

THE ADIABATIC GRADIENT IN THE MANTLE TRANSITION ZONE*

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Assuming that there are penetrative convective currents and using the data on the MgO-SiO₂ system to model the chemical transformations, we have constructed the temperature profile in the mantle transition zone. The roles of chemical and phase transformations as heat sources are examined. The roles of these sources vary in accordance with the convection rate, which enables us to formulate models for adiabatic and isothermal heterophase boundaries. The formulas are used to estimate the temperature step in the interphase layer and the width of that layer. An analysis is performed on the variations in mineral composition in the transition zone during the evolution of the planet within the framework of the quasistatic model.

Considerable advances have been made in seismic sounding of the Earth and in interpreting the resulting data, which has given rise to reasonably reliable ideas of the pressure and density distributions in the planet. The paradoxical situation has arisen where the mechanical picture is largely detached from the thermodynamic data. The fact is, the temperature distribution cannot be recovered unambiguously from the known pressure and density distributions, and this hinders any study of the chemical composition.

As a rule, the density section is constructed by solving the hydrostatic-equilibrium equations for a spherically symmetrical self-gravitating body [1-3]:

$$\frac{dP}{dr} = -\frac{Gm\rho}{r^2}, \quad \frac{dm}{dr} = 4\pi r^2 \rho, \quad (1)$$

where P is pressure, ρ density, $m(r)$ the mass of a spherical layer of radius r , and G the gravitational constant. System (1) is clearly not closed. To close it we need to add the equation of state for the material of the Earth, $P = P(\rho, T, x_1, \dots, x_A)$, and we also need to write equations to define the temperature $T(r)$ and the concentrations of the chemical components $x_i(r)$, $i = 1, \dots, A$. There is however another way of finding the pressure and density distributions. From independent sources (usually seismological data), we know the relation between the pressure and density within the Earth, for example, $dP/d\rho$ is given as a function of ρ or r . In that case, equations (1) can be integrated. The commonest model at the present time is that for an effectively one-component adiabatic planet in the regions of homogeneity. This means that in the zones separated by the seismic boundaries the function $P(\rho)$ describes the adiabatic behavior of a certain substance (Earth material), and $dP/d\rho$ can be calculated from the seismic velocities known from experiment [1-3]:

$$dP/d\rho = v_p^2 - \frac{4}{3}v_s^2.$$

The adiabatic (isentropic) condition is used to determine the temperature:

$$S(\rho, T) = S_0,$$

where S is the specific entropy. There is an ambiguity in determining the temperature because the explicit form of $S(\rho, T)$ is dependent on the unknown

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distribution of the composition over the radius. In that sense, the problems of the temperature and composition are closely related. Another source of ambiguity arises from the possible deviations from the adiabatic condition [1-3]. The thermal-expansion coefficient is small, so such deviations have virtually no effect on the structure of the solution to (1); therefore, the density profile found in that way is generally accepted. On the other hand, there is considerable uncertainty as to the temperature distribution [1-7]. We see that the mechanical and thermochemical problems separate within the framework of the adiabatic model. In particular, we need to construct the adiabat for the Earth material in P - T coordinates, which is then readily transformed into the geotherm $T(r)$ by means of the known $P(r)$ relation. Particular interest attaches to the structure of the adiabat in the regions of the chemical and phase transformation zones, where the temperature gradients may exceed the mean value by large factors, which is due to the presence of localized heat sources there.

The adiabatic character of the temperature distribution in the mantle is usually ascribed to vigorous convective motion. However, there is the open question of the size of the region involved in subsolidus convective mixing [8-10]. Three points of view are common: 1) the convection occurs only in the upper mantle, 2) the upper and lower parts of the mantle are independently convecting layers, and the thermal boundary layer separating them is associated with a chemical (phase) boundary at a depth of ~ 670 km, and 3) the convection extends to the entire mantle. The choice of model has a substantial effect on the calculated temperature profile in the mantle. The adiabatic gradient changes only slightly when the equation of state alters in the homogeneous parts, whereas the presence of boundaries with no flow through them results in high temperature gradients, which may amount to hundreds of degrees over narrow regions [7, 8]. Therefore, it is important to determine whether a density boundary associated with chemical or phase transformations is an obstacle to convection or whether convection is penetrative in relation to this boundary [3, 11-13]. It would be impossible to solve this problem without a detailed description of the transformation chemistry. In essence it is necessary to simulate the detailed chemical and mechanical structures of the region in which the degree of transformation varies from 0 to 1 (heterophase zone). We naturally start with a simplified formulation based on a *a priori* definition of the hydrodynamic flow structure.

There are two major approaches to describing the flow of a continuous medium through heterophase (interphase) zones: the isothermal approximation and the adiabatic one. In the first case, it is assumed that the temperature is constant in the interphase region and that the heat of the chemical transformation is carried off by a convective (conductive) flux, so that heat effect does not appear locally. The second approach is based on the assumption that the particles are adiabatically heated (cooled) as a result of the heat change in the chemical transformation, so there is a nonzero resultant temperature step in a fairly narrow heterophase zone. The choice between the approximations is substantially dependent on the speed of the convective flows.

Here we will consider a model for fairly extensive penetrative convection. We then have to construct the adiabatic temperature distribution in the transitional two-phase region. The approach derives originally from Ringwood [11] and was developed in [12-14]. A similar question of constructing an adiabat arises in considering decompression in rising diapirs [15].

Here we will consider univariant transformations. Divariant ones will be considered in detail in a separate paper. The examination is free from numerous simplifying assumptions made in [11-15]. The formulas enable us to calculate the temperature step at the phase boundary and also to determine the extent of the interphase layer. Considerable evidence has accumulated on the thermodynamic characteristics of high-pressure phases [16-20], so this detailed consideration is feasible.

The data are used in analyzing the thermal structure of the mantle transition zone [21, 22]. Let us examine the applicability of the adiabatic approximation.

ADIABATIC CONSTRUCTION

Hydrodynamic convection theory indicates that the temperature gradient is close to the adiabatic value throughout a region of vigorous convection, apart from the thermal boundary layers [7, 8]. Then the temperature distribution can

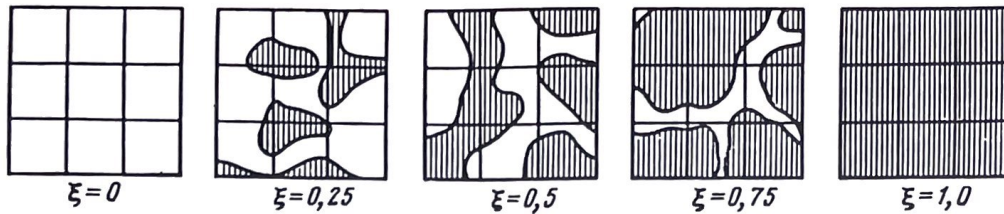


Fig. 1. Schematic representation of an element in a continuous medium for various values of the degree of transformation ξ .

be found from the following equation for any region homogeneous in composition:

$$dS(P, T) = \frac{\partial S}{\partial P} dP + \frac{\partial S}{\partial T} dT = 0. \quad (2)$$

If we introduce the thermal-expansion coefficient $\alpha = -\rho \partial \rho / \partial P = (1/V) (\partial V / \partial T)_P$, the specific volume $V = 1/\rho$, and the specific heat at constant pressure $c_p = T(\partial S / \partial T)_P$, then from (2) we get the standard relation [1-3]:

$$\frac{dT}{dP} = \frac{\alpha T}{\rho c_p}. \quad (3)$$

Equation (3) enables us to construct the adiabat $T(P)$ if the thermodynamic functions $\alpha(P, T)$, $c_p(P, T)$, $V(P, T)$ are known and a reference point on the adiabat $T_0(P_0)$ is specified. The latter feature occurs because the entropy S_0 , which is constant along the adiabat, must be specified independently. An explicit expression for the temperature

$$T = T_0(S_0, \rho_0) \exp \int_{\rho_0}^{\rho} \frac{\gamma(x, S_0) dx}{x}$$

can be obtained if we introduce the Grueneisen parameter $\gamma = \alpha K_s / \rho c_p$, where

$$K_s = \rho \partial P / \partial \rho |_s.$$

To carry out the calculations we need thermodynamic information on the supposed components of the Earth material. Methods of constructing equations of state have been vigorously developed recently [16-20], and these can be used with the experimental data for high pressures to derive the thermodynamic parameters and construct the adiabat.

Solid phases undergo chemical and phase transformations as the thermodynamic conditions alter, which are accompanied by changes in density, entropy, etc. In the interior of the Earth, where the pressure varies by hundreds of kilobars with depths, while the temperature range is thousands of degrees, such transformations are extremely numerous [2, 3, 19-22]. The regions where transformations are localized require particular consideration in constructing models for the convecting mantle. We assume that the convection is penetrative in relation to these zones, and the convection intensity is such that the temperature distribution within the transformation region can be taken as adiabatic.

The system is heterogeneous in the two-phase transition zone. An average description is possible, which involves introducing an additional parameter: the degree of transformation ξ . Let us divide the medium into elements, each of which contains N mols of substance (phase α). They all participate in the convective motion and at a certain instant reach a region of $P-T$ conditions corresponding to the α - β phase equilibrium. The production of $\Delta N_\beta = \xi N$ mols of phase β causes a deviation from homogeneity and is accompanied by the release or absorption of heat. The value of ξ is equal to the molar concentration of phase β , $0 \leq \xi \leq 1$ (Fig. 1).

Table 1

Thermodynamic Information on Major Transformations in the MgO-SiO₂ System

Parameter	$\alpha\text{-Mg}_2\text{SiO}_4 = \beta\text{-Mg}_2\text{SiO}_4$			$2\text{MgSiO}_3(\text{En}) = \beta\text{-Mg}_2\text{SiO}_4 + \text{SiO}_2$			$\beta\text{-Mg}_2\text{SiO}_4 = \gamma\text{-Mg}_2\text{SiO}_4$			$\gamma\text{-Mg}_2\text{SiO}_4 + 2\text{MgSiO}_3$	
	1000	1273	1500	1000	1273	1500	1000	1273	1500	1000	1273
T, K	1000	1273	1500	1000	1273	1500	1000	1273	1500	1000	1273
P, kbar	134	143	151	160	163	164	152	166	177	134	190
$\frac{dP}{dT}, \frac{\text{kbar}}{\text{K}}$	0,035			0,008			0,05			0,2	
$\frac{dT}{dP}, \frac{\text{K}}{\text{kbar}}$	29			125			20			5	
$\Delta H, \frac{\text{kcal}}{\text{mol}}$	-2,1	-2,7	-3,2	-1,1	-1,4	-1,7	-0,5	-0,6	-0,7	-4,5	-5,70
$\Delta V, \frac{\text{cm}^3}{\text{mol}}$	-2,50	-2,52	-2,53	-5,64	-5,82	-5,95	-0,43	-0,41	-0,4	-0,94	-0,93
$V, \frac{\text{cm}^3}{\text{mol}}$	1 40,99 2 38,49 3 —	41,10 38,58 —	41,19 38,66 —	28,58 38,07 13,45	28,77 38,23 13,49	28,95 38,43 13,52	38,16 37,73 —	38,18 37,77 —	38,20 37,80 —	38,0 13,56 25,31	37,42 13,39 24,94
$c_p, \frac{\text{cal}}{\text{mol}\cdot\text{K}}$	1 41,82 2 40,87 3 —	42,78 42,05 —	43,36 42,76 —	29,86 40,77 17,04	30,58 41,99 17,49	31,04 42,71 17,72	40,79 41,29 —	41,97 42,32 —	42,65 42,93 —	41,36 17,07 29,66	42,22 17,48 30,30
$\alpha, 10^{-5}$	1 2,92 2 2,47 3 —	2,93 2,54 —	2,93 2,58 —	3,00 2,38 1,24	3,09 2,47 1,28	3,16 2,52 1,30	2,40 2,32 —	2,45 2,37 —	2,48 2,39 —	2,39 1,28 2,68	2,28 1,24 2,52
$\rho, \frac{\text{g}}{\text{cm}^3}$	1 3,433 2 3,656 3 —	3,423 3,647 —	3,416 3,640 —	3,513 3,696 4,467	3,490 3,680 4,454	3,468 3,660 4,444	3,687 3,729 —	3,684 3,725 —	3,682 3,722 —	3,703 4,431 3,967	3,760 4,487 4,027
$\Delta\rho, \frac{\text{g}}{\text{cm}^3}$	0,233	0,225	0,224	0,384	0,392	0,397	0,042	0,041	0,040	0,073	0,075
$\frac{\Delta\rho}{\rho}, \%$	6,5	6,6	6,6	10,9	11,2	11,4	1,1	1,1	1,1	1,8	1,9

Note: The numbers 1, 2, and 3 correspond to the reactants in the order in which the

The adiabatic condition* for element N can be written as

$$dS_N(P, T, \xi) = 0,$$

where S_N is the entropy of the element. Let us consider a simple model for the chemically equilibrium phase mixture. In that case,

$$S_N = [\xi S_\beta(P, T) + (1-\xi) S_\alpha(P, T)] N, \quad (4)$$

$$\mu_\alpha(P, T) = \mu_\beta(P, T), \quad (5)$$

where S_α and S_β are the molar entropies of the phases and μ_α and μ_β are the chemical potentials (molar Gibbs energies). Condition (5) defines the relationship between the pressure and temperature, which can also be found from the Clausius-Clapeyron equation

$$dP/dT = \Delta H/T\Delta V = \Delta S/\Delta V,$$

*We neglect dissipative mechanisms.

in the Range of P and T Corresponding to the Transition Zone [16-20]

$+SiO_2$ (Ilm)	$\gamma-Mg_2SiO_4+SiO_2$ $=2MgSiO_3(Pv)$			$\gamma-Mg_2SiO_4=MgSiO_3$ $\cdot(Pv)+MgO$			$\gamma-Mg_2SiO_4$ $=2MgO+SiO_2$			$MgO+SiO_2$ $=MgSiO_3(Pv)$		
1500 233	1000 203	1273 206	1500 208	1000 211	1273 212	1500 213	1000 225	1273 223	1500 221	1000 130	1273 151	1500 169
		0,01			0,004			-0,008			0,08	
		100			250			-125			12	
-6,70	-1,0	-1,20	1,40	-0,3	-0,4	-0,5	0,6	0,7	0,9	-1,1	-1,3	-1,4
-0,94	-4,05	-3,99	-3,94	-3,52	-3,49	-3,47	-2,96	-3,00	-3,01	-0,57	-0,51	-0,49
37,01	37,00	37,19	37,36	36,90	37,11	37,29	36,70	36,95	37,16	10,72	10,70	10,69
13,27	13,30	13,33	13,36	23,08	23,22	23,35	10,26	10,34	10,42	13,57	13,54	13,51
24,67	23,14	23,27	23,39	10,32	10,40	10,46	13,22	13,27	13,31	23,72	23,72	23,70
42,72	41,14	42,20	42,82	41,08	42,17	42,79	41,03	42,12	42,75	11,88	12,27	12,52
17,68	17,02	17,47	17,69	29,12	30,10	30,69	11,30	12,14	12,41	17,07	17,49	17,71
30,68	29,15	30,11	30,70	11,74	12,16	12,41	17,00	17,46	17,69	29,37	30,30	30,84
2,22	2,19	2,25	2,29	2,15	2,23	2,27	2,10	2,19	2,24	3,27	3,30	3,32
1,21	1,19	1,22	1,24	2,39	2,50	2,55	2,76	2,92	3,02	1,29	1,30	1,30
2,45	2,41	2,50	2,56	2,84	2,98	3,06	1,17	1,21	1,23	2,64	2,68	2,70
3,802	3,803	3,783	3,766	3,813	3,792	3,773	3,834	3,808	3,786	3,761	3,768	3,772
4,528	4,518	4,508	4,496	4,350	4,324	4,300	3,931	3,899	3,869	4,427	4,439	4,448
4,069	4,339	4,315	4,292	3,905	3,877	3,855	4,545	4,529	4,514	4,232	4,232	4,236
0,076	0,347	0,340	0,336	0,402	0,393	0,389	0,336	0,336	0,334	0,100	0,090	0,087
1,9	8,7	8,6	8,5	10,5	10,4	10,3	8,8	8,8	8,8	2,4	2,2	2,1

reaction equations are written $A+B=C$; 1-A, 2-B, 3-C.

where $\Delta H=H_\beta-H_\alpha$ is the heat of transformation, $\Delta S=S_\beta-S_\alpha$ is the entropy change, and $\Delta V=V_\beta-V_\alpha$ is the change in molar volume. Therefore, the temperature in the transformation zone is controlled by the chemical equilibrium. Table 1 gives thermodynamic data on the main transformations in the MgO-SiO₂ system in the range of $P-T$ parameters corresponding to the mantle transition zone. It is clear that in the two-phase region the temperature gradient may differ from the mean value for the upper mantle, which is ~ 0.8 K/bar, by more than an order of magnitude.

Using (4) we can rewrite the adiabatic condition as

$$-[\alpha_\alpha V_\alpha - \xi \Delta(\alpha V)] dP + \left[\frac{c_p}{T} - \xi \frac{\Delta c_p}{T} \right] dT + \Delta S d\xi = 0,$$

where α_α and α_β are the thermal-expansion coefficients, $\Delta(\alpha V) = \alpha_\beta V_\beta - \alpha_\alpha V_\alpha$, c_{p_α} and c_{p_β} are the specific heats at constant pressure and $\Delta c_p = c_{p_\beta} - c_{p_\alpha}$.

The additional relationship of (5) between the pressure and temperature provides an equation* for ξ :

$$\frac{d\xi}{dT} = \frac{[\alpha_\alpha V_\alpha - \xi \Delta(\alpha V)] \Delta H - [c_{p_\alpha} - \xi \Delta c_p] \Delta V}{\Delta H \Delta V},$$

*Similar relationships arise in considering isochoric transformations [23].

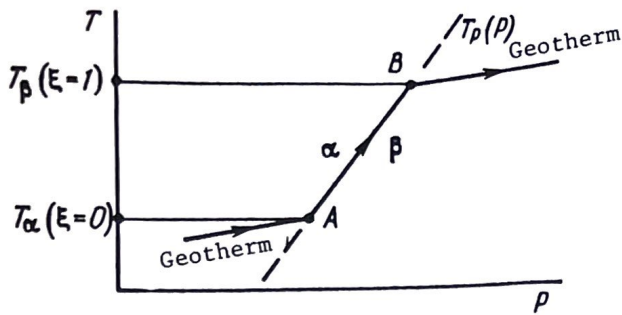


Fig. 2. Characteristic form of the geotherm in the region of an α - β univariant equilibrium. At temperature T_α , the degree of transformation ξ (molar proportion of phase β) is zero, while $\xi = 1$ at $T = T_\beta$. The geotherm shown by the solid line has kinks at points A and B.

which is readily integrated

$$\xi(T) = -\xi_0(T) \exp \left[\int_{T_\alpha}^T \pi(z) dz \right]$$

$$\xi_0(T) = \int_{T_\alpha}^T \sigma(z) \exp \left[\int_z^{T_\alpha} \pi(z') dz' \right] dz. \quad (6)$$

Here we have introduced the symbols

$$\pi(T) = \Delta(\alpha V) / \Delta V - \Delta c_p / \Delta H, \quad \sigma(T) = c_{p\alpha} / \Delta H - \alpha_\alpha V_\alpha / \Delta V$$

as T_α we took the temperature corresponding to the instant where phase β appears: $\xi(T_\alpha) = 0$. At $T = T_\alpha$ the one-phase adiabat (from phase α) intersects the $T(P)$ phase equilibrium curve (Fig. 2). To calculate the resultant temperature change in the transformation zone $\delta T = T_\beta - T_\alpha$, we have to determine T_β from $\xi(T_\beta) = 1$. The width of the two-phase zone can then be found from the $P(r)$ relation.

Methods have been given [16-20] for obtaining information on the behavior of the thermodynamic quantities α , c_p , V , and S along the equilibrium curve. Here we restrict ourselves to simple estimates made from simplifying assumptions. Data attained from the Debye model (Table 1) indicate that the difference in specific heats of the phases is less than 5% for the main transformations in the MgO-SiO₂ system at the T and P corresponding to the mantle transition zone, while the thermal-expansion coefficients on average differ by less than 20%. We therefore put $\alpha_\alpha = \alpha_\beta = \alpha(T)$, $c_{p\alpha} = c_{p\beta} = c_p(T)$. In that case, (6) simplify:

$$\xi(T) = -\xi_0(T) \exp \left[\int_{T_\alpha}^T \alpha(z) dz \right],$$

$$\xi_0(T) = \int_{T_\alpha}^T \left[\frac{c_p}{z\Delta S} - \alpha \frac{V_\alpha}{\Delta V} \right] \exp \left[- \int_{T_\alpha}^z \alpha(z') dz' \right] dz.$$

We neglect the small changes in α , c_p , S , and V along the equilibrium curve to get

$$\xi(T) = -\xi_0(T) \exp[\alpha(T - T_\alpha)],$$

$$\xi_0(T) = \frac{V_\alpha}{\Delta V} \{ \exp[\alpha(T_\alpha - T)] - 1 \} + \frac{c_p}{\Delta S} \exp(\alpha T_\alpha) [\text{Ei}(-\alpha T) - \text{Ei}(-\alpha T_\alpha)],$$

where $\text{Ei}(-x) = - \int_x^\infty e^{-t} t^{-1} dt$ is the Euler function. For small αT ($\alpha \sim 10^{-5} \text{ K}^{-1}$, $T \sim 10^3 \text{ K}$), we use the asymptote for $\text{Ei}(x)$ to get

$$\xi = \frac{\alpha V_\alpha (T - T_\alpha)}{\Delta V} - \frac{c_p}{\Delta S} \ln \frac{T}{T_\alpha}. \quad (7)$$

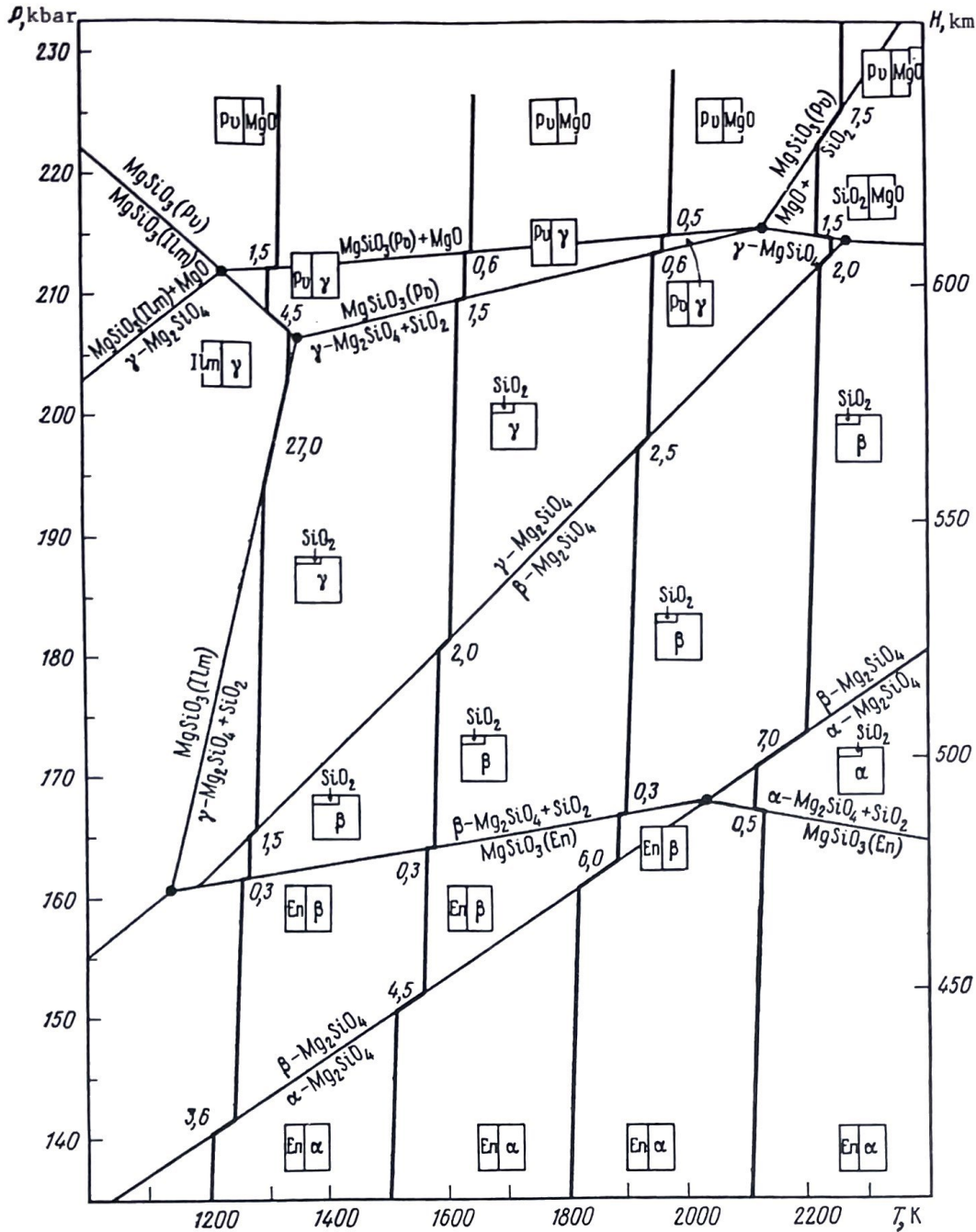


Fig. 3. Temperature distribution in the transition zone at various stages in the Earth's evolution. Phase diagrams for the MgO-SiO₂ system [19, 20]. The mineral compositions are shown schematically in squares; the numbers correspond to the widths l_0 of the interphase zone (km).

If we put $\alpha = 0$, we get Verhoogen's formula [12]. The value of T_β corresponding to the end of the transformation is given by

$$1 = (\alpha V_\alpha / \Delta V) (T_\beta - T_\alpha) - (c_p / \Delta S) \ln (T_\beta / T_\alpha).$$

In most cases (when $T_\beta / T_\alpha \approx 1$) it is sufficient to use the approximate formulas

$$T_\beta = \frac{\alpha V_\alpha T_\alpha \Delta S - c_p \Delta V - \Delta V \Delta S}{c_p \Delta V - \alpha V_\alpha T_\alpha \Delta S} T_\alpha; \quad \delta T = T_\alpha \frac{\Delta S \Delta V}{\alpha V_\alpha T_\alpha \Delta S - c_p \Delta V}.$$

The symbols

$$(dP/dT)_A = c_p / (\alpha V_\alpha T_\alpha), \quad (dP/dT)_P = \Delta S / \Delta V$$

enable us to rewrite the expression for δT as

$$\delta T = - \frac{\Delta H}{c_p} \left[\frac{(dP/dT)_A}{(dP/dT)_A - (dP/dT)_P} \right], \quad (8)$$

where $\Delta H = T_{\alpha} \Delta S$. Simple estimates show that allowance for compressibility is important in considering the transformations for which $(dP/dT)_A$ and $(dP/dT)_B$ are comparable as regards order of magnitude (for example, the transition $\gamma\text{-Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{MgSiO}_3$ (Ilm)).

Figure 3 summarizes the calculations, which shows a model phase diagram for the MgO-SiO₂ system for the P and T of the mantle transition zone (the method of constructing the diagram is discussed in detail in [19, 20]). The diagram also shows the adiabat (geotherms) constructed from (7) and (8), which characterize the temperature distribution in the transition layer at four different (arbitrary) stages in the Earth's evolution. Table 1 summarizes the necessary thermodynamic information on the heat and volume changes in the chemical and phase transitions under equilibrium P and T .

The following are provided by calculations on the adiabatic temperature variation in the mantle by reference to the MgO-SiO₂ system, which simulates the chemical composition of the transition layer to a first approximation:

- 1) Tracing the temperature variation in the transition zone in an early stage of the Earth's evolution (about 3×10^9 years ago) and at the current stage;**
- 2) Indicating the mineral composition of the transition zone at various stages and tracing its variations during heating or cooling of the planet;
- 3) Identifying the roles of chemical energy sources in producing the temperature profile in the transition zone;
- 4) Estimating the temperature step in the transition zone associated with the chemical and phase transformations; and
- 5) Estimating the width of the interphase region.

To characterize the mineral composition in the transition zone let us consider four adiabats for which the temperatures are $T_1 = 1200$ K, $T_2 = 1500$ K, $T_3 = 1800$ K, $T_4 = 2100$ K at $P = 133$ kbar. This pressure corresponds to a depth of ~ 400 km in the Earth on the PREM model [24], at which the temperature is ~ 1800 K [4-6]. The chemical composition at this depth will be represented by an association close to the peridotite one (60 mol.% forsterite and 40 mol.% enstatite) [11]. Clearly, the addition of $\sim 10\%$ of iron to the system and also of Al and Ca would refine the data, but this is the subject of a special study [20]. The following is the sequence of phase relations in the transition zone for each of these stages:

1200 K Adiat:

forsterite + enstatite \rightarrow β -spinel + enstatite \rightarrow
 β -spinel + stishovite \rightarrow γ -spinel + stishovite
 γ -spinel + ilmenite \rightarrow γ -spinel + perovskite \rightarrow perovskite + periclase

Over-All Temperature Change ΔT_{1200} 119 K

1500 K and 1800 K Adiabats:

forsterite + enstatite \rightarrow β -spinel + enstatite \rightarrow β -spinel + stishovite
 γ -spinel + stishovite \rightarrow γ -spinel + perovskite \rightarrow perovskite + periclase

Over-All Temperature Change ΔT_{1500} 145 K, ΔT_{1700} 175 K

2100 K Adiat:

forsterite + enstatite \rightarrow forsterite + stishovite \rightarrow
 β -spinel + stishovite \rightarrow γ -spinel + stishovite \rightarrow
periclase + stishovite \rightarrow periclase + perovskite

Over-All Temperature Change ΔT_{2100} 160 K

*Alternative forms of the phase diagram are possible, see [19, 20].

**For definiteness, in what follows we use the model for the thermal evolution that involves planetary heating. It is readily seen that this does not restrict the generality of the discussion. However, recently it has become widely believed that the Earth has cooled [8-10].

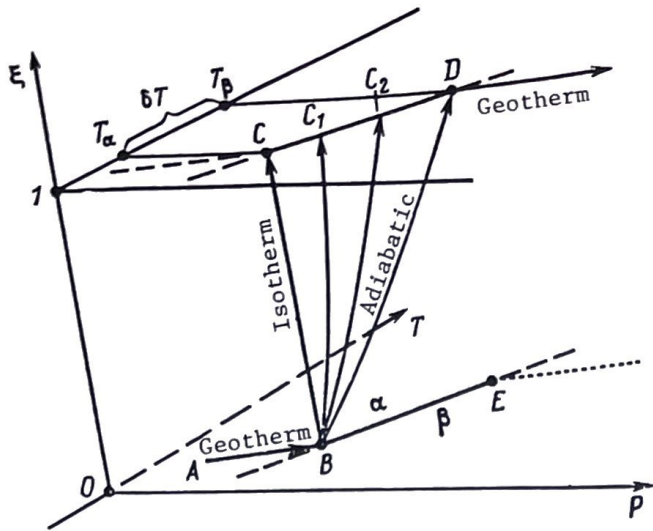


Fig. 4. Schematic representation of the adiabat (geotherm) in $P-T-\xi$ coordinates, where ξ is the degree of transformation, BC is the isothermal path, BD is the adiabatic one, and BE is a segment of the α - β equilibrium curve.

This analysis not only shows how the mineral composition of the transition zone has altered during evolution but also what processes occur and at what depths for the boundary with the lower mantle. While the currently recorded inhomogeneity at the 670 km boundary may be due to chemical transformations involving the formation of the perovskite association, in an early stage of the Earth's evolution these transformations involved the formation of the ilmenite structure. Note that the composition of the lower mantle in all cases corresponded to the perovskite+periclase association.

The invariant point in the phase diagram ($P \sim 215$ kbar, $T \sim 2100$ K), at which four phases coexist: perovskite + γ -spinel + periclase + stishovite, requires particular attention. The P and T in this invariant association correspond within the errors of the calculations to the P and T of the seismic boundary at a depth of ~ 670 km. It is suggested that the discontinuities in physical properties at this boundary observed in seismic experiments are due to a localized inhomogeneity arising from several simultaneous chemical reactions occurring in a narrow region. Some confirmation of this is provided by the density discontinuities at the 670 km boundary and the discontinuities calculated as caused by chemical transformations. For example, according to the PREM model [24] $\Delta\rho = 0.389$ g/cm³ and $\Delta\rho/\rho \simeq 9.7\%$, which agrees well with the data of Table 1 for the four latter reactions characterizing the phase composition at the invariant point.

It is readily established that there is a family of geotherms (adiabats) corresponding to a finite range in a parameter such as the average temperature passing through the invariant point. The geotherm enters the invariant point and coincides with one of the equilibrium curves, and the degree of transformation corresponding to the point of intersection may vary from zero to one. Therefore, we can say that this situation (invariant point on the adiabat) is structurally stable.

The passage through the invariant point can be represented as follows within the framework of the local-equilibrium model. When the appropriate P and T are reached, all possible transformations occur in the invariant association. The temperature and pressure remain fixed, and the heat is distributed between the exothermic and endothermic reactions, with a degree of transformation in each reaction and the sense of reaction controlled by the adiabatic-isolation condition. Emergence from the invariant point occurs along the equilibrium curve for the dominant reaction under conditions where their reactants participating in the competing transformations are exhausted. A detailed discussion will be given for each of the invariant points in Fig. 3.

ISOTHERMAL AND ADIABATIC TRANSFORMATION

For simplicity, let us consider the univariant phase equilibrium curve in a one-component system. We supplement the two-dimensional $P-T$ diagram with a third coordinate axis corresponding to ξ (the mole fraction of phase β or the degree of transformation). The phase transition can be represented schematically as the path of a particle in this three-dimensional diagram. The single-phase states correspond to the planes $\xi = 0$ and $\xi = 1$ (Fig. 4).

Let the point representing an element move along the adiabat (phase α) from point A to point B , which corresponds to the point where phase β arises. Curve BE is the phase-equilibrium line defined by (5). If the heat of the phase transition is removed or supplied sufficiently rapidly, the transition occurs under isothermal conditions (segment BC).^{*} If on the other hand, the heat transfer is difficult and the element continues to move because it is entrained by descending or rising flows, the P and T conditions will alter, and the transformation will occur with varying temperatures (paths BC_1 and BC_2). Under conditions of vigorous convection, the transformation will occur essentially under adiabatic conditions. We denote the corresponding curve defined by (6) by BD .

The isothermal and adiabatic processes are limiting idealized ones. Let the two-phase layer have a width l_0 . We introduce the dimensionless Peclet number $Pe = v_0 l_0 / k_0$, where v_0 is the characteristic velocity of the convective motion and k_0 is the effective thermal diffusivity in the layer. This dimensionless quantity characterizes the ratio of the times for convective and conductive heat transfer in the layer. If $Pe \gg 1$, convection predominates and thermal conduction can be neglected. In that case, the adiabatic condition is obeyed as a particle passes through the two-phase region. If $Pe \ll 1$, thermal conduction is important and one cannot speak of an adiabatic temperature gradient in the layer. In (25), the structure of an isothermal interphase layer was considered, i.e., the limiting case $Pe \rightarrow 0$, which corresponds to a model with infinite thermal conductivity. The intermediate case (paths BC_1 and BC_2) was considered in (14) while neglecting the volume change in the transformation.

To formulate these assumptions more accurately, let us consider the complete hydrodynamic problem for planar stationary flow of a viscous thermally conducting liquid capable of undergoing chemical transformation. We write the basic equations on the assumption that the x axis coincides with the line of action of the gravitational force $g = \text{constant}$. The equations of continuity and momentum take the form [26]

$$\frac{d}{dx} \rho v = 0, \quad \frac{d}{dx} \left[P + \rho v^2 - \mu \frac{dv}{dx} \right] = \rho g, \quad (9, 10)$$

where ρ is density, v velocity, P pressure and μ viscosity. We integrate (9) and eliminate the velocity from (10) to get

$$P + m_0^2/\rho + (\mu m_0/\rho^2) (d\rho/dx) = P_0 + \int_{x_0}^x \rho g dx, \quad (11)$$

where m_0 is the constant characterizing the mass flux and

$$P_0 = P(x_0) + m_0^2/\rho(x_0) + (\mu m_0/\rho^2(x_0)) (d\rho/dx)|_{x_0}.$$

Let us introduce the parameter ξ (degree of transformation) as an additional argument in the internal-energy function, this arising on average description of the heterogeneous system within the framework of a model for a homogeneous continuous medium. We neglect mixing effects, and in particular surface ones, and put

$$U = \xi U_\beta(\rho_\beta, S_\beta) + (1-\xi) U_\alpha(\rho_\alpha, S_\alpha), \quad (12)$$

$$S = \xi S_\beta + (1-\xi) S_\alpha, \quad (13)$$

$$V \equiv 1/\rho = \xi/\rho_\beta + (1-\xi)/\rho_\alpha. \quad (14)$$

Let the following equations of state apply locally for each of the phases:

$$\partial U_\alpha / \partial S_\alpha = T_\alpha, \quad \partial U_\beta / \partial S_\beta = T_\beta, \quad \rho_\alpha^2 \partial U_\alpha / \partial \rho_\alpha = P_\alpha, \quad \rho_\beta^2 \partial U_\beta / \partial \rho_\beta = P_\beta,$$

with $T_\alpha = T_\beta = T$, $P_\alpha = P_\beta = P$. The internal energy increment can be put as

$$dU = T dS - P dV + (\mu_\beta - \mu_\alpha) d\xi, \quad (15)$$

^{*}We assume that the transformation is not limited by kinetic factors, which is reasonable because of the high temperature in this region [12].

where $\mu_\beta = U_\beta - TS_\beta + P/\rho_\beta$, $\mu_\alpha = U_\alpha - TS_\alpha + P/\rho_\alpha$ are the chemical potentials of the phases. Let us write out the energy equation:

$$\rho v \frac{d}{dx} \left(U + \frac{v^2}{2} \right) = - \frac{d}{dx} \left(P v - \mu v \frac{dv}{dx} \right) - \frac{dq}{dx} + \rho g v, \quad (16)$$

where $q = -\kappa(dT/dx)$ is the heat-flux vector. Using (10) and (16) we get

$$\rho v dU/dx = -P dv/dx + \mu (dv/dx)^2 + d/dx (\kappa dT/dx), \quad (17)$$

which is known as the heat-flux equation. From (9) we readily find that $P(dv/dx) = (Pd(1/\rho)/dx)\rho v$. We then combine (15) and (17) to get the entropy-balance equation:

$$\rho v T \frac{dS}{dx} = \mu \left(\frac{dv}{dx} \right)^2 + (d/dx) \left(\kappa \frac{dT}{dx} \right) + (\mu_\alpha - \mu_\beta) \rho v \frac{d\xi}{dx}. \quad (18)$$

According to (18), the change in entropy of a particle is associated with the influx of heat through its surface and with dissipation due to viscosity and thermal conduction, and also to disequilibrium in the chemical transformation, ($\mu_\alpha - \mu_\beta \neq 0$). A standard consideration of (18) in dimensionless form [27] shows that for large values of the Peclet number the terms associated with the thermal conduction can be discarded. The low values for the velocity gradient in the interphase zone make it natural to neglect the viscous dissipation. Therefore, the condition for conservation of entropy in a particle is equilibrium transformation: $\mu_\alpha = \mu_\beta$.

The equation $dS = 0$ is a purely thermodynamic one, and the thermal and mechanical problems are separated. If we possess the corresponding thermodynamic information, we can find the functions $T(P)$, $\xi(P)$, $\rho(P)$, as is evident from (6) and (14), which when substituted into (11) enable us to calculate $P(x)$. It is readily shown that we can neglect the contribution from the dynamic terms in (11) for these flows ($\rho v^2 \ll P$).

Let us now estimate the characteristic velocity of the convective flows needed to maintain the adiabatic gradient in the two-phase region. Figure 3 gives values of l_0 for each of the transformations, and we take the mean value of $0.006 \text{ cm}^3/\text{sec}$ for k_0 . On existing concepts on mantle convection, the speed is of the same order as that of continental drift, i.e., 1-4 cm/y. We calculate the Peclet number from this to get that $Pe \geq 1$ for virtually all the transformations in Fig. 3. The closeness of the value to one indicates that the adiabatic model is not entirely logical at such speeds and the actual situation is more complicated. However, we can say that these results for δT give an upper bound to the corresponding quantity. On the other hand, estimates show that at speeds of $< 0.1 \text{ cm/y}$ we should use the isothermal model [25].

These differences between the adiabatic and isothermal cases must be borne in mind in modeling penetrative convection. A final decision on the penetration can be obtained only by modeling the structure of the interphase region and considering all the different chemical processes.

TRANSITION-ZONE STRUCTURE

Phase relations. A major problem in constructing a model for the inner structure of the planet is to explain the anomalous seismic-wave speeds at depths of 400-700 km. When the detailed structure of the transition zone is known, we will be able to resolve many problems concerning the evolution of the mantle. It appears to have been established that the features of this zone are associated with heterophase boundaries, or rather with regions in which chemical or phase transformations are localized.

A geophysical solution is made difficult by the lack of data on the detailed seismic structure of this region. The difficulties are associated mainly with inadequate resolution in deep seismic sounding [28-30]. For this reason, thermodynamic modeling of the transition zone is very important. Our knowledge of the phase diagram for a fairly general $\text{MgO-SiO}_2\text{-FeO-CaO-Al}_2\text{O}_3$ system enables us to predict seismic anomalies and to determine their intensities [19, 20].

Let us perform a preliminary comparison of the thermodynamic results with the seismological data by reference to the simplified MgO-SiO₂ system (Fig. 3).

At the boundary between the upper mantle and the transition zone (~400 km) there is a phase transformation in olivine, which is the most abundant mineral in the upper mantle. This phase transition involves the formation of a modified spinel structure, which evidently makes the main contribution to the discontinuities in the density and elastic moduli: * $\Delta\rho/\rho \approx 6.5\%$ for the forsterite- β -spinel transition (Table 1), while according to the PREM model this ratio is ~5.1% at the 400 km boundary. The slight excess in the density step indicates that there is dilution of the mineral composition by other components.

At a depth of ~500 km, enstatite disproportionates into β -spinel + stishovite, as Fig. 3 shows, which is accompanied by a density step of ~10%. However, it should be borne in mind that the enstatite content in the mantle is estimated as having an upper limit of 40 mol.% [11]. At depths of 570-600 km, there is the phase transformation of β spinel to γ spinel, which involves a volume change of only 1%; it is likely that for this reason it is with difficulty indicated by seismic methods.

The largest seismic anomaly occurs at a depth of ~670 km (640-720 km according to various sources [24, 28-30]). The phase diagram indicates that there are two chemical transformations in this region: γ -Mg₂SiO₄ + SiO₂ = 2MgSiO₃(Pv) and γ -Mg₂SiO₄ = MgSiO₃(Pv) + MgO, which lead to the transformation of spinel and the production of a dense modification of MgSiO₃ with the perovskite structure. The two reactions occur in a narrow pressure range ($\Delta P \leq 0.5$ kbar) and are accompanied by sharp density increases (8 and 10% correspondingly).** The mineral composition is substantially simplified at high pressures; according to the phase diagram, the lower mantle consists mainly of periclase MgO and perovskite MgSiO₃, and also possibly of corresponding high-pressure phases if such exist [11, 22].

This comparison incorporates only the most important and persistent features of the phase diagram. Information can be obtained on the detailed transition-zone structure by using the model temperature distribution. According to [28], seismic methods indicate perturbations at depths of 411, 512, 610, 630, and 645 km. If we take the temperature at a depth of ~400 km as 1800 K, we get the following transformation sequence (Fig. 3): α -Mg₂SiO₄ = β -Mg₂SiO₄ (pressure $P \approx 161$ kbar, depth $h \approx 475$ km, width of interphase zone $l_0 = \Delta h \approx 6$ km), 2MgSiO₃(En) = β -Mg₂SiO₄ + SiO₂ ($P \approx 167$ kbar, $h \approx 495$ km, $\Delta h \approx 0.3$ km), β -Mg₂SiO₄ = γ -Mg₂SiO₄ ($P \approx 198$ kbar, $h \approx 575$ km, $\Delta h \approx 2.5$ km), 2MgSiO₃(Pv) = γ -Mg₂SiO₄ + SiO₂ ($P \approx 213$ kbar, $h \approx 600$ km, $\Delta h \approx 0.6$ km), γ -Mg₂SiO₄ = MgSiO₃ + MgO ($P \approx 215$ kbar, $h \approx 610$ km, $\Delta h \approx 0.5$ km). Therefore, the thermodynamic results for the MgO-SiO₂ system derived from independent data confirm the seismic evidence for the series of density steps in the transition zone. The inadequate resolution in seismic methods makes it premature to perform any detailed comparison of the thermodynamic structure with the seismic one, and the same applies on account of the model character of the system (absence of Fe, Ca, and Al).

Temperature distribution. There is a close relationship between the construction of the temperature profile in the mantle and the definition of the rock composition. The identification of a polymorphic transformation or chemical reaction at a given depth provides a reference point on the geotherm by reference to the phase diagram; establishing the entire $T(r)$ curve in this way, we obtain an essentially new basis for all geodynamic constructions. On the other hand, by specifying the model composition we can construct the adiabat and thus determine the positions of the phase boundaries.

*Here we restrict ourselves to a density comparison. An analysis of the seismic-wave velocity correlations requires in particular a study of the compressibilities of multiphase heterogeneous elastic media, which is a separate problem.

**A study of the phase relationships in the MgO-FeO-CaO-Al₂O₃-SiO₂ system shows that substantially more chemical transformations are localized in the region of the second seismic step, and these produce additional complications in the model for the transition-zone structure. The most important common feature is the transformation of the spinels Mg₂SiO₄ and Fe₂SiO₄ together with diopside, larnite, and garnets into the (Mg, Fe, Ca)SiO₃ (perovskite structure) + oxide (CaO, Al₂O₃, magnesiowüstite association), which is accompanied by appreciable change in the elastic parameters [19, 20].

Features of the temperature profile are associated with the chemical and phase transformations. The localized heat sources or sinks alter the temperatures of particles taking part in convective motion through the heterophase boundary. Figure 3 shows adiabats that simulate the temperature distribution in the transition zone. These take the form of piecewise-smooth curves. There are anomalies in the temperature gradient associated with the chemical and phase transformations; the over-all temperature change in the transition zone may be 120-200 K, depending on the curve chosen. Let us now elucidate this element of choice.

There are two time scales in the evolution of the planet, which involve fast and slow processes [7, 31].* Global evolution as a quasistatic process involves transition from one equilibrium configuration to another and occurs on the slow scale and is accompanied by change in the average temperature. Therefore, the constant arising on integrating (3) and which indicates the adiabat is a function of the slow time, while the curves shown in Fig. 3 represent four stages of evolution separated by time intervals of $\sim 10^9$ years. Figure 3 therefore enables us to follow the composition change at a given depth during the planetary heating or cooling.

The adiabat is deformed in a complicated way when the average temperature changes. The corresponding curves cannot be derived one from another by simple multiplication by a factor. At certain stages, it is even possible that the adiabat had parts that were not monotonic, which was related to transformations accompanied by the absorption of heat on passing from a less dense phase to a denser one. To demonstrate the changes in transition-zone fine structure due to change in the average temperature in the mantle we give the sequence of chemical and phase transformations based on the 2100 K adiabatic: $2\text{MgSiO}_3(\text{En}) = \alpha\text{-Mg}_2\text{SiO}_4 + \text{SiO}_2$ ($P \simeq 167$ kbar, $h \simeq 495$ km, $\Delta h \simeq 0.5$ km), $\alpha\text{-Mg}_2\text{SiO}_4 = \beta\text{-Mg}_2\text{SiO}_4$ ($P \simeq 171$ kbar, $h \simeq 500$ km, $\Delta h \simeq 7$ km), $\beta\text{-Mg}_2\text{SiO}_4 = \gamma\text{-Mg}_2\text{SiO}_4$ ($P \simeq 212$ kbar, $h \simeq 600$ km, $\Delta h \simeq 2$ km), $\gamma\text{-Mg}_2\text{SiO}_4 = 2\text{MgO} + \text{SiO}_2$ ($P \simeq 215$ kbar, $h \simeq 605$ km, $\Delta h \simeq 1.5$ km), $\text{MgO} + \text{SiO}_2 = \text{MgSiO}_3(\text{Pv})$ ($P \simeq 222$ kbar, $h \simeq 630$ km, $\Delta h \simeq 7.5$ km). This sequence should be compared with that given above for the 1800 K adiabatic. The substantial differences are associated with the possibility that the phase boundaries migrate and new phases appear on passing through the invariant point. The standard discussion, which is based on ignoring the complicated phase composition, results in only a slight change in the density when the average temperature changes.

Invariant points. The MgO-SiO₂ phase diagram indicates that the invariant points occur in a fairly narrow region around $h \sim 600\text{-}700$ km, and their position is correlated with that of the main seismic anomaly.**

The main interest attaches to the invariant point at $P \simeq 215$ kbar and $T \simeq 2100$ K, where the following four reactions may occur in parallel:

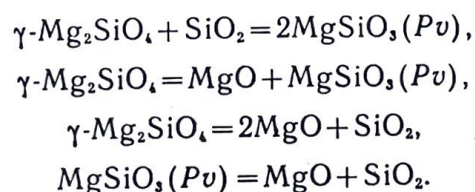


Table 1 gives the corresponding heats of reaction and volume changes. A major feature of these reactions is that most of them are exothermic, because a denser phase association is produced as the pressure rises ($\Delta V < 0$), and the slopes

*The fast time with the scale of $10^7\text{-}10^8$ years is associated with nonequilibrium relaxation, and in particular characterizes the period of convective circulation. The slow time differs from the fast one by an order of magnitude (10^9 years) and in Peltier's expression [32] controls the scale of the change in planetary climate, whereas the fast time may be related to weather changes.

**The addition of FeO results in two new invariant points above 200 kbar, at which there may be five-phase associations $\text{MgSiO}_3(\text{Pv}) + \gamma\text{-Mg}_2\text{SiO}_4 + \gamma\text{-Fe}_2\text{SiO}_4 + \text{FeO} + \text{SiO}_2$ and $\text{MgSiO}_3(\text{Pv}) + \gamma\text{-Mg}_2\text{SiO}_4 + \gamma\text{-Fe}_2\text{SiO}_4 + \text{FeO} + \text{MgO}$. Similarly, the addition of CaO and Al₂O₃ produces a family of invariant points that complicate the phase diagram and at the same time add detail to the mineral composition of the transition zone [19, 20].

of the univariant curves in this system are usually positive [19, 20], so $\Delta H < 0$ and the reactions release heat. Therefore, the parallel occurrence of several reactions at the invariant points may lead to substantial over-all extensive effects (thermal and volume ones). Also, passage through the invariant point is characterized by stepwise change in the elastic parameters of many mineral associations over a narrow pressure range.

On the other hand, the analysis shows that the adiabat passing through the invariant point is a structurally stable situation. For each invariant point one can distinguish a capture region, which means that over a finite time interval, which may amount to hundreds of millions of years, the adiabat passes through a given invariant point while in general undergoing considerable changes at other points. Therefore, invariant transformations are typical of convection in the planet.

We note finally that the seismic anomaly related to the invariant point on the geotherm will have the character of a gradient layer of finite thickness with a marked singularity at the upper (in pressure) boundary; the latter agrees well with the results of [29, 30].

The above indicates the following hypothesis: that the major seismic anomaly at a depth of ~ 670 km may be ascribed to the presence of invariant points in the phase diagram for the model system and is associated not with any single transformation but with a set of them.

CONCLUSIONS

Experimental and theoretical studies on the thermodynamics of equilibria at high pressures and temperatures have recently led to a substantial improvement in our concepts of the chemical processes within the Earth. It has become possible to construct equilibrium diagrams for multicomponent systems involving high-pressure phases. This has made it important to consider geodynamic processes on the basis of the complicated mantle composition and all the various chemical transformations, whose role in planetary evolution has not yet been thoroughly evaluated [20, 31].

The present study concerns modeling the transition zone by reference to the fundamental MgO-SiO₂ system. The assumption that there are penetrative convection currents makes it necessary to consider the temperature distribution in the presence of heat sources related to chemical and phase transformations. The roles of these sources vary with the convection rate, which provides models for adiabatic and isothermal interphase boundaries. The thermal and mechanical problems separate in the adiabatic approximation, and therefore we have to use equilibrium chemical thermodynamics to construct the relationship between temperature and pressure in the two-phase region. This problem is discussed for a case of univariant equilibrium.

The results allow us to follow the behavior of the geotherm in the transition zone and the changes in mineral composition during planetary evolution, and to determine the local role of chemical energy sources in producing the temperature pattern. The formulas enable us to estimate the temperature step and the width of the interphase layer for univariant transformation.

The following are some features of these systems that appear to be of interest and which require further discussion.

1. The presence of transformations with positive heats ($\Delta H > 0$) may lead to nonmonotonic temperature profiles.
2. The possibility of kinks on the adiabat (geotherm) and of regions of high temperature gradient (steps) is related to the chemical and phase transformations. If the volume effect of a transformation is small, the density change on the corresponding mechanical $\rho(r)$ curve will be small and it will be difficult to observe by seismological methods. These seismically unobservable temperature steps may be responsible for the high resultant temperature difference between the core and the upper mantle.
3. Passage of the adiabat through an invariant point is a structurally stable situation. In this system, the composition in the main corresponds to that of the mantle, and the invariant points are concentrated in the range of

P and T corresponding to the observed seismic boundary at a depth of ~ 670 km. Special discussion is needed on the penetration of convection through such zones, which are characterized by a substantial density inhomogeneity.

4. There may be substantial lateral inhomogeneities associated with the chemical and phase boundaries in the transition zone as indicated by seismic methods [30]. For example, in the region of a cold descending flow, the boundary corresponding to a univariant transformation with $dT/dP > 0$ will lie at a smaller depth than that in a region of hot ascending flow. A difference of 300 K for the $\alpha\text{-Mg}_2\text{SiO}_4 = \beta\text{-Mg}_2\text{SiO}_4$ transition produces a relative drift in the phase boundary of 30 km.

5. In the case of divariant transformations in solution, the presence of additional degrees of freedom means that the chemical-equilibrium conditions do not define the relationship between pressure and temperature, i.e., the temperature in the divariant region is not controlled by the transformation but is determined by the adiabatic condition. A characteristic feature is also that heats of mixing are superimposed on the usual picture of heat production in phase transformation. The divariant regions may be of substantial width, which may be comparable as regards order of magnitude with the over-all width of the transition zone.

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