



Theoretical prediction for the validity of isothermal EOS for geophysical minerals

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ABSTRACT

The validity of equation-of-state (EOS) of geophysical minerals is very important for various scientific fields including geophysics, material science and high-pressure physics. In the present work we have calculated pressure P , isothermal bulk modulus K_T , first pressure derivative of isothermal bulk modulus K_T' and second order pressure derivative of isothermal bulk modulus in terms of $K_T K_T''$ for MgO and Al₂O₃, using different equation of state. Using the values of these parameters we have computed the values of Gruneisen parameter (γ) corresponding to different values of V/V_0 and graphs are plotted for Gruneisen parameter (γ) vs. v/v_0 for MgO and Al₂O₃. From these plots it is clear that the Brennan-Stacey and Shanker EOS is compatible both low and high compression ranges for calculating Gruniesen parameter where as Vinet EOS is not compatible for calculating the Gruniesen parameter at low compression ranges.

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Introduction

Knowledge of the P - V - T equation-of-state EOS of relevant materials is very important for scientific investigations in the various fields including geophysics, material science and high-pressure physics [1, 2]. Experimentally, the EOS of a material can be determined by both static diamond anvil cell DAC [3] and dynamic shock wave experiments [4-5] at high pressures and temperatures. Alternatively, the pressure, especially under high pressure and high temperature conditions, can be obtained from the diffraction line shifts in a standard material which is mixed with the sample and whose P - V - T EOS is well known. Therefore, the knowledge of the P - V - T EOS of relevant standard materials is one of the most basic information required for pressure calibration.

The purpose of the present study is to assess the validity of some important Equation of states (EOS) for mantle minerals. A comparison of the result for P - V relationships, bulk modulus, its pressure derivative and Gruneisen parameter has been presented with those obtained from Brennan and Stacey EOS [6], Shanker EOS [9, 10] and Vinet EOS [11-13] at different compression ranges.

In present paper an attempt has been made for theoretical prediction of validity of three different phenomenological isothermal EOS viz. Shanker EOS, Vinet EOS and Brennan-Stacey EOS to determine the compression dependence pressure of two different mantle minerals viz. MgO and Al₂O₃.

Theory

The derivation of equation of state (EOS) of a thermodynamic system is based on a fundamental theorem which equates the negative of pressure to the isothermal volume derivative of a Helmholtz free energy function F . The function F consists of two terms in the case of solids, the first of which represents the potential energy of a non vibrating lattice while the second owes its origin to the pressure of the thermal vibrations.

An EOS can be derived from the volume derivative of lattice potential energy by using the relation;

$$P = - \left(\frac{dW}{dV} \right)_T \quad \text{where } W \text{ for an ionic crystal can be written as the sum of electrostatic energy and short range overlap}$$

repulsive energy.

Using the free volume formula [7] for the Gruneisen parameter γ and assuming that the Gruneisen parameter γ is proportional to volume, Brennan and Stacey obtained an EOS [6, 8] which is given as -

$$P = \frac{3K_0 \left(\frac{V}{V_0} \right)^{\frac{4}{3}}}{(3K_0' - 5)} \left[\left\{ \exp \left(\frac{3K_0' - 5}{3} \right) \left(1 - \frac{V}{V_0} \right) \right\} - 1 \right] \quad (1)$$

On the basis of Born lattice theory taking the volume derivative of short range force constant Shanker obtained a equation of state known as Shanker EOS [9,10] which are as;

$$P = \frac{3K_0 \left(\frac{V}{V_0}\right)^{-\frac{4}{3}}}{(3K_0' - 8)} \left[\left\{ \left(1 - \frac{1}{t} + \frac{2}{t^2}\right) (\exp ty - 1) \right\} + \left\{ y \left(1 + y - \frac{2}{t}\right) \exp ty \right\} \right] \quad (2)$$

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

Vinet proposed a new equation of state on account of relating binding energy with inter-atomic distances known as Vinet EOS [11-13] given as-

$$P = 3K_0 x^{-2} (1-x) \exp \{ \eta (1-x) \} \quad (3)$$

$$\text{Where, } x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}} \text{ and } \eta = \frac{3}{2} (K_0' - 1)$$

Expression for isothermal bulk modulus corresponding to equation (1), (2) and (3) can be obtained by using the relation, $K_T = -V \left(\frac{\partial P}{\partial V}\right)_T$ are given as under;

$$K_T = \frac{4}{3} P + K_0 \left(\frac{V}{V_0}\right)^{-\frac{1}{3}} \exp \left\{ \left(K_0' - \frac{5}{3}\right) \left(1 - \frac{V}{V_0}\right) \right\} \quad (4)$$

$$K_T = \frac{4}{3} P + K_0 \left(\frac{V}{V_0}\right)^{-\frac{4}{3}} \exp \left\{ \left(K_0' - \frac{8}{3}\right) \left(1 - \frac{V}{V_0}\right) \right\} \quad (5)$$

$$K_T = K_0 x^{-2} [1 + \{(1 + \eta x)(1 - x)\}] \exp \eta (1 - x) \quad (6)$$

The first order pressure derivative of isothermal bulk modulus K_T' can be obtained by using the relation $K_T' = \left(\frac{\partial K_T}{\partial P}\right)$,

corresponding to equation (4), (5) and (6) expression for K_T' are given as follows;

$$K_T' = \frac{16}{9} \frac{P}{K_T} + \left(1 - \frac{4}{3} \frac{P}{K_T}\right) \left[\left\{ \left(K_0' - \frac{5}{3}\right) \left(\frac{V}{V_0}\right) \right\} + \frac{5}{3} \right] \quad (7)$$

$$K_T' = \frac{16}{9} \frac{P}{K_T} + \left(1 - \frac{4}{3} \frac{P}{K_T}\right) \left[\left\{ \left(K_0' - \frac{8}{3}\right) \left(\frac{V}{V_0}\right) \right\} + \frac{8}{3} \right] \quad (8)$$

$$K_T' = \frac{1}{3} \left[\frac{x(1-\eta) + 2\eta x^2}{1 + (\eta x + 1)(1-x)} + \eta x + 2 \right] \quad (9)$$

The corresponding expression for second order pressure derivative of isothermal bulk modulus $K_T'' = \frac{\partial K_T'}{\partial P}$, obtained from

further derivation of expression for K_T' . Corresponding to three different EOS, on making further derivation of (7), (8) and (9) we obtain K_T'' , in terms of $K_T K_T'$ given as follows;

$$K_T K_T'' = \frac{4}{3} \left(1 - \frac{PK_T'}{K_T}\right) \left[\frac{4}{3} - \left\{ \frac{V}{V_0} \left(K_0' - \frac{5}{3}\right) + \frac{5}{3} \right\} \right] - \left(\frac{V}{V_0}\right) \left(K_0' - \frac{5}{3}\right) \left(1 - \frac{4}{3} \frac{P}{K_T}\right) \quad (10)$$

$$K_T K_T'' = \frac{4}{3} \left(1 - \frac{PK_T'}{K_T}\right) \left[\frac{4}{3} - \left\{ \frac{V}{V_0} \left(K_0' - \frac{8}{3}\right) + \frac{8}{3} \right\} \right] - \left(\frac{V}{V_0}\right) \left(K_0' - \frac{8}{3}\right) \left(1 - \frac{4}{3} \frac{P}{K_T}\right) \quad (11)$$

$$K_T K_T'' = -\frac{x}{9} \left[\frac{\{(1-\eta) + 4\eta x\} - \{(3K_T' - \eta x - 2)(\eta - 2\eta x - 2)\}}{\{1 + (\eta x + 1)(1-x)\}} + \eta \right] \quad (12)$$

Borton and Stacey find correlation for Gruneisen Parameter γ [14,15], leading to-

$$\gamma = \frac{\left(\frac{1}{2}\right)K_T' - \frac{1}{6} - \frac{f}{3} \left[1 - \frac{1}{3} \left(\frac{P}{K_T}\right)\right]}{1 - \left(\frac{4}{3}\right) \frac{P}{K_T}} \quad (13)$$

Where, $f=2.35$ a constant, K_T is isothermal bulk modulus and K_T' is the first pressure derivative of isothermal bulk modulus.

Result and Discussion:

In the present work we did calculations for pressure P , isothermal bulk modulus K_T , first pressure derivative of isothermal bulk modulus K_T' and second order pressure derivative of isothermal bulk modulus in terms of $K_T K_T''$ for geophysical minerals viz. MgO and Al_2O_3 by using Brennan Stacey, Shanker and Vinet Equation of States. All the three equation of state contains only two parameters K_0 and K_0' both at zero pressure. These values of K_0 and K_0' have been recommended by Anderson. The value of input parameters K_0 and K_0' are given in Table-1, taken from literature [16, 17].

The values of pressure P (GPa) for different geophysical minerals were computed for given increments of V/V_0 by using equation (1), (2) and (3). Using the value of pressure P (GPa) as computed above, the value of isothermal bulk modulus K_T has been calculated by using equation (4), (5) and (6). Substituting these values of P and K_T in equation (7), (8) and (9) the value of first order pressure derivative of K_T i.e. K_T' has been obtained. Further substituting the values of P , K_T and K_T' in equation (10), (11) and (12) second order pressure derivative of K_T i.e. K_T'' has been calculated in terms of $K_T K_T''$. The values of different parameters calculated with the use of Brennan-Stacey EOS is given by P (a), K_T (a), K_T' (a), $K_T K_T''$ (a) and γ (a); values calculated with the use of Shanker EOS is designated with the suffix (b) as P (b), K_T (b), K_T' (b), $K_T K_T''$ (b) and γ (b) and suffix (c) corresponding to Vinet EOS viz. P (c), K_T (c), K_T' (c), $K_T K_T''$ (c) and γ (c).

We have plotted the graphs for P vs V/V_0 displayed in Fig. (1-2), P vs K_T displayed in Fig. (3-4), P vs K_T' displayed in Fig. (5-6), P vs $K_T K_T''$ displayed in Fig. (7-8) and γ vs V/V_0 displayed in Fig. (9-10) for different geophysical minerals. From graph we observe that as $V/V_0 \rightarrow 0$, P goes to infinity. Isothermal bulk modulus increases regularly and continuously with increase in pressure. Pressure derivative of isothermal bulk modulus K_T i.e. K_T' decreases progressively with the increase in pressure and $K_T K_T''$ is always negative.

The expression γ/Ω leads to equation of straight line ($y = mx+c$). Hence the graph between Gruniesen parameter γ vs. Ω must be a straight line which strongly supports the Brennan-Stacey EOS and Shanker EOS both under low and high compression where as Vinet EOS is applicable only at high compression ratio. Thus it is concluded that Brennan-Stacey and Shanker EOS is compatible at both low and high compression ranges for calculating Gruniesen parameter where as Vinet EOS is incompatible for calculating the Gruniesen parameter at low compression ranges.

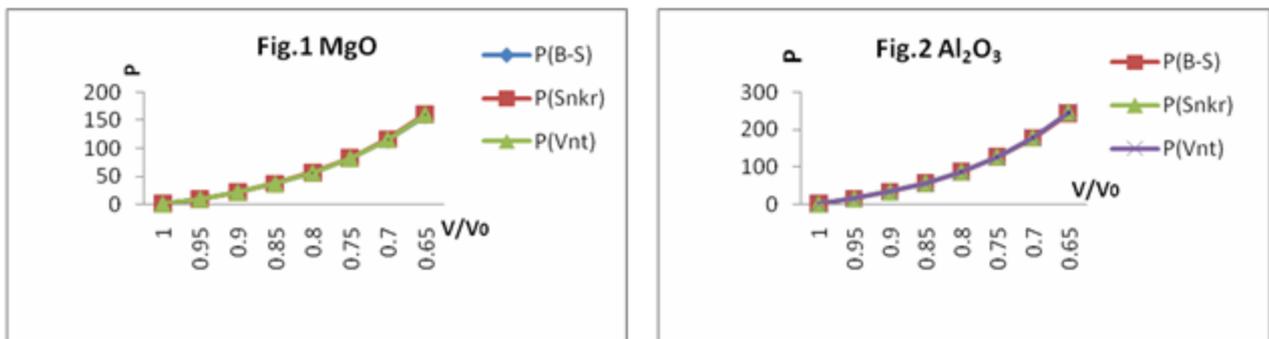


Figure (1-2): The variation of pressure P versus V/V_0 by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al_2O_3 and Olivine

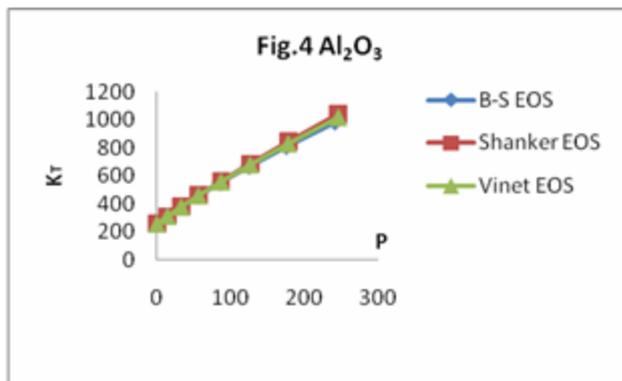
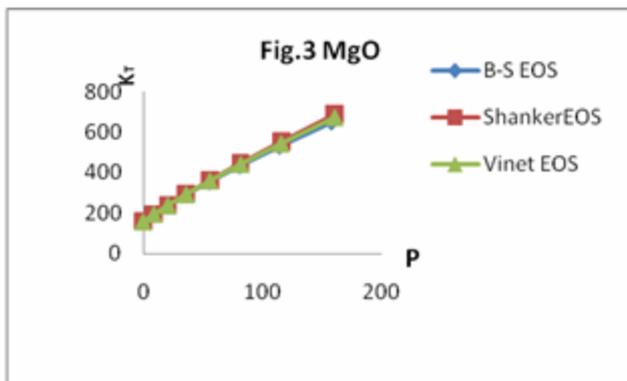


Figure (3-4): The variation of pressure P versus KT by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al₂O₃ and Olivine

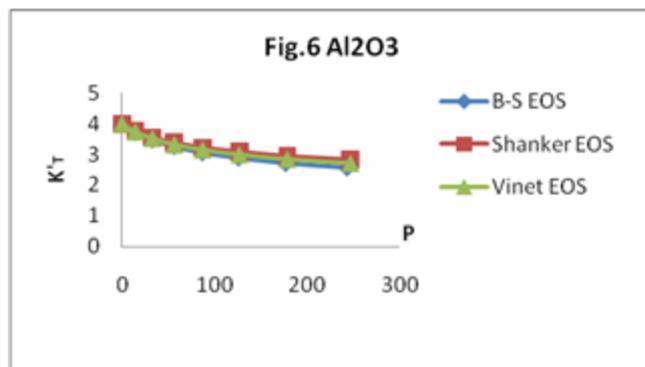
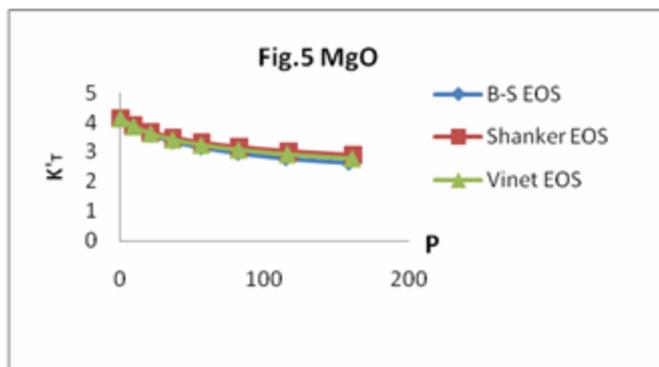


Figure (5-6): The variation of pressure P versus K'_T by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al₂O₃ and Olivine

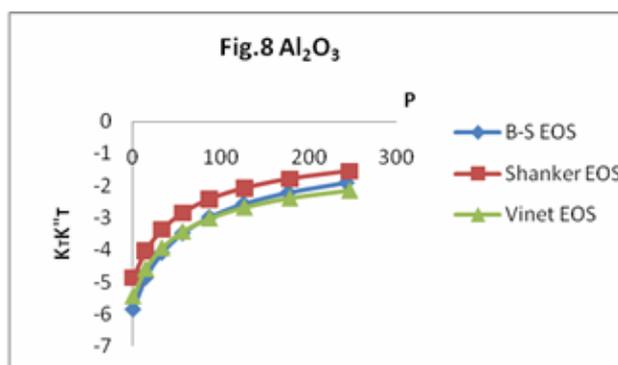
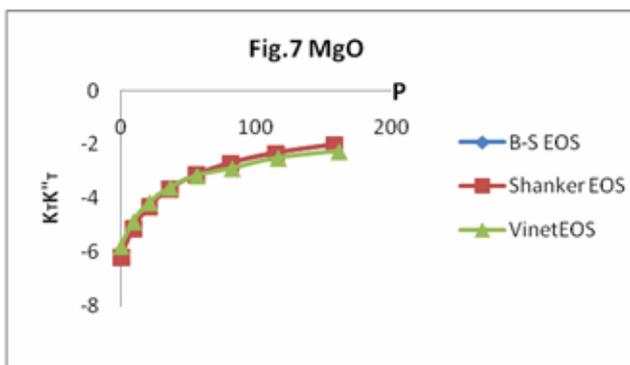


Figure (7-8): The variation of pressure P versus $K_T K_T''$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al₂O₃ and Olivine

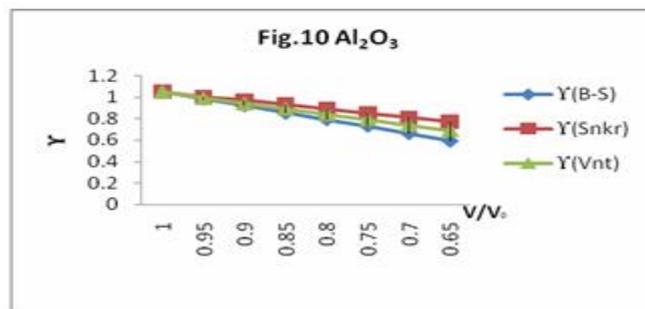
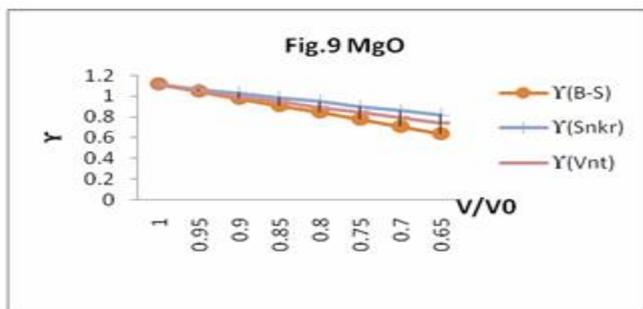


Figure (9-10): The variation of γ versus V/V_0 by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al₂O₃ and Olivine

Table-1 : Input values of K_0 and K_0' for geophysical minerals

Sample	K_0 (Gpa)	K_0'
MgO	160.5	4.13
Al ₂ O ₃	253	3.99

Table- 2 : Calculated values of different parameters for MgO

V/V ₀	P(a)	P(b)	P(c)	K _T (a)	K _T (b)	K _T (c)	K _T '(a)	K _T '(b)	K _T '(c)	K _T K _T ''(a)	K _T K _T ''(b)	K _T K _T ''(c)	Y(a)	Y(b)	Y(c)
1	0	0	0	160.5	160.5	160.5	4.13	4.13	4.13	-6.19	-5.19	-5.8	1.12	1.12	1.12
0.95	9.15	9.15	9.15	196.86	197.1	196.96	3.84	3.89	3.86	-5.12	-4.28	-4.87	1.05	1.07	1.06
0.9	20.94	20.98	20.96	240.59	241.79	241.12	3.59	3.68	3.62	-4.29	-3.57	-4.16	0.98	1.03	1
0.85	36.17	36.29	36.25	293.4	296.66	294.93	3.36	3.49	3.42	-3.64	-3.01	-3.6	0.91	0.99	0.95
0.8	55.86	56.19	56.08	357.45	364.53	360.92	3.16	3.32	3.24	-3.12	-2.56	-3.16	0.85	0.95	0.89
0.75	81.39	82.14	81.94	435.54	449.1	442.5	2.97	3.17	3.08	-2.68	-2.19	-2.89	0.78	0.9	0.85
0.7	114.67	116.16	115.88	531.38	555.43	544.25	2.79	3.03	2.93	-2.31	-1.88	-2.5	0.71	0.86	0.79
0.65	158.34	161.05	160.84	649.92	690.46	672.47	2.64	2.9	2.79	-2	-1.64	-2.25	0.64	0.82	0.74

Table- 3: Calculated values of different parameters for Al₂O₃

V/V ₀	P(a)	P(b)	P(c)	K _T (a)	K _T (b)	K _T (c)	K _T '(a)	K _T '(b)	K _T '(c)	K _T K _T ''(a)	K _T K _T ''(b)	K _T K _T ''(c)	Y(a)	Y(b)	Y(c)
1	0	0	0	253	253	253	3.99	3.99	3.99	-5.86	-4.87	-5.45	1.05	1.05	1.05
0.95	14.36	14.37	14.37	308.22	308.59	308.38	3.72	3.76	3.74	-4.87	-4.03	-4.59	0.98	1	0.99
0.9	32.78	32.83	32.8	374.28	376.13	375.13	3.48	3.56	3.52	-4.09	-3.37	-3.94	0.92	0.97	0.94
0.85	56.39	56.59	56.5	453.63	458.66	456.03	3.26	3.39	3.32	-3.48	-2.85	-3.43	0.85	0.93	0.89
0.8	86.73	87.25	87.07	549.38	560.23	554.77	3.06	3.23	3.15	-2.98	-2.42	-3.02	0.79	0.89	0.84
0.75	125.85	127.01	126.69	665.56	686.22	676.2	2.89	3.09	2.99	-2.56	-2.08	-2.68	0.73	0.85	0.79
0.7	176.56	178.83	178.42	807.49	843.88	826.87	2.72	2.95	2.84	-2.21	-1.79	-2.39	0.66	0.81	0.74
0.65	242.73	246.85	246.51	982.26	1043.17	1015.72	2.57	2.83	2.71	-1.9	-1.55	-2.15	0.59	0.77	0.69

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