CONSTRUCTING SUBSOLIDUS P-T DIAGRAMS FOR MULTICOMPONENT MINERAL SYSTEMS*

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A method is discussed for constructing the subsolidus $P-T$ diagram for a multicomponent multiphase system containing solid solutions. The algorithm is based on calculating univariant equilibrium curves. The method involves constructing a series of subsystem diagrams with increasing numbers of components. The algorithm is implemented beginning with the analysis of a stoichiometric subsystem that includes phases of constant composition. Metastable univariant curves are excluded by transferring to a system of higher dimensions via the degenerate invariant points relating to the edge subsystems. A network of univariant curves intersecting at the invariant points is constructed to define regions in $P-T$ coordinates with certain compositions for the possible assemblages, which enables us to distinguish the mineral facies. The implementation is discussed in detail for the $MgO-FeO-SiO_2$ system in the subsolidus region, which corresponds to the lower boundary ($\sim$ 650 km) of the transitional mantle zone. The topology of this phase diagram is examined for the appropriate P and T, which agrees with measurements and also with theoretical diagrams for the $MgO-SiO_2$ and $FeO-SiO_2$ edge subsystems.

By complete $P-T$ phase diagram we mean one indicating the stable mineral assemblage at each point in $P-T$ coordinates, where the compositions of the coexisting phases are indicated for all overall system compositions [1-4]. Even for a three-component system, it is impossible to represent the relationships in a plane, so one is restricted to two-dimensional sections or projections, the most important of which is the projection of the univariant equilibrium lines on the $P-T$ plane. A complete diagram is thus possible only as a set of numerical computer procedures.

We have devised an algorithm for constructing $P-T$ diagrams for subsolidus systems containing solid solutions. If the system contains only stoichiometric phases that do not form solutions, there are no problems in determining the compositions of the coexisting phases, and the construction is much simplified; the Gibbs energy by classical linear programming can be minimized [5, 6]. Solid solutions complicate the task, mainly because there is substantial nonlinearity in the minimized function.

There are many papers on general methods of constructing such phase diagrams, which are widely used in metallurgy, chemical engineering, and the mechanics of materials [7]. In geochemistry, the topic of equilibrium phase assemblages has been discussed repeatedly, and some novel algorithms have been proposed [8-13]. However, no special methods have been devised for constructing $P-T$ diagrams for solid-solution systems over wide ranges.

Interest in phase diagrams for multicomponent systems at ultrahigh pressures and temperatures is stimulated primarily by the need for an adequate chemical interpretation of the geophysical data in constructing a geochemical model for the Earth. Many measurements have accumulated on the elastic and thermal parameters of high-pressure phases, and numerous equilibria have been identified under laboratory conditions corresponding to the pressures and temperatures in the upper mantle and the transition zone [14]. Methods have been devised for constructing thermal equations of state for solid phases, which enable us to extrapolate thermodynamic parameters reliably [6, 15, 16]. This makes it important to construct a complete $P-T$ diagram for the $MgO-FeO-CaO-Al_2O_3-SiO_2$ system. The most interesting subsystem here is $MgO-FeO-SiO_2$, which provides over 90% of the actual composition and retains all the essential complexities of the full system.

EQUILIBRIUM CONDITIONS

We begin with some standard formulas subsequently required. Let us consider an n-component phase α and denote by n_α^i the number of mols of component i in phase α, $i = 1, \ldots, n$. Let $G^\alpha(n_\alpha{}^i, P, T)$ be the Gibbs energy of phase α, while $\mu_i^\alpha = \partial G^\alpha / \partial n_\alpha{}^i$ is the chemical potential of component i in phase α. G^α is a uniform function of the first degree in the arguments $n_\alpha{}^i$, so $G^\alpha = \sum_i \mu_i^\alpha n_\alpha^i$. It is often convenient to convert to the molar quantities: $g^\alpha = G^\alpha / n^\alpha$, $x_\alpha{}^i = n_\alpha{}^i / n^\alpha$, where n^α is the number of mols of phase α. We write G^α in the form

$$\left(\sum_k n_\alpha^k \right) g^\alpha \left(n_\alpha^i \Big/ \left(\sum_k n_\alpha^k \right), P, T \right),$$

to get

$$\mu_i^\alpha = g^\alpha - \sum_k x_\alpha^k (\partial g^\alpha / \partial x_\alpha^k) + \partial g^\alpha / \partial x_\alpha^i. \tag{1}$$

We now assume that there is a set of r phases having Gibbs energies $G^\alpha(n_\alpha{}^i, P, T)$; $\alpha = 1, \ldots, r$. The total Gibbs energy of the mixture $G = \sum_\alpha G^\alpha$ is dependent on $nr + 2$ variables $n_\alpha{}^i$, P and T. If the overall chemical composition of the mixture is given, there are n constraints on the $n_\alpha{}^i$

$$\sum_\alpha n_\alpha^i = \overset{o}{n}{}^i, \tag{2}$$

where $\overset{o}{n}{}^i$ are the numbers of mols of the components in the mixture. The phase-equilibrium state at given P and T corresponds to the minimum in G with respect to $n_\alpha{}^i$. Then we use (2) and introduce the Lagrange multipliers μ_i, $i = 1, \ldots, n$, and consider the unconditional turning point in the function

$$\Lambda(\mu_i, n_\alpha{}^i) = G - \sum_i \mu_i \left(\sum_\alpha n_\alpha^i - \overset{o}{n}{}^i \right).$$

In terms of the molar values, the necessary turning-point conditions (the conditions for Gibbs phase equilibrium) can be written as

$$\mu_i^1 (x_1^j, P, T) = \mu_i^2 (x_2^j, P, T) = \ldots = \mu_i^r (x_r^j, P, T) \; (= \mu_i), \tag{3}$$

$$\sum_\alpha x_\alpha^i \xi^\alpha = \overset{o}{x}{}^i, \tag{4}$$

$$\sum_i x_\alpha^i = 1, \tag{5}$$

where ξ^α are the molar fractions of the phases and $\overset{o}{x}{}^i$ are the molar fractions of the components in the mixture. For given P and T, the number of equations here coincides with the number of unknowns, which is known as Duhem's theorem. If we discard (4), which expressed the mass balance, the number of unknowns (including P and T) exceeds the number of equations by $n - r + 2$ (Gibbs phase rule).

We now derive some consequences of (3); we combine (3) and (1) to get

$$\frac{\partial g^\alpha}{\partial x_\alpha^i} - \frac{\partial g^\alpha}{\partial x_\alpha^j} = \frac{\partial g^\beta}{\partial x_\beta^i} - \frac{\partial g^\beta}{\partial x_\beta^j} . \tag{6}$$

It is readily tested that equations (6), of which only $(r - 1)(n - 1)$ are independent, express the equilibrium conditions in the exchange reactions (the redistribution of components i and j between phases α and β). In analyzing silicate solid solutions in the subsolidus region it is desirable to distinguish one of the solution components as that forming the framework (the additive component [17]), while the others are considered as interstitial. We assume for definiteness that the framework one is component n (e.g., SiO_2 in the $MgO-FeO-SiO_2$ system). We introduce the new functions

$$\tilde{g}^\alpha(x_\alpha^1, \ldots, x_\alpha^{n-1}) = g^\alpha\left(x_\alpha^1, \ldots, x_\alpha^{n-1}, 1 - \sum_{i=1}^{n-1} x_\alpha^i\right).$$

By virtue of (1) and (3) we have

$$\mu_n = \tilde{g}^\alpha - \sum_{k=1}^{n-1} x_\alpha^k (\partial \tilde{g}^\alpha / \partial x_\alpha^k), \quad \partial \tilde{g}^\alpha / \partial x_\alpha^i = \mu_i - \mu_n, \quad i = 1, \ldots, n-1. \tag{7}$$

Conditions (6) can be rewritten as

$$\partial \tilde{g}^\alpha / \partial x_\alpha^i = \partial \tilde{g}^\beta / \partial x_\beta^i, \quad i = 1, \ldots, n-1. \tag{8}$$

These are equilibrium equations for the exchange reactions involving the interstitial components. The other independent equilibrium equations number $r - 1$ and can be represented as conditions for the equality of the chemical potentials of the framework component in the phases:

$$\tilde{g}^\alpha - \sum_{i=1}^{n-1} x_\alpha^i (\partial \tilde{g}^\alpha / \partial x_\alpha^i) = \tilde{g}^\beta - \sum_{i=1}^{n-1} x_\beta^i (\partial \tilde{g}^\beta / \partial x_\beta^i). \tag{9}$$

We now assume that the concentrations of one of the components in all the phases have been fixed (but are different), which means that the concentration space of dimensions $n - 1$ has the phases corresponding to hypersurfaces of dimensions $n - 2$. We take the concentrations of component k as fixed $k(x_\alpha^k \equiv c_\alpha^k)$ and introduce the functions

$$\tilde{\tilde{g}}^\alpha(x_\alpha^1, \ldots, x_\alpha^{k-1}, x_\alpha^{k+1}, \ldots, x_\alpha^{n-1}) = \tilde{g}^\alpha(x_\alpha^1, \ldots, c_\alpha^k, \ldots, x_\alpha^{n-1}).$$

Equations (9) can then be rewritten as

$$\tilde{\tilde{g}}^\alpha - \sum_{\substack{i=1 \\ i \neq k}}^{n-1} x_\alpha^i (\partial \tilde{\tilde{g}}^\alpha / \partial x_\alpha^i) - c_\alpha^k \left(\frac{\partial \tilde{g}^\alpha}{\partial x_\alpha^k}\right) = \tilde{\tilde{g}}^\beta - \sum_{\substack{i=1 \\ i \neq k}}^{n-1} x_\beta^i \frac{\partial \tilde{g}^\beta}{\partial x_\beta^i} - c_\beta^k \frac{\partial \tilde{g}^\beta}{\partial x_\beta^k} . \tag{10}$$

If we introduce the partial Gibbs energies of the phases

$$\hat{G}^\alpha = \widetilde{\tilde{g}}^\alpha - \sum_{\substack{i=1 \\ i \neq k}}^{n-1} x_\alpha^i (\partial \widetilde{\tilde{g}}^\alpha / \partial x_\alpha^i), \tag{11}$$

we get the following necessary equilibrium conditions* from (10):

$$(c_\gamma^k - c_\beta^k)\, \hat{G}^\alpha + (c_\beta^k - c_\alpha^k)\, \hat{G}^\gamma + (c_\alpha^k - c_\gamma^k)\, \hat{G}^\beta = 0. \tag{12}$$

Equation (12) can be interpreted as an equilibrium condition in a three-phase reaction (between phases α β and γ)**. The number of independent reactions of the type of (12) is $r - 2$. In conjunction with the $(r - 1)(n - 2)$ relations (8)

$$\partial \widetilde{\tilde{g}}^\alpha / \partial x_\alpha^i = \partial \widetilde{\tilde{g}}^\beta / \partial x_\beta^i, \quad i = 1, \ldots, k-1, k+1, \ldots, n-1 \tag{15}$$

we have in all a total of $(r - 1)n - r$ equilibrium conditions. For $r \leqslant n$, these equations are sufficient to define the unknowns $x_\alpha^i (i \neq k)$ (possibly not uniquely), which are related by the constraints

$$\sum_{i=1, l \neq k}^{n-1} x_\alpha^i - 1 - c_\alpha^k.$$

Let us now generalize (12) and (15). In subsolidus systems of this type, in addition to the independent components, we can introduce phase components [17] or minals, which are stoichiometric compounds of specified composition representing the end-members of the solid solutions for each of the phases. We introduce the symbols ξ_α^A for the molar fraction of minal A in phase α, $A = 1$, ..., n; $\bar{x}_A^i$ for the molar fraction of component i in minal A. The matrix for the latter is specified, while the values of $\bar{x}_A^i$ are the unknown variables. We have

$$\sum_{A=1}^m \xi_\alpha^A = 1, \quad \sum_{i=1}^n \bar{x}_A^i = 1. \tag{16}$$

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*If there is a pair of phases for which $c_\alpha^k = c_\beta^k$, the corresponding equilibrium is singular, and the equilibrium condition analogous to (12) takes the form $\hat{G}^\alpha = \hat{G}^\beta$.

**Reactions of the type of (12) should not be confused with phase reactions, which occur for example in the univariant association having $r = n + 1$; the latter are characterized by the stoichiometric coefficients being dependent on the compositions of the coexisting phases. For example, for a univariant phase reaction

$$\sum_{\alpha=1}^{n+1} \nu_\alpha A^\alpha = 0 \tag{13}$$

the stoichiometric coefficients ν_α are defined (apart from a common factor) by the system

$$\sum_{\alpha=1}^{n+1} \nu_\alpha x_\alpha^i = 0, \quad \sum_{\alpha=1}^{n+1} \nu_\alpha = 0, \tag{14}$$

whose solution can be written out explicitly (Korzhinskiy's determinant rule [3]). The equilibrium equation for (13) is

$$\sum_{\alpha=1}^{n+1} \nu_\alpha g^\alpha = 0$$

and can be derived as a consequence of (3).

The molar fractions of the minals in the mixture are

$$y^A = \sum_{\alpha=1}^{r} \xi^\alpha \xi_\alpha^A;$$

and according to (16) we have

$$\sum_{A=1}^{m} y^A = 1.$$

The Gibbs energy of a phase is represented as the sum of the partial molar Gibbs energies of the minals:

$$g^\alpha = \sum_{A=1}^{m} \xi_\alpha^A \bar{g}_A(\xi_\beta^A, \ P, \ T),$$

so the energy of the phase mixture is

$$G = \sum_{A=1}^{m} \bar{g}_A y^A.$$

The constraints of (4) can now be written as

$$\sum_{A=1}^{m} y^A \bar{x}_A^i = \overset{0}{x}{}^i. \tag{17}$$

We note that these equations are linear in the unknown functions, so we can shift to a reaction basis [7, 17] and formulate the equilibrium conditions in terms of the minal reaction set:

$$\sum_{A=1}^{m} v_A^l \ B^A = 0, \ l = 1, \ldots, R, \tag{18}$$

where B^A are the symbols for the minals and v_A^l are the stoichiometric coefficients in the reactions, which are defined by

$$\sum_{A=1}^{m} v_A^l \ \bar{x}_A^i = 0, \ i = 1, \ldots, n; \ l = 1, \ldots, R. \tag{19}$$

Introducing the activities enables us to write the corresponding equilibrium conditions

$$\sum_{A=1}^{m} \bar{g}_A v_A^l = 0$$

in the form of the law of mass action [7].

The number of independent reactions R clearly coincides with the number of linearly independent solutions to (19); we take the ranks of the concentration matrix $\bar{X} = \|\bar{x}_A^i\|$, as n and get that $R = n - 1$. Thus the stoichiometric matrix $W = \|v_A^l\|$ has m columns and $m - n$ rows.*. As each minal belongs only to one phase, we conclude that the number of ξ_α^A to be determined is m, of which only $m - r$

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are independent. There are $m - n$ equilibrium equations to define these quantities, and the number of equations coincides with the number of unknowns for $r = n$. The compositions of the coexisting phases for given $\xi_\alpha{}^A$ are defined by

$$x_\alpha^i = \sum_{A=1}^{m} \xi_\alpha^{A} \overline{x}_A^i,$$

and the phase fractions ξ^α are then found from (4).

Thus the phase-equilibrium conditions here have been formulated by three methods. The first method, that of (3)-(5), requires a solution to equations expressing equality of the chemical potentials for the components in the phases. The second, from (12) and (15), is based on considering two phase (exchange) and three-phase minal reactions. The third, (16)-(19), is an extension of the second and involves considering any reactions between minals. Although the second is based on a special design for the stoichiometric matrix and is thus less general, it gives the best means of incorporating the specific features of these subsolidus systems.

These equations can be used with the known phase composition to determine the chemical compositions of the coexisting phases, but the determination of the phase composition remains an unsolved problem. To discuss methods for this, we must turn to a general formulation of Gibbs energy minimization:

$$G(\xi^\alpha, x_\alpha^i, P, T) = \sum_\alpha \xi^\alpha g^\alpha(x_\alpha^i, P, T) \to \min_{\xi^\alpha, x_\alpha^i} \qquad (20)$$

subject to the constraints of (4) and (5); one chooses the $\overset{\circ}{x}{}^i$ such that $\sum_i \overset{0}{x}{}^i = 1$, so $\sum_\alpha \xi^\alpha = 1$. There are also inequality constraints on the ξ^α and x_α^i:

$$\xi^\alpha \geqslant 0, \quad x_\alpha^i \geqslant 0. \qquad (21)$$

The problem of (4), (5), (20), and (21) is complicated by the presence of parameters* whose variations affect the solution structure substantially (assemblage variability). This nonlinear parametric optimization is extremely complicated in such a general formulation and there are no universal algorithms for handling it at present (see however [7-13]).

For what comes next we need to consider a particular case: a system containing pure (stoichiometric) phases. In this case the compositions of the coexisting phases are given, and the task is that of minimizing the linear function

$$G = \sum_\alpha \xi^\alpha g^\alpha(P, T)$$

subject to linear constraints on the ξ^α in (4) (a classical problem in linear programming [5, 6]). We assume for definiteness that $rk\|x_\alpha^i\| = n$, where n is the number of components. The constraints of (4) define a subspace of dimensions $M - n$ in the M-dimensional space of ξ^α. Shift to the reaction basis of (19) denotes in essence a natural parameterization of this subspace. The constraints of (21) define a certain polyhedron there, and the initial problem concerning the minimization conditions reduces to one of unconditional minimization on that polyhedron. As G is linear, its minimal value is attained at one of the vertices; the vertices correspond to n-phase divariant assemblages (sets of numbers ξ^α, $\alpha = 1, \ldots, M$, of which only n are different from zero). We can thus derive the

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optimal assemblage by surveying the vertices. The phase composition of the assemblage changes when we vary the parameters. For example, let P increase for fixed T, which may tilt the optimal hyperplane for the level of the target function with respect to the permissible-state polyhedron. A shift from one vertex to another occurs when the two vertices and the segment joining them lie in the optimal hyperplane. That situation corresponds to special values of P, and in that case we get a univariant equilibrium of $n + 1$ phases. Any variation in the second group of parameters, which expressed the overall mixture composition, also changes the equilibrium assemblage, but the changes have a different nature. In that case, the polyhedron itself is deformed, so the switch from one equilibrium assemblage to another occurs at a degenerate vertex corresponding to $n - 1$ phase assemblages.

For a stoichiometric system the concentration space of nn is discrete so the construction of the P-T phase diagram can be reduced to linear optimization on a finite number of points in P-T-x coordinates, with subsequent refinement of the positions for the univariant curves. When a P-T diagram for a system containing solid solutions is constructed, the direct minimization must be supplemented with special procedures for searching for the univariant curves and invariant points, since the latter are characterized by certain compositions for the coexisting phases; if we specify the overall chemical composition and steps* through P and T, we may simply jump over them. Such procedures are considered in the second part of the paper. To determine the variability in the phase assemblage during the minimization, with P, T and $\overset{o}{x^i}$ specified, we may begin by distinguishing the possible regions in P-T coordinates characterized by a single qualitative picture for the phase relationships. This task is equivalent to identifying mineral facies.

ALGORITHM FOR CONSTRUCTING A P-T PHASE DIAGRAM: MgO-FeO-SiO$_2$ SYSTEM

The method of constructing the P-T phase diagram is based on the connectedness of the network in P-T coordinates that consists of stable univariant curves (M curves)**, lines for univariant equilibria, and can start (end) only at invariant points (H points) or diverge to infinity. It is clear that if we know some stable M curves and H points, we can construct curve bundles to represent the missing M curves and then define on them points corresponding to new stable invariant equilibria, from which we can construct the complete P-T diagram. Further, if we determine the compositions of the invariant and univariant assemblages, we can use Schreinemaker's rules [2] to recover the qualitative picture of the phase equilibria in the divariant regions for the entire range of possible overall compositions. Enumeration of the phases participating in the equilibrium then allows us to define their compositions. Here we can use direct minimization or can utilize the necessary equilibrium conditions directly.

A phase diagram is constructed by this method by beginning with analyzing subsystems of fewer dimensions. The basic concept is that stable M curves and H points corresponding to a subsystem remain stable in the diagram for the complete system and can be used to start the "sliding" process***. As a rule, subsolidus systems of this type include stoichiometric subsystems, and we will show that the corresponding diagrams can be constructed by standard methods.

We now illustrate the algorithm on the MgO-FeO-SiO$_2$ system, which is very characteristic as it has MgO-SiO$_2$ and FeO-SiO$_2$ as stoichiometric subsystems. The complete (ternary) system has three series of solid solutions: MgO-FeO, Mg$_2$SiO$_4$-Fe$_2$SiO$_4$, and MgSiO$_3$-FeSiO$_3$, and the corresponding end members may be taken as phase components (minals). The MgO-SiO$_2$ and FeO-SiO$_2$ subsystems have been examined in considerable detail. The corresponding P-T diagrams were first

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*That method enables us to construct a P-T section for the complete phase diagram corresponding to a specified mixture composition. There is a discussion in [18] of the structures of such sections or subsolidus systems that are close to stoichiometric.
   **The network may consist also of a set of connected components.
   ***This also enables us to distinguish the stable M curves from the metastable ones, with the latter usually causing the most difficulty.

constructed by means of the simplex method [6] for the range corresponding to the upper mantle and transition zone.

The H points in a binary subsystem correspond to four-phase equilibria and lie on M curves for the ternary system; from each such H point, there emerges a univariant four-phase equilibrium line, which either terminates at an analogous H point in the alternative subsystem (FeO-SiO$_2$ for MgO-SiO$_2$) or else diverges to infinity. Such curves intersect at H points in the ternary system. We calculate $P(T)$ along a M curve by solving (12) and (15) at each step in T, where each time we use the calculations from the previous step as an approximation. The numerical implementation is simplified because dP/dT can be calculated from the Clausius-Clapeyron equation:

$$\mathrm{d}P/\mathrm{d}T = \left(\sum_\alpha \nu_\alpha s^\alpha\right) \Big/ \left(\sum_\alpha \nu_\alpha v^\alpha\right), \qquad (22)$$

where s^α and v^α are the molar entropies and volumes of the phases, while ν_α are the stoichiometric coefficients of the univariant phase reaction, which can be calculated from the known compositions of the coexisting phases from (13) and (14).

If we have a complete set of the potential phases, we can readily enumerate the H points that lie on the stable or metastable parts of a given M curve. To distinguish the stable H points, we note that the M curve arising from a stable H point remains stable as far as the next H one; here we essentially use the connectivity of the net. Thus the first H point encountered (after the initial one) is stable.

Let us now examine this in more detail. The analysis is simplified and the most important points are illustrated by restricting consideration to a system of five phases: (Mg, Fe)SiO$_3$ (P), (Mg, Fe)SiO$_3$ (I), (Mg, Fe)O (M), (Mg, Fe)$_2$SiO$_4$ (γ), and SiO$_2$ (S) (Table 1). These phases are of the main interest as regards interpreting a second seismic boundary at $\sim$ 670 km [6, 14].

This five-phase system has five H points within the MgO-SiO$_2$ system; the phase diagram [6] shows that only three of them are stable in the range of interest here (190-250 kbar and 1500-2500 K): (P, M, S, γ), (I, P, M, γ), (I, P, γ, S)*. Figure 1 shows also the metastable H points (P, I, M, S) and (γ, I, M, S). The FeO-SiO$_2$ system is much simpler at these P and T: there are no H points, and only the FeO + SiO$_2$ assemblage is stable [6].

In the MgO-FeO-SiO$_2$ system, there are four phases of variable composition (I, P, γ, M), which for definiteness we consider as ideal solutions [19], together with a phase of constant compositions (S). This is a unique nondegenerate H point (I, P, γ, M, S), whose position is to be determined.

We begin, following the algorithm, with the four-phase M curves emerging from the stable H points in the MgO-SiO$_2$ subsystem**. There are four possible positions for the four-phase univariant-equilibrium curve in the region of the H point (P, M, S, γ) (cf. Fig. 2), but even the qualitative analysis indicates preference for form a, since only it agrees with the data on the FeO-SiO$_2$ system and satisfies the empirical regularity $x_M^{FeO} > x_\gamma^{FeO} > x_I^{FeO} > x_P^{FeO}$ [14]. Similar arguments enable us to construct curves for the other stable H points, which are degenerate (singular) and contain indifferent phases [2] (Fig. 3).

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*As there are uncertainties in the thermodynamic data and equations of state, it has been suggested [6] that there may be two topologically different forms of diagram for the MgO-SiO$_2$ system. To illustrate our algorithm, we examined one of these in detail, namely the simpler one. We give only the summary P-T diagram for the alternative (Fig. 7).

**The H points considered below are of the degenerate type [20, 21]; see the Appendix for an analysis of this type of H point, which explains the subsequent constructions.

Table 1

Solid Phases in the MgO-FeO-SiO$_2$ System Stable at the
P and T of the Lower Boundary (670 km) of the
Transition Zone in the Earth's Mantle

Formula	Mineral	Abbreviation
SiO$_2$	Stishovite	S
(Mg, Fe)$_2$SiO$_4$	Spinel	γ
(Mg, Fe)$_2$SiO$_4$	Modified spinel	β
(Mg, Fe)SiO$_3$	Ilmenite structure	I
(Mg, Fe)SiO$_3$	Perovskite structure	P
(Mg, Fe)O	Magnesiowüstite	M
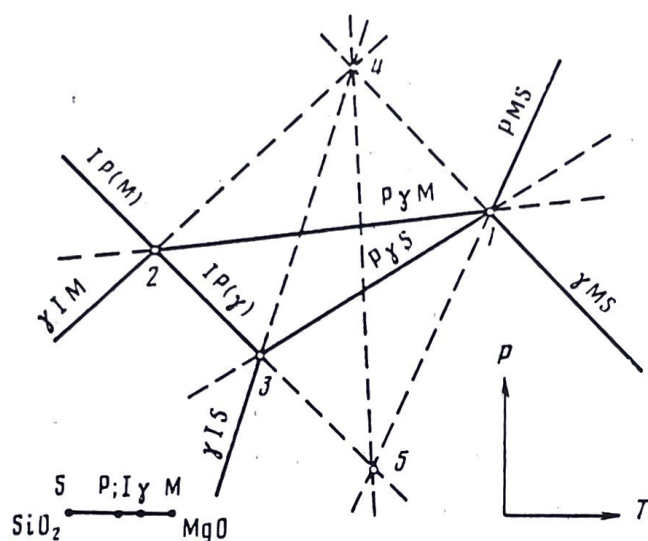
Fig. 1. Part of the phase diagram for the stoichi-
ometric MgO-SiO2 system at the P and T of the lower
boundary in the transitional mantle zone (topologi-
cal scheme, see [6] for details). The numbers de-
note the invariant points: 1) (γ, P, M, S); 2) (I,
P, M, γ); 3) I, γ, S, P): 4) (γ, I, M, S); 5) (P,
I, M, S).

Using the technique developed in the first part, we will write the equations
for $P(T)$ and $x_\alpha{}^i(T)$ on the (P, γ, M, S), (I, P, γ, S), and (P, M, γ, S) univariant
equilibrium lines.

1. FOUR-PHASE (P, γ, M, S) EQUILIBRIUM (Fig. 4a)

We determine the four unknown functions

$$x_\gamma = x_\gamma^{Mg_2SiO_4}(T), \quad x_P = x_P^{MgSiO_3}(T), \quad x_M = x_M^{MgO}(T), \quad P(T)$$

by means of four equations*:

_____

*To derive these equations from (12) and (15), it is necessary to take SiO$_2$ as the compo-
nent whose contents in the phases are fixed, while the component n in (12) and (15) is taken as
FeO. For convenience, the molar fractions of the remaining component MgO have been replaced by
the corresponding minal concentrations. The partial functions $\hat{G}^\alpha$ from (12) correspond to FeO.

Exchange reactions:

1. $\dfrac{1}{2}(g_\gamma^{0\,Mg_2SiO_4} - g_\gamma^{0\,Fe_2SiO_4}) - (g_P^{0\,MgSiO_3} - g_P^{0\,FeSiO_3}) - RT \ln \dfrac{x_P(1-x_\gamma)}{(1-x_P)\,x_\gamma} = 0,$ (23)

2. $\dfrac{1}{2}(g_\gamma^{0\,Mg_2SiO_4} - g_\gamma^{0\,Fe_2SiO_4}) - (g_M^{0\,MgO} - g_M^{0\,FeO}) - RT \ln \dfrac{x_M(1-x_\gamma)}{(1-x_M)\,x_\gamma} = 0.$ (24)

Three-phase minal reactions:

3. $(2g_P^{0\,MgSiO_3} - g_\gamma^{0\,Mg_2SiO_4} - g_S^{0}) - RT \ln \dfrac{x_\gamma^2}{x_P^2} = 0,$ (25)

4. $(g_P^{0\,MgSiO_3} - g_M^{0\,MgO} - g_S^{0}) - RT \ln \dfrac{x_M}{x_P} = 0.$ (26)

The equations contain the standard Gibbs energies of the pure phases, which are taken as known functions of P and T.

We introduce the equilibrium constants

$$K_1(P, T) = \exp\left\{\left[\frac{1}{2}(g_\gamma^{0\,Mg_2SiO_4} - g_\gamma^{0\,Fe_2SiO_4}) - (g_P^{0\,MgSiO_3} - g_P^{0\,FeSiO_3})\right]\Big/RT\right\},$$

$$K_2(P, T) = \exp\left\{\left[\frac{1}{2}(g_\gamma^{0\,Mg_2SiO_4} - g_\gamma^{0\,Fe_2SiO_4}) - (g_M^{0\,MgO} - g_M^{0\,FeO})\right]\Big/RT\right\},$$

$$K_3(P, T) = \exp\left\{(2g_P^{0\,MgSiO_3} - g_\gamma^{0\,Mg_2SiO_4} - g_S^{0})/RT\right\},$$

$$K_4(P, T) = \exp\left\{(g_P^{0\,MgSiO_3} - g_M^{0\,MgO} - g_S^{0})/RT\right\}.$$

When x_P, x_γ and x_M have been eliminated from (23)-(26), the equation for $P(T)$ becomes

$$K_4^2(K_1 - K_2)^2 = K_3(K_2K_1 - K_1K_4 - K_2 - K_1K_2K_4)^2.$$

2. FOUR-PHASE (I, P, γ, S) EQUILIBRIUM (FIG. 4b)

To determine the four unknown functions

$$x_I = x_I^{MgSiO_3}(T),\ x_P(T),\ x_\gamma(T),\ P(T)$$

we have four equations:

Exchange reactions: 1, see (23), and

5. $(g_P^{0\,MgSiO_3} - g_P^{0\,FeSiO_3}) - (g_I^{0\,MgSiO_3} - g_I^{0\,FeSiO_3}) - RT \ln \dfrac{x_I(1-x_P)}{(1-x_I)\,x_P} = 0;$ (27)

Three-phase minal reactions: 3, see (25), and

6. $(g_P^{0\,MgSiO_3} - g_I^{0\,MgSiO_3}) - RT \ln \dfrac{x_I}{x_P} = 0;$ (28)

where the last equilibrium is singular (see footnote 1).

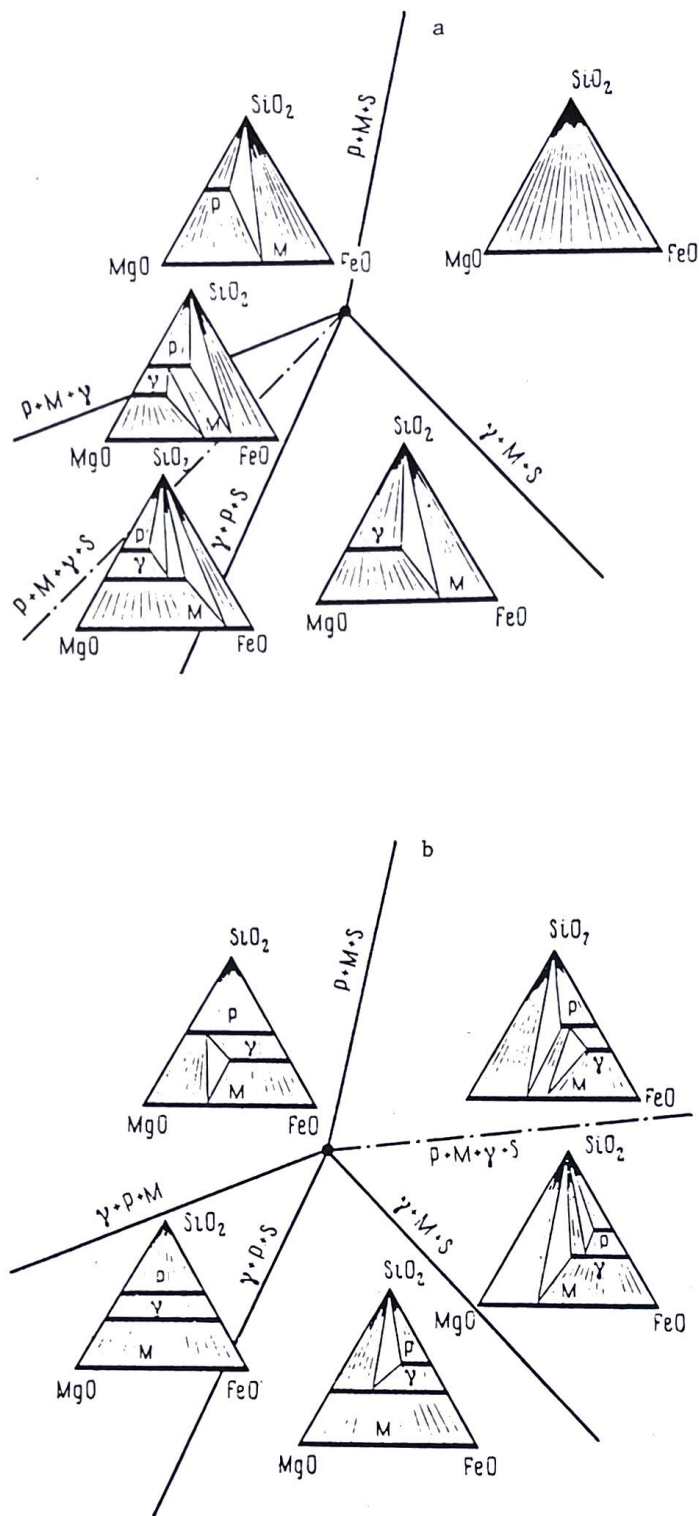We introduce the equilibrium constants for reactions 5 and 6:

Fig. 2. Part of the *P-T* diagram for the MgO–FeO–SiO₂ system. We show schematically the possible forms a–d for the positions of the nondegenerate univariant (P, M, γ, S) curve (dot-dash line) around the singular invariant point relating to the stoichiometric MgO–SiO₂ subsystem (point 1 in Fig. 1). The phase compositions in the divariant regions are shown in the concentration triangles.

$$K_5(P, T) = \exp\{[(g_P^{0\,MgSiO_3} - g_P^{0\,FeSiO_3}) - (g_I^{0\,MgSiO_3} - g_I^{0\,FeSiO_3})]/RT\},$$

$$K_6(P, T) = \exp\{(g_P^{0\,MgSiO_3} - g_I^{0\,MgSiO_3})/RT\},$$
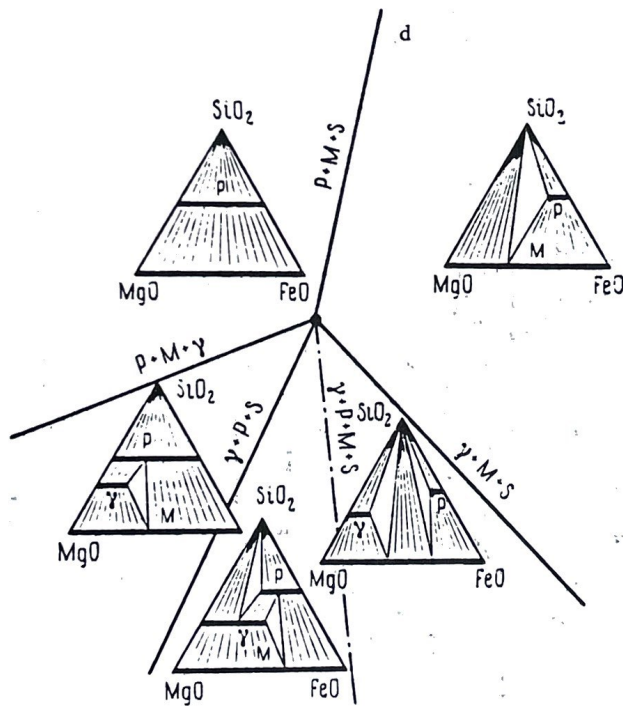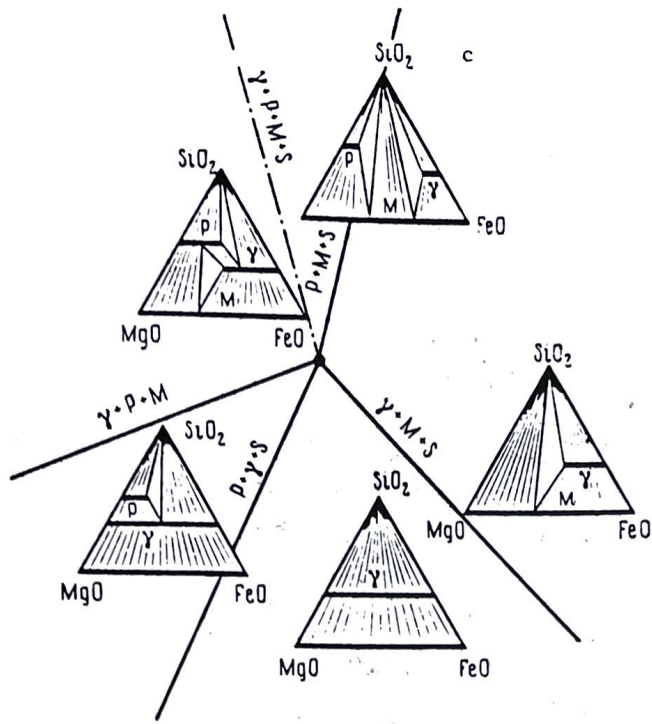
Fig. 2b.

and get the equation for $P(T)$:

$$K_6^2 (K_5 - 1)^2 = K_3 (K_1 K_5 K_6 - K_1 K_5 + K_5 - K_6)^2.$$
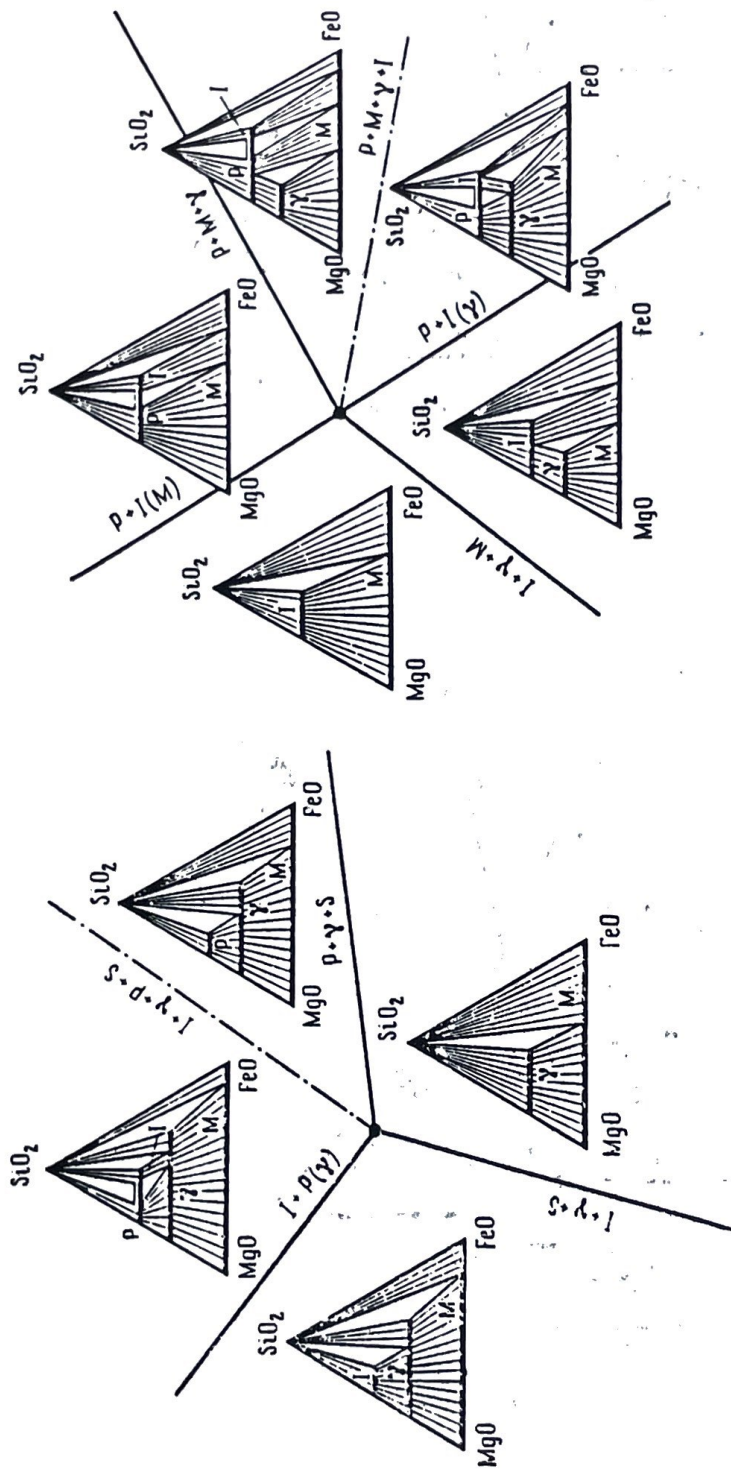
Fig. 3. Part of the *P-T* diagram for the MgO-FeO-SiO$_2$ system. We show schemes consistent with the experimental evidence on the nondegenerate univariant (I, γ, P, S) and (P, M, γ, I) curves (dot-dash lines) around the singular invariant points relating to the stoichiometric MgO-SiO$_2$ subsystem (points 3 and 2 in Fig. 1). The concentration triangles show the phase compositions in the divariant regions; the double lines denote degenerate equilibria corresponding to binary solution subsystems.
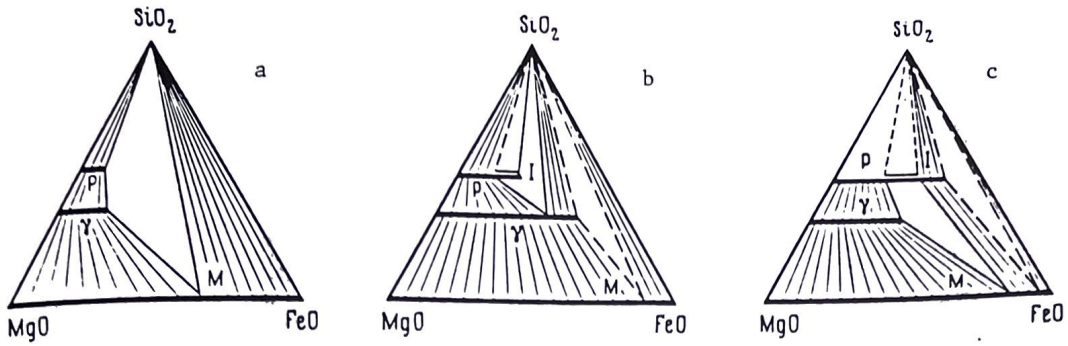
Fig. 4. Structure of the univariant assemblages in concentration space for the MgO–FeO–SiO$_2$ system: a) (P, γ, M, S); b) (I, P, γ, S); c) (P, I, M, γ); the dashed lines show the divariant assemblages existing at the P and T of the univariant equilibrium.

3. FOUR-PHASE (P, M, I, γ) EQUILIBRIUM (FIG. 4c)

To determine the five unknown functions $x_P(T)$, $x_M(T)$, $x_I(T)$, $x_\gamma(T)$, and $P(T)$ we have five equations:

Exchange reactions: 1), see (23); 2, see (24); 5 see (27).

Three-phase minal reactions: 6, see (28) and

$$7. \quad (g_\gamma^{0\,Mg_2SiO_4} - g_P^{0\,MgSiO_3} - g_M^{0\,MgO}) - RT \ln (x_P x_M / x_\gamma^2) = 0. \tag{29}$$

We introduce the equilibrium constant for reaction 7:

$$K_7(P,\,T) = \exp \{(g_\gamma^{0\,Mg_2SiO_4} - g_P^{0\,MgSiO_3} - g_M^{0\,MgO})/RT\} = \frac{K_4}{K_3}\,,$$

and get the equation for $P(T)$:

$$K_2(K_1 K_5 - K_5 + K_6 - K_1 K_5 K_6)^2 =$$
$$= K_6 K_7 (1 - K_5)(K_1 K_5 - K_2 K_6 - K_2 K_5 - K_1 K_5 K_6).$$

Thus the position of each of the M curves can be determined from a unique equation; the H point corresponding to the intersection of two M curves is found by solving a system of two equations. When the pressure is eliminated, this system can be written as a single equation of $\varphi(T) = 0$ type.

The value of dP/dT along the M curve is calculated from (22); (13) and (14) allow us to show that the stoichiometric coefficients for the four-phase univariant reaction $v_\alpha A_\alpha + v_\beta A_\beta + v_\gamma A_\gamma + v_\delta A_\delta = 0$ can be taken as

$$v_\alpha = \frac{(c_\delta^{SiO_2} - c_\beta^{SiO_2})(x_\gamma^{MgO} - x_\beta^{MgO}) - (c_\gamma^{SiO_2} - c_\beta^{SiO_2})(x_\delta^{MgO} - x_\beta^{MgO})}{(c_\alpha^{SiO_2} - c_\beta^{SiO_2})(x_\gamma^{MgO} - x_\beta^{MgO}) - (c_\gamma^{SiO_2} - c_\beta^{SiO_2})(x_\alpha^{MgO} - x_\beta^{MgO})}\,,$$

$$v_\beta = \frac{(c_\delta^{SiO_2} - c_\alpha^{SiO_2})(x_\gamma^{MgO} - x_\alpha^{MgO}) - (c_\gamma^{SiO_2} - c_\alpha^{SiO_2})(x_\delta^{MgO} - x_\alpha^{MgO})}{(c_\beta^{SiO_2} - c_\alpha^{SiO_2})(x_\gamma^{MgO} - x_\alpha^{MgO}) - (c_\gamma^{SiO_2} - c_\alpha^{SiO_2})(x_\beta^{MgO} - x_\alpha^{MgO})}\,,$$

$$v_\gamma = \frac{(c_\delta^{SiO_2} - c_\alpha^{SiO_2})(x_\beta^{MgO} - x_\alpha^{MgO}) - (c_\beta^{SiO_2} - c_\alpha^{SiO_2})(x_\delta^{MgO} - x_\alpha^{MgO})}{(c_\gamma^{SiO_2} - c_\alpha^{SiO_2})(x_\beta^{MgO} - x_\alpha^{MgO}) - (c_\beta^{SiO_2} - c_\alpha^{SiO_2})(x_\gamma^{MgO} - x_\alpha^{MgO})}\,,$$

$$v_\delta = -1.$$

For the case of the (P, γ, M, S) equilibrium, we get

$$v_P = 4(x_\gamma - x_M)/(2x_\gamma - x_M - x_P); \quad v_M = 2(x_P - x_\gamma)/(2x_\gamma - x_M - x_P); \quad v_\gamma = 3(x_M - x_P)/(2x_\gamma - x_M - x_P).$$

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When we write expressions that include molar quantities (Gibbs energies, volumes, and entropies for the phases), we have to incorporate relationships of the type

$$s_\gamma'(x_\gamma^{MgO}, P, T) = 1/3 \hat{s}_\gamma(x_\gamma^{Mg_2SiO_4}, P, T), \quad s_P(x_P^{MgO}, P, T) = \frac{1}{2} \hat{s}_P(x_P^{MgSiO_4}, P, T).$$

The (P, γ, M, S), (I, P, γ, S) and (P, M, γ, I) M curves intersect at a five-phase H point, which is represented schematically in Fig. 5. The two missing M curves arising from the H point are constructed by Schreinemaker's method [2]. This multisystem thus has four stable invariant assemblages, three of which relate to the subsystem and are singular. The complete phase diagram of Fig. 5 enables us to state the possible equilibrium phase assemblages for each of the divariant regions.

We now will explain our method of positioning the M curves near the H point (I, P, γ, S, M). Figure 6 shows that in principle we could have two topologically different schemes for the M curves, both of which satisfy the empirical relation $x_P^{FeO} < x_I^{FeO} < x_\gamma^{FeO} < x_M^{FeO}$. In the first case, the points corresponding to P and I lie in a concentration triangle on one side of the γ-S tie line, while in the second, they lie on opposite sides of it. When one shifts from one form to the other, the order of the (S, γ, I, M) and (P, I, S, γ) M lines changes. Qualitative considerations are inadequate to choose between these two forms, and only the available measurements [22, 23] indicate preference for form a. An analogous choice was made in [14], but the scheme given there for the disposition of the M curves differs from ours: it is a mirror image with respect to the axis T = constant passing through the H point (I, P, γ, S, M). The discrepancy arises from differences in interpreting the measurements [22, 23]*. The decisive feature is that only our scheme agrees with the available data for the MgO-SiO$_2$ subsystem [6] (no such matching was performed in [14]).

We now will show how (12) and (13) can be used to calculate the coexisting-phase compositions in divariant regions; let us consider the region bounded by AB, BC and CA in Fig. 5, where there are the four three-phase assemblages (γ, P, M), (I, S, M), (P, I, M) and (P, I, S), with the last degenerate. We give the formulas for the compositions.

1. <u>Three-phase (γ, M, P) equilibrium</u>: Unknowns x_P, x_γ, and x_M. Exchange reactions: 1 see (23) and 2 see (24). Three-phase minal reaction 7, see (29).

2. <u>Three-phase (I, S, M) equilibrium</u>: unknowns x_I and x_M. Exchange reaction

$$(g_I^{0\,MgSiO_3} - g_I^{0\,FeSiO_3}) - (g_M^{0\,MgO} - g_M^{0\,FeO}) - RT \ln \frac{x_M(1 - x_I)}{(1 - x_M)x_I} = 0. \tag{30}$$

Three-phase minal reaction

$$(g_I^{0\,MgSiO_3} - g_M^{0\,MgO} - g_S^0) - RT \ln \frac{x_M}{x_I} = 0. \tag{31}$$

3. Three-phase (P, I, M) equilibrium: unknowns x_P, x_I, and x_M. Exchange reactions: 5 see (27) and

$$(g_P^{0\,MgSiO_3} - g_P^{0\,FeSiO_3}) - (g_M^{0\,MgO} - g_M^{0\,FeO}) - RT \ln \frac{x_M(1 - x_P)}{(1 - x_M)x_P} = 0 \tag{32}$$

Three-phase minal reaction 6 see (28).

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*The experiments of [22] were performed by diamond anvils and laser heating: recently, there has been firm evidence that the temperature was higher than that given by the authors by 1000° [24], so we suppose that the data of [23] obtained in an apparatus of sectioned sphere type relate to the temperature range below this H point, while the measurements of [22] give the phase relationships above it. The converse sequence was adopted in [14].
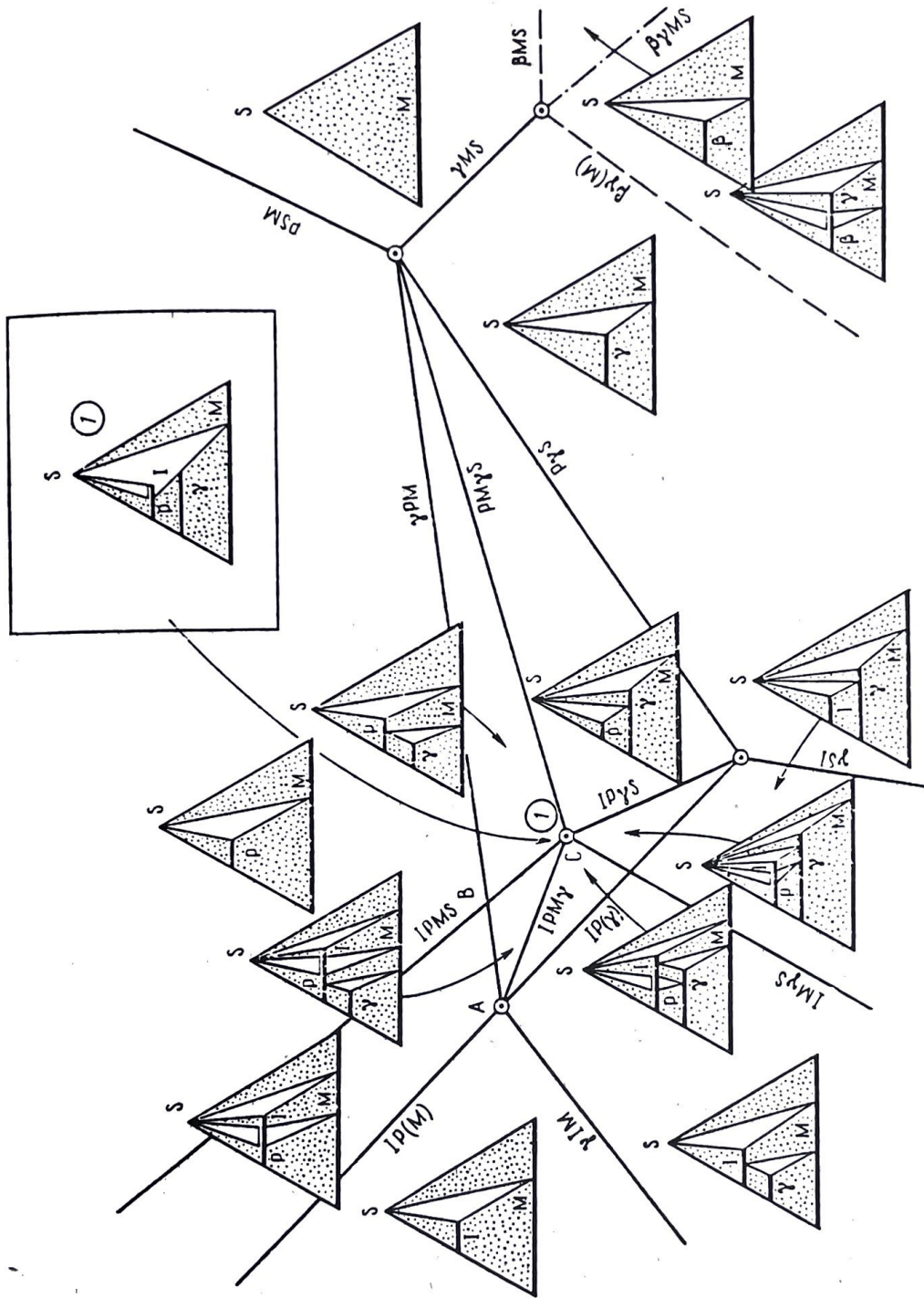
Fig. 5. One of the forms for the $P-T$ diagram for the (P, I, γ, M, S) five-phase multisystem at the P and T of the lower boundary of the transitional mantle zone (topological scheme). The dashed lines show the singular univariant curves and the dot-dash ones show the nonsingular ones, which correspond to the (P, I, γ, M, S, β) six-phase multisystem; the inset shows the disposition of the phases corresponding to the unique nonsingular (P, I, γ, M, I) invariant point.
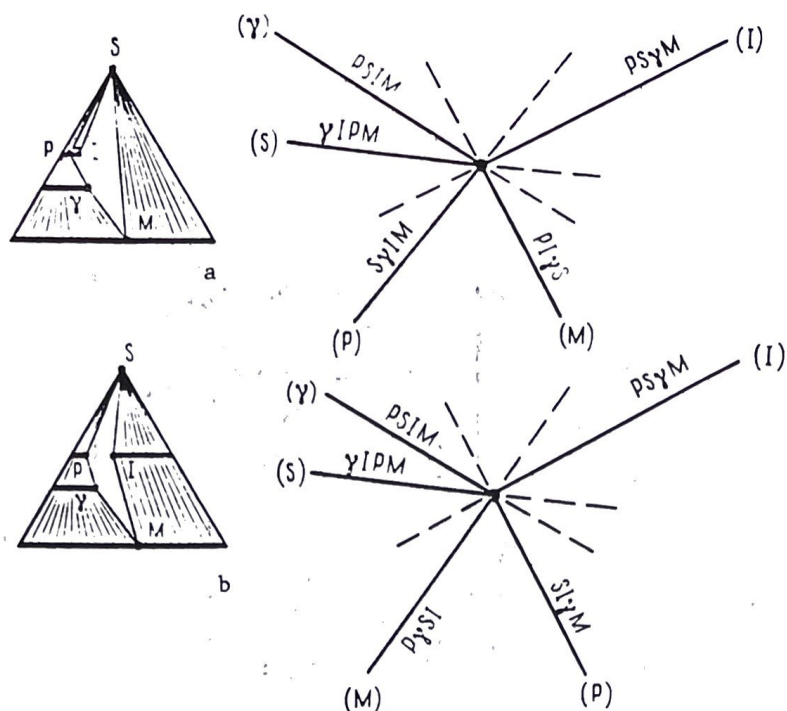
Fig. 6. Topologically distinct schemes for the positions of the univariant curves in the region of the nonsingular (γ, S, P, M, I) invariant point. Forms a and b differ in their phase configurations in the concentration triangle, with form a agreeing with experiment.

We now calculate the phase proportions from the known overall composition. Let phases α, β and γ be in equilibrium. Then we solve (4) to get

$$\xi_\alpha = \frac{(x^{0\text{MgO}} - x_\gamma^{\text{MgO}})(x_\beta^{\text{FeO}} - x_\gamma^{\text{FeO}}) - (x^{0\text{FeO}} - x_\gamma^{\text{FeO}})(x_\beta^{\text{MgO}} - x_\gamma^{\text{MgO}})}{(x_\alpha^{\text{MgO}} - x_\gamma^{\text{MgO}})(x_\beta^{\text{FeO}} - x_\gamma^{\text{FeO}}) - (x_\beta^{\text{MgO}} - x_\gamma^{\text{MgO}})(x_\alpha^{\text{FeO}} - x_\gamma^{\text{FeO}})},$$

$$\xi_\beta = \frac{(x^{0\text{MgO}} - x_\gamma^{\text{MgO}})(x_\alpha^{\text{FeO}} - x_\gamma^{\text{FeO}}) - (x^{0\text{FeO}} - x_\gamma^{\text{FeO}})(x_\alpha^{\text{MgO}} - x_\gamma^{\text{MgO}})}{(x_\beta^{\text{MgO}} - x_\gamma^{\text{MgO}})(x_\alpha^{\text{FeO}} - x_\gamma^{\text{FeO}}) - (x_\alpha^{\text{MgO}} - x_\gamma^{\text{MgO}})(x_\beta^{\text{FeO}} - x_\gamma^{\text{FeO}})}, \tag{33}$$

$$\xi_\gamma = 1 - \xi_\alpha - \xi_\beta.$$

In the particular case of the (P, γ, M) three-phase equilibrium, we must substitute the following into (33):

$$x_P^{\text{MgO}} = \frac{1}{2}x_P, \quad x_\gamma^{\text{MgO}} = \frac{2}{3}x_\gamma, \quad x_M^{\text{MgO}} = x_M,$$

$$x_P^{\text{FeO}} = \frac{1}{2}(1 - x_P), \quad x_\gamma^{\text{FeO}} = \frac{2}{3}(1 - x_\gamma), \quad x_M^{\text{FeO}} = 1 - x_M.$$

The conditions $0 \leqslant \xi_\alpha \leqslant 1$, $0 \leqslant \xi_\beta \leqslant 1$ are in essence constraints on the overall composition $x^{0\text{MgO}}$, $x^{0\text{FeO}}$, for which divariant three-phase equilibrium occurs for the given P and T; if these conditions are not met, the system is in trivariant two-phase equilibrium*. Here there is a unique constraint on the coexisting-phase compositions as the equation for the exchange reaction. The phase compositions can be identified unambiguously only by specifying the overall mixture composition. The additional equation for x_α^{MgO}, x_β^{MgO} is

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*Only one phase may be stable for special overall compositions.

$$(\overset{0}{x}{}^{MgO} - x_\beta^{MgO})(x_\alpha^{FeO} - x_\beta^{FeO}) = (\overset{0}{x}{}^{FeO} - x_\beta^{FeO})(x_\alpha^{MgO} - x_\beta^{MgO}).$$

In the case of (γ, P) equilibrium, we have

$$x_P = \frac{2x_\gamma[2(\overset{0}{x}{}^{MgO} + \overset{0}{x}{}^{FeO}) - 1] - \overset{0}{x}{}^{MgO}}{3(\overset{0}{x}{}^{MgO} + \overset{0}{x}{}^{FeO}) - 2}.$$

This equation in conjunction with (23) enables us to determine $x_P(P, T)$, and $x_\gamma(P, T)$ uniquely.

One additional phase complicates the pattern considerably; let us consider for example the set of P, I, γ, M, S and β, where we have added the phase β-(Mg, Fe)$_2$SiO$_4$ (modified spinel) to the initial five-phase system. The phase relationships in the FeO-SiO$_2$ subsystem are unaltered [6], but the P-T diagram for the MgO-SiO$_2$ subsystem becomes more complicated. The total number of H points increases from 5 to 15. Linear optimization [6] enables us to identify the stable H points, of which there are four in the parameter range of interest.

We will make only some brief comments on the ternary system. For each four-phase M curve we can derive only two five-phase H points; the stable H point (P, M, S, γ, I) considered above remains stable in the extended system. The only four-phase univariant assemblage involving phase β whose stability can be judged reliable is (β, γ, M, S), and the corresponding M curve is shown by the dashed line in Fig. 5. Thus although the P-T diagram for the subsystem becomes more complicated, no new five-phase H points arise in this parameter range on including the β phase.

The situation differs in the alternative diagram (see footnote 8). Without repeating the analysis, we merely give the resultant MgO-FeO-SiO$_2$ diagram (Fig. 7). There are other four-phase H points stable in the MgO-SiO$_2$ subsystem here, although the number of them is unaltered: instead of (P, M, S, γ) and (β, M, S, γ), we have (P, S, γ, β) and (β, γ, P, M). The five-phase H point (I, P, M, γ, S) already considered is here accompanied by a nondegenerate H point (β, γ, M, S, P). At present, the measurements are clearly insufficient to choose unambiguously between these two types, but recent experiments [23] appear to indicate negative slopes for the (I, P) and (P, M, γ) M curves in the MgO-SiO$_2$ system, so we can prefer the form in Fig. 7.

These diagrams are to be considered only as illustrating the algorithm; a quantitative analysis requires a careful discussion of the input thermodynamic parameters and is the subject of a separate paper.

APPENDIX

We will show how the singular H points may be described by Schreinemaker's method [2]. The discussion relates to the general case of an n-component system.

In a divariant assemblage D, given some special compositions of the coexisting phase, a phase reaction can occur that is accompanied by changes in the proportions of the phases for a fixed composition. This is possible if $\det\|x_\alpha^i\|$ becomes zero, so the reaction corresponds to a certain M curve. A typical particular case of such a reaction is the nonsingular univariant transformation in a subsystem containing $n - 1$ components. If there are several such transformations in the subsystem, the corresponding curves may intersect in the P-T plane and define H points. These H points in the $n - 1$ subsystem are nondegenerate and can be described in terms of Schreinemaker's scheme, and the same points will occur in the P-T diagram for the n-component system and denote the bounds to the nonsingular M curves for $n + 1$ phases. Although $n + 2$ M curves arise from such a H point, there are only $n + 1$ phases coexisting there when allowance is made for the indifferent ones.

Let us consider the structure of the D fields near a singular H point of this type.
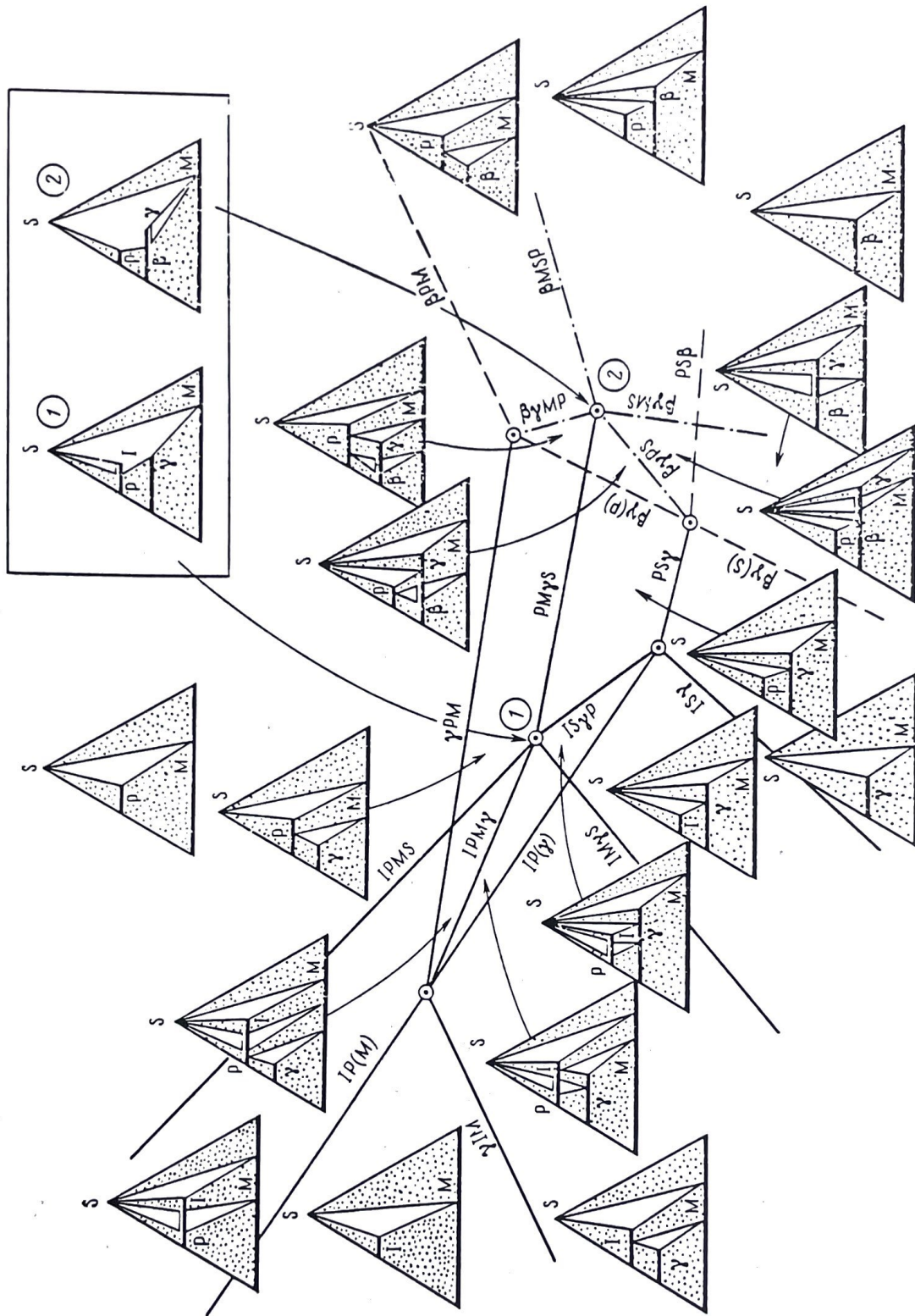
Fig. 7. Alternative form (see Fig. 5) of the P–T diagram for the five-phase (P, I, γ, M, S) multisystem at the P and T of the lower boundary of the mantle transition zone (topological scheme). The dashed lines show the singular univariant curves and the dot-dashed ones show the nonsingular ones corresponding to the six-phase (P, I, γ, M, S, β) multisystem; the inset shows the phase dispositions corresponding to the (P, I, S, M, γ) and (P, β, γ, M, S) nonsingular invariant points.

Schreinemaker's method clearly enables us to recover the disposition of the M curves near this H point: (a), (b), (c), ..., which relate to the subsystem (symbols of [2]). We assume that the position of the nonsingular M curve for the n-component system arising from this H point (equilibrium $a + b + c + \ldots$) can be defined, as the construction method is discussed in the main text. The known compositions of the coexisting phases in the univariant assemblage enable us to determine the dispositions of the D fields, which may also be denoted by (a), (b), (c), and so on in relation to the given M curve [20, 21]; here it must be remembered that D assemblage (a) should lie in the sector bounded by this M curve and the singular M curve of (a). Thus near the nonsingular M curve there are $n + 1$ D fields. When we pass from sector to sector via a singular M curve, the corresponding D assemblage vanishes if it was present previously or appears in the converse case. To solve this problem, it is necessary to begin with a sector adjoining a nondegenerate M curve and complete a circuit around the H point. The corresponding D assemblages are introduced or eliminated on passing through the M curves and can enumerate the D fields in each sector and return to the initial set of D assemblages.

If the phase thermodynamic parameters (molar volumes and entropies) are not available, the solution is not unique, since there are $n + 1$ ways of drawing the nonsingular M curve. The ambiguity arises because the planar polyhedron corresponding to the $n + 1$ phase assemblage in the concentration space of the system containing $n - 1$ components can be transformed in different ways into a volume polyhedron in the concentration space for the n-component system. Clearly, the regularizing factor would be to specify the set of D associations for at least one of the sectors.

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ORGANIC-MATTER TRANSFORMATION IN BOTTOM SEDIMENTS OF THE BERING SEA DEEP-WATER TROUGHS*

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A study has been made of the roles played by organic matter in sediments in the Aleutian and Komandorsky depressions in the processes of petroleum formation by reference to changes in compositional features, accumulation conditions, and bituminous-component distributions. Data have been obtained on the content, composition and distribution of the bitumoids in columns down to a depth of 4.5 m, which show substantial organic-matter transformation that is not characteristic of diagenesis in shallow sediments. The parameters identified, which correspond to the conversion of organic matter as far as the level of protocatagenesis, are related to the unusual diagenetic facies. There are high contents of C_{org} (up to 1.87%) and hydrocarbons (up to 4.0%), while the organic matter is mainly of aline nature, so these sediments may be considered as potential oil-producing ones.

This study concerns organic matter (OM) in sediments in the Komandorsky and Aleutian deep-water trenches, which are associated with an active continental margin. Almost nothing is known about the organic-matter geochemistry of the sediments here, but the composition of the organic matter in such sediments is of interest as regards oil formation, since the main economic oil pools in the North Sakhalin basin are associated with such beds [1, 2]. The region is seismically active. During a week in the 29th voyage of the R/N Dmitriy Mendeleyev, ~ 120 tremors were recorded at a single point. Seismic energy can accelerate OM transformation considerably at low temperatures and favor hydrocarbon formation [3, 4].

In this region, there are very high rates of accumulation of terrigenous and biogenic siliceous material, and very high rates of production by diatom phytoplankton, together with considerable amounts of siliceous spongy benthos

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