

## APPENDIX

### Pressure dependence of heat capacity

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

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

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

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

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

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

A typical  $C_p$  is about  $800 \text{ J} \cdot \text{kg}^{-1} \text{K}^{-1}$  (Stacey 1992),  $T$  about  $10^3 \text{ K}$ ,  $\alpha$  is about  $10^{-5} \text{ K}^{-1}$ , and  $(\partial \alpha / \partial T)_p$  about  $10^{-9} \text{ K}^{-2}$  (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).