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Phase Changes and Convection in the Earth's Mantle

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XXIII. Phase changes and convection in the Earth's mantle

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A phase change may hinder or enhance convection, depending on its characteristics. Univariant transformations such as may occur in the mantle constitute a barrier to convection unless the motion starts at some distance above or below the transition level; an initial temperature gradient in excess of the adiabatic value is also required. Multivariant transformations only require, in the transformation zone, an initial gradient slightly greater than the adiabatic value for a homogeneous layer. The effect on convection of transformation rates is not likely to be serious.

There seems to be general agreement that the occurrence of a reversible phase transformation in a convective system may either impede or enhance instability, depending on the thermodynamic parameters of the transformation. Vening Meinesz (1962) and Brooks (1954) are among those who think that phase transitions in the upper mantle might contribute to convective instability, while Knopoff (1964) states that the inhomogeneous region in the mantle represents a true barrier to convection. Both conclusions appear to be wrong. The main difficulty in approaching the problem is that the nature of the phase transitions occurring in layer *C* (200 to 900 km) of the mantle is not known. The parameters for a few possibly relevant reactions are listed in table 1. (All entries in that table are uncertain, some by as much as a factor of 2.) They suggest that phase transitions in the mantle are likely to be characterized by a volume change ΔV of a few cm^3/mole, and by an entropy change ΔS of a few calories per degree per mole. Characteristically, ΔV and ΔS have the same sign, so that heat is evolved when going from the light to the dense phase (or assemblage of phases), and is absorbed in the opposite reaction. The slope of an univariant equilibrium curve is likely to be of the order of 40 to 50 degC/kb; however, the extension of the transitional zone *C* down to about 900 km, where the pressure is of the order of 350 kb, suggest that there must be at least one transformation that has a much more gentle slope, or a much higher equilibrium pressure at 0 °C, than any listed in table 1, with the possible exception of the last one.

Consider first a univariant system consisting of one component and two phases (e.g. coesite and stishovite), or two components and three phases (e.g. forsterite, stishovite, periclase). The variance is 1, so that the pressure uniquely determines the equilibrium temperature; the slope $\mathrm{d}T/\mathrm{d}P$ of the equilibrium curve is, or course, $\Delta V/\Delta S$.

Let the equilibrium curve and natural temperature distribution curve intersect at *A* (figure 1), and suppose that a small mass of the dense phase (or assemblage of phases) is displaced upwards from *A*. If the transformation dense → light runs adiabatically, the temperature falls as the reaction proceeds, as it is endothermic in that sense. The pressure must therefore also drop, and the system remains on the univariant curve, cooling and expanding along *AB*; at some point *B* the reaction is completed. In the interval *AB* the density of the rising mass is everywhere greater than that of its surroundings because its temperature is lower and because it still contains an untransformed fraction of the original dense phase. Similarly, downward motion starting at *A* proceeds along *AC*, the density being everywhere less than that of the surrounding. The system is thus completely stable with respect to convection starting at *A*. The case where the slope of the equilibrium curve is less than the natural gradient is of no interest, as it cannot occur in the mantle where the undisturbed density increases with depth.

TABLE 1. POSSIBLE VALUES FOR THE PARAMETERS OF SOME POSSIBLE PHASE TRANSITIONS IN THE MANTLE*

reaction	ΔV (cm^3/mole)	ΔS (cal mole^{-1} degC^{-1})	ΔG_{298} (cal/mole)	dT/dP (degC/kb)	equilibrium pressure at 298 °K (kb)
$SiO_2 \rightarrow SiO_2$ coesite → stishovite	−5·9	−3·0	+13·7	47	97·5
$SiO_2 \rightarrow SiO_2$ quartz stishovite	−8·7	−3·7	+15·3	56	73·0
$Mg_2SiO_4 \rightarrow Mg_2SiO_4$ forsterite → spinel	−3·7	−2·0	—	44	—
$Mg_2SiO_4 \rightarrow 2MgO + SiO_2$ forsterite stishovite	−7·3	−3·3	+30·4	53	175
$MgSiO_3 \rightarrow \frac{1}{2}Mg_2SiO_4 + \frac{1}{2}SiO_2$ clinoenstatite forsterite stishovite	−2·65	−1·7	+12·4	37	97·5
$Mg_2SiO_4 \rightarrow MgSiO_3 + MgO$ forsterite corundum	−6·8	—	>20·4	—	> 125
$MgSiO_3 \rightarrow MgSiO_3$ clinoenstatite corundum	−5·8	—	> 14·0	—	> 100
$MgSiO_3 \rightarrow MgO + SiO_2$ corundum stishovite	−0·5	—	< 10·0	—	< 840

* Figures taken or calculated from Sclar, Carrison & Schwartz 1964, Ringwood 1962, and from thermodynamic data listed in Fyfe, Turner & Verhoogen 1958, p. 23.

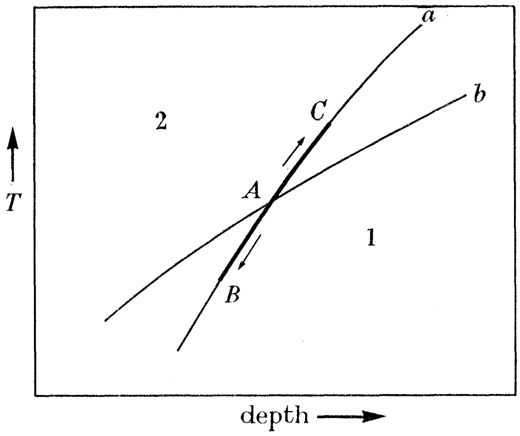

FIGURE 1. Transformation path in a univariant system. Curve *a* is the univariant equilibrium curve; curve *b* is the natural temperature distribution. An adiabatic path through *A* follows the equilibrium curve to *B* (ascending current) or to *C* (descending current).

Suppose, however, that upward motion start at a point *A*, (figure 2) sufficiently below the phase boundary, and that the initial gradient sufficiently exceeds the adiabatic gradient in the lower layer. The temperature of a rising mass drops along the adiabatic line *AB* (neglecting viscous dissipation, etc.), and the phase transformation begins at *B*. If it is completed at *C*, the density of the rising mass will, at all points of the path *ABC*, be less than that of its surroundings (figure 3), and convection may break through the phase boundary.

The depth at which convection must start in order that the transformation be completed at C (figure 2) may be estimated as follows. Assume all gradients to be constant in the range considered; then (figure 2)

$$T_A = T_C + \beta D,$$

where β is the natural gradient. But

$$T_A = T_B + \beta_s (D - d),$$

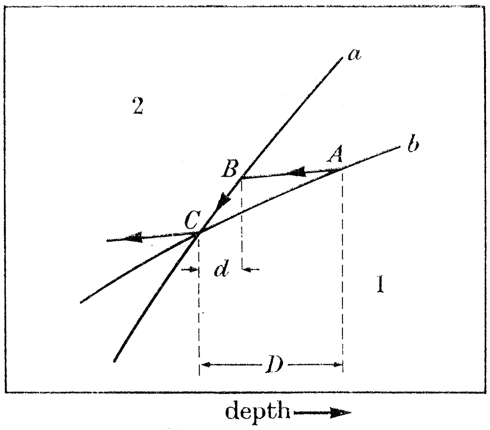

FIGURE 2. Convection through a univariant transformation. Curves a and b represent, as in figure 1, the phase equilibrium curve and the natural temperature distribution, respectively. The curve AB is an adiabatic path in medium 1. Numbers 1 and 2 refer to the dense and light phases, respectively. d is the thickness of the transition zone.

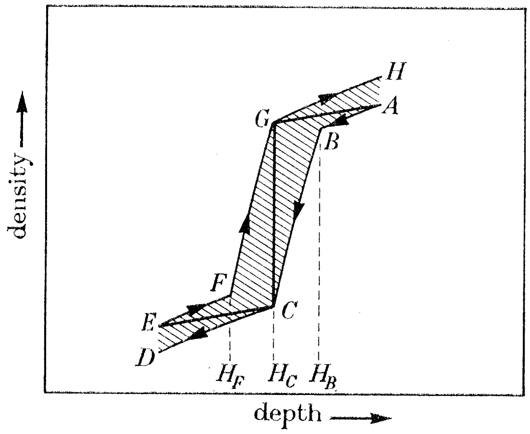

FIGURE 3. Diagram of density against depth in an ascending current ($ABCD$) and descending current ($EFGH$). The density in the descending branch is everywhere greater than the ascending branch. The curve $ECGA$ represents the undisturbed density distribution, with phase transition at depth H_C. The shaded area is proportional to the potential energy released in an overturn.

where β_s is the adiabatic gradient in the lower layer, and d is the thickness of the transition zone BC. Thus

$$D = \frac{1}{\beta'}(T_B - T_C) - \frac{\beta_s}{\beta'} d, \tag{1}$$

where β' is the superadiabatic gradient $\beta - \beta_s$.

To find $T_B - T_C = \Delta T$, one is tempted to write $\Delta T = \Delta H / c$, where ΔH is the latent heat of transformation and c is an appropriate specific heat. This expression, which is frequently used, needs justification. In the first place, ΔH varies nearly linearly with temperature, as the entropy of transformation $\Delta S = \Delta H/T$ is approximately constant. Secondly, c cannot be taken as the specific heat at constant pressure, because the specific heat of a system undergoing a first-order phase transition at constant pressure is infinite (an infinitesimal change in temperature about the equilibrium point causes a finite change in heat content).

Let x be at any point between B and C the molar fraction of untransformed dense phase 1, and $(1-x)$ the fraction of the light phase 2. Thus $x = 1$ at B and $x = 0$ at C, for upward motion. The entropy per mole is

$$S = xS_1 + (1-x)\,S_2 = S_2 + x(S_1 - S_2) = S_2 + x\Delta S, \tag{2}$$

where $\Delta S = S_1 - S_2$ is the entropy of transition (ΔS is generally negative). For an adiabatic change, $\mathrm{d}S = 0$. Thus

$$\left(\frac{\partial S}{\partial P}\right)_{T,\,x}\mathrm{d}P + \left(\frac{\partial S}{\partial T}\right)_{P,\,x}\mathrm{d}T + \left(\frac{\partial S}{\partial x}\right)_{T,\,P}\mathrm{d}x = 0. \tag{3}$$

Using (2), and noting that

$$\left(\frac{\partial S_1}{\partial P}\right)_T = -\alpha_1 V_1, \quad \left(\frac{\partial S_1}{\partial T}\right)_P = c_1/T, \quad \text{etc.}$$

(α = thermal expansion; c_1 = specific heat at constant P of phase 1), we get

$$[-\alpha_2 V_2 + x(-\alpha_1 V_1 + \alpha_2 V_2)]\,\mathrm{d}P + [c_2 + x(c_1 - c_2)]\,(\mathrm{d}T/T) + \Delta S\mathrm{d}x = 0.$$

Along the equilibrium curve $\mathrm{d}P = (\Delta S/\Delta V)\,\mathrm{d}T$. To simplify, suppose that $\alpha_1 = \alpha_2$, $c_1 = c_2 = c$. Then

$$\frac{\mathrm{d}T}{\mathrm{d}x} = 1\Big/\left[x\alpha + \alpha\frac{V_2}{\Delta V} - \frac{c}{T\Delta S}\right] = (1/\alpha)\Big/\left[x + \frac{V_2}{\Delta T} - \frac{c}{\alpha T\Delta S}\right]. \tag{4}$$

Note that $0 \leqslant x \leqslant 1$. The term $V_2/\Delta V$ may be of the order of 10 to 20, whereas $c/(\alpha T\Delta S)$ may be much larger; we might have, for instance, $\alpha \sim 2\times10^{-5}$, $T \sim 2\times10^{3}$, $\Delta S = -3$ cal mole^{-1} degC^{-1} (see table 1), whereas c is close to 0·3 cal g^{-1} degC^{-1}, or 30 cal mole^{-1} degC^{-1}. Neglecting all terms other than the one containing T in the denominator of (4), we get

$$\frac{\mathrm{d}T}{\mathrm{d}x} = -\frac{T\Delta S}{c}.$$

Integrating for x from 1 to 0, and for T from T_B to T_C yields

$$T_B = T_C \exp\,(-\Delta S/c). \tag{5}$$

Now $\Delta S/c$ is of the order of $-0{\cdot}1$ or less; thus $T_B \sim 1{\cdot}1T_C$, and if

$$T_C = 2000\,^{\circ}\mathrm{C}, \quad T_B - T_C = 200\ \mathrm{degC}.$$

To find d, we note that if the slope of the univariant curve is about 50 degC/kb, the pressure at B exceeds that at C by about 4 kb, and $d \sim 10$ km. Suppose that $\beta = 2\beta_s$, or $\beta' = \beta_s = 0{\cdot}5$ degC/km, say. Then from (1) $D \sim 400$ km. But if β' is smaller, or of the order, say, of 0·1 degC/km, $D \sim 2000$ km. Thus we find that a convection current may or may not break through a phase boundary, depending on where it starts; a phase transition acts as a filter which stops small perturbations, but allows large, deep-seated, ones to go through.

The efficiency of the phase transition as an obstacle to convection depends primarily on ΔS. If ΔS is very large, and the univariant equilibrium curve very flat, convection will be hindered; if ΔS is very small and the univariant curve very steep, the inhibition is small. Convection is not affected at all by a phase transition if $\Delta S = 0$ (no latent heat). Figure 3 shows the density as a function of depth in ascending and descending columns. The gravitational energy E released in a cycle is $\int g\delta\rho \,\mathrm{d}h$, where $\delta\rho$ is the difference in density, at the same level, between sinking and rising currents; E is thus proportional to the shaded area in figure 3. We note that if the ascending current starts at a point midway between G and A, while the descending current starts midway between E and C, their density-depth curves would coincide, and no gravitational energy would be released; convection through the transition then becomes impossible.

Consider now a bivariant system consisting of two components and two phases, both of which are solid solutions; the olivine-spinel transformation in the system Fe_2SiO_4–Mg_2SiO_4 may serve as an example. At constant temperature, and for a given composition, the transition starts at a pressure P_1 and ends at a higher pressure P_2. In the interval P_1 to P_2, the composition of both phases and their relative amount change continuously. The molar fraction of the spinel phase increases continuously (but is not a linear function of the pressure (see Meijering & Rooymans 1958); at the same time the density of both the spinel and olivine phases may decrease with increasing pressure, because of their changing composition. Both P_1 and P_2 depend on temperature and gross composition of the system. The curves labelled 1 and 2 in figure 4 represent the P–T conditions under which the transformation starts and ends for a given gross composition. In the P–T field between these two curves the variance is 2, and the system can exist in equilibrium at *any* point in that field. The function $F(z)$ which, according to Vening Meinesz (1962, p. 150), gives the phase equilibrium temperature at depth z does not exist.

Consider now material initially at A (figure 4), and displace it upwards adiabatically. The system is unstable if the adiabatic path AB through the transition zone lies above AC, which represents the natural initial temperature gradient.

To determine the adiabatic path AB, let ΔS be, as before, the entropy of transformation $S_1 \rightarrow S_2$ (subscripts 1 and 2 refer, respectively, to the spinel and olivine phases). Both S_1 and S_2 depend on composition, which we assume to be known. We also assume that ΔS is independent of P and T. We have

$$S_{1,A} = S_{2,A} + \Delta S, \tag{6}$$

$$S_{1,B} = S_{2,B} + \Delta S. \tag{7}$$

But

$$S_{1,A} = S_{1,B} + \int_{T_B}^{T_A} \frac{c_1}{T}\,\mathrm{d}T - \int_{P_B}^{P_A} \alpha_1 V_1 \,\mathrm{d}P. \tag{8}$$

Along an adiabatic path $S_{1,A} = S_{2,B} = S_{1,B} - \Delta S$, by (7). Thus

$$\Delta S = \int_{P_B}^{P_A} \alpha_1 V_1 \,\mathrm{d}P - \int_{T_B}^{T_A} \frac{c_1}{T}\,\mathrm{d}T, \tag{9}$$

from which P_B and T_B may be determined, given P_A and T_A, or vice versa; P_B and T_B must, of course, be related so that the representative point falls on the univariant curve (2). Alternatively, P_A and T_B may be determined from a second equation similar to (8) but relating to the olivine phase:

$$S_{2,A} = S_{2,B} + \int_{T_B}^{T_A} \frac{c_2}{T}\,\mathrm{d}T - \int_{P_B}^{P_A} \alpha_2 V_2\,\mathrm{d}P.$$

Let $P_A - P_B = \Delta P$, and let $\overline{\alpha V}$ be the average value of $\alpha_1 V_1$ in the interval P; similarly, let c be an average value of c_1. Integration of (9) gives

$$\ln(T_A/T_B) = [\overline{\alpha V}\Delta P - \Delta S]/c. \tag{10}$$

The corresponding expression for an adiabatic path in a homogeneous layer would be, of course, $\ln(T_A/T_B) = \overline{\alpha V}\Delta P/c$; the phase transformation merely introduces an additional term $\Delta S/c$ in the expression for the adiabatic gradient. As ΔS is generally negative, the adiabatic gradient is steeper in the transition zone than outside it.

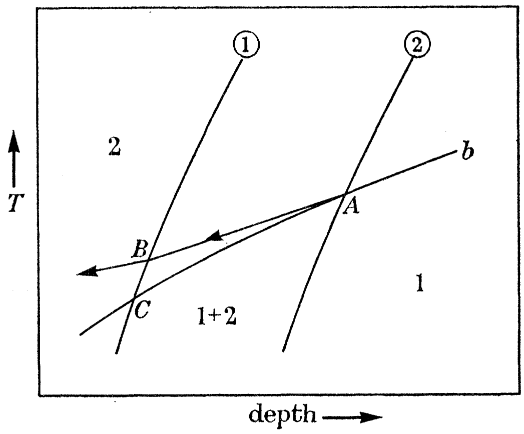

Figure 4. Convection through a divariant transformation. Curves ① and ② represent the beginning and end of the transformation for a given composition. AC is the natural temperature distribution; AB represents an adiabatic path, starting at A, through the transition zone. Phases 1 (dense) and 2 (light) coexist between curves ① and ②; their composition is variable in that interval.

Consider, for example, a multivariant phase transition that spreads, in the mantle, over a pressure range of, say, 100 kb; i.e. $P_A - P_C = 100$ kb (figure 4). Then $\Delta P = P_B - P_A$ is less than this, say 80 kb (figure 3). The term $\overline{\alpha V}\Delta P$ would be of the order of $2\times10^{-5}\times35\times8\times10^{4}$ bar cm^3 mole^{-1} degC^{-1}, or 5·6 cal mole^{-1} degC^{-1}. By comparison, the entropy of the spinel → olivine transition might not be greater than 2 cal mole^{-1} degC^{-1}. Thus, the phase transition steepens the adiabatic gradient, but not very much. Note that at point B, where the adiabatic transformation starting at A is completed, the system is lighter than its surroundings because it consists entirely of the light phase 2 at temperature T_B, whereas the surroundings consist of a mixture of light and dense phases at a lower temperature. Instability above the transition zone is thus enhanced.

It is interesting that if phase transitions and convection both occur in the mantle, it should be possible, theoretically, to map seismologically regions of ascending and descending currents. Indeed, if a univariant transformation occurs in an undisturbed region at depth H_C (figure 3), the transformation starts in an ascending current at the greater depth H_B, and in a descending current at a lesser depth H_F. Similarly, divariant transition extends (figure 5), from F to G in a descending current, and from C to B in an ascending one. Depth differences will, however, presumably be of the order of only a few kilometres.

The preceding discussion assumes that transformation rates are such that the composition of a moving mass remains at all times in equilibrium at the local P–T conditions. If transformations were sluggish and did not run at a rate comparable to the upward or downward velocity, phase transitions would inhibit convection just as a density stratification would. Clearly, if K is the specific reaction rates (fraction transformed per unit time), we must have $K \geqslant v/d$ where v is the vertical velocity and d is the thickness of the transition zone (e.g. d in figure 2). If $v = 10^{-7}$ cm/s, $d = 10^6$ cm, then $K \geqslant 10^{-13}\,\mathrm{s}^{-1}$.

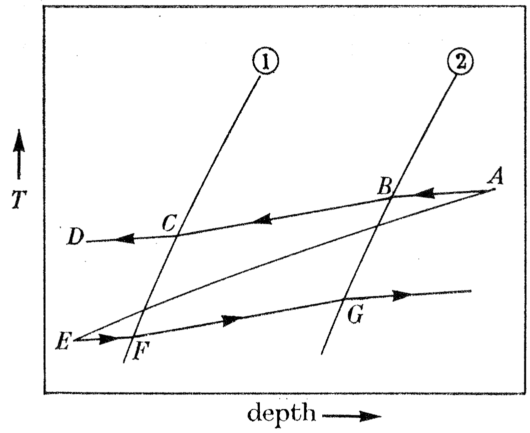

Figure 5. Transition depth for ascending and descending currents, for the case of divariant equilibrium (fixed composition). Curves ① and ② are as in figure 4; EA represents the temperature distribution before convection. $ABCD$ is an adiabatic path for an ascending current; $EFGH$ is a similar path for a descending current. The transition zone in the descending current (F to G) lies above that (BC) for the ascending current.

The geological record shows clearly that phase transformations do not invariably occur at such rates. Metamorphic rocks commonly contain dense phases (e.g. kyanite, garnet, aragonite, etc.) which have failed to revert to their low pressure form when brought to the surface at a rate that cannot be much greater than the rate of isostatic adjustment or of convective motion. This persistence of high pressure forms is commonly attributed to the low temperatures, and therefore slow reaction rates, prevailing near the surface of the Earth; yet one finds in basalts erupted at 1200 °C or so fragments of eclogite which have failed to revert to their low pressure form; and diamonds commonly survive in hot kimberlites. It is of course likely that in the last two instances the rate of upward motion was much greater than 10^{-7} cm/s. But as pressure generally has an adverse effect on rates of transformation, it may be necessary to consider the matter more carefully.

Theory predicts that reaction rates should in general be of the form

$$K = A\,\mathrm{e}^{-\Delta G^*/RT},$$

where ΔG^* is the Gibbs free-energy of activation. But $G = E + PV - TS$, so that K may be written as

$$K = K_0\,\mathrm{e}^{-(E^* + PV^*)/RT},$$

where K_0 is a constant that includes an entropy of activation. E^* is the energy of activation determined by plotting, at $P = 0$, the $\log K$ against $1/T$. V^* is the activation volume which, for processes involving diffusion and growth, is generally of the order of, but smaller than, the molar volume of the diffusing unit.

If P and T are varied simultaneously so as to remain in the neighbourhood of equilibrium,

$$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{\Delta V}{\Delta S} = \beta, \quad \text{say}$$

and

$$\mathrm{d}\ln K = \frac{E^*+PV^*}{RT^2}\,\mathrm{d}T - \frac{V^*}{RT}\,\mathrm{d}P$$

or

$$RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}P} = \beta E^* + V^*(P\beta - T).$$

At equilibrium $P = P_0 + T/\beta$, where P_0 is the equilibrium pressure at $T = 0$. Thus near equilibrium we have, approximately,

$$RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}P} = \beta[E^* + P_0 V^*],$$

and since E^*, V^* and P_0 are generally positive, $\mathrm{d}\ln K/\mathrm{d}P > 0$. This is in accord with the observation that transformation rates generally increase markedly when P and T are raised simultaneously so as to remain near equilibrium.

A typical transformation might be such that $E^* \sim 10^5$ cal/mole, $P_0 \sim 10^5$ b, $V^* = 10\,\mathrm{cm}^3$, $\beta = 5\times10^{-2}\,\mathrm{degC\,b^{-1}}$. Then, at $T = 2\times10^3$ degC, $\mathrm{d}\ln K/\mathrm{d}P \sim 10^{-3}\,\mathrm{b}^{-1}$. Thus, for instance, the rate of the reaction coesite → stishovite at 200 kb (and 5000 °C) might be e^{100} times what it is at 100 kb (and 0 °C). There is, indeed, experimental evidence to show that stishovite may form in shock waves in a time of the order of 10^{-6} s.

We conclude that phase transitions of the kind that may occur in the mantle are likely to slightly inhibit convection, but are not such as to make it impossible. A univariant transition forms no serious obstacle to convection provided that: (1) the entropy of transformation be small enough; (2) the super-adiabatic gradient in the lower layer be large enough; and (3) the upward (downward) motion start sufficiently far below (above) the transition level. Convection through a multivariant transition zone requires a temperature gradient only slightly greater than that needed for convection in a homogeneous layer. Transformation rates are not likely to hinder convection.

Phase transformations have no effect on convection caused by horizontal temperature gradients.

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