Adiabatic decompression and melting of mantle rocks: An irreversible thermodynamic analysis

Jibamitra Ganguly

Department of Geosciences, University of Arizona, Tucson, Arizona, USA

[1] The process of irreversible adiabatic decompression and melting of mantle rocks has been evaluated using the thermodynamic condition of frictionless decompression in a gravitational field. It is found that the melt productivity is significantly greater, thus enhancing the tendency for melt segregation, if a parcel of mantle rock moves upward at nearly constant velocity than that derived for the case of isentropic decompression. The T-Z trajectory of a solid mantle diapir moving upward at a constant velocity has, in general, a smaller slope than the isentropic trajectory, and assumes a negative slope when its density falls below ∼94% of that of the surrounding mantle. The acceleration of upward movement, and the overall density reduction of the material due to phase change that is the likely cause for the acceleration, have qualitatively opposite effects on the deviations of melt productivity and T-Z trajectory of mantle diapir from those under isentropic conditions. **Citation:** Ganguly, J. (2005), Adiabatic decompression and melting of mantle rocks: An irreversible thermodynamic analysis, *Geophys. Res. Lett.*, *32*, L06312, doi:10.1029/2005GL022363.

1. Introduction

[2] Decompression of mantle rocks without any significant loss of heat leads to the intersection of the P-T trajectory of the rock with P-T curve of the solidus, thereby causing melting of the upwelling material (Figure 1). Considering reasonable velocities, distance of upwelling and thermal diffusivity of the rock, the process of decompression of mantle material can be shown to be essentially adiabatic [*McKenzie and Bickle*, 1988]. As discussed by *Stolper* [1996], the adiabatic decompression melting is the most important mechanism by which magmas form in the mantle, and thus "arguably the most significant of all igneous processes". Traditionally the adiabatic decompression process (dq = 0) has been considered to be isentropic (dS = 0), which implies that the process is reversible. As noted, for example by *Stolper* [1996] and *Asimov* [2002], this is at best an approximation, but it has generally been considered to be a good approximation by them and many others in the field [e.g., *McKenzie*, 1984; *McKenzie and Bickle*, 1988; *Iwamori et al.*, 1995; *Asimov et al.*, 1997; *Presnall et al.*, 2002; *Green et al.*, 2001]. A number of interesting conclusions have emerged by considering the adiabatic decompression of mantle rocks to be isentropic. Melt separation and migration, that is the fractional melting process, necessarily implies loss of entropy from the upwelling system. In this case, the process has been considered to be incrementally isentropic. *Asimov* [2002] has presented a comprehensive discussion of the various source terms for entropy production during adiabatic decompression melting, and evaluated the effects of entropy production due to chemical disequilibrium between the melt and the surrounding matrix.

[3] The classic experiment of Joule and Thompson (Lord Kelvin), which is described in practically any introductory text on Physical Chemistry, treated the problem of adiabatic flow of material through a constriction from a uniform pressure, P_1, to another uniform but lower pressure condition, P_2. This is an adiabatic, but an overall irreversible process (dq = 0, dS > 0), which was shown to conserve the enthalpy of the system (dq = dH = 0). *Waldbaum* [1971] drew attention of geologists to this well-known result of thermodynamics and applied it to treat the adiabatic upwelling process of the mantle material. The idea behind this approach was that the upwelling process in a pressure gradient may be considered to be a series of Joule-Thompson experiments with small sequential decrease of pressure. However, as pointed out by *Ramberg* [1972], Waldbaum erred in his thermodynamic treatment of the problem by not incorporating the effect of change of gravitational potential on vertically moving masses over large distance. The purpose of the present paper is to present a treatment of adiabatic upwelling and melting within the framework of Joule-Thompson experiment, but with correction for the effects of change of gravitational potential and kinetic energies, and compare the results with those derived already by others using the isentropic condition. All entropy production other than that due to irreversible decompression has been neglected. Thus, the formulations presented below provide starting points for the treatment of adiabatic upwelling and melting process in the Earth's mantle as *irreversible* processes (dq = 0, dS > 0), which represents a shift from the traditional starting point founded on treating these as reversible processes. As far as possible, the simplicity of McKenzie's treatment [*McKenzie*, 1984] has been preserved in order to be able to estimate the effect of entropy production that is associated with irreversible decompression in a relatively simple way.

2. Irreversible Adiabatic Melting: Thermodynamic Formulation

[4] Conservation of energy for a system of unit mass undergoing irreversible adiabatic decompression (IAD) through vertical but frictionless displacement in a gravitational field, and restricted only to pressure-volume work,
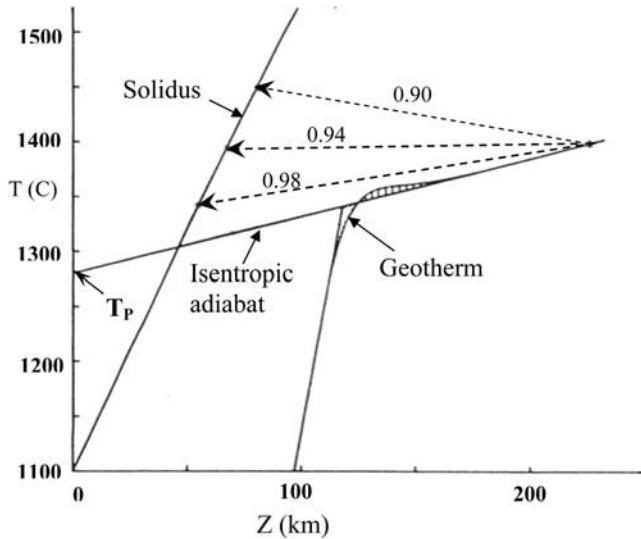
Figure 1. Isentropic (solid line) and IAD (dashed lines) temperature-depth (*T-Z*) paths for ascending mantle material from an arbitrary depth of 225 km. The numbers on the dashed lines stand for the densities of the ascending material relative to that of the surrounding mantle. *Tp* stands for the potential temperature, as defined by *McKenzie and Bickle* [1988]. The geotherm, mantle solidus and isoentropic gradients are from the latter. IAD: Irreversible adiabatic decompression.

leads to the relation [e.g., *Lewis and Randall*, 1961; *Abbott and Van Ness*, 1972]

$$dH + gdh + udu = 0 \qquad (1)$$

where H is the enthalpy per unit mass or specific enthalpy of the system, u is the linear velocity and h is the height. Both h and u are taken to be positive upwards. The enthalpy of a closed system consisting of a mixture of solids (s) and melt (m) is given by

$$H = x^m H^m + \sum_i x^{s_i} H^{s_i} \qquad (2)$$

where x is the mass fraction, H is the specific enthalpy and the superscripts m and s_i stand for melt and ith solid, respectively. All thermodynamic quantities used henceforth are specific quantities.

[5] *McKenzie* [1984] derived an expression of melt productivity with change of pressure, dx^m/dP, under isentropic condition by considering the simplest case of melting of monomineralic rock, but at the same time considering T = T(x, P) as would be the case for melting in a multiphase system (as noted by McKenzie, for the melting of a monomineralic rock, temperature is a function only of depth if melt is present). This approach obviously is not completely adequate to treat melting in a multiphase system, but it is still believed to have captured some of the interesting aspects of isentropic melting of multiphase mantle rock. In McKenzie's approach, equation (2) reduces to H = $x^m H^m$ + (1 − x^m)H^s = $x^m \Delta H_f$ + H^s, where ΔH_f is the specific enthalpy of fusion. This relation would also approximately hold for a multiphase system if the phases have similar specific enthalpies.

[6] A sheared garnet peridotite, PHN 1611, from Thaba Putsua kimberlite, Lesotho, which is believed to be a 'fertile' mantle peridotite, consist of ∼59% olivine, 11% orthpyroxene, 20% clinopyroxene and 10% garnet [*Boyd and McCallister*, 1976]. It is interesting to note that olivine and orthopyroxene, which constitute ∼70% of a mantle rock, have very similar values of specific enthalpies (for example, at 1 bar, 298 K, the specific enthalpy of formation from elements of forsterite and enstatite are −15.45 and −15.40 kJ/mole, respectively, according to the data by *Saxena et al.* [1993]. Clinopyroxene and pyrope garnet have specific enthalpies that differ from those of olivine and orthopyroxene in opposite directions. This scenario is also true for specific (isobaric) heat capacities, entropies and molar volumes [e.g., *Saxena et al.*, 1993]. Thus, as a rough approximation we could write

$$Y \approx x^m Y^m + (1 - x^m)\overline{Y}^s = x^m \Delta Y_f + \overline{Y}^s \qquad (3)$$

where *Y* is a specific property of the system (enthalpy, entropy, volume), ΔY_f is the change of *Y* on fusion and $\overline{Y}^s$ is the average value of *Y* for the solids.

[7] Now writing x for x^m and considering H = H(x, P, T), we have

$$dH = \left(\frac{\partial H}{\partial x}\right)_{P,T} dx + \left(\frac{\partial H}{\partial P}\right)_{x,T} dP + \left(\frac{\partial H}{\partial T}\right)_{P,x} dT \qquad (4)$$

Since *H* = *G* + *TS*, where *G* and *S* are the Gibbs energy and entropy, respectively, we have

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial S}{\partial P}\right)_T = V - T(V\alpha) \qquad (5)$$

where α is the coefficient of thermal expansion. The relation $\partial S/\partial P = -V\alpha$ follows from the application of Maxwell's relation and the definition of α. Writing, in the spirit of equation (3),

$$G \approx xG^m + (1 - x)\overline{G}^s \qquad (6)$$

and

$$S \approx xS^m + (1 - x)\overline{S}^s \qquad (7)$$

where $\overline{G}^s$ and $\overline{S}^s$ are the average specific Gibbs energy and specific entropy of the solids, equation (5) yields

$$\left(\frac{\partial H}{\partial P}\right)_T \approx x(\Delta V_f) + \overline{V}^s - T[x(V^m\alpha^m) + (1-x)\overline{V}^s\overline{\alpha}^s]$$
$$= x(\Delta V_f) + \overline{V}^s - T\varphi \qquad (8)$$

where ΔV_f is the specific volume of fusion, $\overline{V}^s$ and $\overline{\alpha}^s$ are the average values of V^s and α^s, respectively, and φ stands for the collection of terms within the square brackets. Using equations (3) and (8) and the relationship between the isobaric heat capacity, C_p, and H, equation (4) reduces to

$$dH \approx \Delta H_f dx + (x\Delta V_f + \overline{V}^s)dP - T\varphi dP + \left(x\Delta C_{p,f} + \overline{C}_p^s\right)dT \qquad (9)$$

Substituting the above relation in equation (1) and differentiating with respect to P, we get

$$\Delta H_f \frac{dx}{dP} + x\Delta V_f + \overline{V}^s - T\varphi + \left(x\Delta C_{p,f} + \overline{C}_p^s\right)\frac{dT}{dP}$$
$$+ g\frac{dh}{dP} + u\frac{du}{dP} \approx 0 \qquad (10)$$

[8] Following *McKenzie* [1984], we obtain dT/dP from the relation $T = T(x, P)$:

$$\frac{dT}{dP} = \left(\frac{\partial T}{\partial x}\right)_p \frac{dx}{dP} + \left(\frac{\partial T}{\partial P}\right)_x \qquad (11)$$

Substituting equation (11) in equation (10), and rearranging the terms, we finally obtain an expression of melt productivity during adiabatic irreversible decompression under frictionless condition

$$\left[\frac{dx}{dP}\right]_{Q(ir)} \approx \left[\frac{-\left(x\Delta C_{p,f} + \overline{C}_p^s\right)(\partial T/\partial P)_x + T\varphi}{\Delta H_f + \left(x\Delta C_{p,f} + \overline{C}_p^s\right)(\partial T/\partial x)_p}\right]$$
$$- \left[\frac{g(dh/dP) + x\Delta V_f + \overline{V}^s + u(du/dP)}{\Delta H_f + \left(x\Delta C_{p,f} + \overline{C}_p^s\right)(\partial T/\partial x)_p}\right] \qquad (12)$$

[9] *McKenzie* [1984] assumed that $C_p^S = C_p^m = C_p$. In that case, $\Delta C_{p,f} = 0$, and the terms within the first square brackets in the right of the above equation is the same as that derived by him [*McKenzie*, 1984, equation (D7)] for isentropic melting, $(dx/dP)_S$, except that he had $T\Delta S_f$ instead of ΔH_f. Now, very little overstepping was needed even in the laboratory melting experiments of natural peridotite [e.g. *Takahashi*, 1986]. Thus, it is safe to assume that the melting process in nature does not involve any significant overstepping of *P-T* condition. For an one-component system, the temperature of the system becomes effectively buffered along the univariant melting curve during decompression. In a multiphase system, on the other hand, the equilibrium melting temperature varies within a temperature interval defined by the solidus and liquidus. In that case, the assumption of no significant overstepping of melting condition implies that nearly equilibrium fraction and composition of melt are produced at any temperature between the solidus and liquidus. Regardless of whether it is a single component or multiphase system, we have $\Delta H_f(P, T) \approx T_f\Delta S_f(P, T)$ as long as we have a nearly equilibrium situation (i.e. the Gibbs energy of the system is close to the minimum). (When the phases represent solutions, the delta terms above represent changes of the partial molar properties. Also, if the thermodynamic properties of the solids in a multiphase system are significantly different, then ΔH_f and ΔS_f would also be affected by the changing stoichiometry of the melting reaction between solidus and liquidus).

[10] From the above analysis, we conclude that the terms within the second square brackets on the right of equation (12) constitute the effect of *entropy production* during the process of adiabatic irreversible decompression. Now, $g(dh/dP) = -1/\rho = -V$ where V is the specific volume of the mantle rocks, which should be very similar to the specific volume of the solids, V^s, in the upwelling material. Thus, equation (12) reduces to

$$\left[\frac{dx}{dP}\right]_{Q(ir)} \approx \left[\frac{dx}{dP}\right]_S - \left[\frac{x\Delta V_f + u(du/dP)}{\Delta H_f + \left(x\Delta C_{p,f} + \overline{C}_p^s(\partial T/\partial x)_p\right)}\right]$$
$$\approx \left[\frac{dx}{dP}\right]_S - \Lambda \qquad (13)$$

3. Melt Productivity During Decompression

[11] To have a feeling of the probable magnitude of the Λ term in equation (13), we use the values of diopside for ΔV_f (0.38 cm^3/gm [*Asimov et al.*, 1997]) and ΔH_f (637.6 J gm^{-1} [*Stebbins et al.*, 1983]). We also assume, following *McKenzie* [1984] that $C_p^s = C_p^m = C_p$ and that $C_p = 1.2$ J gm^{-1} K^{-1}, as given by *Iwamori et al.* [1995]. Also from these authors [*Iwamori et al.*, 1995, Figure 3a], we obtain $\partial T/\partial x \sim 370$ K for batch melting between 1260 and 1400°C. Now if we assume that the ascending mantle material has essentially constant velocity, then these values yield $\Lambda = 0.04$ GPa^{-1} for $x = 0.10$. *Iwamori et al.* [1995] calculated the melt productivity for isentropic decompression of mantle peridotite. From their data, the average value of $[dx/dP]_S$ is around -0.16 GPa^{-1} at 1400°C for $x = 0.10 - 0.24$. Thus, the melt productivity under IAD is $\sim$25% higher than that under isentropic condition at $\sim$1400°C. Similar exercise for $x = 0.05$ yields 14% increase of melt productivity under IAD relative to the isentropic condition. The increase of melt productivity for $x = 0.06 - 0.08$ is much higher, by $\sim$50%, because of the shallow slope of $(\partial x/\partial P)_s$ within this melting interval. Thus, these calculations suggest that there is a significant increase of melt productivity under IAD, and conveys an approximate impression of the magnitude of the increase. The results are not strongly affected for the case of fractional melting using Figure 3b from *Iwamori et al.* [1995] to calculate $(dx/dP)_s$. A potentially important consequence of increased melt productivity is that melt segregation would take place more quickly than envisaged for the limiting case of isentropic decompression.

4. Irreversible Adiabatic Decompression of Solid Mantle

[12] As in decompression melting, the adiabatic decompression of the solid mantle material has been always considered to be an isentropic process, except by *Waldbaum* [1971], who considered the case of isenthalpic decompression. Here we revisit the problem by satisfying equation (1). Setting x = 0 in equation (9), and substituting the result in equation (1), we obtain

$$C_p dT - V(T\alpha - 1)dP + gdh + udu = 0 \qquad (14)$$

(note that the above identity is exact even though equation (9) has an approximate equality as a result of approximation of properties in the presence of a melt phase). Thus,

$$\left[\frac{dT}{dP}\right]_{Q(ir)} = \frac{T\alpha - 1}{\rho C_p} - \frac{gdh}{C_p dP} - \frac{u}{C_p}\left(\frac{du}{dP}\right) \qquad (15)$$

Using $dZ = -dh = dP/(\rho_r g)$, where Z is the depth (+ ve downwards) and ρ_r is the density of the mantle rock, the above equation yields

$$\left[\frac{dT}{dZ}\right]_{Q(ir)} = \frac{\rho_r}{\rho}\left(\frac{gT\alpha}{C_p}\right) + \frac{g}{C_p}\left(1 - \frac{\rho_r}{\rho}\right) - \frac{u}{C_p}\left(\frac{du}{dZ}\right) \quad (16)$$

The term within the first parentheses on the right equals the isentropic gradient [e.g., *Turcotte and Schubert*, 1982] so that we can write

$$\left[\frac{dT}{dZ}\right]_{Q(ir)} = \frac{\rho_r}{\rho}\left[\frac{dT}{dZ}\right]_S + \frac{g}{C_p}\left(1 - \frac{\rho_r}{\rho}\right) - \frac{u}{C_p}\left(\frac{du}{dZ}\right) \quad (17)$$

Since $\rho < \rho_r$ (otherwise material would not move upward), the second right hand term (<0) somewhat counteracts the first right hand term, which is positive, and may even cause a temperature rise, $[dT/dZ]_{Q(ir)} < 0$, as the material moves upward at a constant velocity. The ratio ρ/ρ_r controls the velocity of upward motion. If the ratio is very close to unity, then the temperature gradient effectively equals isentropic gradient if the adiabatic condition prevails ($u \rightarrow 0$ as $\rho \rightarrow \rho_r$).

[13] Figure 1 shows the *T-Z* trajectories of mantle rocks upwelling at constant velocity, as calculated according to equation (17), with different values of ρ/ρ_r, $C_p = 1.2$ kJ/kg-K, as above, and typical value of isentropic gradient of the mantle rock of ~0.5 K/km (Figure 1). It is found that the ascent of a mantle material with 94% density of the surrounding mantle will be essentially isothermal, if it moves with a constant velocity. If the density of the ascending material is lower, then there will be a net heating during ascent. It may be noted in this connection that extraction of 20% basalt from a garnet peridotite decreases its density by 1.7% [*Jordan*, 1979].

5. Effect of Acceleration

[14] So far, we have limited our numerical results to mantle diapir moving upward at a constant velocity as we have no quantitative idea about the possible acceleration of vertical movement. If there are phase changes within the solid mantle material as it moves upward, which are necessarily to lower density phases, there would be increase of the buoyancy force leading to acceleration of the upward movement. *Ramberg* [1972] suggested that more than 10% melting of a diapir is enough to reduce its viscosity sufficiently to accelerate its upward movement. It is easy to see from equations (13) and (17) that acceleration of upward movement ($du/dP < 0$, $du/dZ < 0$) reduces the departures of both melt productivity and *T-Z* trajectory from the isentropic conditions compared to the case of displacement with constant velocity. However, the density reduction of the mantle diapir, which is responsible for its acceleration, works in the opposite direction (Figure 1). If there is any significant kinetic lag during phase change, then, of course, one would need to take into account the effect of entropy production due to irreversible reaction.

6. Potential Temperature

[15] *McKenzie and Bickle* [1988] introduced the concept of potential temperature of mantle material, T_p, which is the projection of the temperature of the material from its source region to the Earth's surface along an isentropic gradient (Figure 1). Thus, materials with different depths along an isentropic gradient within the Earth have the same T_p. The concept of potential temperature has been widely used in the literature of igneous petrology as a means of comparison of the extent of melting that materials with different temperatures in the source, T_s, would undergo during ascent. If these materials have the same T_p, then the extent of melting is considered to be the same. However, as should be evident from Figure 1, two mantle rocks displaced upward from two different depths located on an isentropic gradient could intersect the solidus at two different temperatures, depending on their original difference of T_s and densities, and thus undergo different extents of partial melting. The practical usefulness of the concept of potential temperature requires a demonstration that the density of the upwelling material differs only slightly from the ambient mantle density.

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J. Ganguly, Department of Geosciences, University of Arizona, 1040 E. Fourth Street, Tucson, AZ 85721, USA. (ganguly@geo.arizona.edu)