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Exploring the High-Pressure Equation of State in Earth's Mantle with a Focus on the $MgSiO_3$–MgO System

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The thermodynamic characteristics of the $MgSiO_3$–MgO system are determined using a modified form of the Shanker equation of state (EOS) known as the 'Higher Order Shanker (HOS) EOS'. This adaptation incorporates higher-order terms into the Shanker EOS. The Higher Order Shanker (HOS) EOS is evaluated against Stacey criteria to ensure consistency in the variation of the pressure dependence of the isothermal bulk modulus. In a comparative analysis, the thermodynamic properties obtained from the Higher Order Shanker (HOS) EOS are contrasted with those derived from established classical EOS models, alongside electronic contribution analysis. This demonstrates the reliability of the proposed Higher Order Shanker (HOS) EOS for computing thermodynamic properties for similar systems under higher pressures. Furthermore, expressions for the bulk modulus and its pressure derivatives are formulated and extended to the theoretical limit of infinite pressure. These

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derived expressions are valuable for conducting more intricate analysis of higher-order thermoelastic properties.

Key words: equation of state, Stacey criteria, thermal expansion, Grüneisen parameter.

Термодинамічні характеристики системи $MgSiO_3$–MgO визначено з використанням модифікованої форми Шенкерового рівняння стану, відомого як «Шенкерове рівняння з урахуванням вищих порядків». Ця адаптація включає члени вищого порядку Шенкерового рівняння стану. Шенкерове рівняння з врахуванням вищих порядків оцінено за критеріями Стейсі, щоб забезпечити узгодженість у зміні залежности ізотермічного об'ємного модуля від тиску. У порівняльній аналізі термодинамічні властивості, одержані з Шенкерового рівняння з урахуванням вищих порядків, порівняно з термодинамічними властивостями, одержаними з відомих класичних моделів Шенкерового рівняння стану, а також з аналізою електронних внесків. Це демонструє надійність запропонованого методу Шенкерового рівняння з врахуванням вищих порядків для розрахунку термодинамічних властивостей подібних систем за високих тисків. Крім того, сформульовано вирази для об'ємного модуля та його похідних за тиском, які поширено на теоретичну границю нескінченного тиску. Ці одержані вирази є цінними для проведення більш складної аналізи термопружніх властивостей вищих порядків.

Ключові слова: рівняння стану, критерії Стейсі, теплове розширення, Ґрюнайзенів параметер.

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1. INTRODUCTION

The exact thermodynamic behaviour of the $MgSiO_3$–MgO system as one of the component of the Earth's lithosphere is the field of interest for modern mineralogical researches. Since 2004 [1, 2], when $MgSiO_3$–MgO was known to be the ultimate phase of the lower mantle of the Earth, different studies are carried out on its thermodynamic properties and its phase boundary conditions, so as to know more about the D-layer of Earth in seismological scenario and are nowadays used as input for geodynamics studies heling us to develop the theory regarding plate tectonics which explain the formation of Earth's lithosphere. Equations of state (EOS) is the powerful tool for the exact determination of thermodynamic variables in terms of pressure, volume and temperature and it is also found helpful for studying the compressibility and pressure induced phase transitions for geophysical minerals at high pressures and temperatures [4–6].

The properties of geophysical minerals at extreme pressures and temperatures recently estimated from EOS's are obtained by simplifying basic thermodynamic expressions like bulk modulus and thermal expansion taking into account of electronic contribution due to Helmholtz free energy and the properties thus computed by varying temperature and pressure conditions are found to have low precision due to its limitation as reported earlier for B–M EOS for solids for higher compressions. This drawback was overcome by proposing EOS universally [10] for solids having distinct kind of chemical bonding at extremely high compressions. The dependences of potential energy $E = E(r)$ (r being the interatomic distance) were in agreement with Rydberg's model of EOS [11, 12].

An EOS based on volume dependent short-range forces in case of interatomic potentials was developed by Shanker *et al.* [13, 14]. However, the results reported earlier [7, 13] were not consistent with the results of Hama Suito EOS [15] derived from the first principle and based on quantum statistical model (QSM-Model) and linearized augmented plane wave method (APW-Method). In view of recent findings about EOS based on potential energy function, focused studies are being made to frame new EOS and require critical assessment to overcome the present challenges of the Earth interior.

For achieving better consistency with the results of Hama Suito, in the present endeavour, the previous developed Shanker EOS [13] has been modified by considering the effect of the higher-order terms of V/V_0, which were excluded in Shanker EOS. The consistency of modified EOS has been mapped with Hama Suito to follow the essential Stacey criteria for pressure dependent bulk modulus dK_T/dP at constant temperature as a function of P/K_T; K_T being the isothermal bulk modulus at pressure P. For rigorous consistency, the derived EOS has been subjected to polymorphic lower mantle material $MgSiO_3$–MgO. This system is of great importance as it provides understanding of evolution of the Earth and helps in comprehending the seismic profile of the Earth. In addition to this, the correctness of modified EOS is verified by comparing the results with (*a*) B–M EOS, (*b*) Vinet–Rydberg EOS, (*c*) Shanker EOS, and (*d*) Stacey EOS.

The thermodynamic properties obtained using modified Shanker EOS known as 'Higher Order Shanker (HOS) EOS' will be useful for various applications of Geosciences and specially to the Earth's behaviour at extreme conditions. For consistency of modify EOS, we have to calculate the values of first-, second-, and third-order Grüneisen parameter using to Stacey EOS and Modified EOS (HOS EOS) values under high compressions.

2. MODIFICATIONS OF SHANKER EOS

Shanker EOS representing the relationship between P and V/V_0 can also be obtained using the volume dependence. The volume dependent force constant is approximated [15] as

$$A = A_0 f\ , \tag{1}$$

where A_0 does not depend on volume and f is volume or compression V/V_0 dependent. Now, using Shanker's approach [16] the expression of P is given by

$$P\left(\frac{V}{V_0}\right)^{4/3} = -\frac{K_0}{f_0 V_0}\int_{V_0}^{V} f dV\ . \tag{2}$$

Equation (2) is the basic equation, which assists in deriving the EOS. Shanker EOS has been obtained [17] using following form for f:

$$f = (1 + y + y^2)\exp(ty)\ , \tag{3}$$

where $y = 1 - \frac{V}{V_0}$ and t is the constant. For $V = V_0$, $f = f_0 = 1$.

Equation (3) is substituted in (2) as

$$P\left(\frac{V}{V_0}\right)^{4/3} = -\frac{K_0}{f_0 V_0}\int_{V_0}^{V} f dV\ . \tag{4}$$

For getting more closer results with Hama Suito results at high compressions, we replaced the value of f inducing the higher-order terms as given by

$$f = (1 + y + y^2 + y^3)\ . \tag{5}$$

Using (4) and (5) resulted in the modified Shanker EOS named as Higher Order Shanker (HOS) EOS.

EOS.

$$P = K_0\left(V/V_0\right)^{-4/3} \times \times\left[\left(1 - \frac{1}{t} + \frac{2}{t^2} - \frac{6}{t^3}\right)\left\{\exp\left(ty\right) - 1\right\} + y\left(1 + y - \frac{2}{t} + y^2 - \frac{3y}{t} + \frac{6}{t^2}\right)\exp\left(ty\right)\right], \tag{6}$$

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-\frac{1}{3}}\left(1 + y + y^2 + y^3\right)\exp\left(ty\right) + \frac{4}{3}P\ , \tag{7}$$

$$K_T' = \frac{4}{3} + \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left[\frac{1}{3} + \frac{V}{V_0}\left\{t + \frac{\left(1 + 2y + 3y^2\right)}{\left(1 + y + y^2 + y^3\right)}\right\}\right], \tag{8}$$

where $t = K_0' - \frac{8}{3}$ and $y = 1 - \frac{V}{V_0}$.

The above-mentioned mathematical relations expressed for P, K_T and K_T' are employed to investigate pressure dependent properties in the present study and the results obtained are explained in the subsequent section.

3. RESULTS AND DISCUSSION

We have obtained pressure P (cold pressure or pressure at reference isotherm) and isothermal bulk modulus K_T for $MgSiO_3$–MgO system (Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite, and Post-perovskite) taking the input data of K_0, K_0' and K_T'' of earlier work [22]. The expressions obtained from various EOSs are written below.

B–M EOS.

$$P = \frac{3}{2}K_0\left(x^{-7} - x^{-5}\right)\left[1 + \frac{3}{4}A_1\left(x^{-2} - 1\right)\right], \quad (9)$$

$$K_T = \frac{1}{2}K_0\left(7x^{-7} - 5x^{-5}\right) + \frac{3}{8}A_1\left(9x^{-9} - 14x^{-7} + 5x^{-5}\right), \quad (10)$$

$$K_T' = \frac{K_0}{8K_T}\left[\left(K_0' - 4\right)\left(81x^{-9} - 98x^{-7} + 25x^{-5}\right) + \frac{4}{3}\left(49x^{-7} - 25x^{-5}\right)\right], \quad (11)$$

where $x = \left(\frac{V}{V_0}\right)^{1/3}$ and $A_1 = K_0' - 4$.

VINET (Rydberg) EOS.

$$P = 3K_0x^2(1 - x)\exp\left[\frac{3}{2}(K_0' - 1)(1 - x)\right], \quad (12)$$

$$K_T = K_0x^2\left[1 + \left\{\frac{3}{2}(K_0' - 1)x + 1\right\}(1 - x)\right]\exp\left[\frac{3}{2}(K_0' - 1)(1 - x)\right], \quad (13)$$

$$K_T' = \frac{1}{3}\left[\frac{x\left(1 - \eta\right) + 2\eta x^2}{1 + \left(\eta x + 1\right)\left(1 - x\right)} + \eta x + 2\right], \quad (14)$$

where $x = \left(\frac{V}{V_0}\right)^{1/3}$ and $\eta = \frac{3}{2}\left(K_0' - 1\right)$.

SHANKER EOS.

$$P = K_0\left(\frac{V}{V_0}\right)^{-4/3}\left[\left(1 - \frac{1}{t} + \frac{2}{t^2}\right)\left\{\exp\left(ty\right) - 1\right\} + y\left(1 + y - \frac{2}{t}\right)\exp\left(ty\right)\right], \quad (15)$$

$$K_T = K_0 (\frac{V}{V_0})^{-\frac{1}{3}} \left(1 + y + y^2\right) \exp\left(ty\right) + \frac{4}{3} P\,, \tag{16}$$

$$K'_T = \frac{4}{3} + \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left[\frac{1}{3} + \frac{V}{V_0}\left\{t + \frac{(1+2y)}{\left(1 + y + y^2\right)}\right\}\right], \tag{17}$$

where $t = K'_0 - \dfrac{8}{3}$ and $y = 1 - \dfrac{V}{V_0}$.

Stacey [18, 19] has established an innovative method representing $K' = \dfrac{dK'}{dP}$ with the dependence with $\dfrac{P}{K}$. Stacey deduced reciprocal of K' as mentioned below:

$$\ln\left(\frac{V}{V_0}\right) = \frac{K'_0}{K'^2_\infty} \ln\left(1 - K'_\infty \frac{P}{K}\right) + \left(\frac{K'_0}{K'_\infty} - 1\right)\frac{P}{K}\,, \tag{18}$$

$$\frac{K}{K_0} = \left(1 - K'_\infty \frac{P}{K}\right)^{-\frac{K'_0}{K'_\infty}}, \tag{19}$$

$$\frac{1}{K'} = \frac{1}{K'_0}\left(1 - \frac{K'_\infty}{K'_0}\right)\frac{P}{K}\,. \tag{20}$$

Several attempts have been to formulate the equations of state. However, they fail to satisfy the Stacey's criterion [8, 19] Shanker EOS and Higher Order Shanker (HOS) EOS, B–M EOS and Vinet EOS are nearly linear supporting the validity of Stacey equations (linear or exponential form).

In addition, the polymorphic $MgSiO_3$–MgO system (Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite, and Postperovskite) and their compressibility and phase transitions were studied by using the different EOSs. Phase equilibria in the $MgSiO_3$–MgO system play a major contribution in the interpretation of the seismic profile of Earth's mantle. Recently, it was observed that olivine (OI) structure converted into Wadsleyite (Wds) structure at the distance of 410 km existing at 14–15 GPa and at the depth of 520 km at 17–18 GPa is categorised by Wadsleyite–Ringwoodite (Rwd) transition [21]. The low boundary present in the upper mantle (550–670 km) around 23–24 GPa is often designated to Ringwoodite (Rwd) to Mg, Perovskite, and Ferropericlase (or Magnesiowistite) transition. This 'layer *D*' can be perceived above the core–mantle boundary using seismic data studies. Such type of studying is done by experimentally and an initial calculation. In the present work, measurements of *P*–*V*–*T* properties were us-

TABLE 1. Values of input data for $MgSiO_3$–MgO System.

Phase	K_0	K'_0	γ_0	$\alpha_0 \times 10^{-6} (K^{-1})$
Forsterite	127.4	4.30	1.066	22.599
Wadsleyite	169.0	4.14	1.185	20.295
Ringwoodite	187.4	3.98	1.210	18.909
Perovskite	252.0	4.38	1.700	22.594
Akimotoite	215.3	4.91	2.000	27.584
Postperovskite	253.7	4.03	1.670	22.274

ing Equations of State and the validity of the proposed equations of state is tested for $MgSiO_3$–MgO system. Subsequently, after assessment of EOSs, we have also studied the equilibria of the transitions OI to Wds, and Rwd to Bdg + Per.

The input data on K, K'_0, γ and γ_0 as used [21, 22] for assessment of EOSs are tabulated in Table 1 with $K'_\infty = 2.41$ (for lower mantle). We have observed the variation of pressure (P), isothermal bulk modulus (K_T) and their derivative with compression (K'_T) and shown in Fig. 1–6, (a–c). The results for obtained equations of state are strongly matched with measured data and are found to be consistent.

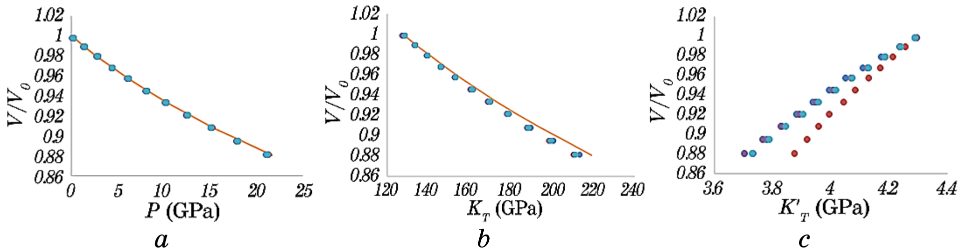

Fig. 1. Variation of pressures (a), K_T (b), K'_T (c) with compression for Forsterite.

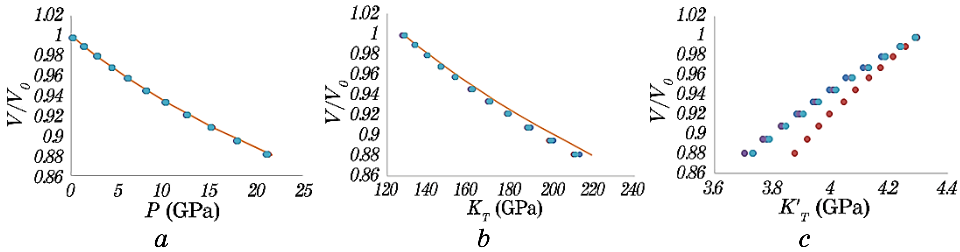

Fig. 2. Variation of pressures (a), K_T (b), K'_T (c) with compression for Wadsleyite.

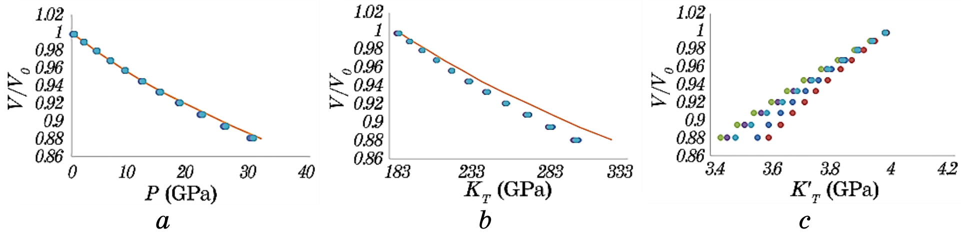

Fig. 3. Variation of pressures (*a*), K_T (*b*), K'_T (*c*) with compression for Ringwoodite.

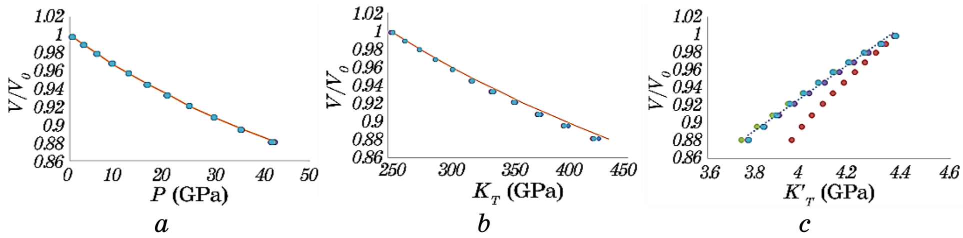

Fig. 4. Variation of pressures (*a*), K_T (*b*), K'_T (*c*) with compression for Perovskite.

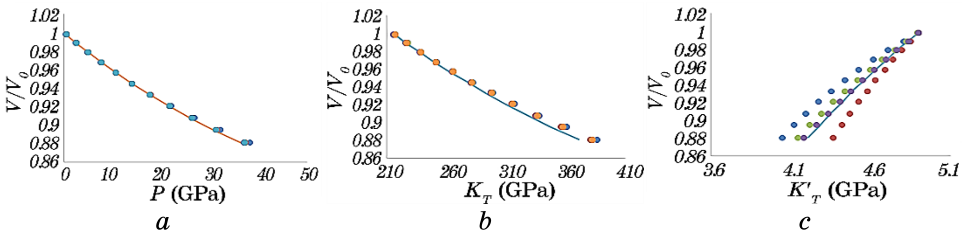

Fig. 5. Variation of pressures (*a*), K_T (*b*), K'_T (*c*) with compression for Akimotoite.

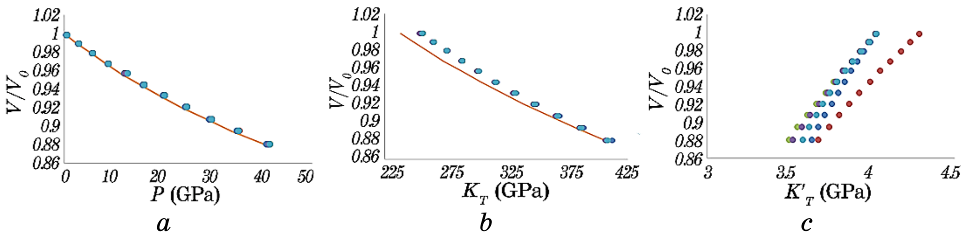

Fig. 6. Variation of pressures (*a*), K_T (*b*), K'_T (*c*) with compression for Postperovskite.

Stacey EOS
BM EOS
Shanker EOS
Vinet (Rydberg) EOS
HOS EOS
— $R_{ef.}$ [21, 22]

In addition, the results of pressure K_T and K'_T are also in good agreement with previously reported data computed using thermodynamic model (electronic configuration) approach equations [21, 22] and are labelled as R_{ef} in Fig. 1–6, (*a–c*).

The B–M EOS is based on Euler's strain theory and the Vinet (Rydberg) EOS is based on the Rydberg potential function. Shanker EOS is derived from the near force constant related to the potential energy derivative [10, 11].

Values of K_0 and K'_0 used in the present calculations are given in Table 1. The results for P, K_T and K'_T as functions of V/V_0 down to 0.1 are given in Fig. 1–6, (*a–c*). Stacey argued that results based on B–M EOS, Vinet (Rydberg) EOS, and Shanker EOS agree well with results for Forsterite, Perovskite, Akimotoite, and Postperovskite studied up to high compressions. For Wadsleyite and Ringwoodite, the results obtained from Shanker EOS are relatively close to those based on the electron contribution equation [21, 22], but fail up to very high compressions. However, the results obtained from Higher Order Shanker EOS (HOS), which uses higher-order terms in this study, are more consistent up to higher-order compression, supporting their claim [21, 22] and further analysis help.

$MgSiO_3$–MgO System

It is evident from Figs. 1–6, (*a–c*) that the values of P and K_T calculated from Eqs. (6) and (7) present close agreement with the values obtained from the HOS EOS, which is consistent with the Stacey EOS and Electronic contribution equation [21, 22] results for the entire range of compressions.

On the other hand, the results obtained from the B–M third-order EOS, the B–M EOS, and the Vinet EOS deviate substantially from the Electronic contribution equation [21, 22] at higher compressions; V/V_0 is somewhat less than 0.80.

An advantage of the present EOS is that it can be written in the inverted form also, *i.e.*, V/V_0 as a function of pressure. We have studied the range of applicability of the present EOS for various solids with different values of K'_0. It has been found that the present EOS is valid up to very high compressions for a material with $K'_0 < 4$ (Ringwoodite—Fig. 3, *a–c*). For materials with $4 < K'_0 < 4.38$, (such as Forsterite, Wadsleyite, and Postperovskite) the EOS holds good down to a compression of $V/V_0 = 0.85$. In the case of solids with $K'_0 \geq 4.38$, such as Perovskite and Akimotoite, the present EOS holds good only for small compressions down to about $V/V_0 = 0.85$.

For the Earth's lower mantle, we have $K'_0 < 4$ [1], and therefore the present EOS is suitable for studying the variation of densities with pressure for the entire depth of the lower mantle.

Variation of First-, Second-, and Third-Order Grüneisen Parameter with Pressure

The ratio of γ is a vital quantity in condensed matter physics as well as Shockwaves and the field of geophysics. The anharmonicity of solids is directly linked to the Grüneisen parameter. The greater the value of γ, the greater is its anharmonic nature.

Important parameters like pressure as well as temperature of the metal and core [8, 25]. One way to get the perfect EOS for a solid from their response to shock-wave loading is to use a specific form of this dependence in conjunction with Hugoniot shock. That is why it is important to achieve an independent form of Hugoniot shock or isotherm. The Grüneisen ratio, used in shock physics, has not been done so far. Therefore, the purpose of the present work we have to find the anharmonic behaviour of Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite, and Postperovskite using the values (P, K_T and K'_T) obtained by HOS.

The Stacey K-primed equation given below:

$$\frac{1}{K'} = \frac{1}{K'_0} + \left(1 - \frac{K'_\infty}{K'_0}\right)\frac{P}{K}. \tag{21}$$

The expressions for higher-order pressure derivatives obtained from (2) due to Stacey [20] are written as follows:

$$KK'' = -\left(\frac{K''^2}{K'_0}\right)\left(K' - K'_\infty\right). \tag{22}$$

The expressions of γ based on Shanker *et al.* [27] are given below:

$$\frac{1}{\gamma} = A + B\frac{P}{k}, \tag{23}$$

where A and B are material dependent constants:

$$A = 1/\gamma_0, \tag{24}$$

$$B = K'_\infty\left(\frac{1}{\gamma_\infty} - \frac{1}{\gamma_0}\right). \tag{25}$$

The subscripts 0 and ∞ present values at zero pressure and infinite pressure, respectively. We have used the following identity at infinite pressure [28].

The most important reason for considering (16) at finite pressures is that it leads to the boundary conditions for higher-order Grüneisen parameters at infinite pressure which are identical to those derived in the preceding section using the principle of calculus. Equation (16), when differentiated with respect to pressure, gives

$$\frac{q}{\gamma} = B\left(1 - K'\frac{P}{K}\right), \tag{26}$$

where q is the second-order Grüneisen parameter (3). Now, differentiating (20) with respect to P, we find

$$\frac{q\lambda}{\gamma} - \frac{q^2}{\gamma} = B\left[\left(KK''\right)\frac{P}{K} + K'\left(1 - \frac{K'P}{K}\right)\right], \tag{27}$$

where λ is the third-order Grüneisen parameter (8). (20) and (21) then yield

$$\lambda = \left(\frac{KK''}{1 - K'\frac{P}{K}}\right)\frac{P}{K} + K' + q\,. \tag{28}$$

The input data used in calculations are taken in Table 1, 2. The input data used in calculations are taken from and P, K_T and K_T' values from HOS EOS ((6)–(8)). Values of KK'' are determined from (22) of Stacey and Davis [25]. Values of γ, q and λ at different values of pressure are calculated from Eqs. (23), (26) and (28) respectively. The results have been given here in Fig. 7–12. Values of γ, q and λ for the Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite and Postperovskite are compared with the corresponding values reported by Stacey EOS and recent developed HOS EOS. Stacey [20] found that K_∞' is nearly equal to $\frac{3}{5}K_0'$. Calculated values of K_∞' reported in Table 2 also vali-

TABLE 2. Values of input data for $MgSiO_3$–MgO System from equations.

Phase	K_0'	A	B	$K_\infty' = \frac{3}{5}K_0'$ [20 and 25]	$\gamma_\infty = \frac{1}{2}K_\infty' - \frac{1}{6}$ [25]
Forsterite	4.30	0.938	–0.123	2.58	1.123
Wadsleyite	4.14	0.843	0.213	2.48	1.075
Ringwoodite	3.98	0.826	0.280	2.38	1.027
Perovskite	4.38	0.588	0.745	2.62	1.147
Akimotoite	4.91	0.501	0.781	2.94	1.307
Postperovskite	4.03	0.598	0.872	2.41	1.042

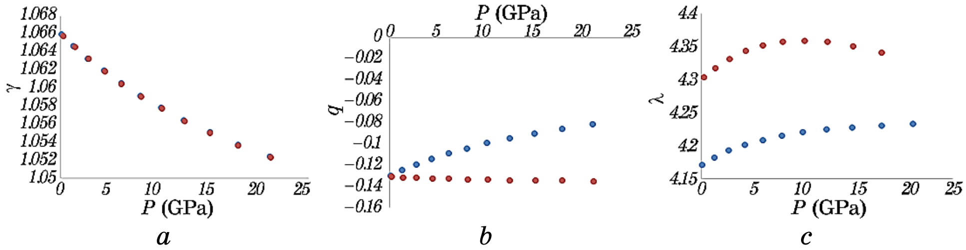

Fig. 7. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Forsterite.

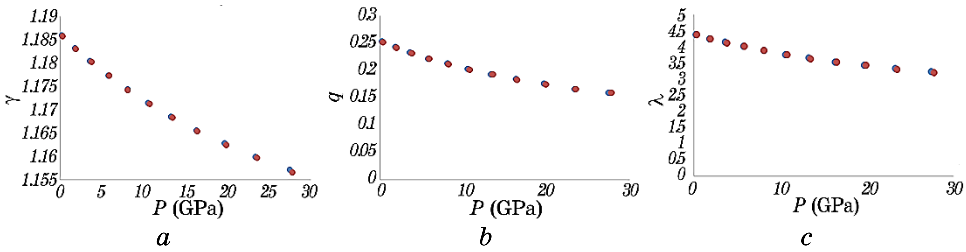

Fig. 8. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Wadsleyite.

date the Stacey thermodynamic constraint [20, 25]: $K'_\infty > 1 + \gamma_\infty$.

Finally, we discuss that the higher-order thermoelastic properties obtained in the present study are useful to estimate the cross derivatives of bulk modulus with respect to pressure and temperature.

The results based on the Higher Order Shanker (HOS) EOS and the Stacey EOS are compared in Fig. 7, *a*–12, *c*. The difference in the two sets of values is substantial at low pressures. The results for the cross derivatives of bulk modulus with respect to P and T are very sensitive to the values of second- and third-order Grüneisen parameter q and appearing in Eq. (19). We have to calculate the higher-order Grüneisen parameters, taking the values P, K_T and K'_T from two sets: (i) HOS EOS, (ii) Stacey EOS. These are in good agreement with values obtained in the present study. The results obtained in the present study and those reported by Stacey EOS both reveal that values of γ, q and λ for the Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite and Post-perovskite shown in Fig. 7, *a*–12, *c*. As pointed out that, the model is not satisfactory for Forsterite because of KK'' values become negative. At finite pressures our values of λ are between 2 and 4 for the lower mantle, and between 2 and 3 for the core. These values of λ are not much different from the Stacey–Davis values which are between 3 and 4 at finite pressures.

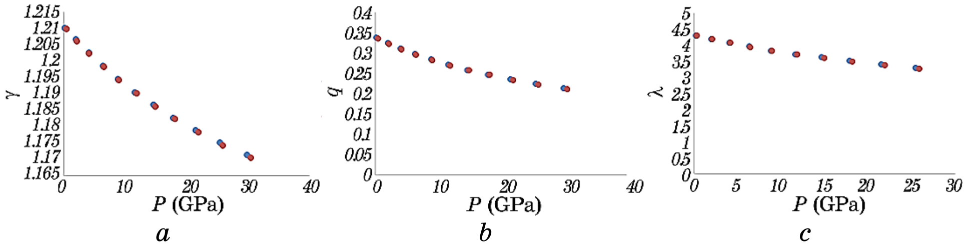

Fig.9. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Ringwoodite.

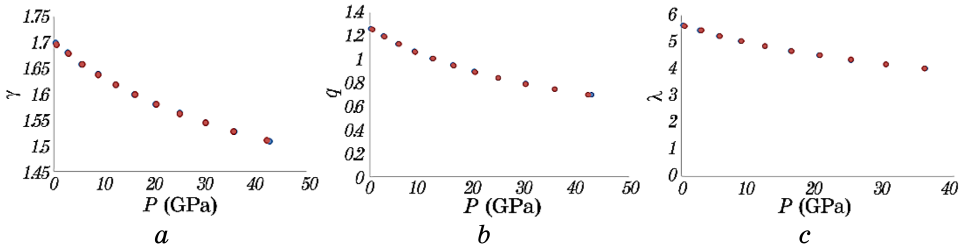

Fig. 10. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Perovskite.

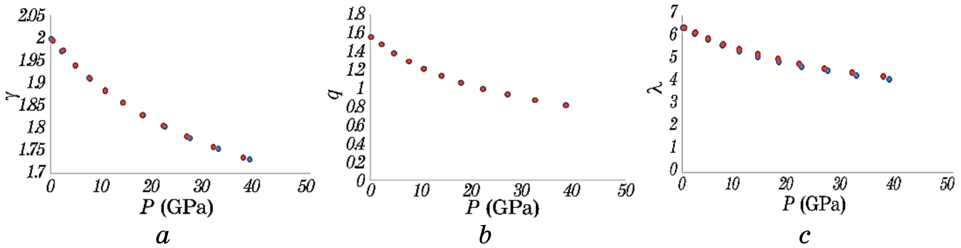

Fig. 11. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Akimotoite.

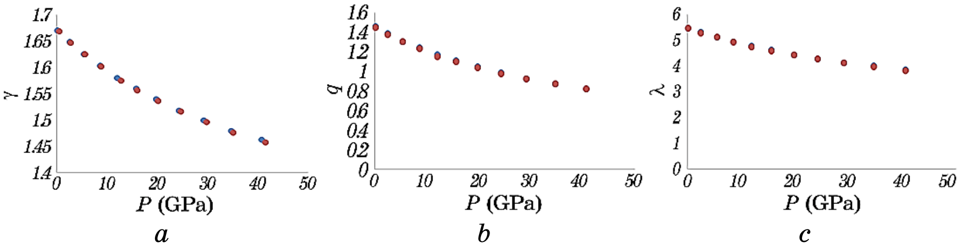

Fig. 12. First- (*a*), second- (*b*), third- (*c*) order Grüneisen parameter for Postperovskite.

● P, K, and K' values of Stacey EOS

● P, K, and K' values of HOS EOS

Most of the calculations for the Earth interior were performed by Stacey and Davis (2004) using the reciprocal K-primed equation. λ_0 and λ_∞ were the exceptions. Subsequently, the method was developed (Shanker and Singh, 2005; Shanker *et al.*, 2009) for determining λ_0 and λ_∞ using the Stacey reciprocal K-primed equation. It should be mentioned that the expressions for KK'' and K^2K''' obtained from the Stacey reciprocal K-primed equation when using Shanker equation at infinite pressure (Shanker *et al.*, 2009) yield.

$$\lambda_\infty = \frac{K'^2}{K_0'}. \tag{29}$$

Equation (29) gives $\lambda_\infty = 1.54$, 1.48, 1.42, 1.56, 1.79 and 1.44 for Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite and Postperovskite respectively (1.38 for the lower mantle, and 1.81 for the core). We note from (29) that $\lambda_\infty < K'_\infty$ since $K_\infty < K'_0$.

The results for the Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite and Postperovskite given in figs are similar to those reported by Stacey EOS values. γ, q and λ all decrease with the increase in pressure. At infinite pressure, q_∞ and λ_∞ remain positive finite. It should be mentioned that (16) is more suitable for geophysical applications since P and K both are available directly from the seismological data.

An equation of state is physically acceptable only when it satisfies the thermodynamic constraints [5] *viz.* K'_∞ must be greater than 5/3, λ_∞ must be positive finite, and λ_∞ must be less than K'_∞. In case of the Birch–Murnaghan equation, we have $K'_\infty = 3$, and $\lambda_\infty = 2/3$ [8]. This equation thus satisfies the thermodynamic constraints, but yields the pressure-volume data [16], which deviate much from the seismological data [5]. For the Vinet–Rydberg equation [14], we have $K'_\infty = 2/3$, and $\lambda_\infty = 1/3$. Although this equation satisfies the constraint that $\lambda_\infty < K'_\infty$, but it fails to satisfy the fundamental constraint [5] $K'_\infty > 5/3$.

This equation thus violates the constraints *viz.* $K'_\infty > 5/3$ and $\lambda_\infty > 0$. To conclude, a physically acceptable equation of state must satisfy all the thermodynamic constraints as specified above, and it should be capable of predicting not only the pressure–volume relationship but also the higher derivative thermoelastic properties of materials in agreement with experimental data. The Stacey reciprocal K-primed equation is found to fulfil these requirements and HOS equations results close to Stacey EOS results.

In the limit of extreme compression $V \to 0$, P tends to infinity, K also tends to infinity, but their ratio P/K remains finite. K decreases with the increase in pressure and attains a minimum constant value K'_∞. This is because K becomes linear in P (directly proportional to P) in the limit of infinite pressure [2, 3]. Under this condition, the following identity has been found to hold [19, 20].

$$\left(\frac{P}{K}\right)_{\infty} = \frac{1}{K''_{\infty}}, \tag{30}$$

where the infinite subscript denotes the respective parameter at infinite pressure. (1) displays that the expression $\left[1 - K'P / K\right]$ reaches zero at extreme pressure and likewise exhibit the variation of α. The subsequent expression for $\alpha(P)$ can be written as [23, 24].

$$\alpha = \alpha_0 \left[1 - K'(P / K)\right]^t, \tag{31}$$

where α_0 is the thermal expansion at $P = 0$ and t is the constant dependent on material properties. The validity of (16) has been demonstrated for the Earth lower mantle [25] with $t = 1.13$. The Higher Order Shanker equation was used for obtaining thermal expansion and the corresponding input parameters [21] are also tabulated in Table 2. Values of $\alpha(P)$ with compressions are shown in Fig. 13. The values of thermal expansion obtained using modified EOS display strong correlation with the measured data [21, 22].

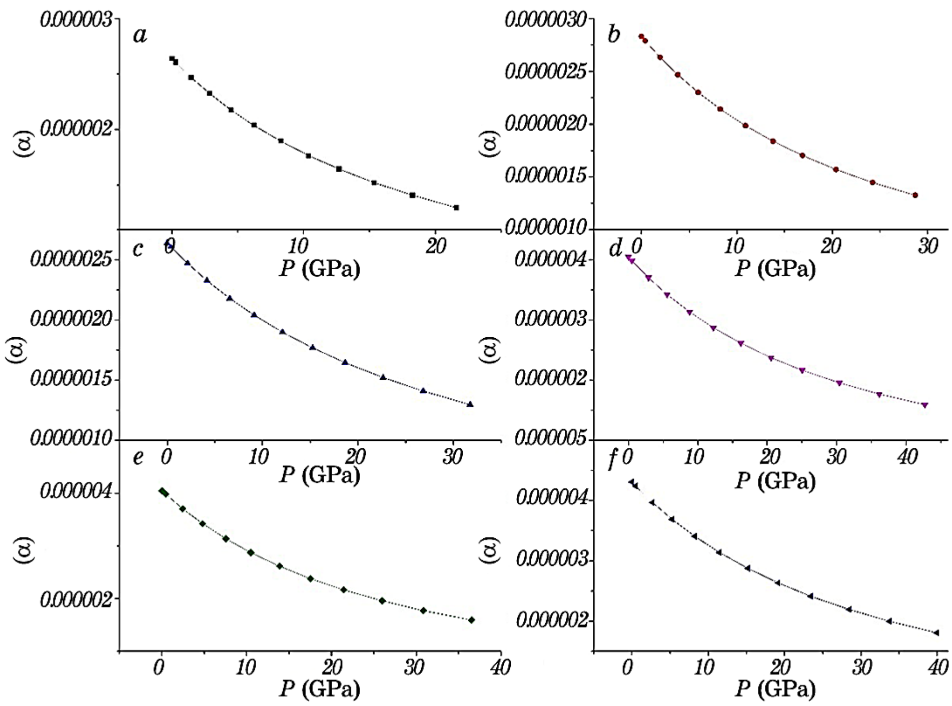

Fig. 13. Variation of thermal expansion (α) for Forsterite (*a*), Wadsleyite (*b*), Ringwoodite (*c*), Perovskite (*d*), Akimotoite (*e*) and Postperovskite (*f*) as a function of pressure MgO–$MgSiO_3$ system.

4. CONCLUSIONS

Shanker Equation of State (EOS) has been modified by including higher-order terms. The modified equation has been studied for fundamental MgO system, and, for validation, it is compared with phenomenological EOSs. The modified EOS for solids follows Stacey formulation under high compressions and is more reliable. The results obtained from modified EOS for $MgSiO_3$–MgO System are found to be in agreement with the experimental data. These results indicates that the correctness of the modified EOS and confirm that it can be used for determining thermoelastic properties of $MgSiO_3$ system at high pressure and high temperatures.

The equation's main feature is fewer input parameters are required, which are easily available by experimental studies. These equations may be frequently employed as the thermal equation of states of Earth's minerals. It uses various advanced quantum methods and simulations at the pressure and temperature of the Earth's interior. This study follows the basic laws of thermodynamic in regard to expressions at high-pressure. It also allows extrapolation to regions for which experimental data are not available.

As fewer studies have been done, so proposed study attempts to investigate the elastic properties of $MgSiO_3$ system under high pressure. The results for the Forsterite, Wadsleyite, Ringwoodite, Perovskite, Akimotoite and Postperovskite, given in Figs. are similar to those reported by Stacey and Davis [25]. As pointed out by Stacey and Davis (2004), the same formula for an equation of state works satisfactorily for different phases provided we use appropriate values of input parameters such as K'_0 and K'_∞ which are different for the lower mantle, outer core and the inner core of the Earth.

The present HOS EOS results are similar to Stacey EOS (6) proves particularly advantageous for geophysical applications, as both P (pressure) and K (isothermal bulk modulus) can be directly obtained from seismological data. The applicability of the Higher Order Shanker Equation of State (HOS EOS) extends beyond geophysics, demonstrating its relevance in the study of Bulk Metallic Glasses [29]. Moreover, the HOS EOS can be reliably extrapolated to high *r* pressures, enhancing its utility for interpreting recent experiments in high-pressure research.

The ability to apply the same methodology to both complex minerals and BMGs underscores its robustness and utility in diverse scientific investigations, making it a valuable tool for researchers exploring a range of materials and their behaviours.

Therefore, the new EOS can contribute to the planning of high-pressure experiments in the future on compression behaviour of Earth-forming minerals and solids.

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