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# Mechanical and phase equilibria in inclusion–host systems

Youxue Zhang<sup>\*</sup>*Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA*

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## Abstract

Mechanical and phase equilibria in inclusion–host systems are investigated in this paper. An inclusion–host system that is initially under lithostatic pressure and in mechanical and phase equilibria may undergo pressure–temperature change. The new elastic and plastic equilibrium, possible viscous relaxation, and phase equilibrium are considered. The new inclusion pressure typically differs from both the initial pressure and the pressure on the outside surface of the host. The inclusion is under isotropic stress (a single pressure) but the host is anisotropically stressed. The relative volume change of the inclusion differs from that of the inclusion-free host by  $0.75(P_{in} - P_{out})/G_h$  where  $P_{in}$  and  $P_{out}$  are the pressures on the inside and outside surfaces of the host, and  $G_h$  is the shear modulus of the host. Different inclusions in a single host may be under different pressures. A simple case of elastic anisotropy is also considered and the result shows that incorporation of elastic anisotropy is necessary for accurate calculations of volume and strain effect. For inclusions with roughly constant bulk modulus, the time scale of viscous relaxation is found to be  $4\eta_h/(3K_i)$  where  $\eta_h$  is the viscosity of the host phase and  $K_i$  is the bulk modulus of the inclusion phase. If the host mineral does not relax viscously and does not fracture into pieces, the host mineral partially protects the inclusion and phase transition in the inclusion–host system is partial and spans a large  $T$ – $P$  range even for one-component systems, in contrast to sharp phase transitions under isobaric and isothermal conditions. For example, a graphite inclusion in a diamond host does not completely convert to diamond when pressure on the diamond host increases. Using the chemical potential formulation of Kamb, about 1% of graphite would convert to diamond for every 1 GPa increase in host pressure. Because the inclusion pressure may be different from the lithostatic pressure on the host, pressure obtained from thermobarometers using inclusion–host pairs may not have depth significance. Correct ‘reading’ of information stored by inclusion–host pairs requires an understanding of mechanical and phase equilibria involving the inclusion and host. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** phase equilibria; elasticity; inclusions; host rocks; P–T conditions

## 1. Introduction

Mineral, melt/glass, and fluid inclusions in a host mineral are common and have been used widely to infer mantle processes, source conditions, and  $P$ – $T$  history. When an inclusion and its host mineral form at some initial temperature and pressure re-

ferred to as  $T_0$  and  $P_0$ , the inclusion pressure may be assumed to be the same as the confining pressure acting upon the host. Subsequently when there is  $P$ – $T$  change, the pressure inside the inclusion is expected to be different from that on the host if compressibilities and thermal expansivities of the inclusion and host are different. Several pioneers have studied the mechanical and phase equilibria of inclusion–host systems. Rosenfeld and coworkers [1–5] pointed out

<sup>\*</sup> Fax: +1 313 763 4690; E-mail: youxue@umich.edu

the importance of elastic effects surrounding mineral inclusions in host minerals. They developed the null curve technique (a null curve is a  $P$ – $T$  curve on which the relative strain disappears) for the inference of  $P$ – $T$  history of the host (see also [6,7]). Gillet et al. [8] and Van der Molen and Van Roermund [9] investigated the pressure inside a mineral inclusion and used the result to model the  $P$ – $T$  history of the host rock based on coesite inclusions in garnet. Tait [10] analyzed stress field surrounding melt inclusions in minerals and applied the result to discuss the selective preservation of melt inclusions in igneous phenocrysts.

Because the host does not transmit pressure perfectly to the inclusion, the phase equilibria between the inclusion and the host can be complicated. In this work, I first examine mechanical equilibria between the host and the inclusion including both elastic and plastic effects. One case of elastic anisotropy is considered. Viscous relaxation of stress is also discussed. Finally phase equilibria between the inclusion and the host are investigated.

## 2. $P$ – $T$ history of inclusion–host systems

The temperature–pressure history for an inclusion–host pair that formed at high  $T_0$  and  $P_0$  and then is sampled on surface at 300 K and a host pressure of 1 bar can be complicated. A typical  $T$ – $P$  history for a mantle-derived inclusion–host system may be as follows.

(1) The inclusion is incorporated in the host at an initial  $P_0$  (that equals both the inclusion and host pressures) and  $T_0$ .

(2) After the formation, the temperature and host pressure may change slowly owing to mantle convection. In this process, the inclusion pressure typically becomes different from the pressure acting on the outside surface of the host and  $P_0$ .

(3) The sample may be brought up rapidly (and roughly adiabatically) to the surface by, e.g., kimberlitic eruption, so that the host pressure changes to 1 bar and the temperature does not change significantly. The inclusion pressure can be very different from 1 bar. Although the rapid ascent does not typically affect chemical equilibrium and hence does not affect thermobarometry based on chemical reac-

tions, this rapid decompression causes large pressure changes and may lead to significant deformation and to decompressional cracks. The sample may also be brought up slowly by tectonic movement along a geotherm to 300 K and a host pressure of 1 bar.

(4) Samples that are rapidly and roughly adiabatically brought up to the surface then rapidly cool down on the surface to  $\sim 300$  K.

When trying to explain features related to inclusion–host systems, it is important to bear in mind the complexity of the  $P$ – $T$  history and to understand which part of the  $P$ – $T$  history caused a given feature. Chemical reactions (especially those that involve diffusion) and viscous relaxation can only happen at high temperatures and when there is enough time. On the other hand, elastic deformation, plastic yielding, and fracturing can happen rapidly regardless of the temperature.

## 3. Elastic equilibrium between the host and the inclusion

This section presents a reanalysis of the stress field in the host mineral and the pressure in the inclusion mineral. The problem has been solved in textbooks of Southwell [11] and Timoshenko and Goodier [12], and discussed in geological literature by Gillet et al. [8], Van der Molen and Van Roermund [9], and Tait [10]. The following analysis differs from these earlier analyses in that the temperature effect is included explicitly and the non-zero initial pressure is highlighted. Small differences with the earlier analyses due to minor errors in them will be pointed out. This section only treats elastic equilibrium. Beyond-elastic processes are discussed in the next section.

### 3.1. Assumptions and general analysis for elastically isotropic inclusion and host

For simplicity, surface tension is ignored. The inclusion and the host are assumed to be concentric spheres (Fig. 1). Both phases are assumed to be elastically isotropic unless otherwise specified. A simple case of elastic anisotropy is considered later.

Following previous authors [8,9], the outer surface of the host crystal is assumed to be under uni-

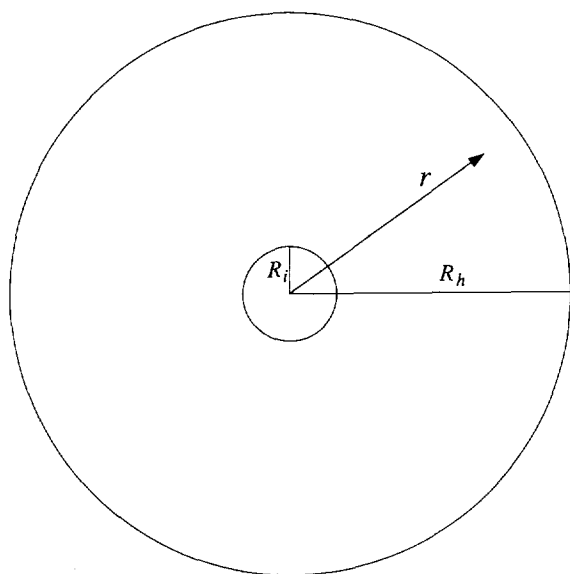


Fig. 1. A spherical inclusion at the center of a spherical host.  $R_i$  is the inclusion radius, and  $R_h$  is the host radius. Pressure in the inclusion is defined to be  $P_{in}$  and that at the outside surface of the host is defined to be  $P_{out}$ . The host and inclusion are assumed to be elastically isotropic.

form isotropic stress. That is, the stress can be represented by a single pressure  $P_{out}$ :  $\sigma_{ij}^{rr}|_{r=R_h} = -P_{out}$ . This assumption deserves some discussion since the rock is a composite material and host crystal is in contact with other elastic crystals. Observational justification for this assumption includes the pronounced birefringent halos (interpreted to be caused by differential strain in the host mineral) often observed in a host isometric mineral (such as garnet) next to an inclusion and the absence of such pronounced birefringent patterns away from the inclusions (e.g., [1]). Other justifications for the assumption can be made in the following cases.

(1) If there is an interconnected fluid phase (though the amount of the fluid may be small) in the pores of a rock, the outer surfaces of crystals will be at uniform isotropic pressure. For rocks in the subduction slab, this is probably the situation owing to dehydration and decarbonation. For other rocks, the presence of a minute amount of fluids is not uncommon either, as evidenced by metasomatism (sometimes cryptic).

(2) If most of the rock matrix has a lower viscosity than the mineral under consideration, the outer

surface of the mineral will be roughly under uniform isotropic pressure. This would apply to garnet and diamond in an olivine-dominated rock since the viscosity of olivine is low compared to that of garnet [13].

In both cases (1) and (2), the stress on the outside surface of the host mineral is expected to be isotropic and the same as the lithospheric pressure but the pressure in the inclusion can be different because the host phase partially protects the inclusion. There may be limitations to this assumption. For example, in a fluid-free rock at low temperatures, the outer surfaces of crystals may be under stress. The effect of the inclusion would be to add an additional stress field to the adjacent host. In the following discussion, nonisotropic stress on the outer surface of the host crystal is not considered.

Consider an inclusion–host system initially at  $(T_0, P_0)$  and then brought to  $(T, P_{out})$  where  $P_{out}$  is the lithostatic pressure acting upon the outer surface of the host crystal. Initially,  $P_{in,0} = P_{host,0} = P_{out,0} = P_0$ . The temperature of the inclusion is expected to be always the same as that of the host. The initial radius of the inclusion is  $R_{i0}$  and that of the host is  $R_{h0}$ , where the subscripts *i* and *h* signify the inclusion and the host, respectively. To be found are the new pressure inside the inclusion ( $P_{in}$ ), the new volume of the inclusion ( $V_i$ ), and the stress distribution in the host phase around the inclusion. The radial displacement is defined in this work as the displacement relative to the initial condition  $(T_0, P_0)$ , not relative to zero stress. Hence the initial displacement is zero. The displacement is assumed to be small and linear to  $\Delta P$ . The stress is still defined relative to zero pressure, not to the initial pressure. The general equation for the radial displacement at elastic equilibrium is [11,12]:

$$(\Delta \mathbf{u})_r = \Delta u - \frac{2}{r^2}u = \frac{d}{dr} \left( \frac{du}{dr} + \frac{2u}{r} \right) = 0 \quad (1)$$

where  $\mathbf{u}$  is the displacement vector relative to the initial state  $(T_0, P_0, R_{i0}, R_{h0})$ ,  $(\Delta \mathbf{u})_r$  is the radial component of the Laplacian of  $\mathbf{u}$ , and  $u$  is the radial component of  $\mathbf{u}$ . The solution to Eq. 1 for each of the inclusion and host phases is:

$$u = Ar + \frac{B}{r^2} \quad (2)$$

where  $A$  and  $B$  are two constants to be determined

for each of the inclusion and host phases. The radial and tangential stress in each phase can be found from:

$$\sigma^{rr} = -P_0 + 3AK - \frac{4BG}{r^3} - \gamma K \quad (3)$$

$$\sigma^{\theta\theta} = -P_0 + 3AK + \frac{2BG}{r^3} - \gamma K \quad (4)$$

where  $K$  and  $G$  are the bulk and shear modulus at  $T$  (not  $T_0$ ) and

$$\gamma = \int_{T_0}^T \alpha dT \quad (5)$$

where  $\alpha$  is the thermal expansivity. If  $\alpha$  is constant, then  $\gamma = \alpha\Delta T$ . The stress equations include the initial pressure term because the displacement is defined relative to the initial condition (instead to zero pressure), whereas the stress is defined relative to zero stress.

The above treatment incorporates the temperature dependence of the elastic constants. However,  $K$ ,  $G$ , and  $\alpha$  of the host phase (but not the inclusion phase) are assumed to be independent of pressure or stress so that linear elasticity theory can be applied. The elastic constants do not depend strongly on  $P$ . For example,  $K$  for pyrope changes by about 10% from 0 to 4 GPa [14]. (The dependence of  $K$  and  $G$  on temperature is also weak [15].) Furthermore, incorporation of the pressure effect would require much more complicated nonlinear elasticity theory.

### 3.2. Stress distribution in the inclusion and host

The solution of  $P_{in}$  (the radial stress component at the inclusion–host boundary) depends on the properties of the inclusion and whether there are reactions in the inclusion or between the inclusion and the host. To determine the radius of the inclusion and the stress distribution in the host,  $P_{in}$  is used as a parameter to be solved later. All other unknowns are expressed as a function of  $P_{in}$ .

For a solid inclusion with constant  $K_i$ , the radial displacement can be expressed as:

$$u_i = A_i r + \frac{B_i}{r^2} = A_i r, \quad \text{for } r \leq R_i \quad (6)$$

where  $B_i$  must be zero because otherwise  $u_i$  would be infinite at  $r = 0$ .  $A_i$  can be obtained from Eq. 3 using the boundary condition  $\sigma_i^{rr}|_{r=R_i} = -P_{in}$ . The

final solutions for the radial displacement and stress distribution in the inclusion are:

$$u_i = r(P_0 - P_{in} + K_i\gamma_i)/(3K_i), \quad \text{for } r \leq R_i \quad (7)$$

$$\sigma_i^{rr} = \sigma_i^{\theta\theta} = -P_{in}, \quad \text{for } r < R_i \quad (8)$$

That is, the stress inside the spherical and elastically isotropic inclusion is uniform and isotropic. The shear modulus of the inclusion phase does not play a role in determining the radial displacement and pressure in the inclusion. Defining  $R_i^*$  to be the radius of the inclusion when  $P_{in} = P_{out}$  at  $T$ ,  $R_i^*$  can be found by letting  $P_{in} = P_{out}$  in Eq. 7. It can be found that

$$\frac{R_i - R_{i0}}{R_{i0}} = \frac{u_i}{R_{i0}} \Big|_{r=R_i} = \frac{\gamma_i}{3} - \frac{P_{in} - P_0}{3K_i} \quad (9a)$$

and

$$\frac{R_i - R_i^*}{R_i} = \frac{u_i - u_i^*}{r} \Big|_{r=R_i} = \frac{P_{in} - P_{out}}{3K_i} \quad (9b)$$

For a liquid or gas inclusion, clearly Eq. 8 is valid. Eqs. 9a and 9b are valid for a liquid inclusion with constant  $K_i$ . For a gas inclusion, Eqs. 9a and 9b do not apply because  $K_i$  depends on  $P$ . For an ideal gas inclusion, using its equation of state ( $P_{in}V_i/T = P_0V_{i0}/T_0$ ), the volume (or radius) change of the inclusion is easy to obtain:

$$\frac{\Delta V_i}{V_{i0}} = \frac{V_i}{V_{i0}} - 1 = \frac{P_0 T}{P_{in} T_0} - 1 \approx \frac{3(R_i - R_{i0})}{R_{i0}} \quad (10)$$

For the host phase, the radial displacement  $u_h$  is given by Eq. 2 where  $A_h$  and  $B_h$  are two constants to be solved from Eq. 3 and the following boundary conditions:

$$\sigma_h^{rr}|_{r=R_i} = -P_{in}, \quad \text{and} \quad \sigma_h^{rr}|_{r=R_h} = -P_{out} \quad (11)$$

The solutions for  $A_h$  and  $B_h$  are:

$$A_h = \frac{1}{3K_h} \left[ \frac{(P_{in} - P_{out})}{1-x} - (P_{in} - P_0) + K_h\gamma_h \right] \quad (12)$$

$$B_h = \frac{(P_{in} - P_{out})}{4G_h(1-x)} R_i^3 \quad (13)$$

where  $x = R_i^3/R_h^3 \approx R_{i0}^3/R_{h0}^3$ . Replacing  $A_h$  and  $B_h$  into Eqs. 2–4 leads to:

$$u_h = \frac{r}{3K_h} \left[ \frac{(P_{in} - P_{out})}{1-x} + K_h\gamma_h + (P_0 - P_{in}) \right] + \frac{(P_{in} - P_{out})R_i^3}{4G_h(1-x)r^2}, \quad \text{for } R_i \leq r \leq R_h \quad (14)$$

$$\sigma_h^{rr} = \left[ \frac{(P_{in} - P_{out})}{1 - x} - P_{in} \right] - \frac{(P_{in} - P_{out})R_i^3}{(1 - x)r^3},$$

for  $R_i \leq r \leq R_h$  (15)

$$\sigma_h^{rr} = \left[ \frac{(P_{in} - P_{out})}{1 - x} - P_{in} \right] + \frac{(P_{in} - P_{out})R_i^3}{2(1 - x)r^3},$$

for  $R_i \leq r \leq R_h$  (16)

and

$$\begin{aligned} \frac{\Delta V_i}{V_{i0}} &\approx \frac{3u_h}{R_{i0}} \Big|_{r=R_i} \\ &= \frac{1}{K_h} \left[ P_0 - P_{in} + \frac{(P_{in} - P_{out})}{1 - x} + K_h \gamma_h \right] \\ &\quad + \frac{3(P_{in} - P_{out})}{4G_h(1 - x)} \end{aligned} \quad (17)$$

Therefore, the stress in the spherical and elastically isotropic host is neither uniform nor isotropic. There is deviatoric stress that changes with  $r$ . If  $P_{in}$  is known,  $\Delta V_i/V_{i0}$  can be calculated using Eq. 17. Comparing Eq. 17 (by letting  $\Delta T = 0$ ) with eq. 6 of Tait [10] reveals errors in his eq. 6. The difference between the right-hand side of Eq. 17 above and that of Tait's eq. 6 is  $(P_0 - P_{out})/K_h$ . This difference arises because Tait did not correctly account for the reference state of zero deformation.

Eq. 15 can be rewritten as:

$$\begin{aligned} \frac{\Delta V_i}{V_{i0}} &\approx \frac{P_0 - P_{out}}{K_h} + \gamma_h \\ &\quad + \frac{(P_{in} - P_{out})}{1 - x} \left[ \frac{x}{K_h} + \frac{3}{4G_h} \right] \end{aligned} \quad (18)$$

Comparing the above equation of relative change of inclusion volume with that of host volume without the inclusion:

$$\frac{\Delta V_h}{V_{h0}} \approx \frac{P_0 - P_{out}}{K_h} + \gamma_h \quad (19)$$

it can be seen that when  $x$  is small,  $\Delta V_i/V_{i0} - \Delta V_h/V_{h0}$  by  $0.75(P_{in} - P_{out})/G_h$ .

### 3.3. Inclusion pressure for several simple cases

To completely determine the stress and strain distribution,  $P_{in}$  must be determined. The method of solution for  $P_{in}$  depends on whether the inclusion is a void (vacuum), an ideal gas, a condensable fluid, or

a mineral. It also depends on whether there are phase transitions or reactions inside the inclusion [8–10] or reactions between the inclusion and the host. Several simple cases are discussed below and cases involving reactions and phase transitions will be discussed in later sections.

(1) If the inclusion is a vacuum (void, or cavity), the initial equilibrium pressure  $P_0$  must be zero. The inclusion pressure  $P_{in}$  is always zero. If  $P_{out}$  is given, the radial displacement, inclusion volume and the stress field can be calculated using Eqs. 14–16. Heating up the host mineral at zero pressure, the inclusion volume expands exactly the same way as the host and the stress in the host adjacent to the inclusion is zero. Pressurizing the host isothermally, the void volume decreases and there is a stress field in the host adjacent to the void.

(2) If an ideal gas is included, combining Eq. 10, Eq. 14 at  $r = R_i$ , and the equation  $u_i|_{r=R_i} = u_h|_{r=R_i}$  (this displacement continuity equation has a simple form because  $u$  is defined as displacement relative to the initial condition instead of the zero stress), and after some manipulation,  $P_{in}/P_0$  satisfies and can be obtained from:

$$\begin{aligned} &\left[ \frac{xP_0}{(1 - x)K_h} + \frac{3P_0}{4(1 - x)G_h} \right] \left( \frac{P_{in}}{P_0} \right)^2 \\ &\quad + \left[ 1 + \gamma_h + \frac{P_0}{K_h} - \frac{P_{out}}{1 - x} \left( \frac{1}{K_h} + \frac{3}{4G_h} \right) \right] \frac{P_{in}}{P_0} \\ &\quad - \frac{T}{T_0} = 0 \end{aligned} \quad (20)$$

(3) For a solid or liquid inclusion with no phase change and no reaction with the host, combining Eq. 7, Eq. 14 at  $r = R_i$ , and  $u_i|_{r=R_i} = u_h|_{r=R_i}$  leads to:

$$\begin{aligned} &\frac{P_0 - P_{in} + K_i \gamma_i}{K_i} = \\ &\quad \frac{1}{K_h} \left[ \frac{(P_{in} - P_{out})}{1 - x} + K_h \gamma_h + (P_0 - P_{in}) \right] \\ &\quad + \frac{3(P_{in} - P_{out})}{4G_h(1 - x)} \end{aligned} \quad (21)$$

Knowing inclusion and host properties,  $P_0$ , and  $P_{out}$ , Eq. 21 can be used to obtain  $P_{in}$ . The dependence of  $P_{in}$  on the inclusion size is weak as long as the inclusion is small. If the inclusion and the host are of the same phase (i.e., if part of the host

is considered as an inclusion), then  $K_i = K_h$  and  $\gamma_i = \gamma_h$  in the above equation. Hence,  $P_{in} = P_{out}$  and the whole mineral is under uniform isotropic pressure of  $P_{out}$  according to the above equation, as expected. If there are several inclusions (they may be fluid inclusions or solid inclusions) in the same host,  $P_{in}$  in the inclusions would be the same as long as the inclusions are far away from each other and have the same  $K_i$  and  $\alpha_i$ .

Eqs. 20 and 21 can also be used to estimate the equilibrium pressure  $P_0$  knowing  $P_{in}$ ,  $P_{out}$ , and  $\Delta T$ . If initially  $P_{in,0} \neq P_{out,0}$ , then a variation of Eq. 21 is:

$$P_{in} = \left\{ (P_{in,0} - P_{out,0} + P_{out}) \left[ \frac{1}{K_h} + \frac{3}{4G_h} \right] + (1-x) \left[ P_{in,0} \left( \frac{1}{K_i} - \frac{1}{K_h} \right) + (\gamma_i - \gamma_h) \right] \right\} \times \left[ \frac{1-x}{K_i} + \frac{3}{4G_h} + \frac{x}{K_h} \right]^{-1} \quad (22)$$

If  $x \rightarrow 0$  and only  $T$  changed (i.e.,  $P_0 = P_{out}$ ), combining Eqs. 9a and 21 leads to:

$$R_i = R_{i0} \left[ 1 + \frac{\gamma_h}{3} + \frac{(\gamma_i - \gamma_h)}{3 + 4G_h/K_i} \right] \quad (23)$$

Comparing the above equation with the equation of Gillet et al. ([8], p. 435) for inclusion radius change due to temperature variation  $R_i = R_{i0}[\exp(\gamma_h)]^{1/3}$  reveals a small error in their simplistic treatment of the temperature effect. For example, for a diamond inclusion in garnet at  $P_0 = P_{out}$ , if  $T_0 = 1400$  K and  $T = 1000$  K, the calculated inclusion volume change is 0.7% using Eq. 23 but would be 1.2% using the simple treatment of Ref. [8].

### 3.4. Calculated stress distribution

Fig. 2a shows calculated stress field for a pyrope inclusion in a diamond host with  $P_0 = 5$  GPa,  $P_{out} = 7$  GPa, and  $\Delta T = 20$  K. The example is chosen because both phases are fairly isotropic. When the pressure on the outer surface of the host (i.e., the lithostatic pressure) is 7 GPa, the pressure inside the inclusion is only 6.06 GPa, lower than the lithostatic pressure by 0.94 GPa (9.4 kbar)! Under other conditions, the pressure difference can be even greater. The inclusion pressure hence may not be interpreted in terms of a depth by simply assuming

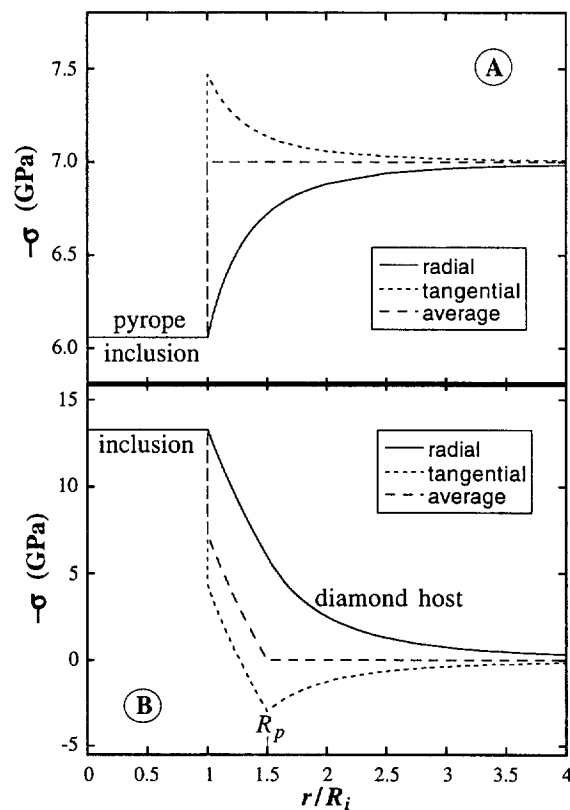


Fig. 2. Calculated radial and tangential stress in diamond host. (A) Stress distribution in a pyrope inclusion ( $r/R_i < 1$ ) and diamond host ( $r/R_i > 1$ ) for the elastic case. The elastic properties are:  $\alpha_h = 1.65 \times 10^{-5} \text{ K}^{-1}$ ,  $K_h = 444 \text{ GPa}$ ,  $G_h = 536 \text{ GPa}$ ,  $\alpha_i = 3.13 \times 10^{-5} \text{ K}^{-1}$ ,  $K_i = 173 \text{ GPa}$  [19,34,35]. Initial conditions:  $T_0 = 1400 \text{ K}$ ,  $P_0 = 5 \text{ GPa}$ ,  $R_{i0} = 0.01 \text{ mm}$ ,  $R_{h0} = 1 \text{ mm}$ . Then the host phase is brought along the geotherm (10 K/GPa) to  $P_{out} = 7 \text{ GPa}$  and  $T = 1420 \text{ K}$ . New  $P_{in}$  and  $R_i$  are calculated to be 6.058 GPa and  $0.998 R_{i0}$ . (B) Stress distribution in an unspecified inclusion (hence  $K_i$  is not known and  $P_{in}$  must be specified) and diamond host including both plastic ( $1 \leq r/R_i \leq 1.5$ ) and elastic ( $r/R_i \geq 1.5$ ) regions.  $T = T_0$ ,  $\gamma_h = 9 \text{ GPa}$  [36],  $K_i = 173 \text{ GPa}$ ,  $R_p/R_i = 1.5$ ,  $R_h/R_i = 100$ ,  $P_{out} = 0 \text{ GPa}$ , and  $P_{in} = 13.3 \text{ GPa}$ .

lithostatic pressure for the inclusion. The radial stress in the host changes continuously from  $-P_{in}$  to  $-P_{out}$ , whereas the tangential stress is discontinuous at the inclusion–host interface. The tangential stress and the radial stress are different in the host adjacent to the inclusion. That is, there is deviatoric stress. The difference between the tangential and radial stresses may cause plastic deformation or failure of the host mineral [16], to be discussed in the next section.

The length scale over which the radial and tangential stresses vary is about the same as the radius of the inclusion. More precisely, for small  $x$  (the volume fraction of the inclusion),  $|\sigma_h^{rr} + P_{out}|$  and  $|\sigma_h^{t\theta} + P_{out}|$  decreases to 1/2 of the corresponding value at the interface when  $r - R_i = 0.26R_i$ , and to 1/8 of the value at the interface when  $r - R_i = R_i$ . The ‘mean host pressure’ is defined as:

$$-\frac{(\sigma_h^{rr} + 2\sigma_h^{t\theta})}{3} = \frac{(P_{out} - xP_{in})}{(1-x)} \approx P_{out} \quad (24)$$

which is a constant throughout the host phase. The approximation in the above equation is valid if  $x$  is small. The density of the host phase is independent of  $r$  despite the stress field, and corresponds to a density at  $P = P_{out}$ .

### 3.5. A simple case of elastic anisotropy

The assumption of elastic isotropy for the host mineral is important for simple solutions to be obtained and is often employed [8–12], but, to my knowledge, its accuracy has never been examined before. Recently, Schmidt et al. [17] carried out experiments to examine the variation of volume and pressure of an H<sub>2</sub>O fluid inclusion in quartz as a function of temperature and pressure (I.-M. Chou, pers. commun.). The pressure inside the inclusion is determined by observing the complete disappearance of the vapor phase in a vapor–liquid inclusion by varying the temperature at a given host pressure. The pressure in the inclusion is the saturation pressure at the given temperature. They found that for an initial condition of  $P_{out,0} = 0.1$  MPa and  $P_{in,0} = 2.45$  MPa at  $T_0 = 222.9^\circ\text{C}$ ,  $P_{in} = 1.91$  MPa when  $P_{out} = 253.5$  MPa and  $T = 210^\circ\text{C}$ . Since the mass of H<sub>2</sub>O in the inclusion is conserved (ignoring water diffusion into quartz at such low temperatures), the percentage of volume variation of the inclusion can be calculated to be about  $-2.0\%$  using the liquid molar volume variation along the saturation curve. Without considering the elastic effects, the volume variation of quartz itself is only  $-0.7\%$ , not enough to account for the inclusion volume decrease. Using Eq. 17 but accounting for the initial difference in  $P_{in,0}$  and  $P_{out,0}$ , the calculated inclusion volume variation is  $-1.2\%$  when elastic effects are considered assuming elastic isotropy for quartz. The agreement with the

observed  $-2.0\%$  variation is better, demonstrating that considering elastic effects is in the right direction. However, the agreement with the observation is still not good, suggesting that elastic anisotropy of quartz may have to be considered. Love [18] gave a solution for a spherical inclusion in an elastically anisotropic solid with transverse isotropy about the radius vector. Even though quartz does not even possess transverse isotropy, this solution is expected to approximate the elastic properties of quartz better than simple elastic isotropy. After incorporating the temperature and non-zero initial pressure effects, the solution for the volume variation of a spherical inclusion (eq. 30 in [18], p. 165) can be rewritten as:

$$\begin{aligned} \frac{\Delta V_i}{V_{i0}} &= \frac{P_0}{K_h} + \alpha_h(\Delta T) + \frac{3}{(1-x')y'} \\ &\times \left[ \frac{P_{in}x'y' - P_{out}}{(n-0.5)C_{33} + 2C_{13}} + \frac{P_{in}y' - P_{out}}{(n+0.5)C_{33} - 2C_{13}} \right] \end{aligned} \quad (25)$$

where  $C_{ij}$ ’s are elastic constants [19],  $n = 0.5[1 + 8(C_{11} + C_{12} - C_{13}/C_{33})^{1/2}]$  ( $n = 1.5$  for cubic minerals but  $1.33$  for quartz),  $x' = (R_i/R_h)^{2n}$ , and  $y' = (R_i/R_h)^{1.5-n}$ . Using the above equation, the calculated inclusion volume variation is  $-1.8\%$ , in good agreement with observed  $-2.0\%$ . Therefore, for accurate treatment of the elastic effects involving an elastically anisotropic host, anisotropy must be incorporated. Because solutions for elastically anisotropic materials are few and complex (e.g. [18]), the following discussion still assumes elastic isotropy.

## 4. Beyond elasticity

The difference in  $P_{in}$  and  $P_{out}$  may lead to beyond-elasticity changes, including (1) viscous relaxation of the stress when the time scale under consideration is long, or (2) plastic deformation and fracture when  $|P_{in} - P_{out}|$  and the deviatoric stress increases on a short time scale. Following mechanical engineering literature [16], in this work ‘plastic deformation’ means plastic yield when the deviatoric stress exceeds the elastic limit and does not mean plastic flow. Plastic yielding does not relax the stress but does limit the deviatoric stress. Viscous relaxation

means viscous flow that relaxes stress. The result of viscous relaxation is for  $P_{in}$  to become the same as  $P_{out}$  and for the stress field around the inclusion to become simply the fluidstatic pressure of  $P_{out}$ . This section briefly treats these possibilities.

#### 4.1. Stress relaxation due to viscous flow

When  $P_{in} \neq P_{out}$  and there is a stress distribution in an inclusion, Tait [10] solved the viscous flow velocity  $\dot{R}_i = (P_{in} - P_{out})R_i/(4\eta_h)$  near the inclusion–host boundary by assuming (1) that the host is an incompressible Newtonian fluid that flows radially, and (2) that the host is much more viscous than the inclusion. Using the velocity, he assumed that the characteristic time scale for viscous relaxation is  $R_i/\dot{R}_i$  and found the relaxation time scale to be  $4\eta_h/(P_{in} - P_{out})$ . This relaxation time scale is in error because particles in the host phase around the inclusion do not have to flow a distance of  $R_i$  to release the stress; instead, particles only have to move such a distance that the volume of the inclusion changes from that corresponding to  $P_{in}$  to that corresponding to  $P_{out}$ . This distance is  $\Delta R_i = R_i^* - R_i = (P_{in} - P_{out})R_i/(3K_i)$  (Eq. 9b) for a solid or liquid inclusion with constant  $K_i$  (assuming  $\Delta R_i/R_i \ll 1$ ). Hence the relaxation time scale for the inclusion–host system is:

$$\tau_h = \Delta R_i/\dot{R}_i = 4\eta_h/(3K_i) \quad (26)$$

Compared with the viscous relaxation time scale of the host phase without the presence of inclusions, the Maxwell relaxation time scale  $\eta_h/G_h$  [20], the relaxation time scale for the inclusion–host system is  $4G_h/3K_i$  times that of the host alone.

If the inclusion is an ideal gas, the inclusion volume must change from  $V_i$  to  $V_i(P_{in}/P_{out})$  for it to relax to  $P_{out}$ . The radius change is  $\Delta R_i = R_i[(P_{in}/P_{out})^{1/3} - 1]$ . Hence, the relaxation time scale is:

$$\tau = \frac{\Delta R_i}{\dot{R}_i} = \frac{4\eta_h[(P_{in}/P_{out})^{1/3} - 1]}{P_{in} - P_{out}} \quad (27)$$

For a typical upper mantle mineral olivine at  $\sim 1600$  K with a viscosity of  $10^{21}$  Pa s (e.g. [21]) and a typical solid inclusion bulk modulus of  $\sim 10^{11}$  Pa at 1600 K [22], the relaxation time scale is  $10^{10}$  s  $\approx 400$  years, a short time geologically. Hence the

stress in an olivine crystal that contains inclusions is expected to be lithostatic in much of the upper mantle with normal temperatures. However, if a mantle xenolith is brought up rapidly by volcanic eruption, there would not be enough time for stress relaxation [10] and there will be anisotropic stress in an inclusion-bearing olivine crystal due to rapid decompression. This stress field should not be confused with the stress field in the mantle.

Mineral viscosity increases rapidly with decreasing temperature. For example, Karato [13] estimated that at 700°C, mantle mineral viscosity is  $\sim 10^{32}$  Pa s. At such a viscosity, the stress relaxation time scale would be  $4 \times 10^{13}$  years, 4 orders of magnitude greater than the age of the earth. Hence under such low temperatures, anisotropic stress would be common if there are inclusions in a mineral. For diamond, garnet and many other minerals, the viscosity is not well-known but presumably very high [13]. Hence viscous relaxation for inclusions in these minerals is often negligible.

#### 4.2. Plastic deformation

The development in this subsection follows that of Hill [16]. There are two commonly used criteria of plastic yield for a solid: the Tresca criterion and the von Mises condition (e.g. [16]). The two yield criteria do not differ much (a few percent) and ease of application is often the deciding factor in choosing a yield function. Using the Tresca criterion, plastic deformation occurs when  $|\sigma_h^{rr} - \sigma_h^{tt}| \geq Y_h$  where  $Y_h$  is the yield strength of the host mineral. Plastic deformation limits  $|\sigma_h^{rr} - \sigma_h^{tt}|$  to be  $Y_h$ . Since  $|\sigma_h^{rr} - \sigma_h^{tt}|$  is greatest at the interface between the inclusion and host, plastic deformation begins when

$$|\sigma_h^{rr} - \sigma_h^{tt}|_{r=R_i} = \frac{3|P_{in} - P_{out}|}{2(1-x)} = Y_h \quad (28)$$

The first equality in the above equation is obtained from Eqs. 15 and 16. As  $|P_{in} - P_{out}|$  increases further,  $|\sigma_h^{rr} - \sigma_h^{tt}|$  is still  $Y_h$  but it no longer equals  $1.5|P_{in} - P_{out}|/(1-x)$ . The plastic yield region expands at the expense of the elastic region. Define  $R_p(\leq R_h)$  to be the elastic–plastic boundary such that the region  $R_i < r < R_p$  undergoes plastic deformation and the region  $R_p < r < R_h$  undergoes elastic deformation. In the elastic region ( $R_p \leq r \leq R_h$ ), Eqs. 3 and 4

apply in which the constants  $A$  and  $B$  can be solved using the following two boundary conditions:

$$\sigma_h^{rr}|_{r=R_h} = -P_{\text{out}} \quad (29)$$

$$(\sigma_h^{tt} - \sigma_h^{rr})|_{r=R_p} = \delta Y_h \quad (30)$$

where  $\delta = \text{sign}(P_{\text{in}} - P_{\text{out}})$  that equals 1 when  $P_{\text{in}} - P_{\text{out}} > 0$ , and equals  $-1$  when  $P_{\text{in}} - P_{\text{out}} < 0$ . Obtaining  $A$  and  $B$ , and letting  $y = (R_p/R_h)^3$ , then:

$$\sigma_h^{rr} = -P_{\text{out}} - \frac{2\delta Y_h}{3} \left( \frac{R_p^3}{r^3} - y \right), \quad R_p \leq r \leq R_h \quad (31)$$

$$\sigma_h^{rr} = -P_{\text{out}} + \frac{2\delta Y_h}{3} \left( \frac{R_p^3}{2r^3} + Y \right), \quad R_p \leq r \leq R_h \quad (32)$$

In the plastic region ( $R_i \leq r \leq R_p$ ), the condition that  $\sigma_h^{tt} - \sigma_h^{rr} = \delta Y_h$  leads to:

$$\frac{\partial \sigma_h^{rr}}{\partial r} = \frac{2(\sigma_h^{tt} - \sigma_h^{rr})}{r} = \frac{\delta 2Y_h}{r} \quad (33)$$

Solving the above equation,

$$\sigma_h^{rr} = 2\delta Y_h \ln r + C_h \quad (34)$$

where  $C_h$  is a constant that can be determined from the boundary condition (continuity for  $\sigma_h^{rr}$ )  $\sigma_h^{rr}|_{r=R_p-0} = \sigma_h^{rr}|_{r=R_p+0}$ :

$$2\delta Y_h \ln R_p + C_h = -P_{\text{out}} - \frac{2\delta Y_h}{3}(1 - y) \quad (35)$$

Obtaining  $C_h$  leads to:

$$\sigma_h^{rr} = 2\delta Y_h \ln \frac{r}{R_p} - \frac{2\delta}{3} Y_h (1 - y) - P_{\text{out}}, \quad R_i \leq r \leq R_p \quad (36)$$

$$\sigma_h^{tt} = 2\delta Y_h \ln \frac{r}{R_p} - \frac{2\delta}{3} Y_h (1 - y) + \sigma Y_h - P_{\text{out}}, \quad R_i \leq r \leq R_p \quad (37)$$

Fig. 2b shows a calculated case for stress distribution in diamond next to an unspecified inclusion when both plastic and elastic deformations are present. In the region  $R_p \leq r \leq R_h$ , the stress distribution is elastic with ‘mean pressure’ identical to  $P_{\text{out}}$ . In the region  $R_i \leq r \leq R_p$ , the stress distribution is plastic with ‘mean pressure’ increases toward the inner surface.

Elastic strain disappears after removal of stress. Hence elastic strain depends only on the current stress state, and is independent of the elastic stress/strain history. However, if plastic deformation occurs, residual strain remains after removal of stress. Hence the exact strain state depends not only on the present stress state but also on the plastic stress/strain history of the solid. This complexity makes the strain–stress relation, and the analytical solution for the strain almost impossible to treat for complex stress history involving plastic deformation. The above solutions of the elastic and plastic problems apply only when there was no prior residual strain (that is, no prior plastic deformation).

#### 4.3. Fractures

Fractures develop when the stress intensity factor or the crack extension force exceeds a critical value [23]. Because an isotropic spherical inclusion is under isotropic stress but the host next to the inclusion is under deviatoric stress, fractures are expected to develop in the host under the right conditions, but not the inclusion. When the inclusion is not spherical, stress is concentrated at sharp corners. Hence fractures more often develop from these sharp corners. Fractures in the host phase radiating from the inclusion are often observed, e.g., [8]. In many cases, these fractures are decompressional cracks.

In studying inclusions in garnet crystals brought up by ultramafic diatremes from the Four Corners area, it was found (Wang, Ph.D. thesis, in prep.) that radiating fractures in the garnet host often develop around composite inclusions (consisting of carbonate, amphibole, mica, etc.), pyroxenes, and olivine, but not around spinel or rutile inclusions. That is, fractures develop when  $K_i < K_h$  but not when  $K_i > K_h$ . Because radiating cracks form when  $P_{\text{in}} > P_{\text{out}}$ , that the cracks occur only when  $K_i < K_h$  means that  $P_{\text{out}} < P_0$ . Hence these are decompressional cracks. Furthermore, calculations show that the decompression is roughly adiabatic or isothermal. If the decompression is accompanied by temperature decrease along a typical geotherm (such as slow upward tectonic motion due to obduction), calculations show that the pressure and temperature effects would roughly cancel out for an olivine inclusion in garnet host so that  $P_{\text{in}}$  would be roughly the

same as  $P_{\text{out}}$  and there would be no radiating cracks. (For other inclusions such as pyroxene inclusion, the pressure and temperature effects do not cancel out.) This example shows that it is possible to infer from the presence of decompressional cracks that the garnet host decompressed rapidly and roughly isothermally. Of course, it is already known from field relations that the garnet crystals were brought up rapidly by ultramafic diatremes. The investigation of the cracks confirms this understanding and also shows the potential to constrain whether the ascent is rapid or slow by understanding the formation of cracks.

### 5. Phase equilibria and reactions in inclusions: graphite inclusion in diamond

If the inclusion can react with the host or undergo a phase transition, the extent of the reaction or phase transition, the inclusion pressure, and the stress field in the host affect one another. In this section, the case of a graphite inclusion in a diamond host is considered. For simplicity, only elastic deformation is considered, diamond and graphite are assumed elastically isotropic, and graphite inclusion is assumed to be spherical. Suppose that initially in a subducting slab there is some graphite. When the pressure is high enough, diamond grows from graphite. In this process, a piece of graphite is included in a diamond crystal at a  $T$ – $P$  condition that roughly corresponds to graphite–diamond equilibrium. The diamond crystal then goes to greater pressure with the subducting slab. As long as the host diamond crystal maintains its integrity, the graphite inclusion cannot completely change into diamond. Otherwise, the inclusion would occupy much less volume (due to the higher density of diamond) and there would be free space in the inclusion. That would mean a zero pressure in the inclusion and hence the conversion of diamond back to graphite. That is, the graphite inclusion cannot completely convert to diamond even when  $(T, P_{\text{out}})$  is well into the stability field of diamond, contrary to what one may expect. Hence, the graphite–diamond two-phase equilibrium at the inclusion–host boundary controls the pressure in the inclusion.

Unfortunately, the chemical potential of a stressed solid is still under debate. For example, Kamb [24] avoided using the term ‘the chemical potential of a

stressed solid’, and derived that the chemical potential of the component of the solid dissolved in a fluid (not of the component in the solid itself) that is in contact with surface  $k$  of the solid is:

$$\mu_k = \mu^0 + P_k \bar{V} + w \bar{V}_0 \quad (38)$$

where  $\mu^0$  is the chemical potential of the component in the solid under zero stress ( $P = 0$ ),  $P_k$  is the fluid pressure applied normal to the solid surface  $k$  and  $P_{\text{in}}$  for diamond host next to a graphite inclusion,  $\bar{V}$  and  $\bar{V}_0$  are the molar volume and unstressed molar volume, and  $w$  is the strain energy density ( $w = 0.5 \sum \sigma_{ij} e_{ij}$  with  $\sigma_{ij}$  and  $e_{ij}$  being the components of the stress and strain tensors). For fluidstatic pressure  $P$ , Eq. 38 reduces to  $\mu = \mu^0 + P \bar{V} + 0.5 P (\bar{V}_0 - \bar{V}) = \mu^0 + P (\bar{V}_0 + \bar{V})/2$ . That is,  $w \bar{V} \sim 0.5 P (\bar{V}_0 - \bar{V})$  and is typically a small term (because  $e_{ij}$ ’s are  $\ll 1$ ). Hence, to a first order approximation,  $\mu_k = \mu^0 + P_k \bar{V}$ . For a graphite inclusion in a diamond host,  $\mu_{\text{C}}^{\text{dia}}|_{r=R_i} \approx \mu_{\text{C}}^{\text{dia},0} + P_{\text{in}} \bar{V}_{\text{C}}^{\text{dia}}$ . Because carbon chemical potential in graphite also depends on  $P_{\text{in}}$  as  $\mu_{\text{C}}^{\text{gra}} = \mu_{\text{C}}^{\text{gra},0} + P_{\text{in}} \bar{V}_{\text{C}}^{\text{dia}}$ , the phase equilibrium at the inclusion–host boundary can be roughly treated as isobaric equilibrium. Therefore,  $P_{\text{in}}$  can be calculated simply from the isobaric phase equilibrium between graphite and diamond. This  $P_{\text{in}}$  depends only on  $T$  but not on  $P_{\text{out}}$ . When  $P_{\text{in}} \neq P_{\text{out}}$ , the chemical potential of carbon on the outer surface of the diamond host would be different from that in the inclusion. Therefore, the whole inclusion–host system is not in chemical equilibrium even when the inclusion and the adjacent host are in equilibrium.

Bartholomeusz [25], however, argued that the derivations of Kamb [24] and other similar derivations overlooked energy changes associated with maintaining fluid pressure. Because Bartholomeusz did not provide an explicit simple formula for the chemical potential, application of his theory would require second-guessing. Therefore, the treatment of Kamb [24] is used in the following discussion.

Consider a graphite inclusion in diamond host formed at  $(T_0 = 1497.15 \text{ K}, P_0 = 5 \text{ GPa})$ . The phase boundary is at  $P = 1.94 + (T - 273.15)/400$  [26]. If the inclusion–host system is brought isothermally to a  $P_{\text{out}} = 8 \text{ GPa}$ , the inclusion pressure would be 6.44 GPa if there was no phase transition. However, if phase equilibrium at the inclusion–host boundary is reached,  $P_{\text{in}}$  depends simply on  $T$  and stays at 5

GPa. If the same inclusion–host system is brought instead along a geotherm of 10 K/GPa to 1527.15 K and  $P_{\text{out}} = 8$  GPa,  $P_{\text{in}}$  would change to 6.50 GPa without a phase transition but only change by 0.075 GPa to 5.075 GPa if phase equilibrium at the inclusion–host boundary is reached. Because mechanical equilibrium is reached rapidly but phase transition can be slow, the actual  $P_{\text{in}}$  at a given instant may lie between 6.50 and 5.075 GPa.

Knowing  $P_{\text{in}}$ , it is possible to calculate stress distribution, radial displacements, and volume of the inclusion. Since diamond and graphite interconvert, the mass of graphite in the inclusion is not necessarily the same as the initial mass. To avoid confusion, I define two inclusion volumes: one is the volume associated with the initial graphite mass, the virtual inclusion volume  $V_{\text{vi}}$  (or radius  $R_{\text{vi}}$ ); the other is the actual volume of the graphite inclusion  $V_{\text{ai}}$  (or radius  $R_{\text{ai}}$ ). The solutions for radial displacements become:

$$u_i = \frac{r(P_0 - P_{\text{in}} + K_i \gamma_i)}{3K_i}, \quad \text{for } r \leq R_{\text{ai}} \quad (39)$$

$$u_h = \frac{r}{3K_h} \left[ \frac{(P_{\text{in}} - P_{\text{out}})}{1 - x} + K_h \gamma_h + (P_0 - P_{\text{in}}) \right] + \frac{(P_{\text{in}} - P_{\text{out}}) R_i^3}{4G_h(1 - x)r^2}, \quad \text{for } R_{\text{vi}} \leq r \leq R_h \quad (40)$$

Using Eq. 39 at  $r = R_{\text{ai}}$  and Eq. 40 at  $r = R_{\text{vi}}$  leads to:

$$\frac{u_i}{R_{\text{ai}}} \Big|_{r=R_{\text{ai}}} = 1 - \frac{F^{1/3} R_{i0}}{R_{\text{ai}}} = \frac{P_0 - P_{\text{in}} + K_i \gamma_i}{3K_i} \quad (41)$$

$$1 - \frac{R_{i0}}{R_{\text{vi}}} = \frac{1}{3K_h} \left( P_0 - P_{\text{in}} + \frac{P_{\text{in}} - P_{\text{out}}}{1 - x} + K_h \gamma_h \right) + \frac{P_{\text{in}} - P_{\text{out}}}{4G_h(1 - x)} \left( \frac{R_{\text{ai}}}{R_{\text{vi}}} \right)^3 \quad (42)$$

where  $F (= M_{\text{ai}}/M_{i0})$  is the mass fraction of graphite still remaining in the inclusion (if  $F > 1$ , then some diamond transformed into graphite) and can be related to other parameters as:

$$\left( \frac{R_{\text{vi}}}{R_{i0}} \right)^3 = F \frac{\bar{V}_{\text{i,gr}}}{\bar{V}_{i0,\text{gr}}} + (1 - F) \frac{\bar{V}_{\text{vi,dia}}}{\bar{V}_{i0,\text{gr}}} \quad (43)$$

$F$ ,  $R_{\text{ai}}$  and  $R_{\text{vi}}$  can be solved simultaneously from Eqs. 41–43 using  $P_{\text{in}}$  from phase equilibrium constraint. A numerical example is given in Fig. 3,

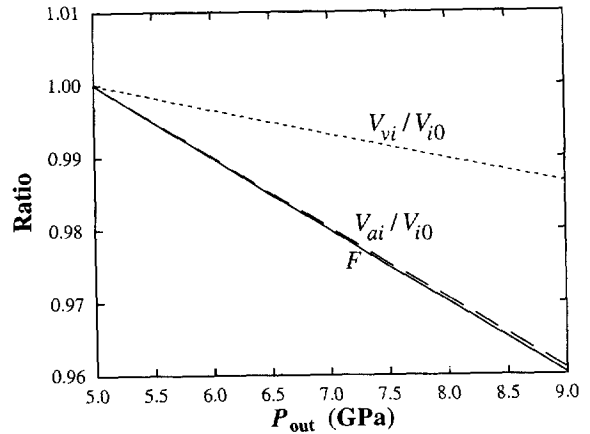


Fig. 3. Calculated mass and volume ratios of graphite in the inclusion as a function of  $P_{\text{out}}$ .  $T_0 = 1497$  K,  $P_0 = 5$  GPa,  $R_{i0} = 0.01$  mm,  $R_{h0} = 1$  mm. The host diamond is brought along the geotherm (10 K/GPa) to greater pressures.  $\alpha_h = 1.86 \times 10^{-5}$  K $^{-1}$ ,  $K_h = 444$  GPa,  $G_h = 536$  GPa,  $\alpha_i = 3.24 \times 10^{-5}$  K $^{-1}$ ,  $K_i = 161$  GPa [19,34,35]. Mass ratio ( $F$ ) variation with  $P_{\text{out}}$  is shown as the solid line. Shown are also the variations of virtual and actual inclusion volumes relative to the initial inclusion volume (short and long dashed lines). The calculations are based on Kamb's formulation of the chemical potential.

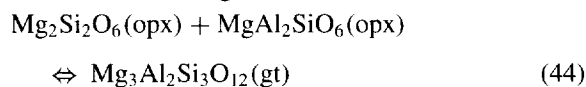
which shows how  $F = M_{\text{ai}}/M_{i0}$ ,  $V_{\text{ai}}$  and  $V_{\text{vi}}$  vary as a function of  $P_{\text{out}}$ . At  $P_{\text{out}} = 9$  GPa, the mass of graphite inclusion has decreased by only 4%. During the phase transition process,  $P_{\text{in}}$  is not known, but  $P_{\text{in}}$ ,  $R_{\text{ai}}$  and  $R_{\text{vi}}$  can be solved simultaneously from Eqs. 41–43 from the extent of phase transition  $F$ .

Most of us are used to considering phase equilibria under isobaric and isothermal conditions. Under such conditions, a phase transition between condensed phases occurs at a single temperature for a given pressure or at a single pressure for a given temperature in a one-component system (ignoring kinetics). That is, as temperature or pressure varies, the phase transition is sharp, complete and total. However, inside an inclusion, due to the protection of the host phase and the volume constraint, the pressure in the inclusion can be different from the pressure on the outside surface of the host. The transition between condensed phases in a one-component system is partial and almost never goes to completion. Hence, once a piece of graphite is included in diamond, the graphite will survive almost all conceivable  $T$ – $P$  paths unless the host diamond relaxes (flows viscously) or fractures into pieces.

This example demonstrates differences in the phase equilibria of inclusion–host systems and those under isobaric and isothermal conditions. To a first-order approximation, the inclusion mass and volume can be regarded as constant, and the thermodynamics and phase equilibria in inclusion–host systems are similar to those under isochoric (e.g., [8–10]) and isothermal conditions instead of the more familiar isobaric and isothermal conditions. An instructive diagram for examining isochoric phase transitions is a temperature–volume diagram (instead of a  $T$ – $P$  diagram) if there is a large variation in  $T$ , which is similar to the pressure–entropy diagram used by Asimow et al. [27] to examine isentropic melting. However, in detail, the process is not perfectly isochoric, and volume change must also be considered for more accurate description of the phase transition.

## 6. Thermobarometry using inclusion–host systems

The above example, graphite in diamond, shows the complexity of phase transitions in inclusions. There are many other possible phase transitions and reactions in an inclusion or between an inclusion and a host. For example, for an orthopyroxene inclusion and a garnet host, there are at least two reactions between the inclusion and the host. One reaction is the  $\text{Fe}^{2+}$ –Mg exchange. Because the cation exchange does not have a significant volume effect, its effect on the inclusion pressure is ignored in the following consideration (even though small volume effect may affect the inclusion pressure in a significant way). The second reaction between the inclusion and the host is the following:



This reaction has a large  $\Delta V$ . The right hand side has a higher density and smaller volume than the left hand side. Therefore, as pressure increases, the  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  component dissolved in orthopyroxene decreases (that is, the Al content in orthopyroxene coexisting with garnet is a barometer [28]) if the orthopyroxene is not an inclusion. However, when orthopyroxene is an inclusion in garnet, using Kamb's theory, the Al content in orthopyroxene

inclusion will be related to the inclusion pressure, instead of the host pressure. The difference between  $P_{\text{in}}$  and  $P_0$  depends on the activity–composition relation and the partial molar volume of each component in both phases.

Inclusions in minerals have often been used to infer temperature and pressure. Owing to protection of inclusions by the host phase, some applications are valid while others are questionable. It is necessary to understand the elastic effects on phase equilibrium to determine whether a specific kind of equilibrium can be used to infer  $T$ – $P$  conditions. Several applications can be distinguished:

(1) If the temperature is high (e.g.,  $T \geq 1000^\circ\text{C}$ ), stress around an inclusion is relaxed in a short time scale for typical mantle minerals with relatively low viscosity. Therefore, inclusion–host equilibrium can be treated in the usual manner and thermobarometry can be used to infer the peak temperature and pressure or the closure  $P$ – $T$ . (If the inclusion–host is rapidly brought to the surface, there will be a stress field around the inclusion due to the decompression. This stress field is not necessarily that in the mantle.) However, for a mineral such as diamond, the viscosity is not known and it is not clear whether deviatoric stress would relax in a short time ( $\leq 10^8$  years).

(2) For most metamorphic rocks with temperatures below  $800^\circ\text{C}$ , for a part of the upper mantle that is relatively cold ( $\leq 800^\circ\text{C}$ ), and for some minerals with very high viscosity (possibly garnet and diamond), the host phase may not relax viscously at the peak temperature and pressure. Under such conditions, the following statements can be made.

(a) A valid application is to use the inclusions to infer or constrain the formation conditions (instead of equilibrium after formation) if there is no reaction between the host and the inclusions or if the reaction is so slow that original inclusion composition is preserved in the core. For example, separate single-phase silicate and sulfide inclusions in diamond do not react with diamond. Therefore, they can be used to infer or constrain the  $P$ – $T$  conditions of formation for the part of diamond next to the inclusion (e.g. [29,30]). Another example is coesite inclusion in garnet [6,7] and other separate inclusions in garnet [31].

(b) If a single inclusion contains several phases, the equilibria between the several phases can be used to infer  $T$  (peak temperature or closure temperature)

and  $P_{in}$  at the  $T$ . However, the inclusion pressure may not have a depth significance.

(c) If the host and the inclusion can react, the observed compositions of the inclusion and host reflect the long  $P_{out}-P_{in}-T$  history experienced by the pair and cannot be simply used to infer  $P_0-T_0$  of formation or the peak  $P_{out}-T$ . Hunter and Smith [32] and Smith and Barron [33] used the Fe–Mg exchange equilibrium between orthopyroxene inclusion and garnet host and the Al content in orthopyroxene inclusion in garnet to infer  $T-P$  conditions or paths for the inclusion–host pairs. However, because their estimated temperatures are low (500 to 800°C), viscous relaxation in the garnet host is negligible. Using Kamb's thermodynamic formulation, the estimated pressures are inclusion pressures that do not have depth significance. Such  $T$  and  $P$  may not be used to construct a geotherm.

(d) When there are several separate inclusions in a host mineral, the pressure in one inclusion (such as an orthopyroxene inclusion in a garnet) may not be the same as the pressure in another inclusion (such as a clinopyroxene inclusion in the same garnet) unless the host has viscously relaxed. Therefore, one may not combine several inclusions to solve for both peak  $T$  and  $P$ .

Use of the above understanding can help us to correctly apply thermobarometry methods and to avoid incorrect applications. Understanding of how inclusion pressure depends on the initial ( $T_0$ ,  $P_0$ ) and the new ( $T$ ,  $P_{out}$ ) may eventually lead to methods capable of inferring both ( $T_0$ ,  $P_0$ ) and ( $T$ ,  $P_{out}$ ). Before such an understanding, caution must be exercised in such applications.

## 7. Conclusions

Mechanical and phase equilibria involving inclusion–host phases are complicated. As the temperature and/or pressure on the host phase vary, the pressure in an inclusion may become different from the host pressure unless the host mineral relaxes. Each inclusion is at uniform isotropic stress but different inclusions may have different pressures. The host is anisotropically stressed. In the elastic regime of deformation, there is a gradient in the radial and tangential stress, but the 'mean pressure' of the host

is uniform. In the plastic region, there is a gradient in radial, tangential and 'mean pressure' in the host. At normal mantle temperatures and for normal mantle minerals, it is expected that stress relaxation through viscous flow is the norm. However, at temperatures below 800°C or for minerals with high viscosity, stress relaxation is not expected to be effective. If stress does not relax, phase transition in an inclusion can be roughly treated as isochoric and isothermal transitions. Even in a one-component system, the phase transition is partial and almost never goes to completion.

Caution must be exercised in applying inclusion–host equilibrium to infer temperature and pressure. If there is no reaction between the host and the inclusion, inclusions may be used to infer formation conditions. If the temperature is high enough and viscous relaxation is rapid, inclusion–host pairs can be used to infer the closure  $P-T$  condition (instead of the formation condition). However, if the host–inclusion reaction altered the inclusion composition and if the temperature is below 800°C, (1) the inferred pressure using an inclusion–host pair may be the inclusion pressure, which may not have depth significance, and (2) different inclusions cannot be combined to infer both temperature and pressure. The examples given in this paper demonstrate the richness of mechanical and phase equilibria in inclusion–host systems.

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