadsleyite at high-pressure conditions (Li and Liebermann, 2000; Wang et al., 2014). Besides, by using ultrasonic interferometry in conjunction with synchrotron X-ray diffraction measurements, Liu et al. (2009) presented the elastic wave velocity and unit-cell volume of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> to 12 GPa and 1073 K. Here, we fit the *P*- and *S*- wave velocities by Liu et al. (2009) with Eq. 10, and the fitting coefficients and their uncertainties are listed in Table 1.

$$v(P, T) = v_0 + v_1 P + v_2 (T - 273) + v_3 P^2 + v_4 (T - 273)^2 + v_5 P (T - 273) \quad (10)$$

where pressure is expressed in GPa, temperature is expressed in K, *P*- and *S*- wave velocity are expressed in m/s. The differences are less than 0.5% and 1.5% compared with the results reported by Li and Liebermann (2000) and Wang et al. (2014), respectively.

### Thermodynamic Properties at High-Temperature and Ambient Pressure Conditions

At present, there is no experimental or theoretical data for the thermal expansion, heat capacity, or entropy of Fe-bearing wadsleyite yet. Since it is suggested that the volume and heat capacity are linearly proportional to the Fe/(Mg + Fe) ratio

( $X_{Fe}$ ) (Xu et al., 2004), the thermal expansion and heat capacity of Fe-bearing wadsleyite as a function of temperature can be estimated from the data of Mg end-member wadsleyite ( $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>) and Fe end-member ( $\beta$ -Fe<sub>2</sub>SiO<sub>4</sub>) wadsleyite.

However,  $\beta$ -Fe<sub>2</sub>SiO<sub>4</sub> is a virtual mineral since fayalite ( $\alpha$ -Fe<sub>2</sub>SiO<sub>4</sub>) is transformed directly to Fe end-member ringwoodite ( $\gamma$ -Fe<sub>2</sub>SiO<sub>4</sub>) with increasing pressure (Akimoto et al., 1967). According to the studies on  $\alpha$ -Fe<sub>2</sub>SiO<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>SiO<sub>4</sub> (Fei and Saxena, 1986), Saxena (1996) published the molar volume and heat capacity of  $\beta$ -Fe<sub>2</sub>SiO<sub>4</sub> at ambient conditions. Besides, Saxena (1996) also concluded the results from previous studies on  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> (Akimoto et al., 1978; Watanabe, 1982), and provided the thermodynamic data. Here, we use the database presented by Saxena (1996). For the Fe-bearing wadsleyite with a  $X_{Fe}$  as 0.13, the temperature dependence of heat capacity is represented by a polynomial equation as shown in Eq. 11. The molar volume data is analyzed using the EoSfit software (Gonzalez-Platas et al., 2016), and the equation for the thermal expansion as a function of temperature is defined as Eq. 12. Additionally, the standard entropy is determined as 99.3 J/mol K.

$$C_P(T) = 179.59(21) + 1.10(1) \times 10^{-2} T - 19171(297) T^{-1} + 1.05(149) \times 10^6 T^{-2} - 4.34(24) \times 10^8 T^{-3} \quad (11)$$

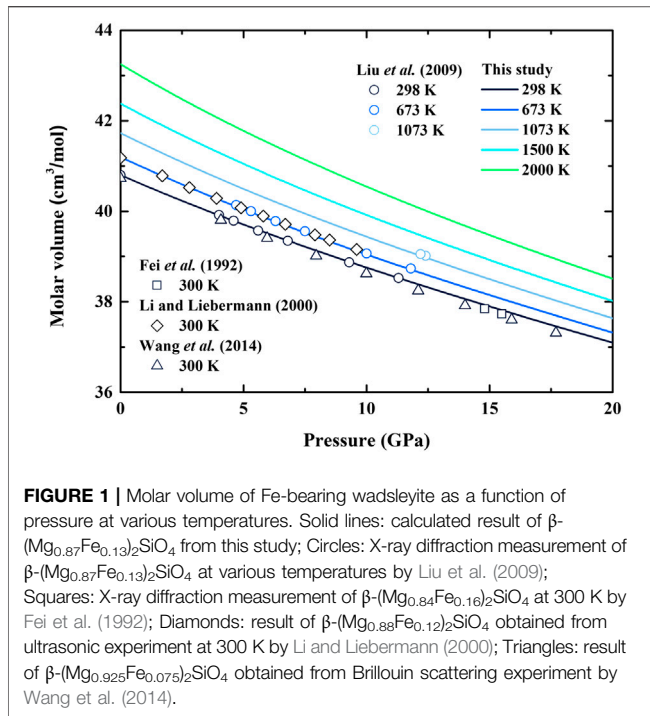
$$\alpha(T) = 2.520(112) \times 10^{-5} + 0.902(55) \times 10^{-8} T - 0.755(269) T^{-2} \quad (12)$$

## RESULTS

Based on the calculation procedure and experimental data discussed in *Methods*, the molar volume, adiabatic bulk modulus, shear modulus, thermal expansion, heat capacity, and entropy of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> are derived. All the calculated parameters are provided in **Supplementary Tables S1–S3**, together with their uncertainties approximated using the error propagation calculations.

### Molar Volume at High-Temperature and High-Pressure Conditions

The calculated molar volume of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> as a function of pressure at various temperatures is shown in **Figure 1**. The unit-cell volumes of  $\beta$ -(Mg<sub>0.84</sub>Fe<sub>0.16</sub>)<sub>2</sub>SiO<sub>4</sub> and  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> were measured by Fei et al. (1992) and Liu et al. (2009) using X-ray diffraction,



**FIGURE 1** | Molar volume of Fe-bearing wadsleyite as a function of pressure at various temperatures. Solid lines: calculated result of  $\beta$ -( $\text{Mg}_{0.87}\text{Fe}_{0.13}$ ) $_2\text{SiO}_4$  from this study; Circles: X-ray diffraction measurement of  $\beta$ -( $\text{Mg}_{0.87}\text{Fe}_{0.13}$ ) $_2\text{SiO}_4$  at various temperatures by Liu et al. (2009); Squares: X-ray diffraction measurement of  $\beta$ -( $\text{Mg}_{0.84}\text{Fe}_{0.16}$ ) $_2\text{SiO}_4$  at 300 K by Fei et al. (1992); Diamonds: result of  $\beta$ -( $\text{Mg}_{0.88}\text{Fe}_{0.12}$ ) $_2\text{SiO}_4$  obtained from ultrasonic experiment at 300 K by Li and Liebermann (2000); Triangles: result of  $\beta$ -( $\text{Mg}_{0.925}\text{Fe}_{0.075}$ ) $_2\text{SiO}_4$  obtained from Brillouin scattering experiment by Wang et al. (2014).

respectively. Also, the densities of  $\beta$ -( $\text{Mg}_{0.88}\text{Fe}_{0.12}$ ) $_2\text{SiO}_4$  and  $\beta$ -( $\text{Mg}_{0.925}\text{Fe}_{0.075}$ ) $_2\text{SiO}_4$  were presented by Li and Liebermann (2000) and Wang et al. (2014) based on ultrasonic and Brillouin scattering measurements, respectively. Based on the molar mass of the Fe-bearing wadsleyite from those previous studies mentioned above, we convert the units of the unit-cell volume ( $\text{\AA}^3$ ) and density ( $\text{g/cm}^3$ ) to molar volume ( $\text{cm}^3/\text{mol}$ ), and the results are also illustrated in **Figure 1**.

Our result shows good consistency with the X-ray diffraction measurement by Liu et al. (2009), and the difference is less than 0.1% at room temperature. The excellent agreement also holds at high-temperature conditions, and the largest difference is 0.1% at 1073 K compared with that by Liu et al. (2009). In the meantime, our obtained molar volume is  $\sim$ 0.3% higher than the result by Wang et al. (2014),  $\sim$ 0.12% higher than that by Fei et al. (1992), and  $\sim$ 1.9% lower than that by Li and Liebermann (2000). Overall, except for the result by Li and Liebermann (2000), the molar

volume of Fe-bearing wadsleyite seems to increase with the value of  $X_{\text{Fe}}$ .

## Elastic Properties at High-Temperature and High-Pressure Conditions

Based on the molar volume, the calculated elastic moduli of  $\beta$ -( $\text{Mg}_{0.87}\text{Fe}_{0.13}$ ) $_2\text{SiO}_4$  are shown in **Table 2**; **Figure 2**, along with the previous results of Fe-bearing wadsleyite with different values of  $X_{\text{Fe}}$  (Sinogeikin et al., 1998; Li and Liebermann, 2000; Katsura et al., 2001; Mayama, 2004; Liu et al., 2009; Isaak et al., 2010; Wang et al., 2014).

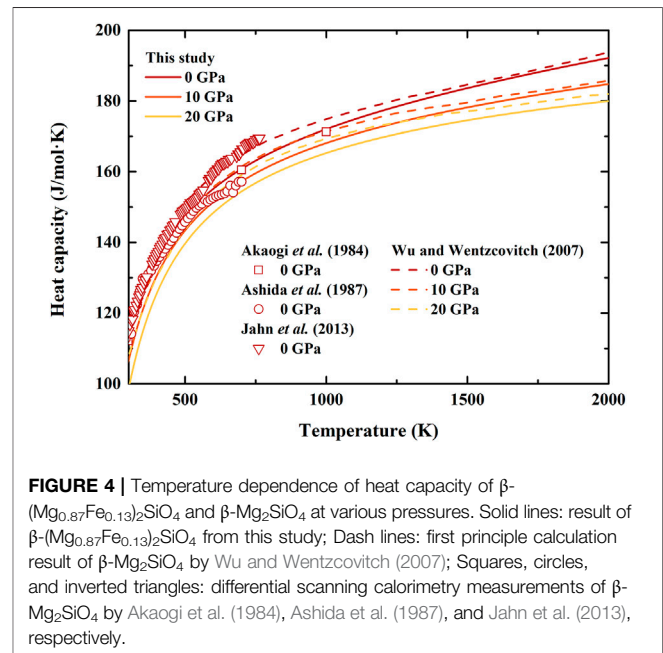
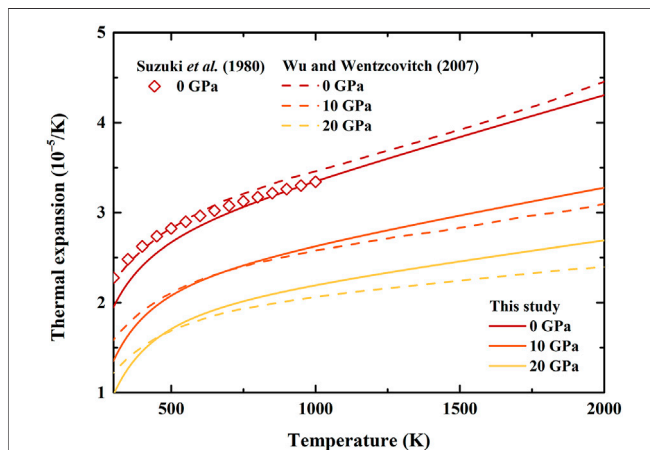
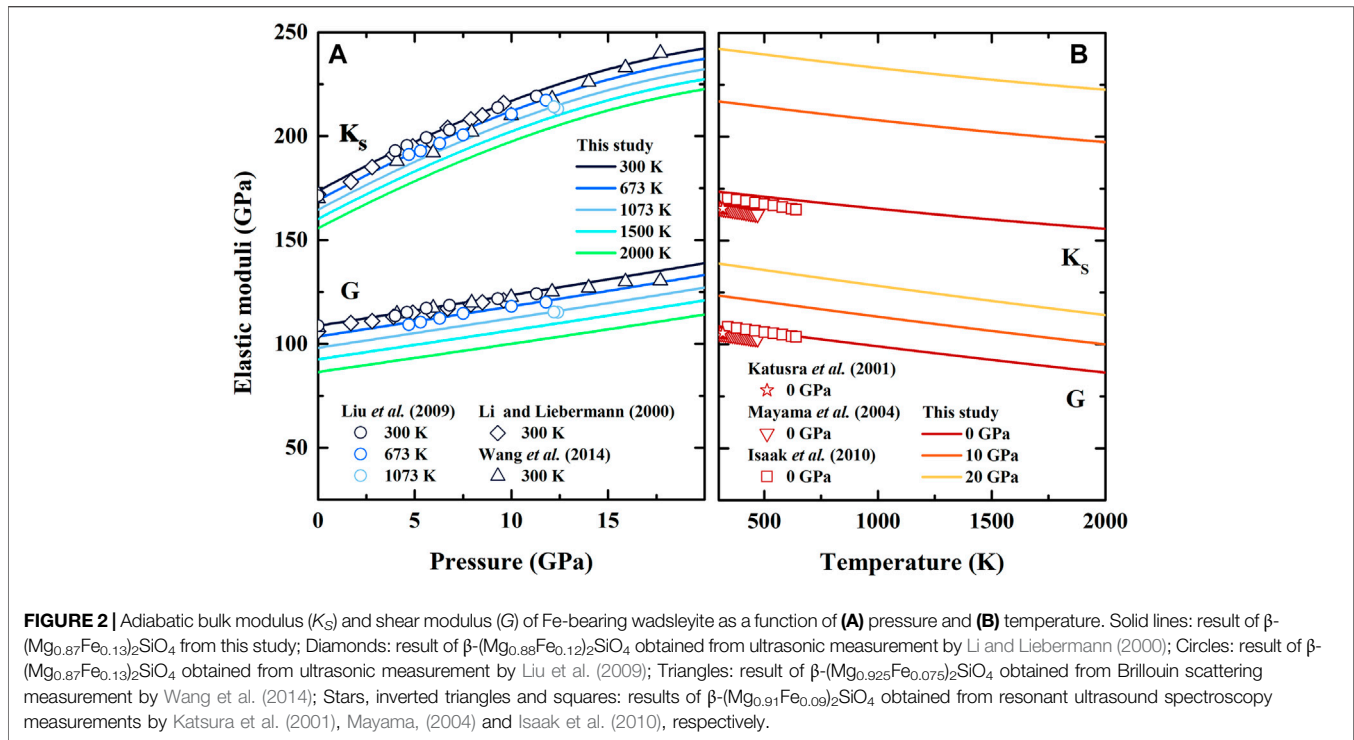
In this study, the adiabatic bulk modulus and shear modulus at ambient conditions are determined as  $K_{S0} = 173.4$  (12) GPa and  $G_0 = 108.6$  (5) GPa, respectively. In **Table 2**, our  $K_{S0}$  is consistent within the uncertainties of Liu et al. (2009), in which  $X_{\text{Fe}} = 0.13$ , and generally larger than those with less Fe contents (Isaak et al., 2010; Katsura et al., 2001; Li and Liebermann, 2000; Mayama, 2004; Sinogeikin et al., 1998; Wang et al., 2014). On the other hand, the values of  $G_0$  listed in **Table 2** do not show apparent  $X_{\text{Fe}}$  dependence. Our  $G_0$  also agrees well with the result by Liu et al. (2009). Although our  $G_0$  is larger than those with  $X_{\text{Fe}} = 0.12$  (Li and Liebermann, 2000) and  $X_{\text{Fe}} = 0.09$  (Katsura et al., 2001; Mayama, 2004), it is nearly the same as those with  $X_{\text{Fe}} = 0.08$  (Isaak et al., 2010) and  $X_{\text{Fe}} = 0.075$  (Sinogeikin et al., 1998; Wang et al., 2014).

In **Figure 2A**, our adiabatic bulk modulus exhibits significant nonlinear variation with the increasing pressure, whereas shear modulus shows the opposite trend. Both of the derived adiabatic bulk modulus and shear modulus are generally comparable with the data obtained from ultrasonic measurements (Li and Liebermann, 2000; Liu et al., 2009), and the largest separation is 1%. Though our adiabatic bulk modulus is  $\sim$ 2.5% larger than that by Wang et al. (2014) in the pressure range of 5–12 GPa, it agrees well with the result by Wang et al. (2014) with the differences less than 1%. Also, the first and second pressure derivatives of adiabatic bulk modulus and shear modulus are obtained as  $\partial K_S/\partial P = 5.28$ (1),  $\partial^2 K_S/\partial P^2 = -0.0991$ (2)  $\text{GPa}^{-1}$ ,  $\partial G/\partial P = 1.48$ (1) and  $\partial^2 G/\partial P^2 = -0.0171$ (6)  $\text{GPa}^{-1}$ , respectively.

The temperature dependences of adiabatic bulk modulus and shear modulus are shown in **Figure 2B**. Our adiabatic bulk modulus is  $\sim$ 2% larger than that of Isaak et al. (2010), while shear modulus is consistent with Isaak's result, and the

**TABLE 2** | Elastic moduli of  $\beta$ -( $\text{Mg}_{0.87}\text{Fe}_{0.13}$ ) $_2\text{SiO}_4$  and their pressure and temperature derivatives.

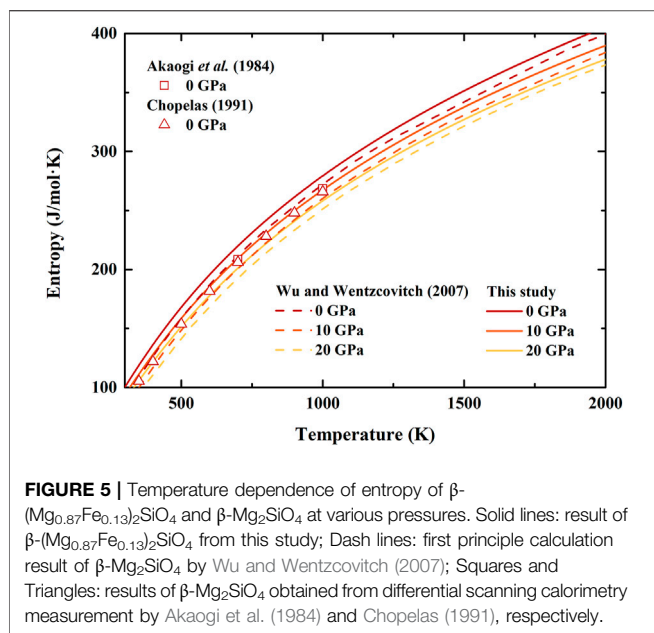
$X_{\text{Fe}}$	$K_{S0}$ GPa	$(\frac{\partial K_S}{\partial P})_T$	$(\frac{\partial^2 K_S}{\partial P^2})_T$ $\text{GPa}^{-1}$	$(\frac{\partial K_S}{\partial T})_P$ $\text{GPa K}^{-1}$	$G_0$ GPa	$(\frac{\partial G}{\partial P})_T$ $\text{GPa}^{-1}$	$(\frac{\partial^2 G}{\partial P^2})_T$ $\text{GPa}^{-1}$	$(\frac{\partial G}{\partial T})_P$ $\text{GPa K}^{-1}$	References
0.075	170 (3)				108 (2)				Sinogeikin et al. (1998)
0.075	170 (3)	4.1 (1)			108 (2)	1.45 (4)			Wang et al. (2014)
0.08	170.8 (1.2)			-0.0175 (7)	108.9 (0.4)			-0.0155 (6)	Isaak et al. (2010)
0.09	165.7 (1)			-0.016 (3)	105.66 (3)			-0.012 (1)	Katsura et al. (2001)
0.09	165.72 (1)			-0.0175 (3)	105.43 (2)			-0.0159 (1)	Mayama (2004)
0.12	172 (2)	4.6 (1)			106 (1)	1.6 (1)			Li and Liebermann (2000)
0.13	175.4 (7)	4.10 (11)		-0.0135 (10)	108.0 (4)	1.56 (5)		-0.0144 (8)	Liu et al. (2009)
0.13	173.4 (12)	5.28 (1)	-0.0991 (2)	-0.0145 (1)	108.6 (5)	1.48 (1)	-0.0171 (6)	-0.0210 (1)	This study



differences are within 0.6%. The obtained adiabatic bulk modulus and shear modulus are 5.4% and 3.5% larger than that of Katsura et al. (2001) and Mayama (2004), respectively. The temperature derivatives of adiabatic bulk modulus and shear modulus are determined as  $\partial K_S/\partial T = -0.0145(1)$  GPa/K and  $\partial G/\partial T = -0.0210(1)$  GPa/K, respectively, which are comparable with those obtained by resonant ultrasound spectroscopy (Katsura et al., 2001; Mayama, 2004; Isaak et al., 2010) (Table 2).

## Thermodynamic Properties at High-Temperature and High-Pressure Conditions

The thermal expansion, heat capacity, and entropy of  $\beta$ - $(Mg_{0.87}Fe_{0.13})_2SiO_4$  as a function of temperature at various pressures are illustrated in Figures 3–5, respectively. Since there is no thermodynamic data of Fe-bearing wadsleyite at



**FIGURE 5 |** Temperature dependence of entropy of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\beta$ - $\text{Mg}_2\text{SiO}_4$  at various pressures. Solid lines: result of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  from this study; Dash lines: first principle calculation result of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  by Wu and Wentzcovitch (2007); Squares and Triangles: results of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  obtained from differential scanning calorimetry measurement by Akaogi et al. (1984) and Chopelas (1991), respectively.

present, here we only show the available thermal expansion, heat capacity, and entropy of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  for comparisons (Suzuki et al., 1980; Akaogi et al., 1984; Ashida et al., 1987; Chopelas, 1991; Wu and Wentzcovitch, 2007; Jahn et al., 2013).

In **Figure 3**, our calculated thermal expansion of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  at ambient condition is determined as  $\alpha_0 = 1.952 (428) \times 10^{-5} \text{ K}^{-1}$ , which is lower than the results by Suzuki et al. (1980) ( $2.27 \times 10^{-5} \text{ K}^{-1}$ ) and Wu and Wentzcovitch (2007) ( $2.21 \times 10^{-5} \text{ K}^{-1}$ ). With increasing temperature, the difference between our and Suzuki's result becomes smaller, and decreases to 0.12% at 1000 K. Also, our thermal expansion shows a similar trend with that of Wu and Wentzcovitch (2007) at ambient pressure conditions over  $\sim 700$  K, with an average difference of  $\sim 3\%$ . For high-pressure conditions, our result becomes larger than the result by Wu and Wentzcovitch (2007) over  $\sim 700$  and  $\sim 450$  K at 10 and 20 GPa, respectively, and causes a difference of 5% and 11% at 2000 K at 10 and 20 GPa, respectively.

The calculated heat capacity of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  as a function of temperature at various pressures is shown in **Figure 4**, together with the ambient pressure results of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  measured using differential scanning calorimetry (Akaogi et al., 1984; Ashida et al., 1987; Jahn et al., 2013), as well as high-pressure results determined using first principle calculation (Wu and Wentzcovitch, 2007). At ambient pressure conditions, the separations between these previous results of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  are quite large. Our heat capacity is close to that by Akaogi et al. (1984) with a difference of  $\sim 0.5\%$ , while larger than that by Ashida et al. (1987), and smaller than those by Wu and Wentzcovitch (2007) and Jahn et al. (2013). Moreover, our obtained heat capacity is smaller than the result by Wu and Wentzcovitch (2007) at high-pressure conditions as well.

Furthermore, the determined entropy of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  is illustrated in **Figure 5**, which is generally larger than previous experimental (Akaogi et al., 1984; Chopelas, 1991) and theoretical (Wu and Wentzcovitch, 2007) results. Though at ambient conditions, the differences between our and previous results are pretty significant, which is  $\sim 13\%$ ,  $\sim 15\%$ , and  $\sim 10\%$  compared to that by Akaogi et al. (1984), Chopelas (1991), and Wu and Wentzcovitch (2007), respectively. Nevertheless, the separations decrease with increasing temperature, and the average differences are  $\sim 5\%$ ,  $\sim 8\%$ , and  $\sim 4\%$  compared to the results by Akaogi et al. (1984), Chopelas (1991), and Wu and Wentzcovitch (2007), respectively. In addition, our calculated entropy of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  is  $\sim 5\%$  larger than that of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  by Wu and Wentzcovitch (2007) at 10 and 20 GPa.

Based on the database by Saxena (1996), the values of thermal expansion, heat capacity, and entropy of  $\beta$ - $\text{Fe}_2\text{SiO}_4$  are larger than those of  $\beta$ - $\text{Mg}_2\text{SiO}_4$ . Theoretically the thermal expansion, heat capacity, and entropy of the Fe-bearing wadsleyite should be slightly larger than those of  $\beta$ - $\text{Mg}_2\text{SiO}_4$ . But according to the results, only entropy shows a noticeable increase with the Fe content. Since the differences of the thermal expansions and heat capacities between the available results for  $\beta$ - $\text{Mg}_2\text{SiO}_4$  are pretty large (**Figures 3, 4**), it is difficult to identify the effect of Fe on thermal expansion and heat capacity of wadsleyite based on existing results. More experimental and theoretical investigations are needed to clarify the Fe effects on the thermodynamic properties of wadsleyite.

## DISCUSSION AND IMPLICATIONS

### Comparisons on Thermodynamic Properties of $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$ and $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$

The thermoelastic properties, including molar volume, thermal expansion, and heat capacity of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  at HT-HP have been determined in our previous work (Su et al., 2018). The standard entropy of forsterite ( $\alpha$ - $\text{Mg}_2\text{SiO}_4$ ) and fayalite at 298 K were defined by Robie et al. (1982a; 1982b), from which the entropy of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  can be derived as 99.8 (1) J/mol K. Here, we re-analysis the data and present the entropy of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  at HT-HP, as well as the uncertainties of the determined parameters. The obtained data is shown in **Supplementary Tables S4–S6**.

To investigate the pressure effects on the thermodynamic properties of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ , we fit the thermodynamic parameters, including thermal expansions, heat capacities, and entropies to an equation of  $N = N_0 + \partial N / \partial P \times P + \partial^2 N / \partial P^2 \times P^2$  at different temperatures, where  $N$  refers to the thermodynamic properties,  $N_0$  refers to  $N$  at ambient pressure,  $\partial N / \partial P$  and  $\partial^2 N / \partial P^2$  refer to the first and second pressure derivatives of  $N$ , respectively. The fitting coefficients are listed in **Table 3**.

In **Table 3**, all the thermodynamic parameters, including thermal expansions, heat capacities, and entropies of  $\beta$ -

**TABLE 3** | The thermal expansions, heat capacities, and entropies of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> and  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub>, and their pressure derivatives at various temperatures.

T K	Fe-Bearing wadsleyite ( $\beta$ -(Mg <sub>0.87</sub> Fe <sub>0.13</sub> ) <sub>2</sub> SiO <sub>4</sub> )			San Carlos olivine ( $\alpha$ -(Mg <sub>0.9</sub> Fe <sub>0.1</sub> ) <sub>2</sub> SiO <sub>4</sub> )		
	$\alpha_0$ 10 <sup>-5</sup> /K	$\partial\alpha/\partial P$ 10 <sup>-7</sup> /K GPa	$\partial^2\alpha/\partial P^2$ 10 <sup>-8</sup> /K GPa <sup>2</sup>	$\alpha_0$ 10 <sup>-5</sup> /K	$\partial\alpha/\partial P$ 10 <sup>-7</sup> /K GPa	$\partial^2\alpha/\partial P^2$ 10 <sup>-8</sup> /K GPa <sup>2</sup>
300	1.952 (428)	-7.01 (2)	1.11 (1)	2.213 (390)	-12.25 (2)	1.39 (1)
700	2.997 (206)	-7.46 (2)	1.21 (1)	3.308 (188)	-13.31 (3)	1.48 (1)
1100	3.449 (196)	-8.84 (3)	1.50 (1)	3.867 (178)	-15.33 (4)	1.81 (2)
1500	3.839 (207)	-10.33 (3)	1.81 (2)	4.369 (189)	-17.45 (5)	2.19 (3)
2000	4.304 (230)	-12.22 (4)	2.19 (2)	4.978 (210)	-20.14 (6)	2.66 (3)
T K	$C_{P0}$ J/mol K	$\partial C_p/\partial P$ J/mol K GPa	$\partial^2 C_p/\partial P^2$ 10 <sup>-3</sup> J/mol K GPa <sup>2</sup>	$C_{P0}$ J/mol K	$\partial C_p/\partial P$ J/mol K GPa	$\partial^2 C_p/\partial P^2$ 10 <sup>-3</sup> J/mol K GPa <sup>2</sup>
300	114.57 (377)	-0.804 (1)	0.09 (1)	120.38 (280)	-0.835 (1)	1.94 (1)
700	160.76 (105)	-0.387 (1)	3.56 (3)	164.64 (78)	-0.487 (1)	6.30 (4)
1100	174.78 (68)	-0.474 (1)	6.18 (5)	179.30 (50)	-0.640 (1)	10.57 (8)
1500	183.61 (56)	-0.625 (2)	8.94 (8)	189.41 (41)	-0.865 (3)	15.27 (12)
2000	192.17 (50)	-0.853 (2)	12.79 (11)	200.13 (37)	-1.196 (3)	21.96 (18)
T K	$S_0$ J/mol K	$\partial S/\partial P$ J/mol K GPa	$\partial^2 S/\partial P^2$ J/mol K GPa <sup>2</sup>	$S_0$ J/mol K	$\partial S/\partial P$ J/mol K GPa	$\partial^2 S/\partial P^2$ J/mol K GPa <sup>2</sup>
300	99.3	-0.74 (1)	0.010 (1)	99.8 (1)	-0.89 (1)	0.021 (1)
700	219.1 (17)	-1.17 (1)	0.012 (1)	223.1 (14)	-1.37 (1)	0.024 (1)
1100	295.0 (21)	-1.36 (1)	0.014 (1)	300.9 (17)	-1.62 (1)	0.027 (1)
1500	350.6 (23)	-1.53 (1)	0.016 (1)	358.1 (18)	-1.85 (1)	0.032 (1)
2000	404.6 (24)	-1.74 (1)	0.019 (1)	414.1 (19)	-2.14 (1)	0.037 (1)

(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> and  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> show negative and nonlinear relationships with the pressure. The thermal expansion of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> is generally smaller than that of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> at the same temperature, which coincides with the principle that wadsleyite has a more densely packed structure than olivine. Also, the pressure effects on the thermal expansions of both  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> and  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> increase with the temperature. Also, the pressure derivative of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> is larger than that of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> at the same temperature. In the temperature range of 300–2000 K, the  $\partial\alpha/\partial P$  of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> decreases from -7.01 (2) 10<sup>-7</sup>/K GPa to -12.22 (4) 10<sup>-7</sup>/K GPa, and the  $\partial\alpha/\partial P$  of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> decreases from -12.25 (2) 10<sup>-7</sup>/K GPa to -20.14 (6) 10<sup>-7</sup>/K GPa.

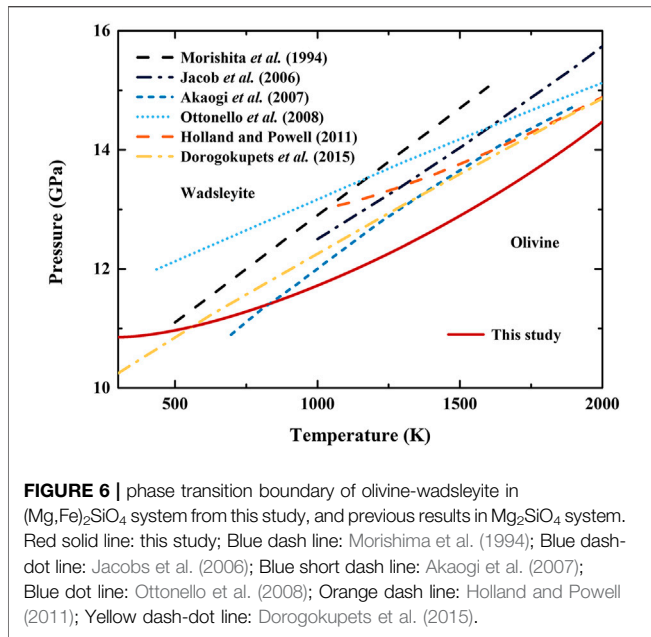
For the heat capacity, the  $\partial C_p/\partial P$  of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> at 300 K ( $\partial C_p/\partial P = -0.804$  (1) J/mol K GPa) is smaller than that at 700 K ( $\partial C_p/\partial P = -0.387$  (1) J/mol K GPa). Then, with the temperature increasing to 2000 K, the  $\partial C_p/\partial P$  of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> decreases to -0.853 (2) J/mol K GPa. The pressure effect on the heat capacity of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> shows the same pattern with the temperature, but generally, the  $\partial C_p/\partial P$  of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> is smaller than that of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub>.

Similar to thermal expansion, the entropy of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> is generally lower than that of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> at the same condition. The pressure effect on the entropy of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub> is also smaller than that of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub>. The  $\partial S/\partial P$  of  $\beta$ -(Mg<sub>0.87</sub>Fe<sub>0.13</sub>)<sub>2</sub>SiO<sub>4</sub>

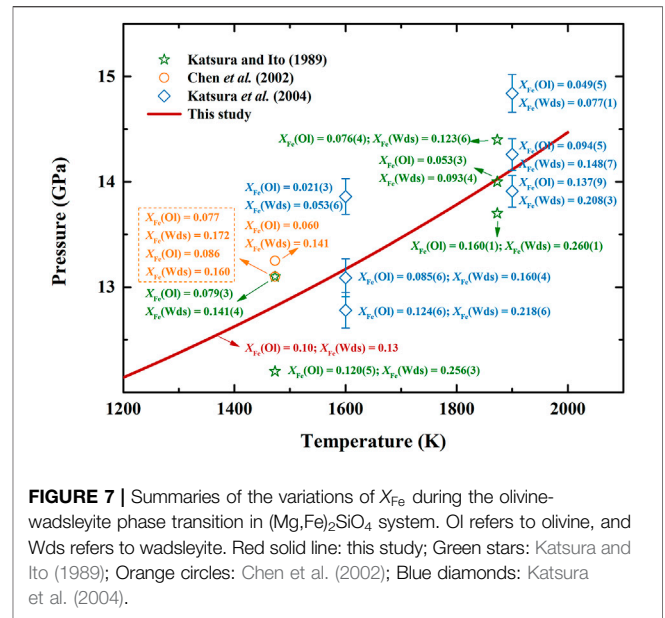
decreases from -0.74 (1) J/mol GPa to -1.74 (1) J/mol GPa with the temperature increases from 300 to 2000 K. Besides, the  $\partial S/\partial P$  of  $\alpha$ -(Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub> decreases from -0.89 (1) J/mol GPa to -2.14 (1) J/mol GPa in the temperature range of 300–2000 K.

## Phase Transition Boundary of Olivine-Wadsleyite in (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> System

The global seismic discontinuity at the depth of 410 km, which separates the upper mantle from the transition zone, is most likely caused by the olivine-wadsleyite transition at ~13–14 GPa (Zhang and Bass, 2016). Therefore, the phase transition boundary of olivine-wadsleyite has been widely studied to infer the composition and temperature at the 410 km discontinuity. By normal and reverse runs using *in-situ* X-ray diffraction in a cubic anvil apparatus, the olivine-wadsleyite transition pressures in Mg<sub>2</sub>SiO<sub>4</sub> system from 1073 to 1873 K were proposed by Morishima et al. (1994). Also, the transition pressures of olivine-wadsleyite with different Fe contents were experimentally determined at various temperatures by Katsura and Ito (1989) (1473 and 1873 K), Chen et al. (2002) (1473 K), and Katsura et al. (2004) (1600 and 1900 K). Then, based on the transition pressures determined in Mg<sub>2</sub>SiO<sub>4</sub> system, as well as the thermodynamic properties of  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> and  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>, the phase transition boundary was calculated using Eq. 13 (Jacobs et al., 2006; Akaogi et al., 2007; Ottonello et al., 2008; Holland and Powell, 2011; Dorogokupets et al., 2015).



**FIGURE 6** | phase transition boundary of olivine-wadsleyite in  $(\text{Mg,Fe})_2\text{SiO}_4$  system from this study, and previous results in  $\text{Mg}_2\text{SiO}_4$  system. Red solid line: this study; Blue dash line: Morishima et al. (1994); Blue dash-dot line: Jacobs et al. (2006); Blue short dash line: Akaogi et al. (2007); Blue dot line: Ottonello et al. (2008); Orange dash line: Holland and Powell (2011); Yellow dash-dot line: Dorogokupets et al. (2015).



**FIGURE 7** | Summaries of the variations of  $X_{\text{Fe}}$  during the olivine-wadsleyite phase transition in  $(\text{Mg,Fe})_2\text{SiO}_4$  system. Ol refers to olivine, and Wds refers to wadsleyite. Red solid line: this study; Green stars: Katsura and Ito (1989); Orange circles: Chen et al. (2002); Blue diamonds: Katsura et al. (2004).

$$\Delta G(P, T) = \Delta H(P_0, T) - T\Delta S(P_0, T) + \int_{1 \text{ atm}}^P \Delta V(P, T)dP = 0 \quad (13)$$

Eq.13 is derived based on the Gibbs free energy equation, in which  $\Delta H(P_0, T)$  and  $\Delta S(P_0, T)$  are enthalpy and entropy changes between the low and high-pressure phases at high-temperature and ambient pressure conditions, respectively,  $\Delta G(P, T)$  and  $\Delta V(P, T)$  are the Gibbs free energy and volume changes at HT-HP, respectively. In previous studies, the volumes of olivine and wadsleyite as a function of temperature and pressure were obtained from either theoretical calculations (Jacobs et al., 2006; Ottonello et al., 2008; Dorogokupets et al., 2015), or X-ray diffraction experiments with the combination of the third-order Birch–Murnaghan equation of state (3BM EoS) (Akaogi et al., 2007; Holland and Powell, 2011). The empirical EoS such as 3BM EoS and Mie–Grüneisen–Debye EoS undoubtedly provide convenient ways for determining volumes at specific  $P$ - $T$  conditions, but the assumptions in the derivation processes of these empirical EoS might cause uncertainties at high  $P$ - $T$  range (Anderson, 1995; Angel et al., 2021).

Meanwhile, the Clausius-Clapeyron equation (Eq. 14) is also one of the classic equations for estimating the phase transition boundaries:

$$\frac{dP}{dT} = \frac{\Delta S(P, T)}{\Delta V(P, T)} \quad (14)$$

where  $dP/dT$  is the Clapeyron slope,  $\Delta S(P, T)$  and  $\Delta V(P, T)$  are, respectively, the entropy and volume changes between the two coexisting phases at HT-HP. Since previous measurements on the transition pressures in  $(\text{Mg,Fe})_2\text{SiO}_4$  system were usually conducted at high-temperature conditions (Katsura and Ito, 1989; Chen et al., 2002; Katsura et al., 2004), once the transition pressure at an arbitrary temperature is determined,

the transition boundary can be simply derived with the entropy and volume changes between olivine and wadsleyite at HT-HP. The Clausius-Clapeyron equation was barely applied to the solid-solid phase transitions because the entropy variations with pressure in solids were often ignored in early studies (Ovrutsky et al., 2014). Here, with our obtained molar volumes and entropies of  $\alpha$ - $(\text{Mg}_{0.9}, \text{Fe}_{0.1})_2\text{SiO}_4$  and  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  at HT-HP, we try to determine the phase transition boundary of olivine-wadsleyite in  $(\text{Mg,Fe})_2\text{SiO}_4$  system using the Clausius-Clapeyron equation. Note that the uncertainties of the transition pressure and Clapeyron slope are estimated using a Taylor series expansion.

In this study, the  $X_{\text{Fe}}$  are 0.13 and 0.1, respectively, for our wadsleyite and olivine, and the partition coefficients of Fe and Mg between  $\alpha$  and  $\beta$  phases ( $K_{\text{Fe-Mg}}^{\alpha-\beta} = (X_{\text{Fe}}^\alpha/X_{\text{Fe}}^\beta)/[(1 - X_{\text{Fe}}^\alpha)/(1 - X_{\text{Fe}}^\beta)]$ ) is calculated as 0.74. The  $X_{\text{Fe}}$  of our wadsleyite and olivine are close to one of the experimental results proposed by Katsura et al. (2004) that the  $X_{\text{Fe}}$  increased from 0.094 (5) to 0.148 (7) during the olivine-wadsleyite transition, and the transition temperature and pressure were determined as 1900 K and 14.26 (15) GPa. Since our  $K_{\text{Fe-Mg}}^{\alpha-\beta}$  is slightly higher than that by Katsura et al. (2004) [0.60 (5)], the start  $P$ - $T$  point for our calculation is placed at 1900 K and 14.11 GPa, which is the lower limit of the transition pressure determined by Katsura et al. (2004).

Figure 6 illustrates our determined phase transition boundary, along with previous results determined in  $\text{Mg}_2\text{SiO}_4$  system (Morishima et al., 1994; Jacobs et al., 2006; Akaogi et al., 2007; Ottonello et al., 2008; Holland and Powell, 2011; Dorogokupets et al., 2015). Generally, the transition pressures obtained in  $\text{Mg}_2\text{SiO}_4$  system are higher than ours over  $\sim 850$  K (Ottonello et al., 2008). Also, the transition pressures of most previous studies tend to be linear with increasing temperature (Morishima et al., 1994; Jacobs et al., 2006; Akaogi et al., 2007; Ottonello et al., 2008; Dorogokupets et al., 2015). In contrast, our



obtained transition pressure shows obvious nonlinear temperature dependence, which is caused by the nonlinear relationship between determined  $dP/dT$  and temperature. At room temperature, the transition pressure is estimated as 10.85 (1) GPa, with the  $dP/dT$  as 0.0005 (2) GPa/K. Then, the  $dP/dT$  increases with the temperature and reaches 0.0036 (3) GPa/K at 2000 K, where the transition pressure is estimated as 14.47 (18) GPa. The obtained transition pressure can be approximated modeled by a polynomial function of  $p = 10.78 (1) + 6.73 (2) \times 10^{-4} (T-273) + 8.49 (1) \times 10^{-7} (T-273)^2$ , where  $P$  in GPa and  $T$  in K. Detailed data of the calculated transition pressure,  $dP/dT$ , and their uncertainties is provided in **Supplementary Table S7**.

Furthermore, to investigate the effect of Fe content on the phase transition boundary of olivine-wadsleyite, we collect the variations of  $X_{\text{Fe}}$  during the transition from previous work (Katsura and Ito, 1989; Chen et al., 2002; Katsura et al., 2004), and the data is summarized in **Figure 7**. We find that the transition pressures with the  $X_{\text{Fe}}^{\alpha} < 0.1$  from previous work are generally higher than our estimation. Also, except for the two data points (1873 K and 14.4 GPa; 1873 K and 14.0 GPa) by Katsura and Ito (1989), the transition pressure decreases with the increasing  $X_{\text{Fe}}^{\alpha}$  at the same temperature condition.

## Implication for the Temperature at the 410 km Discontinuity

Temperature is one of the essential parameters for modeling the dynamics of the Earth's interior. Nearly 4 decades ago, the mantle temperature profiles were presented with the constructions of Earth models (Stacey, 1977; Brown and Shankland, 1981), in which the temperature at the 410 km discontinuity was estimated in a wide range of ~1700–2000 K. Then, by comparing the depth of the 410 km discontinuity with the pressures of the olivine-wadsleyite transition, Katsura et al. (2004) proposed the temperature as  $1760 \pm 45$  K for a pyrolite model assuming a bulk composition of  $X_{\text{Fe}} = 0.11$ . And later, the value was re-evaluated as  $1830 \pm 48$  K (Katsura et al., 2010).

In this study, we regard the globally averaged depth of the 410 km discontinuity as  $411 \pm 2$  km following the results of seismic investigations (Gu et al., 1998; Chambers et al., 2005), and the pressure can be estimated as  $13.76 \pm 0.05$  GPa according to the depth-pressure conversion (Stacey and Davis, 2008). Therefore, the temperature at the 410 km discontinuity is obtained as  $1795 \pm 70$  K on the basis of our phase relations.

It is worth noting that our temperature at the 410 km discontinuity is determined under anhydrous conditions. It has been confirmed that there is water existing in both olivine and wadsleyite in their crystal structure, which would not only reduce their bulk sound velocity (Jacobsen et al., 2008; Mao et al., 2008), but also enlarge their thermal expansion (Ye et al., 2009) and the heat capacity of wadsleyite (Jahn et al., 2013). Evidence has shown that the presence of water would reduce the pressure interval of olivine-wadsleyite phase transformation by

0.3–0.6 GPa (Chen et al., 2002), which leads to an increase of ~90–176 K in temperature.

Additionally, in this study, we regard  $K_{\text{Fe-Mg}}^{\alpha-\beta}$  as a constant and only present the olivine-wadsleyite phase transition boundary of a simple model in  $(\text{Mg,Fe})_2\text{SiO}_4$  system. Previous studies concluded that the values of  $K_{\text{Mg-Fe}}^{\alpha-\beta}$  are in the ranges of 0.38–0.57, 0.52–0.69, and 0.60–0.62 at 1473, 1873, and 1900 K, respectively, which indicates that  $K_{\text{Fe-Mg}}^{\alpha-\beta}$  may decrease with the increasing temperature during the phase transition (Katsura and Ito, 1989; Katsura et al., 2004). Therefore, more complicated systems need to be taken into account in future studies.

## CONCLUSION

In the present study, the self-consistent molar volume, elastic moduli, thermal expansion, heat capacity, and entropy of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  have been determined up to 2000 K and 20 GPa based on existing experimental data and thermodynamic relations. The calculated parameters were generally consistent with available results. The thermodynamic properties, including entropy of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  were also reanalyzed on account of our recent work. The thermal expansions, heat capacities, and entropies of both  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  show negative and nonlinear relationships with the pressure. Also, the pressure effects on the thermodynamic properties of  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  are larger than that of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$ .

Using the Clausius-Clapeyron equation, the olivine-wadsleyite phase transition boundary with the  $K_{\text{Fe-Mg}}^{\alpha-\beta}$  as 0.74 was estimated with the combination of the obtained molar volumes and entropies of  $\beta$ - $(\text{Mg}_{0.87}\text{Fe}_{0.13})_2\text{SiO}_4$  and  $\alpha$ - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ . The transition pressure can be approximately expressed by a polynomial equation of  $P$  (GPa) =  $10.78 (1) + 6.73 (2) \times 10^{-4} (T(K)-273) + 8.49 (1) \times 10^{-7} (T(K)-273)^2$ , which is generally lower than the previous studies on  $\text{Mg}_2\text{SiO}_4$  system at the same temperature condition. For instance, the temperature at the 410 km discontinuity is obtained as  $1795 \pm 70$  K based on our obtained olivine-wadsleyite phase transition boundary under anhydrous conditions, and it would increase by ~90–176 K if the water effect was considered. The results indicate that both Fe and water contents would influence the transition pressure of olivine-wadsleyite phase transition, which probably leads to a higher temperature at the 410 km discontinuity.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

## AUTHOR CONTRIBUTIONS

Conceptualization, CS, YL, and WS; methodology, CS, YL, and DF; software, GY; resources, JJ. and ZS; data curation, WS;

writing-original draft preparation, CS; writing-review and editing, YL, WS, and DF; supervision, YL and WS; project administration, YL; funding acquisition, YL. All authors have read and agreed to the published version of the manuscript.

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## SUPPLEMENTARY MATERIAL

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