Earth Planets Space, **50**, 1029–1034, 1998

A note on latent heat release from disequilibrium phase transformations and deep seismogenesis

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(Received May 8, 1998; Revised October 19, 1998; Accepted October 23, 1998)

Latent heat release by equilibrium mineralogical transformations in an adiabatically subducting slab reversibly perturbs temperatures and pressures so as to conserve entropy. However, latent heats of metastable transformations in such a slab yield irreversible isobaric temperature changes which increase entropy despite adiabatic constraints. As a result, latent heat release by metastable exothermic transformations can yield local superheating above the background adiabat, with the degree of potential superheating increasing with extent of metastable overstep. In real slabs, however, regions of metastably persisting low-pressure phases should undergo conductive warming from surrounding transformed material. Such warming should proceed more rapidly than warming of the bulk slab from the surrounding mantle, and the resulting decrease in metastable transition pressures will slightly decrease the degree of local superheating. Nonetheless, such local temperature increases may trigger seismic release of accumulated strain energy via a number of proposed mechanisms of shear instability. Adiabatic instability, in the form of shear localization in material with temperature-dependent rheology, is one mechanism which may be triggered by such latent heat release in metastable regions yet produce rupture that extends beyond the boundaries of such regions.

1. Introduction

A variety of phenomena, such as thermal deflection of phase boundaries or viscosity stratification, may contribute to significant stresses within subducting lithospheric slabs (Goto *et al.*, 1987; Vassiliou and Hager, 1988; Bina, 1996, 1997; Yoshioka *et al.*, 1997). Release of the associated strain energy in the form of deep seismicity, however, requires a mechanism that will allow slip to occur despite the large confining pressures prevailing at depth (Green and Houston, 1995). A number of mechanisms for such shear instabilities have been proposed, including dehydration, strain concentration in material with temperature-dependent rheology, formation of weak zones due to fine-grained material arising from phase transition or dynamic recrystallization, and runaway phase transformation arising from latent heat release (Bridgman, 1945; Kirby *et al.*, 1991; Rubie and Ross, 1994; Green and Houston, 1995; Green and Zhou, 1996; Karato, 1997). Each of these mechanisms requires either localized heating or a mineralogical phase transition (under equilibrium or metastable conditions) or both.

Here I review the temperature effects associated with latent heat release from phase transformations under both equilibrium and metastable conditions in idealized adiabatically subducting slabs, noting that metastable exothermic transformations under such conditions can yield anomalously large local temperature increases, and I comment on the extent to which useful work may thereby be obtained. I then introduce the effects of conductive heating of small regions of material that may have persisted metastably beyond their stability field, noting that such heating slightly decreases the degree of local superheating associated with metastable exothermic transition. Finally, I consider the extent to which possible triggering of seismicity by such local superheating, due to latent heat release during transformation of metastable phases, may be consistent with observed patterns of deep seismicity.

2. Subduction along an Adiabat

2.1 Equilibrium transformations

The P-T path of idealized slab material subducting along an adiabat (i.e., assuming no heat exchange with adjacent material) follows the standard adiabatic gradient:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha V}{C_P} \tag{1}$$

where T is temperature, V volume, C_P isobaric heat capacity, and α volume coefficient of thermal expansion. When the material undergoes an equilibrium phase transformation, such as the exothermic $\alpha \rightarrow \beta$ transition in olivine near 400 km depth, the adiabat is deflected along the equilibrium boundary of the phase transition (Fig. 1) in accordance with the Clapeyron relation:

$$\frac{dT}{dP} = \frac{\Delta V^{\alpha\rightarrow\beta}}{\Delta S^{\alpha\rightarrow\beta}} \tag{2}$$

where ΔV and ΔS are the changes in volume and entropy, respectively, across the phase transition. This refraction of the adiabat, which is based upon the assumption (discussed below) that rates of reaction and attendant latent heat release significantly exceed rates of conductive heat transfer, results in a net temperature and pressure increment across the phase

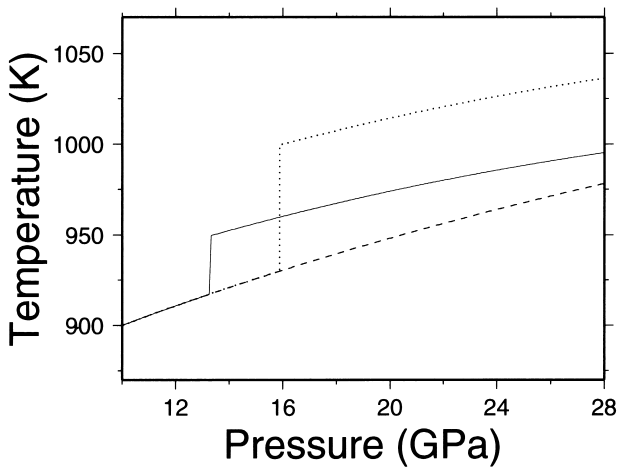

Fig. 1. Temperature as a function of pressure for a portion of a lithospheric slab subducting along an adiabat that is refracted by an equilibrium exothermic phase transition (solid). Regions in which low pressure phases persist metastably continue to follow their own adiabat (dashed). Eventual metastable transformation (here at 930 K) yields isobaric superheating (dotted) above the background equilibrium adiabat. Diagram calculated for the $\alpha \rightarrow \beta$ transition in forsterite.

transition:

$$\Delta T \approx \frac{-\Delta H^{\alpha\rightarrow\beta}}{C_P - \frac{T\alpha V \Delta S^{\alpha\rightarrow\beta}}{\Delta V^{\alpha\rightarrow\beta}}} = \frac{-T\Delta S^{\alpha\rightarrow\beta}}{C_P - \frac{T\alpha V \Delta S^{\alpha\rightarrow\beta}}{\Delta V^{\alpha\rightarrow\beta}}}, \quad (3)$$

$$\Delta P \approx \frac{\Delta S^{\alpha\rightarrow\beta}}{\Delta V^{\alpha\rightarrow\beta}}\Delta T \approx \frac{-T(\Delta S^{\alpha\rightarrow\beta})^2}{C_P \Delta V^{\alpha\rightarrow\beta} - T\alpha V \Delta S^{\alpha\rightarrow\beta}} \quad (4)$$

where C_P, α, and V are for the high-pressure phase. These increments are often approximated as:

$$\Delta T \sim \frac{-T\Delta S^{\alpha\rightarrow\beta}}{C_P}, \quad \Delta P \sim \frac{-T(\Delta S^{\alpha\rightarrow\beta})^2}{C_P \Delta V^{\alpha\rightarrow\beta}} \quad (5)$$

and called the "Verhoogen effect" (Jeanloz and Thompson, 1983).

The ΔT value given by the expression (5) for the Verhoogen effect simply reflects the conversion of the latent heat of equilibrium phase change ($\Delta H = T\Delta S$) into temperature via the isobaric heat capacity. However, since the reaction possesses a finite Clapeyron slope, such heating at equilibrium cannot be isobaric, and the more complete expression (3) for ΔT above reflects the additional contribution of adiabatic compression. These increments in T and P serve to maintain adiabaticity (i.e., constant entropy S) within the slab across the transition.

2.2 Metastable transformations

In the non-equilibrium case, α persists metastably into the stability field of β, because temperatures within the cold slab material are insufficient to overcome the activation energy barrier to transformation (Sung and Burns, 1976a,b). Metastably persistent α will continue to follow its own adiabat, given by Eq. (1), which remains colder than the refracted adiabat of the transformed material. In this case, when the transformation eventually does occur, it takes place in the absence of such equilibrium constraints as the Clapeyron equation (2) above, and it results in simple isobaric heating:

$$\Delta T \approx \frac{-\Delta H}{C_P} = \frac{-(T\Delta S + \Delta G)}{C_P} \quad (6)$$

where G is the Gibbs free energy, in which the latent heat of phase change induces a temperature change through the isobaric heat capacity.

Thus, ΔH is the relevant isobaric potential for heat in both equilibrium and metastable processes (Klotz, 1964). However, the expression for ΔH in the metastable case (6) differs from that in the equilibrium case (3) by ΔG, which is identically zero at equilibrium but negative for metastable transformation. The effect upon ΔH of metastable postponement of the transition can be described in terms of the oversteps in pressure and temperature:

$$d\Delta H(P,T) = [\Delta V - T\Delta(\alpha V)]dP + \Delta C_P dT \quad (7)$$

where the pressure dependence has occasionally been approximated by omission of the αV term (Rubie and Ross, 1994; Kirby *et al.*, 1996). Both expressions (6) and (7) show that an exothermic subsolidus phase transition under metastable conditions yields a greater latent heat release than under equilibrium conditions (Fig. 1), an effect which also has been observed in numerical simulations (Daessler and Yuen, 1993; Daessler *et al.*, 1996). Furthermore, a greater degree (i.e., depth) of metastable persistence, corresponding to greater ΔG of eventual transition, will generate a greater ΔT and so greater local heating above the slab background.

Thus, exothermic latent heat release in an adiabatically subducting slab yields local superheating by raising the temperature of any metastable material above the level of the ambient adiabat upon eventual transformation. While equilibrium transformation is a reversible process in which S remains constant under adiabatic conditions, metastable transformation is an irreversible process in which a net increase in S occurs despite adiabatic conditions preventing heat exchange with the surroundings (Klotz, 1964).

Since the Gibbs free energy change of reaction, ΔG, is zero for equilibrium transformation but negative for metastable transformation, it has been suggested that additional useful work may be available from the latter (Kirby *et al.*, 1996). Indeed, G is a potential for the net work W_{net} reversibly performed by the system at constant pressure and temperature, exclusive of the necessary PdV work of expansion or contraction:

$$W_{\text{net,irrev}} < W_{\text{net,rev}} = -(\Delta G)_{P,T} \quad (8)$$

where the work performed irreversibly is always less than the reversible value, and the heat Q liberated by the system will be correspondingly reduced:

$$Q = -\Delta H - W_{\text{net}} \quad (9)$$

thereby reducing the degree of local superheating. However, to the extent that the reaction rates of irreversible transformation exceed the characteristic rates of any processes for recovering useful work, such transformations are likely to approach the limit of explosively irreversible processes in which W_{net} is zero.

Since most studies involving latent heats of mantle phase transformations have assumed, explicitly or implicitly, that reaction rates of transformation significantly exceed both rates of heat conduction and rates of work recovery, some discussion of this assumption may be in order. Exothermic olivine polymorphic transformations that occur under conditions of significant metastable overstep exhibit rapid growth (Brearley and Rubie, 1994; Kubo *et al.*, 1998). For the $\alpha \rightarrow \beta$ transformation, two completing primary mechanisms have been revealed experimentally. The first mechanism involves the incoherent nucleation of β on grain boundaries of α and exhibits interface-controlled growth (Rubie and Ross, 1994; Kerschhofer *et al.*, 1996). Kinetically, greater overstep of the equilibrium boundary results in a smaller required critical nucleus (Burnley, 1995), and the larger driving force (ΔG) for transformation enhances both nucleation and growth rates (Rubie and Ross, 1994). Furthermore, the small activation volume (Kubo *et al.*, 1998) falls with increasing pressure (Rubie and Ross, 1994), becoming negative at large overstep pressures (Burnley, 1995), thus enhancing the growth rate by decreasing the effective activation energy (Rubie and Ross, 1994). The second mechanism involves coherent intracrystalline nucleation of γ lamellae on shear-induced stacking faults followed by nucleation of β on the γ (Kerschhofer *et al.*, 1996; Chai *et al.*, 1998). For this mechanism, which may be more important in cold subducting slabs (Burnley, 1995; Kerschhofer *et al.*, 1996), a large pressure overstep enhances the shear-induced transformation (Burnley, 1995; Kerschhofer *et al.*, 1996), both because greater overstep of the equilibrium boundary provides a greater driving force for transformation (Burnley, 1995) and because smaller strain energies are required to form γ lamellae at high pressures due to the greater compressibility of α (Burnley, 1995).

All of the above effects conspire to elevate reaction rates for olivine transformations under conditions of large metastable overstep. For transformation under near-equilibrium conditions, on the other hand, the small driving force (ΔG) of transition will depress reaction rates. Furthermore, the $\alpha \rightarrow \beta$ transformation exhibits diffusion-controlled growth under such conditions (Rubie and Ross, 1994), and the consequent necessity for diffusion of cations through bulk crystals rather than simply across grain boundaries will further depress the kinetics of near-equilibrium transformation. Thus, the conditions under which the assumption of rapid rates of reaction (relative to rates of thermal conduction) is likely to be most accurate are precisely those prevailing in the case of metastably persistent phases.

2.3 Multiple transformations

The examples thus far have featured a single phase transformation. In complex multicomponent systems such as the mantle, however, a series of multiple phase transformations may occur with increasing depth. In mantle olivine, for example, the exothermic $\alpha \rightarrow \beta$ transition is followed by the exothermic $\beta \rightarrow \gamma$ and endothermic $\gamma \rightarrow pv + mw$ transitions. Tabulated thermodynamic parameters for these phases (Fei *et al.*, 1991) allow determination of the relevant pressure-temperature paths for the associated phase transformations, where for simplicity these have been calculated for pure forsterite (Fig. 2) rather than for a forsterite-90 solid solution. The metastable $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions are exothermic and so yield local superheating above the ambient adiabat. The metastable $\alpha \rightarrow \gamma$ transition, being essentially a combination of the previous two, is significantly more exothermic and so yields a greater degree of local superheating. The metastable $\alpha \rightarrow pv + mw$ transition is also strongly exothermic, yielding local superheating.

On the other hand, the metastable $\gamma \rightarrow pv + mw$ transition is endothermic and so yields local cooling. However,

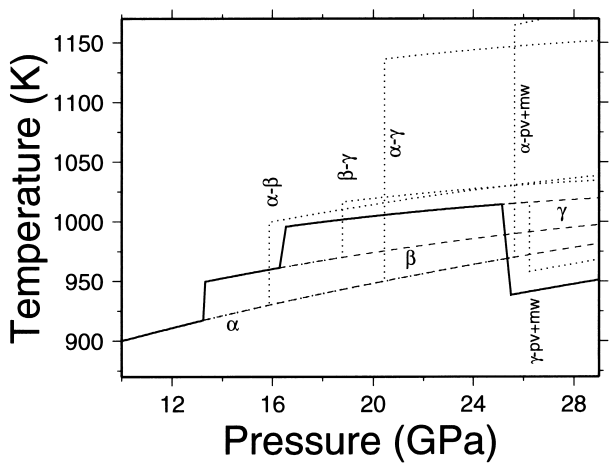

Fig. 2. Temperature as a function of pressure for a portion of a lithospheric slab subducting along an adiabat that is refracted by multiple equilibrium phase transitions (solid). Regions in which low pressure phases (α, β, γ) persist metastably continue to follow their own adiabats (dashed). Eventual metastable transformations ($\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, $\alpha \rightarrow \gamma$, $\alpha \rightarrow pv + mw$, $\gamma \rightarrow pv + mw$) yield isobaric superheating (dotted) above the background equilibrium adiabat. Diagram calculated for transitions in forsterite.

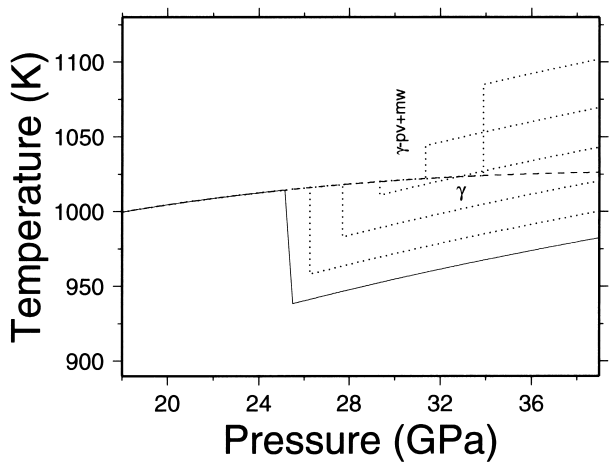

Fig. 3. Temperature as a function of pressure for a portion of a lithospheric slab subducting along an adiabat that is refracted by an endothermic equilibrium phase transition (solid). Regions in which the low pressure phase (γ) persists metastably continue to follow their own adiabat (dashed). Eventual metastable transformation ($\gamma \rightarrow pv + mw$) initially yields isobaric cooling (dotted). However, the transformation becomes exothermic at higher pressures, according to Eq. (7), thus eventually yielding isobaric superheating (dotted). Diagram calculated for transitions in forsterite.

the metastable $\gamma \rightarrow pv + mw$ transition, while initially endothermic, becomes exothermic at higher pressures (Fig. 3) due to the dominance of the ΔV term in Eq. (7). This behavior, too, is derived from a standard thermochemical database (Fei *et al.*, 1991), but better constraints may be provided by more recent experimental data on the thermochemistry of the post-γ phase transitions (Akaogi *et al.*, 1998).

Moreover, transitions among phases other than the olivine polymorphs, such as those between pyroxenes and garnet-majorite solid solutions, may also exhibit disequilibrium behavior under subduction zone conditions. Enstatite, for example, has been shown to persist metastably at low temperatures (Hogrefe *et al.*, 1994). The latent heats of such additional transitions will also perturb the local temperature structure. Furthermore, the presence of one phase may alter the metastable behavior of another. The stability of high-pressure clinopyroxenes in the mantle (Woodland, 1998), for example, may serve to enhance the kinetics of the olivine transformations (Sharp and Rubie, 1995).

3. Subduction with Heat Conduction

3.1 Exothermic transformations

While an idealized subducting slab may be considered to transform under equilibrium conditions and so to follow an adiabat refracted along the phase boundary as discussed above, in reality its edges will warm by conduction from the surrounding mantle. Moreover, any regions of α which persist metastably into the β field (or subsequent fields) will also warm by conduction from the surrounding transformed slab material, rather than continuing along their own adiabat as in the idealized adiabatic case above. In both cases, the temperature of the colder material will approach that of the surrounding warmer material with a thermal lag λ (Fig. 4) which depends upon time t and distance from the edge y as follows:

$$\lambda(y,t) \approx \frac{2\Delta T}{\pi} \sum_{n=1}^{\infty} e^{-(\frac{n\pi}{L})^2 \kappa t} \left[\frac{1-(-1)^n}{n} \right] \sin \frac{n\pi y}{L} \quad (10)$$

where ΔT is the initial temperature difference between the two materials and L is the characteristic spatial extent of the warming region (Pinsky, 1991). The characteristic time τ required for such material to be substantially heated above its adiabat thus depends upon spatial extent as L^2. Hence, a 10-km-wide region of metastable material, for example, will rise in temperature by conduction from the surrounding hotter slab material approximately 100 times faster than the 100-km-thick bulk slab will heat by conduction from the surrounding mantle.

As a result, when a region of metastably persisting material does undergo an exothermic phase transformation, its initial temperature will already have risen somewhat above its adiabat by conduction from surrounding transformed material. However, if transformation is triggered by attaining a critical temperature, the material will attain that temperature at a lower pressure than would material which adhered to the adiabat. The net result, via Eq. (7), is a slight decrease in the degree of local superheating attending metastable transformation (Fig. 4). Again, greater depths of metastable persistence will generate greater degrees of local superheating.

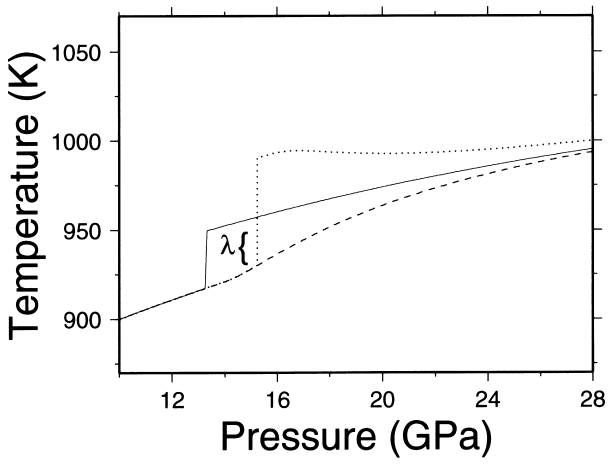

Fig. 4. Temperature as a function of pressure for a portion of a lithospheric slab subducting along an adiabat that is refracted by an equilibrium exothermic phase transition (solid). Regions in which low pressure phases persist metastably continue to follow their own geotherm (dashed), but this departs from an adiabat due to conductive heating from the surrounding warmer transformed material with a thermal lag λ according to Eq. (10). Eventual metastable transformation (here at 930 K) yields isobaric superheating (dotted) above the background equilibrium adiabat. Diagram calculated for the $\alpha \rightarrow \beta$ transition in forsterite, for 30-km-diameter metastable regions with 6 cm/yr vertical descent rate.

3.2 Endothermic transformations

In the case of an endothermic phase transition (e.g., $\gamma \rightarrow pv + mw$ near 670 km depth), any metastably persisting material would find itself surrounded by colder slab material, and subsequent heat conduction would lower its temperature (Green and Houston, 1995; Green and Zhou, 1996) with the same sort of lag λ as described (10) above. Subsequent endothermic transformation of the metastable material would also yield cooling, which would be unlikely to effectively trigger a seismogenic mechanism involving thermal runaway. However, conductive heating of slab material from the surrounding mantle would eventually overcome such cooling, so that other seismogenic mechanisms (such as dehydration) would remain possible at greater depths (Green and Houston, 1995; Okal and Bina, 1998). Moreover, a sufficient degree of metastable overstep of an endothermic phase boundary may cause the metastable transformation to become exothermic (Fig. 3).

4. Discussion and Conclusions

In summary, the temperature of metastable material that subducts adiabatically should, upon eventual exothermic transformation, rise via latent heat effects above the adiabatic temperature of the transformed bulk material surrounding it. However, regions of metastable material will not subduct strictly adiabatically, since they will warm by conduction from the hotter transformed material surrounding them (Devaux *et al.*, 1997), and the resulting decrease in transformation pressure will slightly reduce the effective magnitudes of the latent heats. Nonetheless, eventual transformation of metastable material can yield local superheating above the temperature of the surrounding material, with greater depths of metastable persistence generating greater

degrees of local superheating. Such superheating could trigger release of strain energy through a variety of proposed mechanisms of seismogenic shear instability, such as dehydration, runaway phase transformation (possibly with attendant crystallization of fine-grained weak material), or temperature-dependent rheological weakening. Regardless of the particular mechanisms of shear instability, thermal control of the failure process is consistent with the observation that the statistical properties of deep earthquakes and their aftershock sequences exhibit a greater temperature dependence than do those of shallow earthquakes, with colder slabs exhibiting a greater frequency of small earthquakes as well as more substantial aftershock sequences for deep earthquakes (Wiens and Gilbert, 1996).

It is instructive to contrast two proposed mechanisms in the context of latent heat release. In the runaway phase transformation model, latent heat release enhances reaction kinetics in neighboring metastable material via conductive heating, giving rise to locally rapid reaction rates (Kirby *et al.*, 1991; Rubie and Ross, 1994; Green and Houston, 1995; Green and Zhou, 1996; Kirby *et al.*, 1996). Such a failure mechanism, however, cannot operate outside the region of metastable material, contrary to observations constraining the actual rupture extent of deep seismicity (Wiens *et al.*, 1994; Myers *et al.*, 1995; Silver *et al.*, 1995).

In the temperature-dependent rheological weakening model, on the other hand, shear localization occurs through ductile deformation. Consequent shear heating, arising from concentrated conversion of elastic strain energy (Regenauer-Lieb and Yuen, 1998), leads to weakening in material with temperature-dependent rheology. This further focuses additional shear deformation, and such a feedback cycle leads to "adiabatic instability" as a potential mechanism for deep seismicity (Ogawa, 1987; Hobbs and Ord, 1988; Karato, 1997). Indeed, in addition to this subsolidus temperature-induced rheological weaking, such shear localization may induce partial melting (Ogawa, 1987; Karato, 1997) leading to even greater local reductions in viscosity. While there is no direct evidence of such melting in the transition zone, shear localization appears in some cases to have induced high degrees of partial melting within the lithosphere (Austrheim and Boundy, 1994; Obata and Karato, 1995; Austrheim *et al.*, 1996; Jin *et al.*, 1998), and frictional melting has also been suggested recently as an adjunct to deep seismicity (Kanamori *et al.*, 1998). Local superheating arising from latent heat release due to disequilibrium transformation of metastable phases could initiate such adiabatic instability by locally depressing viscosities within the superheated zone, and consequent shear localization could induce failure beyond the extent of the metastable material in which it was initially triggered.

Furthermore, it is interesting to compare the anomalous heating behavior expected for a series of phase transitions in a subducting slab and the observed distribution of deep seismicity (Green and Houston, 1995). Increasingly metastable persistence of α below an uplifted (exothermic) $\alpha \rightarrow \beta$ transition in the slab is consistent with increasing seismicity with depth below 400 km, and onset of a depressed (endothermic) $\gamma \rightarrow pv + mw$ transition is consistent with cessation of seismicity below 700 km. Of the various metastable olivine transformations considered herein (Fig. 2), those involving the metastable persistence of α, rather than of β or γ, may be the most important in subducting slabs, because the lowest temperatures in the slab are found initially within the α stability field. Of these, the metastable $\alpha \rightarrow \gamma$ transition yields the greatest latent heat release in the upper mantle.

If α can persist metastably into the lower mantle, then the metastable $\alpha \rightarrow pv+mw$ transition will release even greater latent heat. Also, any metastable persistence of γ leads to a $\gamma \rightarrow pv + mw$ reaction that, while initially endothermic, grows progressively more exothermic at greater depths in the lower mantle (Fig. 3). Thus, if lower pressure phases can persist metastably below the depth of the equilibrium $\gamma \rightarrow pv + mw$ transition, a mechanism for generating local superheating can also operate below this depth, and the apparent absence of seismicity in the lower mantle (Okal and Bina, 1998) may simply be due to a dearth of high strain energies below the transition zone (Bina, 1997).

Finally, because conductive heating of the slab occurs initially at the edges rather than in the interior, the edge regions initially possess a greater potential for local thermal anomalies due to metastable transformations, possibly consistent with occasional observation of double Wadati-Benioff zones at intermediate depths (Wiens *et al.*, 1993). However, heating of the slab edges leaves little scope for metastable persistence in these regions at greater depths, and the large degree of overstep associated with any metastable areas in the cold slab interior confers upon this region the greatest potential for initiation of seismicity at large depths.

Acknowledgments. I am grateful to the personnel of Tokyo University's Earthquake Research Institute for their kind hospitality and to the U.S. National Science Foundation (INT-9603234 and EAR-9706152) for financial support. I thank Harry Green, Fred Marton, and Dave Rubie for helpful comments on the manuscript.

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