1. Thermodynamic properties

4. Grüneisen parameter

4.1 Thermal pressure

Thermodynamic properties of rock-forming minerals are the kunderstandingerstand dynamics of interiors of planets. Materials of planetary interior are under high-temperature and high-pressure conditions. It is necessary to investigate behaviors of minerals under such a high-temperature and high-pressure conditions and the pressure (P) and temperature (T) dependence of thermodynamic properties of each mineral.

In thermodynamics, thermal pressure means the rate of pressure (P) increase by temperature (T) increase at constant volume (V). In other words, thermal pressure is defined by partial derivative of the pressure , or pressure increase, with temperature increase at a constant volume:

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \\ &= \left\{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right\}\left[-V\left(\frac{\partial P}{\partial V}\right)_T\right] \\ &= \alpha K_T \end{aligned} \tag{1.4.1}$$

where P is the pressure, T is the temperature, V is the volume, α is the thermal expansivity (thermal expansion coefficient), and K_T is the isothermal bulk modulus. As shown in the equation (1.4.1), thermal pressure can be expressed as a product of thermal expansivity (α) and isothermal bulk modulus (K_T).

Thermal pressure is relatively constant at high temperature because thermal expansivity (α) and isothermal bulk modulus K_T increases and decreases with temperature, respectively. Figure 1 shows thermal pressure (αK_T) of periclase and forsterite and they are nearly constant at high temperatures.

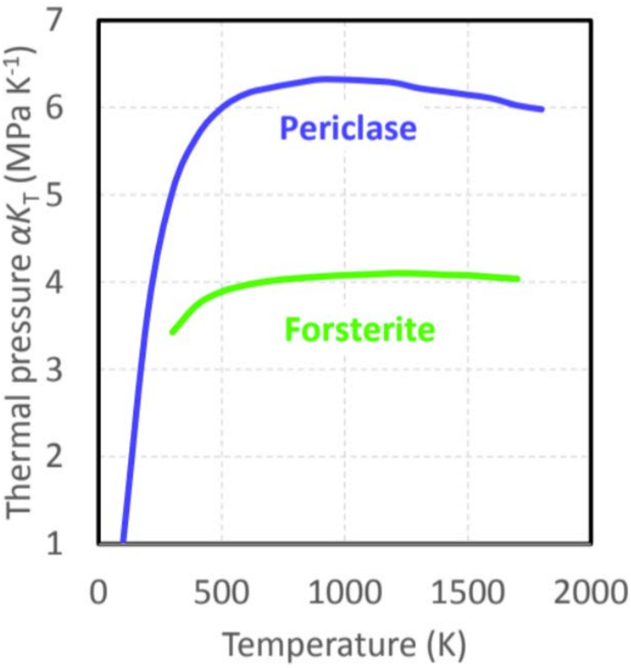

Fig. 1. Diagram of thermal pressures of periclase (marked in blue) and forsterite (marked in green) at ambient pressure (P_0). Thermal pressure of periclase at low temperature increases with temperature increase, while thermal pressures of periclase and forsterite at high temperature are relatively constant because of cancellation of α increase and K_T decrease with T. The diagram is originally from Anderson (1995).

4.2 Definition of Grüneisen parameters

Grüneisen parameter describes the anharmonic effects of lattice vibration at high temperature and the parameter is helpful to precisely estimate thermodynamic behaviors of rock-forming minerals, especially at Earth's mantle. Thermodynamic properties of high-pressure minerals are measured at limited conditions which can be reproduced in a laboratory. The crystal structure of high-pressure minerals breaks down at relatively low temperatures at a lower pressure than atmospheric pressure. Therefore, thermodynamic parameters such as thermal expansivity and heat capacity of high-pressure minerals are measured at much lower temperatures at laboratory than at the mantle. To discuss thermodynamics of mantle minerals at high-temperature and high-pressure conditions as well as planetary interiors, the thermodynamic parameters measured at laboratory should be extrapolated theoretically with Grüneisen parameter.

Grüneisen parameter γ is defined by the product of the volume and partial derivative of the pressure with respect to the internal energy (E) at a constant volume:

$$\gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_V \cong \left[\frac{\Delta P}{\Delta E/V}\right] \qquad (1.4.2)$$

where V is the volume, P is the pressure, and E is the internal energy.

Thermodynamic Grüneisen parameter γ_{th} is defined as shown below:

$$\gamma_{th} = \frac{\alpha K_T V}{C_V} \qquad (1.2.20)$$

where α is the thermal expansivity, K_T is the isothermal bulk moduli, V is the volume, C_V is the isochoric heat capacity (heat capacity at constant volume). Thermodynamic Grüneisen parameter can be calculated with these thermodynamic properties obtained by laboratory measurements and the equation (1.2.20).

4.3 Equivalency of Grüneisen parameters

Grüneisen parameters can be expressed in many formulations with various thermodynamic parameters. These different formulations provide various interpretations of Grüneisen parameters. From here, let's confirm the equivalency of Grüneisen parameters expressed by the equation (1.4.2) and (1.2.the 20). The second factor of the right side of equation for Grüneisen parameter (1.4.2) $\gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_V$ is modified as shown below:

$$\left(\frac{\partial P}{\partial E}\right)_V = \left(\frac{\partial P}{\partial T}\right)\left(\frac{\partial T}{\partial E}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V / \left(\frac{\partial E}{\partial T}\right)_V \qquad (1.4.3)$$

where P is the pressure, E is the internal energy, V is the volume, and T is the temperature. Note that this modification follows derivative the composite function: if $y = f(g(x)), \frac{df}{dx} = \frac{df}{dg}\frac{dg}{dx}$

The denominator of the equation (1.4.3) is the definition of isochoric heat capacity C_V:

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V \qquad (1.2.1)$$

where C_V is the isochoric heat capacity, E is the internal energy, and T is the temperature.

By substituting (1.4.1), (1.4.3), and (1.2.1) into (1.4.2), the equivalency of Grüneisen parameter (γ) and thermodynamic Grüneisen parameter (γ_{th}) can be confirmed as follows:

$$\gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_V = V\left(\frac{\partial P}{\partial T}\right)_V / \left(\frac{\partial E}{\partial T}\right)_V = \frac{\alpha K_T V}{C_V} = \gamma_{th} \qquad (1.4.4)$$

where V is the volume, P is the pressure, E is the internal energy, K_T is the isothermal bulk moduli, and C_V is the isochoric heat capacity.

4.4 Meaning of Grüneisen parameter

Grüneisen parameter is the indicator showing the rate of pressure increase by internal energy density increase at constant volume. Grüneisen parameter γ can be divided to the two parts: αK_T and V/C_V. These two parts have each meaning in thermodynamics. The factors which composes Grüneisen parameter and/or thermodynamic Grüneisen parameter are shown in Table 1. The factor αK_T means pressure increase by temperature increase, therefore, higher αK_T means larger pressure increase by a given temperature increase and thermodynamic Grüneisen parameter γ_{th} increases in proportion to αK_T. The factor V/C_V means larger temperature increase by a given internal energy increase, therefore, thermodynamic Grüneisen parameter γ_{th} increases in proportion to V/C_V.

Table. 1. Meaning of each factor of Grüneisen parameter

	factors	**meaning**
α	thermal expansivity	The matter attempts to increase V by T increase
K_T	isothermal bulk modulus	The efforts for V increase is converted to P increase
αK_T		P increase by T increase ➔ Higher αK_T: larger P increase by a given T increase ➔ $\gamma_{th} \propto \alpha K_T$
C_V	isochoric heat capacity	E increase by T increase
C_V/V		E density increase by T increase
V/C_V		T increase by E density increase ➔ Larger V/C_V: T increase by a given E density increase ➔ $\gamma_{th} \propto V/C_V$

4.5 Relative constancy of Grüneisen parameter

As discussed in the equation (1.2.20), Grüneisen parameter can be described as:

$$\gamma_{th} = \frac{\alpha K_T V}{C_V} \tag{1.2.20}$$

Figure 2 shows thermal expansivity and Grüneisen parameter of periclase and forsterite with respect to temperature. At lower temperature (0-500 K), thermal expansivity α of periclase and forsterite increases with temperature increase, and at higher temperature (>500 K), thermal expansivity of periclase and forsterite slightly but still increases with temperature increase. This properties of minerals are explained by the behavior of each factors such as αK_T and V/C in

Grüneisen parameter at high/low temperatures. At high temperatures with temperature increase, increases in thermal expansivity and decreases in isothermal bulk modulus result in nearly constant αK_T. The isochoric heat capacity is also nearly constant at high temperatures. At low temperature, Grüneisen parameter shows no constancy because of much larger temperature dependence of thermal expansicvity than that of isothermal bulk modulus. Thermal expansivities of periclase and forsterite are in the order of 10^{-5} K^{-1}, while Grüneisen parameters of those minerals are dimensionless.

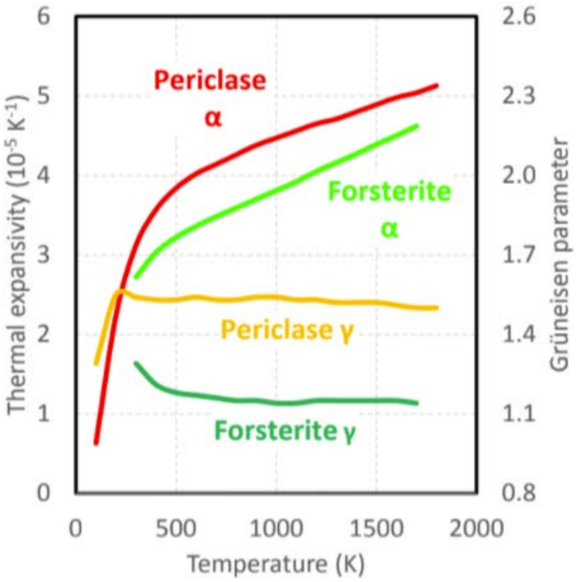

Fig. 2. Diagram of thermal expansivity (α) and Grüneisen parameters (γ) of periclase (marked in red and orange, respectively) and forsterite (marked in green and forest-green, respectively). Thermal expansivity of periclase rapidly increases with temperature increase at low temperature (<500 K), while that of periclase and forsterite gradually increase with temperature increase at higher temperature. Grüneisen parameter of periclase rapidly increases with temperature increase at low temperature (<250 K) and that is nearly constant at high temperature (>250 K). Grüneisen parameter of forsterite gradually decreases at low temperature (250-500K) and is nearly constant at high temperature (>500 K).

4.6 1+$\alpha\gamma T$ factor

The factor shown below is helpful to discuss anharmonicity of lattice at high temperature:

$$\frac{K_S}{K_T} = \frac{C_P}{C_V} = 1 + \alpha\gamma_{th}T \qquad (1.3.13)$$

This factor $1+\alpha\gamma_{th}T$ is a measure of the anharmonicity of a lattice. Thermal expansivity increases with temperature increase, while Grüneisen parameter is independent from temperature. It is therefore the factor $1+\alpha\gamma_{th}T$ increases with increasing temperature. Figure 3 shows the factor $1+\alpha\gamma_{th}T$ with respect to temperature. Assuming the factor is equal to 1, isochoric heat capacity (C_V) and isobaric heat capacity (C_P) are equal. In low-temperature regions in Figure 3, the factor $1+\alpha\gamma_{th}T$ of periclase and forsterite are almost 1, and with increasing temperature, the factor increases up to 1.1 at around 1500 K (temperature at upper mantle), indicating C_P and K_S is larger by 10% than C_V and K_T respectively.

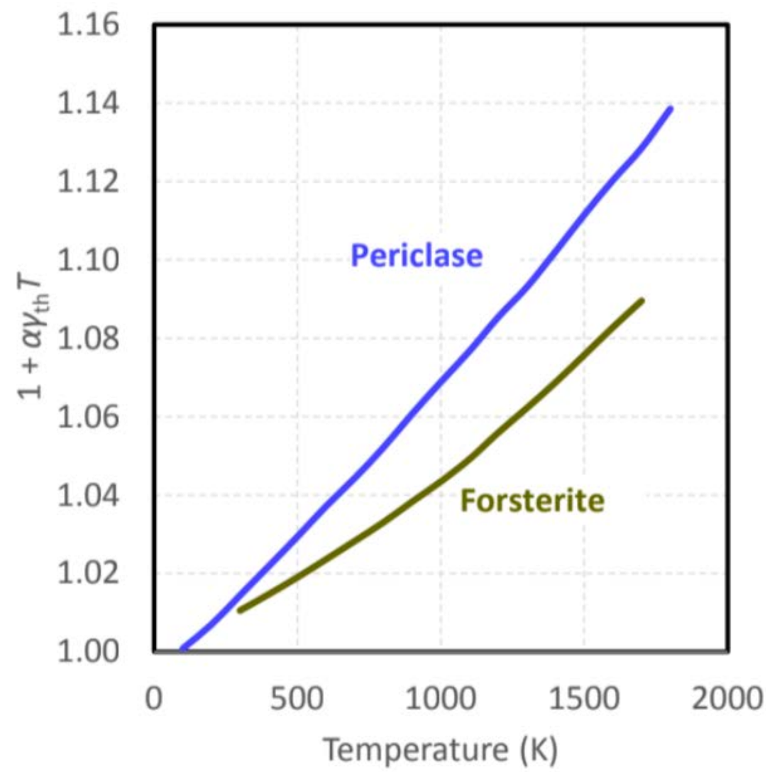

Fig. 3. Diagram of 1+$\alpha\gamma T$ of periclase (marked in blue) and forsterite (marked in olive green). The factors of periclase and forsterite monotonously increase with temperature increase.