

Analysis of temperature dependence of volume thermal expansion of geophysical minerals at high pressure

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ABSTRACT

A method for estimating temperature dependence of volume thermal expansion of geophysical minerals at high pressures has been developed by modifying the formulation originally due to Suzuki [5]. The formulation modified in the present study becomes applicable upto very high temperatures close to the melting temperatures of the minerals under high pressures. The method has been applied to predict volumes of pyrope, MgSiO_3 and CaSiO_3 perovskites at simultaneously elevated pressures and temperatures upto their melting temperatures. Values of pressure P , isothermal bulk modulus K_T and its pressure derivative dK_T/dP at different compressions have been used those derived from the Rydberg-Vinet [9] equation of state. It has been found that the rate of increase of volume thermal expansion with temperature decreases at high pressures. This has been correlated with the melting temperatures of the minerals under high pressures.

1. INTRODUCTION:

An adequate understanding of thermoelastic properties of geophysical minerals requires the knowledge of temperature dependence of volume thermal expansion at high pressures [1, 2]. A multi-step method has been developed by Anderson et al [3] for estimating the volumes of minerals at high pressures and high temperatures. This method

is based on the equation for isobaric volume thermal expansion formulated by Suzuki et al [4, 5]. However, there is a shortcoming in the original derivation of the Suzuki equation which is rectified in the present study. By expressing the modified Suzuki equation in terms of thermal pressure, we estimate the temperature dependence of volume thermal expansion along isobars at $P=0$ and also at higher pressures for three important minerals viz., pyrope, MgSiO_3 – perovskite and CaSiO_3 – perovskite. The input data on K_0 , K'_0 , V_0 , $\overline{\alpha K_T}$ for these minerals have been reported by Wang et al [6]. The values of P , K_T and K'_T corresponding to different compressions needed in the calculations are estimated using the Rydberg-Vinet equation of state.

2. REVISION OF THE SUZUKI FORMULATION

The Suzuki equation has been derived from the Mie-Grüneisen equation of state (EOS) :

$$P(V, T) = P(V, 0) + \frac{\gamma E_{th}}{V} \quad (1)$$

where $P(V, 0)$ represents the pressure as function of volume only at $T=0$ K. γ is the Grüneisen parameter, and E_{th} is the thermal energy evaluated at different temperatures with the use of the Debye theory. At zero pressure, i.e. $P(V, T) = 0$, equation (1) reduces to the following form

$$-\gamma E_{th} = VP(V, 0) = f(V) \quad (2)$$

Suzuki et al expanded the right – hand side of equation (2) in powers of change in volume $(V-V_0)$. Thus we can expand the function f given on the right hand side of equation (2) as follows:

$$-\gamma E_{th} = f_0 + \left. \frac{\partial f}{\partial V} \right|_{V_0} (V - V_0) + \frac{1}{2} \left. \frac{\partial^2 f}{\partial V^2} \right|_{V_0} (V - V_0)^2 + \dots \quad (3)$$

By truncating the series past the squared term, a quadratic equation was found for $(V - V_0)$. The coefficients in the Taylor series expansion in equation (3) were evaluated in terms of the isothermal bulk modulus and its pressure derivative both at $P=0$. The Suzuki equation thus obtained is

$$\frac{V - V_0}{V_0} = \frac{\left[1 + 2k \left(1 - \frac{4\gamma_0 k E_{th}}{K_{T_0} V_0} \right) \right]}{2ka_V} \quad (4)$$

where

$$k = \left(\frac{1}{2} \right) (K'_0 - 1)$$

and a_V is the ratio of volumes at 300 K and 0 K. Equation (4), originally due to Suzuki has been used widely in the field of geophysics [1, 7]. It is pointed out here that when we review the derivation of equation (4) from equation (3) it is found that γ has been replaced by γ_0 , the value of Grüneisen parameter at initial conditions of pressure and temperature. However this is not justified in view of the fact that γ depends on volume and its volume dependence is expressed as

$$\frac{\gamma}{\gamma_0} = \left(\frac{V}{V_0} \right)^q \quad (5)$$

where q is known as the second Grüneisen parameter. For most of the minerals the value of q is nearly equal to 1. When we take $q=1$, we get an equation also quadratic in $(V - V_0)$ and yields the following solutions.

$$\frac{V}{V_0} - 1 = \frac{A_1}{A_2} \left[1 - \left(1 - \frac{2A_2 \gamma_0 E_{th} / V_0}{A_1^2} \right)^{1/2} \right] \quad (6)$$

where

$$A_1 = K_0 - (\gamma_0 E_{th}) / V_0$$

$$A_2 = K_0 (K'_0 - 1)$$

It should be emphasized that equation (6) corresponds to $q=1$ in equation (5), whereas the Suzuki equation corresponds to $q=0$. It should also be mentioned that equation (6) reduces to Singh -Suzuki equation obtained recently by Singh [8] where $(\gamma_0 E_{th}) / V_0$ is replaced by thermal pressure P_{th} . Thus we have [8].

$$\frac{V}{V_0} - 1 = \frac{A_1}{A_2} \left[1 - \left(1 - \frac{2A_2 \Delta P_{th}}{A_1^2} \right)^{1/2} \right] \quad (7)$$

where

$$A_1 = K_0 - \Delta P_{th}$$

$$A_2 = K_0 (K'_0 - 1)$$

3. TEMPERATURE DEPENDENCE OF VOLUME AT HIGH PRESSURES:

Equation (6) or (7) can be used to estimate the volume as a function of temperature along isobars at $P=0$ as well as along higher pressures. When we use equation (7) along isobars at finite pressures ($P>0$), the parameters A_1 and A_2 appearing in equation (7) have modified meaning i.e. $A_1 = K_T(T_0, P) - \Delta P_{th}$ and $A_2 = K_T(T_0, P) [K'_T(T_0, P) - 1]$. The volume ratio V/V_0 appearing in equation (7) is now $V(T, P)/V(T_0, P)$. Values of $V(T_0, P)$, $K'_T(T_0, P)$, $K_T(T_0, P)$ at 300K are estimated with the help of equations given below based on the Rydberg -Vinet equation of state [9].

$$P=3K_0(1-x)x^{-2} \exp[\eta(1-x)] \quad (8)$$

$$K_T = K_0x^{-2}[1+(\eta x+1)(1-x)] \exp \{\eta(1-x)\} \quad (9)$$

$$K'_T = \frac{1}{3} \left[\frac{x(1-\eta)+2\eta x^2}{1+(\eta x+1)(1-x)} + \eta x + 2 \right] \quad (10)$$

where

$$x = \left[\frac{V(T_0, P)}{V(T_0, 0)} \right]^{1/3}$$

and

$$\eta = \frac{3}{2}(K'_0 - 1)$$

The three minerals namely pyrope, $MgSiO_3$ and $CaSiO_3$ perovskites have recently been studied by Wang et al [6]. The input data reported by them are given in Table-1. Values of P , $K_T(T_0, P)$ and $K'_T(T_0, P)$ at different compressions, calculated from equations (8) – (10) using input data given in Table-1 are reported in Table- 2. For determining the values of thermal pressure to be used in equation (7), we consider the following expression [Equation (5) of Wang et al, [6]]

$$\Delta P_{th} = P_{th}(T) - P_{th}(300K) = \overline{\alpha K_T} [T-300K] \quad (11)$$

Values of $\overline{\alpha K_T}$ are given in Table 1. for the minerals under study.

4. RESULTS AND CONCLUSIONS

Values of volumes $V(T, P)$ calculated with the help of equation (7) using the data given in Tables 1 and 2 and the values of ΔP_{th} estimated from equation (11) at different temperature are reported in Table 3-5. The range of compressions down to $V/V_0 =$

0.60 considered in the present study corresponds to a much wider range of pressures upto 231 GPa, 375 GPa and 390GPa in case of pyrope, MgSiO_3 perovskite and CaSiO_3 perovskite respectively. These values of pressures are much higher than their isothermal bulk modulus K_T at ambient pressure which are 172.8 GPa, 261 GPa and 232 GPa respectively. It should be mentioned that the range of pressures in the lower mantle is well within the range of these pressures.

The volume-temperature relationships have been used to predict the values of volumes (V_m) at melting temperatures T_m for different minerals under high pressures. The results are shown in Figures 1-3. The values of melting temperature have been taken from Wang et al. [6]. They have obtained critical volume at different pressures and reference volume at 300K at higher pressure by exchanging the values of isothermal bulk modulus at 300K and at the critical temperature. The melting temperatures for minerals under study thus obtained by Wang et. al. [6] are in close agreement with the experimental values reported in the literature.

It is evident from Figures 1-3 that the rate of volume expansion with increasing temperature reduces significantly as the pressure is increased, this would imply that the thermal expansivity decreases at high pressures. At relatively lower pressure the variation of volume with temperature becomes nonlinear at high temperature ($T > 4000\text{K}$). This is particularly evident from figures 2 and 3 for silicate perovskites for which we have calculated variation of volume with temperature upto 7000K. The non-linearity is reduced and is almost eliminated at higher pressures. This finding seems to be related with the effect of anharmonicity. Karki et al. [10] have found that the effect of anharmonicity is dominant at high temperatures and lower pressures. The effect of anharmonicity is suppressed at simultaneously elevated high pressure and high temperatures. Thus the

findings of the present study are supported by the work of Karki et al. [10] and Panwar et al. [11].

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TABLE -1 : Input data on volume V_0 ($\text{cm}^3 \text{mol}^{-1}$), isothermal bulk modulus K_0 (GPa), and pressure derivative K'_0 all at reference pressure P_0 and 300K, and product αK_T (average) [where α is $\overline{\alpha}$ thermal expansivity and K_T is isothermal bulk modulus][6].

Minerals	P_0 (GPa)	V_0 ($\text{cm}^3 \text{mol}^{-1}$)	K_0 (GPa)	K'_0	$\overline{\alpha K_T}$ (Average) (10^{-3}) GPa K ⁻¹
Pyrope (Mg ₃ Al ₃ Si ₃ O ₁₂)	0	113.31	172.8	4.0	4.45
MgSiO ₃ perovskite	26	142.52	261	4.0	6.92
CaSiO ₃ perovskite	16	41.59	232	4.8	7.20

TABLE -2 : Values of pressure P (GPa) isothermal bulk modulus K_T (GPa) and $K'_T = (dK_T/dP)$ for Pyrope, $MgSiO_3$ and $CaSiO_3$ perovskites calculated from Rydberg - Vinet EOS.

V/V ₀	Mineral								
	Pyrope			MgSiO ₃			CaSiO ₃		
	P (GPa)	K_T (GPa)	K'_T	P (GPa)	K_T (GPa)	K'_T	P (GPa)	K_T (GPa)	K'_T
1	0	172.8	4.000	26	261	4.000	16	232	4.800
0.95	9.82	211	3.746	40.82	318.3	3.75	29.45	294.0	4.452
0.90	22.4	256.5	3.525	59.86	387.4	3.525	47.37	371.0	4.159
0.85	38.6	312	3.330	84.34	471.1	3.330	71.24	467.0	3.906
0.80	59.54	379.6	3.155	116	573.4	3.155	103	587.8	3.685
0.75	86.66	462.9	2.996	157	699.1	2.996	146	740.7	3.488
0.70	122	566.2	2.851	210	855.3	2.851	203	936.3	3.309
0.65	169	695.9	2.716	281	1051	2.716	282	1189.0	3.145
0.60	231	860.3	2.589	375	1299.5	2.589	390	1520	2.993

TABLE -3 : Values of volumes $V(T, P)$ {cm³ mol⁻¹} for Pyrope [Mg₃Al₂Si₃O₁₂] at simultaneously elevated temperature and pressure calculated from Rydberg-Vinet EOS and Singh-Suzuki equation.

P(GPa)	V(T,P) {cm ³ mol ⁻¹ }								
	300 K	500 K	1000 K	1500 K	2000 K	2500 K	3000 K	3500 K	4000 K
0.0	113.31	113.90	115.45	117.12	118.94	120.94	123.16	125.71	128.72
9.8	107.65	108.11	109.29	110.55	111.90	113.32	114.86	116.53	118.36
22.4	101.98	102.34	103.25	104.21	105.21	106.26	107.37	108.54	109.78
38.6	96.31	96.59	97.30	98.03	98.78	99.57	100.38	101.23	102.11
59.5	90.65	90.87	91.41	91.96	92.53	93.12	93.73	94.35	94.99
86.7	84.98	85.14	85.56	85.99	86.42	86.86	87.31	87.78	88.25
122	79.32	79.44	79.76	80.08	80.40	80.73	81.07	81.42	81.77
169	73.65	73.75	73.98	74.23	74.47	74.72	74.97	75.22	75.48
231	67.99	68.05	68.23	68.41	68.59	68.78	68.96	69.15	69.33

TABLE -4 : Value of volumes $V(T,P)$ $\{\text{cm}^3\text{mol}^{-1}\}$ for MgSiO_3 perovskite at simultaneously elevated temperature and pressure calculated from Rydberg-Vinet EOS and Singh-Suzuki equation.

P (GPa)	V (T,P) $\{\text{cm}^3\text{mol}^{-1}\}$														
	300K	500K	1000K	1500K	2000K	2500K	3000K	3500K	4000K	4500K	5000K	5500K	6000K	6500K	7000K
26.0	142.52	143.29	145.30	147.47	149.83	152.46	155.39	158.77	162.80	168.17	177.62	-	-	-	-
40.8	135.39	135.99	137.53	139.17	140.92	142.77	144.79	146.98	149.41	152.13	155.26	159.05	164.06	173.56	-
59.9	128.27	128.73	129.92	131.17	132.46	133.84	135.27	136.81	138.44	140.18	142.07	144.14	146.42	149.01	152.01
84.3	121.14	121.51	122.98	123.36	124.35	125.37	126.42	127.53	128.69	129.89	131.16	132.51	133.92	135.45	137.07
116	114.02	114.29	115.0	115.72	116.47	117.23	118.02	118.83	119.66	120.53	121.43	122.35	123.32	124.32	125.37
157	106.89	107.10	107.64	108.19	108.75	109.33	109.92	110.51	111.12	111.75	112.41	113.07	113.74	114.45	115.16
210	99.76	99.92	100.33	100.75	101.17	101.60	102.04	102.49	102.94	103.41	103.87	104.35	104.84	105.34	105.85
281	92.64	92.76	93.07	93.38	93.69	94.02	94.34	94.67	95.00	95.34	95.69	96.03	96.39	96.74	97.10
375	85.51	85.61	85.84	86.07	86.30	86.54	86.78	87.02	87.26	87.50	87.75	88.01	88.27	88.52	88.78

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TABLE -5 : Values of volumes $V(T,P)$ $\{\text{cm}^3\text{mol}^{-1}\}$ for CaSiO_3 perovskite at simultaneously elevated temperature and pressure calculated from Rydberg-Vinet EOS and Singh-Suzuki equation.

P (GPa)	V (T,P) $\{\text{cm}^3\text{mol}^{-1}\}$														
	300K	500K	1000K	1500K	2000K	2500K	3000K	3500K	4000K	4500K	5000K	5500K	6000K	6500K	7000K
16.0	41.59	41.85	42.536	43.35	44.25	45.32	46.69	48.85	-	-	-	-	-	-	-
29.5	39.51	39.71	40.22	40.78	41.39	42.06	42.82	43.70	44.78	46.26	-	-	-	-	-
47.4	37.43	37.58	37.96	38.36	38.79	39.25	39.74	40.27	40.86	41.52	42.28	43.19	44.38	46.47	-
71.2	35.35	35.46	35.74	36.04	36.35	36.67	37.01	37.36	37.74	38.14	38.57	39.04	39.55	40.12	40.77
103	33.27	33.36	33.57	33.78	34.00	34.23	34.47	34.72	34.98	35.24	35.52	35.81	36.12	36.45	36.79
146	31.19	31.26	31.41	31.57	31.73	31.89	32.07	32.24	32.42	32.60	32.79	32.99	33.19	33.40	33.62
204	29.11	29.16	29.27	29.39	29.51	29.63	29.75	29.87	30.00	30.13	30.26	30.39	30.53	30.67	30.82
282	27.03	27.07	27.15	27.23	27.32	27.40	27.49	27.58	27.67	27.76	27.85	27.95	28.04	28.14	28.24
390	24.95	24.98	25.04	25.10	25.16	25.22	25.28	25.34	25.41	25.47	25.54	25.60	25.67	25.74	25.80

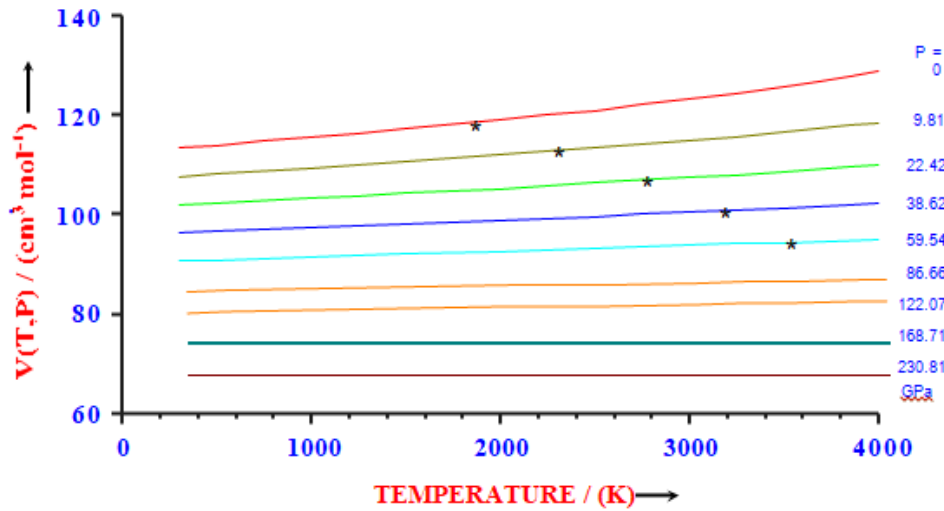


FIGURE 1 : PLOTS OF $V(T,P)$ VERSUS TEMPERATURE T FOR PYROPE ($Mg_3Al_2Si_3O_{12}$) AT DIFFERENT PRESSURES. MELTING TEMPERATURES T_m AT DIFFERENT PRESSURES ARE MARKED BY (*)



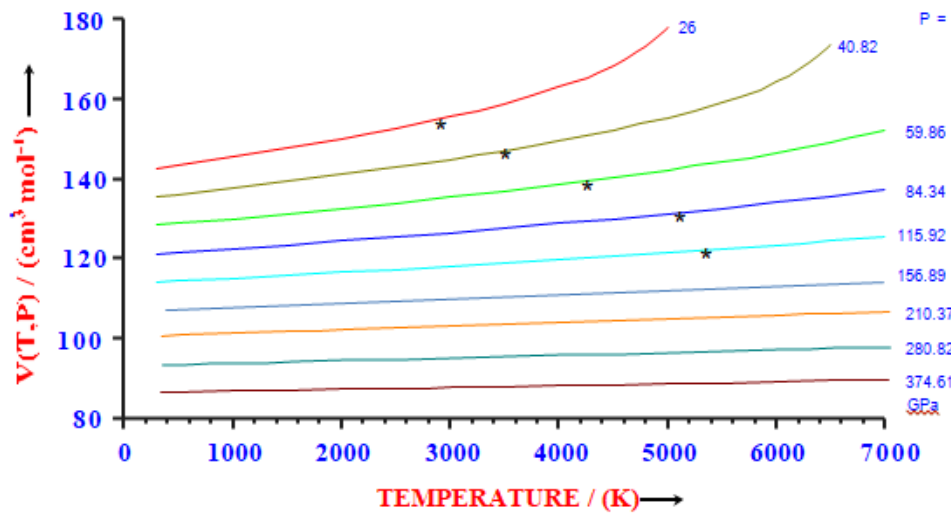


FIGURE 2: PLOTS OF $V(T,P)$ VERSUS TEMPERATURE T FOR $MgSiO_3$ PEROVSKITE AT DIFFERENT PRESSURES. MELTING TEMPERATURES T_m AT DIFFERENT PRESSURES ARE MARKED BY (*)



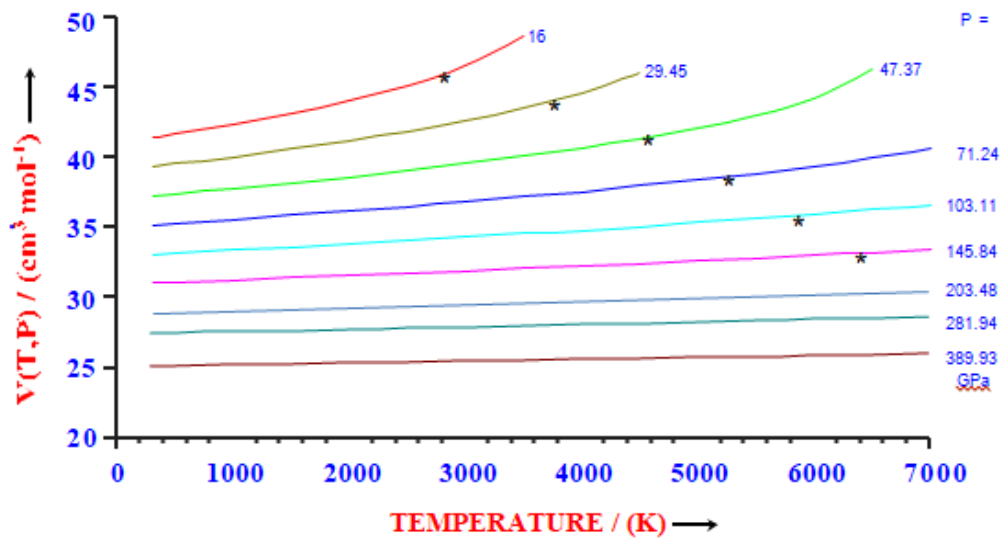


FIGURE 3.: PLOTS OF $V(T,P)$ VERSUS TEMPERATURE T FOR $CaSiO_3$ PEROVSKITE AT DIFFERENT PRESSURES. MELTING TEMPERATURES T_m AT DIFFERENT PRESSURES ARE MARKED BY (*)

