

APPENDIX

Pressure dependence of heat capacity

The constant pressure heat capacity, C_p , is defined as (Stacey 1992),

$$C_p = (\partial H / \partial T)_p \quad (\text{A1})$$

the partial derivative of enthalpy H with respect to temperature T (at constant pressure). To examine its pressure dependence, take its pressure derivative

$$\left(\partial C_p / \partial P \right)_T = \frac{\partial}{\partial P} \left[\left(\frac{\partial H}{\partial T} \right)_p \right]_T \quad (\text{A2})$$

and exchange the order of differentiation. Because $(\partial H / \partial P)_T = V(1 - \alpha T)$,

$$\begin{aligned} \left(\partial C_p / \partial P \right)_T &= \frac{\partial}{\partial T} \left[V(1 - \alpha T) \right]_p = \alpha V(1 - \alpha T) - VT \left[\frac{\partial \alpha}{\partial T} \right]_p - \alpha V \\ &= -T \alpha^2 V \left[1 + \frac{1}{\alpha^2} \left[\frac{d\alpha}{dT} \right]_p \right]. \end{aligned} \quad (\text{A3})$$

A typical C_p is about $800 \text{ J} \cdot \text{kg}^{-1} \text{K}^{-1}$ (Stacey 1992), T about 10^3 K , α is about 10^{-5}K^{-1} , and $(\partial \alpha / \partial T)_p$ about 10^{-9}K^{-2} (Fei 1995) and a typical V is $10 \text{ cm}^3 \text{mol}^{-1} = 1 \text{ J} \cdot \text{mol}^{-1} \text{bar}^{-1}$. If the molar mass of the material is $\sim 50 \text{ g} \cdot \text{mol}^{-1}$, this volume becomes $V = 2 \times 10^{-4} \text{ J} \cdot \text{kg}^{-1} \text{Pa}^{-1}$. Hence $(\partial C_p / \partial P)_T = 2 \times 10^{-2} \text{ J} \cdot \text{kg}^{-1} \text{K}^{-1} \text{GPa}^{-1}$. For a maximum planetary pressure of 400 GPa, C_p will change by 10%. This is typically the uncertainty in the value used due to it representing a property of an aggregate whose constituent oxide components or alloying elements are not specified, for example “granite,” “basalt,” “peridotite,” “pyrolite,” “chondrite,” or, for that matter, “pure iron” (Birch 1952; Stacey 1992; Turcotte and Schubert 2002).