

Computer Simulation of the Phase Diagram for the MgO–SiO₂ System at *P–T* Parameters of the Mantle Transition Zone

O.L. Kuskov, O.B. Fabrichnaya, R.F. Galimzyanov, L.M. Truskinovsky

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, 19, Kosygin Street, Moscow 117334, USSR

Abstract. The paper reports an attempt to study the topologies of the phase diagram for the MgO–SiO₂ system at high pressure and temperature using computer simulation. Phase equilibria at MgSiO₃ stoichiometry is investigated, demonstrating that the invariant point Gr + Ilm + Pv is stable at 21.6 GPa and 2270 K. A thermodynamic data base for minerals in the MgO–SiO₂ system is established by supplementing the calorimetric data for low pressure phases and equations of state for low and high pressure phases with data calculated from high pressure synthesis experiments. A refined set of standard free energies of formation and phase transformations in the MgO–SiO₂ system is presented. The proposed phase diagram covers a wide range of pressure (up to 25 GPa) and temperature (up to 2500 K) and forms the basis for a geochemical interpretation of the nature of seismic discontinuities in the mantle.

Introduction

The picture of phase equilibria in the mantle and in silicate systems modeling its composition at pressures over 10 GPa has not yet been clearly outlined. The binary MgO–SiO₂ system fundamental to mantle petrology is known within a wide range of temperatures and pressures (1000–2000° C, 10–30 GPa) as a result of experimental investigations due to Ringwood (1975), Suito (1977), Akaogi and Akimoto (1977), Yagi et al. (1979), Ohtani (1979), Liu (1979), Ito and Yamada (1982), Ito and Navrotsky (1985), Sawamoto (1986). Studies of individual phase transformations in this system form the basis of a geochemical interpretation of the nature of seismic discontinuities in the mantle. However, the post-spinel transformations have been established as a first approximation only and are still largely subject to debate, while there is as yet no exhaustive picture of the phase diagram of the MgO–SiO₂ system.

The availability of experimental data on phase equilibria, parameters of equations of state, and calorimetry now make it possible to calculate phase diagrams using the methods of chemical thermodynamics (Liu 1979, Kuskov et al. 1983a, Ito and Navrotsky 1985, Kuskov and Galimzyanov 1986, Ostrovsky et al. 1986).

Galimzyanov and Kuskov (1988) have developed a consistent approach to the problem of predicting the mineral composition of the mantle, so that an analysis of the topology of a phase diagram as a whole can be made instead

of an examination of univariant curves for individual equilibria. The construction of a phase diagram becomes a completely formalized procedure and the search for an internally consistent diagram is realized by changing input data within the uncertainty ranges.

The present paper reports the first attempt to use imitation modelling as a method of study in the topology of a phase diagram for the MgO–SiO₂ system at the *P–T* parameters typical for the mantle transition zone. The method of direct minimization of Gibbs energy is used to construct the diagrams. The input data are equations of state for all phase of the system, standard free energies of formation of low-pressure phases, and the *P–T* parameters of basic univariant equilibria. The approach has revealed topologically stable variants of the *P–T* diagram for the MgO–SiO₂ system for use in modeling the structure and evolution of planetary shells, in order to connect the phase transition of minerals to the observed seismic discontinuities in the mantle, as well as in planning new experiments at ultrahigh pressures and temperatures.

Phase Relations in the MgO–SiO₂ System from Experimental Data

Since reviews of experimental studies relating to the MgO–SiO₂ system can be found in Kuskov and Galimzyanov (1986), we shall consider here only new information obtained in recent years. The parameters of phase equilibria¹ are given in Table 1.

Ito and Navrotsky (1985) have found that enstatite decomposes into an association of β -spinel + stishovite at 1000° C and 15 GPa, that is, 1.5–2.0 GPa below the previous determinations of Akaogi and Akimoto (1977) and Liu (1979). The *P–T* parameters have been improved for the reaction $\gamma + \text{St} = 2 \text{Ilm}$ ($P = 19.5\text{--}20.5$ GPa at 1100° C) by Ito and Yamada (1982) and Ito and Navrotsky (1985).

It has been found that the univariant curves for $\text{Ilm} = \text{Pv}$ and $\gamma = \text{Pv} + \text{MgO}$ have a negative slope (Ito and Yamada 1982), but the resolution available in these experiments did not permit the *P–T* parameters of these two (most highest)-pressure transformations to be distinguished. At temperatures above 1700° C within the range 18 to 22 GPa, a gar-

¹ The following notation is adopted in the text; for polymorphic modifications of Mg₂SiO₄: forsterite- α , β -spinel- β , γ -spinel- γ ; for polymorphic modifications of MgSiO₃: enstatite-En, MgSiO₃ in the structures of ilmenite, perovskite, and garnet-Ilm, Pv, Gr respectively; for SiO₂ (stishovite)-St.

Table 1. Phase relationships in the MgO–SiO₂ system from experimental evidence

Transformation	$P(1273\text{ K}), \text{ GPa}$	$P(T) = A + BT$ $P, \text{ GPa}; T, \text{ K}$	Apparatus type	Reference
I Composition: Mg ₂ SiO ₄				
$\alpha = \beta$	12.0	–	1	Rinwood 1975
	12.3	$6.4 + 0.0046 T$	1	Akimoto et al. 1976
	12.6	$6.2 + 0.005 T$	1	Kawada 1977
	14.3	$9.8 + 0.0035 T$	2	Suito 1977
	13.0	–	2	Malinovsky et al. 1981
$\beta = \gamma$	18.6	$7.8 + 0.0085 T$	2	Kawada 1977
	16.0	–	3	Yagi et al. 1979
	17	$10.0 + 0.0055 T$	2	Suito 1977
	16.1	$10.6 + 0.0043 T$	2	Ohtani 1979
	15.7	$7.9 + 0.0061 T$	2	Sawamoto 1985
$\gamma = \text{Pv} + \text{MgO}$	27	–	3	Liu 1976 ^b
	25.5	–	3	Yagi et al. 1979
	25.3	$27.8 - 0.002 T$	2	Ito Yamada 1982
II Composition: MgSiO ₃				
2 En = β + St	17.5	$13.7 + 0.003 T$	2	Akaogi and Akimoto 1977
	17.0	–	2	Ito and Matsui 1977
	17.5	–	3	Liu 1976 ^a , 1979
	15.2	–	2	Ito and Navrotsky 1985
$\gamma + \text{St} = 2 \text{ Ilm}$	19–22	–	3	Liu 1976 ^a , 1979
	20.5(1373 K)	–	2	Ito and Yamada 1982
	19.5(1373 K)	–	2	Ito and Navrotsky 1985
Ilm = Pv	21.0–25.0	–	3	Liu 1976 ^a , 1979
	25.3	$27.8 - 0.002 T$	2	Ito and Yamada 1982

Apparatus types are numbered thus: (1) Bridgeman anvil, (2) multipunch device, (3) diamond anvil with laser heating

net-like modification of MgSiO₃ was discovered with tetragonal symmetry and a slightly higher density than cubic garnet (Sawamoto and Kohzaki 1985). Experiments of Kato and Kumazawa (1986) at 20 GPa have shown stability of the β -phase within the range 1700 to 2250° C; the association $\beta + \text{Ilm}$ is stable up to temperatures of 1800° C, while at still higher temperatures (2000–2100° C) β -spinel and a noncubic garnet-like modification coexist.

Sawamoto (1986), Logvinov (1983), Malinovsky et al. (1981) have refined the positions of the phase boundaries $\alpha = \beta$ and $\beta = \gamma$ for the Mg₂SiO₄ system (see Table 1); the pressures they report are 0.5–1.5 GPa below those given by Suito (1977).

The most reliable data are for the equilibria α -forsterite = β -spinel and β -spinel = γ -spinel; these can be used as basic phase boundaries to compute phase diagrams for the MgO–SiO₂ system.

However, there are some discrepancies with respect to the P – T parameters of all transformations (Table 1) related to the use of different equipment, different methods of pressure calibration and temperature measurement, as well as to measurement errors. It should also be taken into account that the investigations were into the fields of phase synthesis, not the true boundaries of phase equilibria. For this reason one must analyse changes in the topology of the resulting P – T diagrams due to varying input data within the limits of experimental uncertainty. This can be taken into account and investigated, during the operation if the construction of the phase diagram is a completely formalized procedure.

Chemographic Approach

The topology of the phase diagram of the system MgO–SiO₂ for pressures over 20 GPa and high temperatures is not known. In this range of parameters five phases are found experimentally Ilm, Pv, MgO, St, γ . This multisystem has a negative dimension of -1 , possessing not more than five invariant points and nine univariant curves in P – T coordinates. By using the chemographic approach it is possible to construct all topologically correct variants of P – T diagram for this five-phase subsystem of MgO–SiO₂. The topological structure of the real diagram is sure to be met among these variants.

If we admit only straight univariant lines, the number of topologically different variants of the P – T diagram for the system under consideration is equal to 20. This is less than the maximal number of variants, equal to $(n+3)(n+2)+2$ for the nondegenerative n -component ($n=2$) system with $n+3$ phases (Mohr and Stout 1980). The degenerative character of our subsystem is due to equal composition of two phases – Ilm and Pv.

All 20 possible potential variants may be generated, having one initial potential solution, by the transposition of invariant points – the general chemographic procedure developed by Mohr and Stout (1980). These distinct topologies are displayed in Figure 1. Invariant points are designated by the symbol of the missing phase placed within square brackets. Solid lines represent stable univariant reactions, dotted lines – metastable reactions.

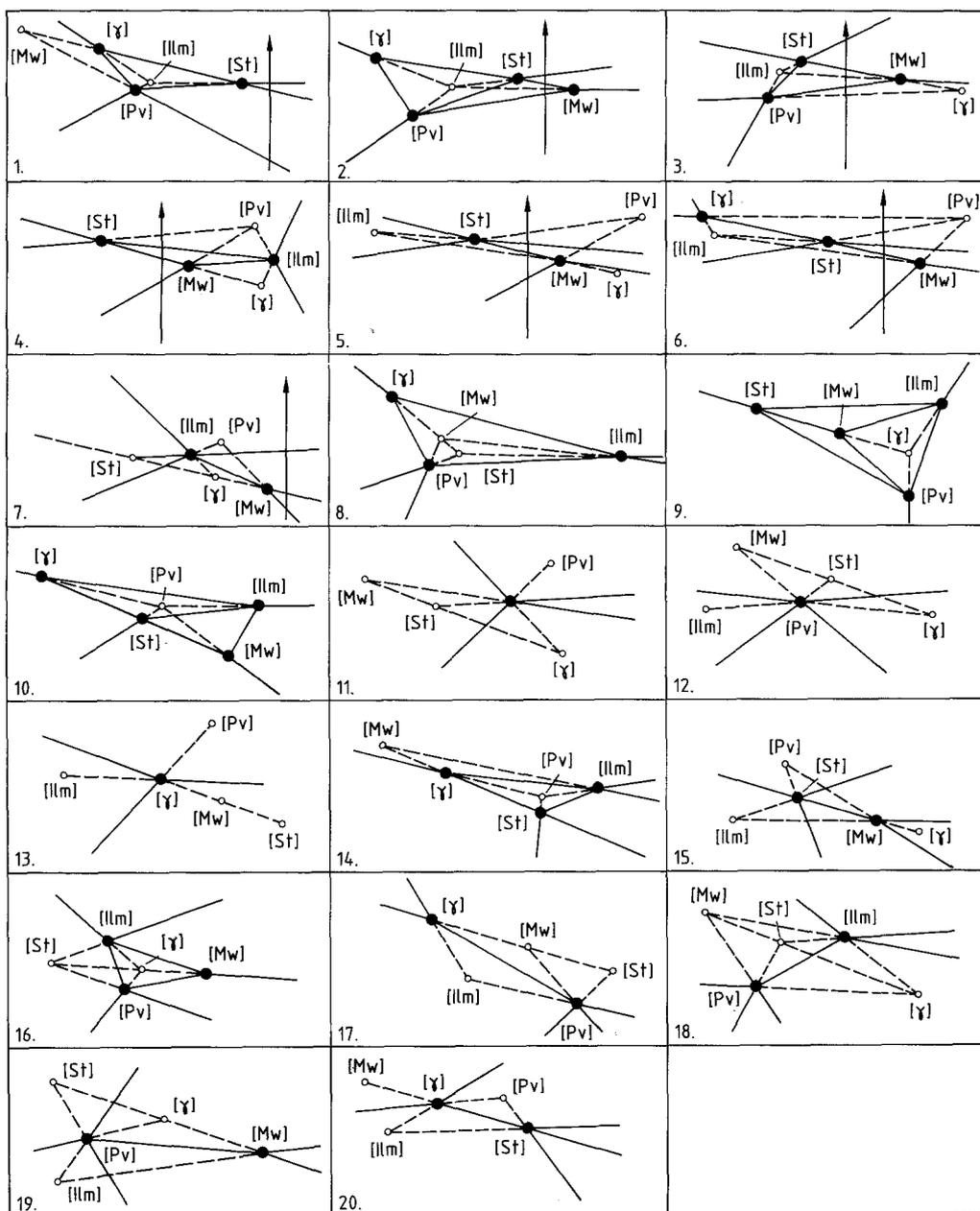
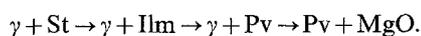


Fig. 1. The set of 20 potential topologies for the chemography of five phases Ilm, Pv, MgO, St, γ . Only seven of them (numbers 1–7) agree with experimental constraints

Analysis of the variants makes it possible to choose seven of them (from number 1 to 7 at Fig. 1) that agree with the experimental sequence of phase transformations at $T \approx 1273$ K with increasing pressure



It will be shown that the topological nonuniqueness which still exists, can be considerably diminished by use of additional thermodynamic constraints.

Thermodynamics of Minerals in the MgO–SiO₂ System

Standard Thermodynamical Functions. The experimental values of entropy (S_{1000}^0) and enthalpy of formation from oxides ($\Delta H_{f,1000}^0$) for low-pressure phases are given in Table 2.

α -Mg₂SiO₄. The data on ΔH_f^0 from the solution calorimetry of forsterite (Brousse et al. 1984, Charlu et al. 1975, King et al. 1967, Kiseleva et al. 1979) are fairly consistent with one another within the experimental uncertainty. In this work we adopted the mean value $\Delta H_{f,1000}^0 = -60.86 \pm 1.44$ kJ·mol⁻¹.

MgSiO₃ (enstatite). In view of incompleteness or absence of information relating to the thermodynamical properties and the equation of state of clinoenstatite, we shall consider a single modification of MgSiO₃ (enstatite). The mean value of ΔH_f^0 as given in Table 2 is practically identical with the value $\Delta H_{f,1000}^0 = -35.23 \pm 1.28$ kJ·mol⁻¹ calculated by Wood and Holloway (1984) from the P - T parameters of phase equilibria and adopted in our work.

MgSiO₃ (ilmenite, perovskite, garnet). Ito and Navrotsky (1985) have determined the heat of the phase transformation

Table 2. Standard thermodynamical functions for low-pressure phases of the MgO–SiO₂ system

Mineral	ΔH_{f1000}^0 kJ·mol ⁻¹	Source	S_{1000}^0 J·K ⁻¹ mol ⁻¹	Source
SiO ₂ (quartz)	0		116.02	Robinson et al. (1982)
MgO	0		82.29	Robinson et al. (1982)
α -Mg ₂ SiO ₄	-60.44 ± 1.26	King et al. (1967)	277.61	Robinson et al. (1982)
	-62.51 ± 1.13	Charlu et al. (1975)		
	-60.63 ± 1.38	Kiseleva et al. (1979)		
	-59.85 ± 1.88	Brousse et al. (1984)		
	-60.86 ± 1.44	mean		
	-60.86 ± 1.44	adopted		
MgSiO ₃ (En)				
Ortho	-33.89 ± 1.76	Brousse et al. (1984)		
Ortho	-35.94 ± 1.3	Chatillon-Colinet et al. (1983)		
Clino	-35.10 ± 1.13	Kiseleva et al. (1979)		
Ortho	-36.86 ± 0.71	Charlu et al. (1975)		
Ortho	-35.15 ± 1.3	Gasparik and Newton (1984)		
Ortho	-35.23 ± 1.28	Wood and Holloway (1984)	195.62	Wood and Holloway (1982)
	-35.36 ± 1.34	mean		
	-35.23 ± 1.28	adopted		

orthoenstatite = ilmenite as $\Delta H_{1000}^0(\text{En} = \text{Ilm}) = 71.797 \pm 3.140$ kJ·mol⁻¹. No thermochemical determinations are available for modifications of MgSiO₃ in the perovskite and garnet structures.

SiO₂(*coesite, stishovite*). The change in the standard free energy of the phase transformation quartz-coesite-stishovite was calculated from the P - T parameters of phase equilibria by Kuskov and Fabrichnaya (1987).

β, γ -Mg₂SiO₄. Akaogi et al. (1984) have determined the heat of phase transformations in Mg₂SiO₄ by calorimetry as $\Delta H_{1000}^0(\alpha = \beta) = 29.96 \pm 2.93$; $\Delta H_{1000}^0(\beta = \gamma) = 6.82 \pm 3.76$ kJ·mol⁻¹ and calculated changes in entropy of phase transformations by two methods giving $\Delta S_{1000}^0(\alpha = \beta) = -11.72$; $\Delta S_{1000}^0(\beta = \gamma) = -5.44$ J·K⁻¹·mol⁻¹ according to Kieffer's (1980) model; $\Delta S_{1273}^0(\alpha = \beta) = -10.46$; $\Delta S_{1273}^0(\beta = \gamma) = -6.28$ J·K⁻¹·mol⁻¹ based on the P - T parameters of phase equilibria according to Suito (1977).

Equations of State. The potential method for construction of the equation of state for solids is described in detail by Kuskov et al. (1983b) and Kuskov and Galimzyanov (1986). The parameters of the *equation of state* (EOS) for minerals are summarized in Table 3.

Computer Simulation of Phase Relations in the MgO–SiO₂ System

Below we study changes in the topologies of phase diagrams of the MgO–SiO₂ system and an internally consistent data set based on different assumptions and input data.

Calculations Based on Thermochemical Determinations

Figure 2 presents the phase diagram for a simplified part of the MgO–SiO₂ system that includes six phases (periclase, stishovite, forsterite, β -spinel, γ -spinel, enstatite). The

calculations are based on calorimetric determinations of the heat of phase transformations in Mg₂SiO₄ (Akaogi et al. 1984) and changes in entropy calculated in the same work according to Kieffer's model (1980):

$$\Delta G^0(\alpha = \beta) = 29960 + 11.72 T \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G^0(\beta = \gamma) = 6820 + 5.44 T \text{ J} \cdot \text{mol}^{-1}$$

The data of Table 2 and the equations of state for the minerals were also used in the calculations; the EOS for γ -1 was adopted for γ -spinel.

The results of calculations for phase diagrams based on the data from Akaogi et al. (1984) lead to discrepancies with the experimental data. The diagram contains the stable univariant equilibria $\alpha = \gamma$, 2 En = γ + St and $\gamma = 2$ MgO + St in a temperature range (1000–1600 K) in which they must be metastable according to all the experimental evidence available (Suito 1977, Akaogi and Akimoto 1977, Yagi et al. 1979, Ohtani 1979, Liu 1979, Sawamoto 1986, Akimoto et al. 1976, Ito and Yamada 1982).

It should be emphasized that the use of thermochemical information inconsistent with data for equations of state and phase equilibria results in deformations in the stability fields of minerals relative to those determined in the experiment. The same can be said with respect to the calculations reported by Ostrovsky et al. (1986). It should be noted at the same time that the calculations of portions of the phase diagram made by Ito and Navrotsky (1985) on the basis of thermochemical determinations of ΔH_T^0 , as well as the values of ΔS_T^0 calculated using the simplest EOS from data on phase equilibria at a fixed temperature are in agreement with the experimental data at pressures of 13–20 GPa.

Calculations Based on Fei and Saxena's Data

Fei and Saxena (1986) have used the Murnaghan's EOS for minerals and the P - T parameters of a number of basic

Table 3. Parameters of equations of state for minerals in the MgO–SiO₂ system at 1 bar and 298.15 K

	MgO ^a		α -quartz ^b		SiO ₂ coesite ^b		stishovite ^b	
ρ	3.583	(0.001)	2.648	(0.001)	2.92	(0.005)	4.289	(0.005)
α	31.2	(0.5)	35	(0.5)	7.5	(0.5)	16.5	(1.0)
C_p	37.78	(0.08)	44.43	(0.21)	44.98	(0.4)	42.97	(0.08)
K_s	163	(0.5)	37.1	(0.5)	96	(3.0)	316	(7.5)
K'	4.5	(0.2)	6.0	(0.2)	8.4	(1.0)	4.0	(1.0)
θ	936	(10)	570	(5)	675	(25)	1190	(25)
Mg ₂ SiO ₄								
	α		β		$\gamma-1$		$\gamma-2$	
ρ	3.213	(0.001)	3.474	(0.01) ^c	3.559	(0.01) ^c	3.549	(0.005)
α	26	(1.0)	20.6	(1.0)	19.0	(1.0)	19.0	(1.0)
C_p	118.11	(0.16)	110.12	(1.0)	106.94	(1.0)	106.94	(1.0)
K_s	128.8	(1.0)	174.0	(6.0) ^c	184.0	(5) ^c	210	(5)
K'	5.1	(0.2)	4.3	(0.5)	4.0	(0.5)	4.0	(0.5)
θ	763	(5)	893	(25) ^c	902	(25)	900	(25)
MgSiO ₃								
	En ^a		Ilm		Pv ^f		Gr	
ρ	3.198	(0.005)	3.795	(0.005) ^d	4.1	(0.01)	3.556	(0.01) ^h
α	28	(2.5)	22	(5) ^e	25	(5) ^e	15	(5) ⁱ
C_p	82.22	(0.08)	79.29	(0.8)	79.5	(4.0)	79.5	(4.0)
K_s	108	(3)	212	(5) ^d	250	(10)	170	(10) ^j
K'	5	(0.5)	4	(0.5)	3.8	(0.5)	4.0	(0.5)
θ	734	(30)	944	(25) ^d	985	(50)	800	(50) ^j

ρ in g·cm³, α ·10⁶ in K⁻¹, C_p in J·K⁻¹·mol⁻¹, K_s in GPa, θ in K.

^a Kuskov and Galimzyanov (1986);

^b Kuskov and Fabrichnaya (1987);

^c Weidner et al. (1984);

^d Weidner and Ito (1985);

^e Ashida et al. (1985) for MgGeO₃(Ilm);

^f Kuskov and Galimzyanov (1986), Knittle and Jeanloz (1987), Matsui et al. (1987), Kudoh et al. (1987);

^g $\alpha_{298}(\text{Pv})$ is adopted $25 \cdot 10^{-6} \text{ K}^{-1}$ because the calculations on the Debye theory give $\alpha_{1000}(\text{Pv}) = 44 \cdot 10^{-6} \text{ K}^{-1}$, which is consistent with averaged value of $\alpha(\text{Pv}) = 40 \cdot 10^{-6} \text{ K}^{-1}$ according to Knittle et al. (1986);

^h Sawamoto and Kohzaki (1985);

ⁱ $\alpha(\text{Gr})$ is adopted as for Al₂O₃ according to Suzuki (1975) and Anderson (1980);

^j Babuska et al. (1978). Irifune (1987);

C_p from Kuskov and Galimzyanov (1986) and Watanabe (1982); other data are from Kuskov and Galimzyanov (1986).

equilibria for the calculations of standard free energies of formation of high-pressure phases for the MgO–SiO₂ system. Figure 3 shows the phase diagram for the MgO–SiO₂ system which we have calculated on the basis of Fei and Saxena's (1986) data. A peculiar feature of this diagram is curvature in the lines of univariant equilibria. The change in the sign of the slope of dP/dT for the number of curves is related to the change of sign in the ΔS , the latter being due to the use of unsubstantiated values of the coefficients in the polynomial dependence of the heat capacity on temperature for phases with the ilmenite or perovskite structure. The phase diagram calculated from the data of Fei and Saxena (1986) is in disagreement with an experimental sequence of phase transformations at pressures above 23 GPa. The fact that the equilibrium $\gamma = \text{Pv} + \text{MgO}$ which Fei and Saxena (1986) adopt as the basic one became metastable (see Fig. 3) seems to be due to inconsistencies between the

information on MgSiO₃ with the structure of ilmenite. The same equilibrium is metastable within the experimentally studied range of temperature in the calculations of Ostrovsky et al. (1986), while the univariant lines of the reaction $\text{MgSiO}_3(\text{Pv}) = \text{MgO} + \text{SiO}_2(\text{St})$ become stable in two parts of the P – T diagram at once at $T < 1000 \text{ K}$ and $T > 2000 \text{ K}$.

An Algorithm for Calculation and Adjustment of the P – T Diagrams

The discrepancies that have emerged between direct experiments and calculations based on thermochemical data reveal instability in the phase diagram of the MgO–SiO₂ system with respect to variation of $\Delta G_{i,T}^0$ and $\int_0^P V dP$ for the phases.

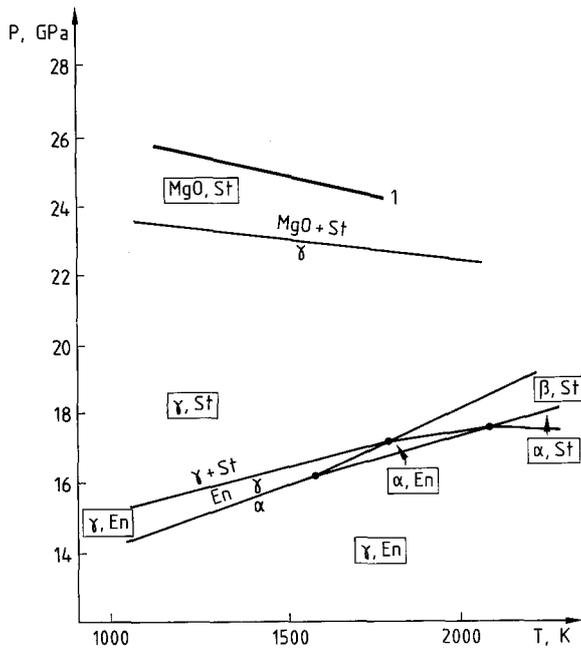


Fig. 2. Phase diagram of the MgO–SiO₂ system constructed from the data of EOS of minerals (see Table 3) and thermochemical data of Akaogi et al. (1984): $\Delta G_T^0(\alpha=\beta)=29960+11.72T$, $\Delta G_T^0(\beta=\gamma)=6820+5.44T$ J·mol⁻¹ 1-equilibrium $\gamma=Pv+MgO$ by Ito and Yamada (1982)

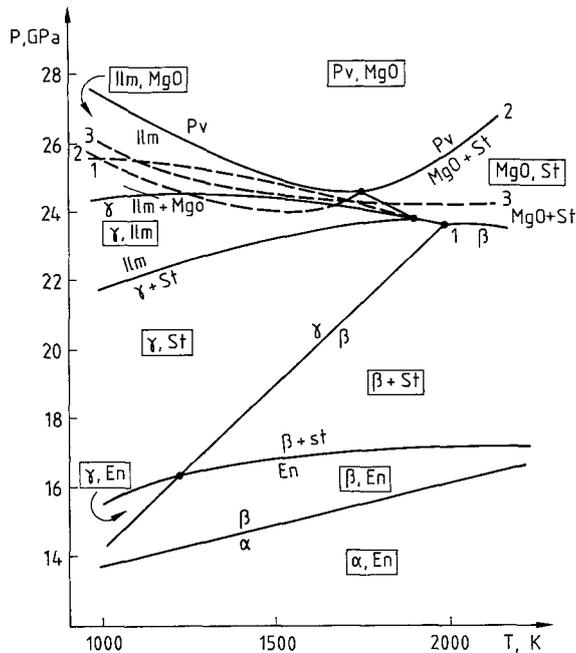


Fig. 3. Phase diagram of the MgO–SiO₂ system constructed from the data of Fei and Saxena (1986) (the Murnaghan's EOS are used)

The algorithm for calculation and adjustment of $P-T$ diagrams for multisystems with phases of constant composition is as follows (Galimzyanov and Kuskov 1988):

- (1) Selection of ΔG_{fT}^0 values for low-pressure phases.
- (2) Construction of equations of state for all phases.
- (3) Calculation of missing information from standard free energies of phase transformations from experimental equi-

librium $P-T$ parameters with subsequent conversion to the ΔG_{fT}^0 of high-pressure minerals.

(4) Calculation of equilibrium phase composition of the system for different P and T values using the method of minimization of Gibbs free energy and construction of $P-T$ diagrams.

(5) Analysis of the effect of the uncertainty intervals of input information on calculation results and the topology of $P-T$ diagrams as a whole.

Thus, the construction and adjustment of $P-T$ diagrams requires three sets of input data: standard free energies of formation for low-pressure phases; equations of state of all phases; $P-T$ parameters of phase equilibria adopted as basic ones. The condition that consistency has been achieved is agreement between the calculated and experimental sequence of phase transformations. Thus, for instance, if polymorphic transformations in SiO₂ and $\alpha=\beta$ Mg₂SiO₄ are taken as basic equilibria, the $P-T$ parameters of the equilibrium $2\text{En}=\beta+\text{St}$ are determined uniquely. The basic equilibrium $\beta=\gamma$ must obviously take place at higher pressures than $2\text{En}=\beta+\text{St}$. Equilibria involving the modification MgSiO₃ with ilmenite and perovskite structures taken as basic must be at lower pressures than the equilibrium $\gamma=2\text{MgO}+\text{St}$. Note also that the results of adjustment depend on the selection of parameters and the method used for constructing the equations of state (Kuskov and Galimzyanov 1986, Kuskov et al. 1983a, Galimzyanov and Kuskov 1988).

A Simplified Model of Phase Diagram

First we construct a $P-T$ diagram for the simplified part of the system restricted to six phases (MgO, stishovite, forsterite β -, γ -spinel, enstatite). The basic equilibria will be

$$\alpha - \text{Mg}_2\text{SiO}_4(\text{forsterite}) = \beta - \text{Mg}_2\text{SiO}_4(\beta\text{-spinel}) \quad (1)$$

$$\beta - \text{Mg}_2\text{SiO}_4(\beta\text{-spinel}) = \gamma - \text{Mg}_2\text{SiO}_4(\gamma\text{-spinel}) \quad (2)$$

The $P-T$ parameters of equilibria (1) and (2), as well as the method used for constructing the equations of state are given in Table 4; the results of calculations can be found in Figure 4.

Decomposition of γ -spinel occurs at 24 ± 1 GPa and 1000–2000 K as shown in Figure 4a. But the equilibrium $\gamma=2\text{MgO}+\text{St}$ must be metastable according to the data of Liu (1979), Yagi et al. (1979), Ito and Yamada (1982) and the pressure of this transformation must be higher than that of the decomposition of γ -spinel into perovskite + periclase in order that the experimentally established sequence of phase transformations with increasing pressure could hold: $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow Pv + \text{MgO}$. From Figure 4a one can see that the use of the $P-T$ parameters of basic equilibria (1) and (2) by Suito (1977) makes the line $\gamma=2\text{MgO}+\text{St}$ lower in pressure than $\gamma=Pv+\text{MgO}$ according to Ito and Yamada (1982), whatever the variation of input constants and the methods for constructing the EOS of γ -spinel. Thus, the $P-T$ parameters of the basic equilibria $\alpha=\beta$, $\beta=\gamma$ according to Suito (1977) and $\gamma=Pv+\text{MgO}$ according to Ito and Yamada (1982) are inconsistent thermodynamically.

Computation shows that the lower the pressure for the basic equilibria (1) and (2), the higher the line of γ -spinel decomposition into oxides; the $P-T$ diagram of variant 1D shown in Figure 4b satisfies these requirements.

The variant 1D was based on the $P-T$ parameters of the basic equilibrium $\beta=\gamma$ taken from Sawamoto (1986)

Table 4. Input information for construction of a simplified part of phase diagram and calculation of free energies of phase transformations in the MgO–SiO₂ system

Input information ^a $P(\text{GPa})=A+B T(\text{K})$	EOS ^b	method of calculation of EOS	$\Delta G_T^0, \text{J} \cdot \text{mol}^{-1}$	Variant
$\alpha=\beta \text{ Mg}_2\text{SiO}_4$; Suito (1977) $9.84+3.5 \cdot 10^{-3} T$	$\gamma-1$	potential	$26267+12.87 T^{(4)}$ $8008+6.06 T^{(5)}$	IA
$\beta=\gamma \text{ Mg}_2\text{SiO}_4$; Suito (1977) $10+5.5 \cdot 10^{-3} T$	$\gamma-2$	potential	$26267+12.87 T^{(4)}$ $6803+3.18 T^{(5)}$	IB
$\alpha=\beta \text{ Mg}_2\text{SiO}_4^c$ $9.16+3 \cdot 10^{-3} T$ $\alpha=\beta \text{ Mg}_2\text{SiO}_4$; Sawamoto (1986) $7.9+6.1 \cdot 10^{-3} T$	$\gamma-1$	Murnaghan	$25857+13.51 T^{(4)}$ $7999+6.19 T^{(5)}$	IC
			$24418+11.72 T^{(4)}$ $6410+6.49 T^{(5)}$	ID

^a ΔG_T^0 for low-pressure phases used in calculating phase diagrams are given in Table 2

^b Parameters of equations of state are given in Table 3

^c The $P(T)$ dependence given for the equilibrium $\alpha=\beta$ is explained in the text

The free energies of transformations are denoted by the indices: 4– $\alpha=\beta \text{ Mg}_2\text{SiO}_4$, 5– $\beta=\gamma \text{ Mg}_2\text{SiO}_4$

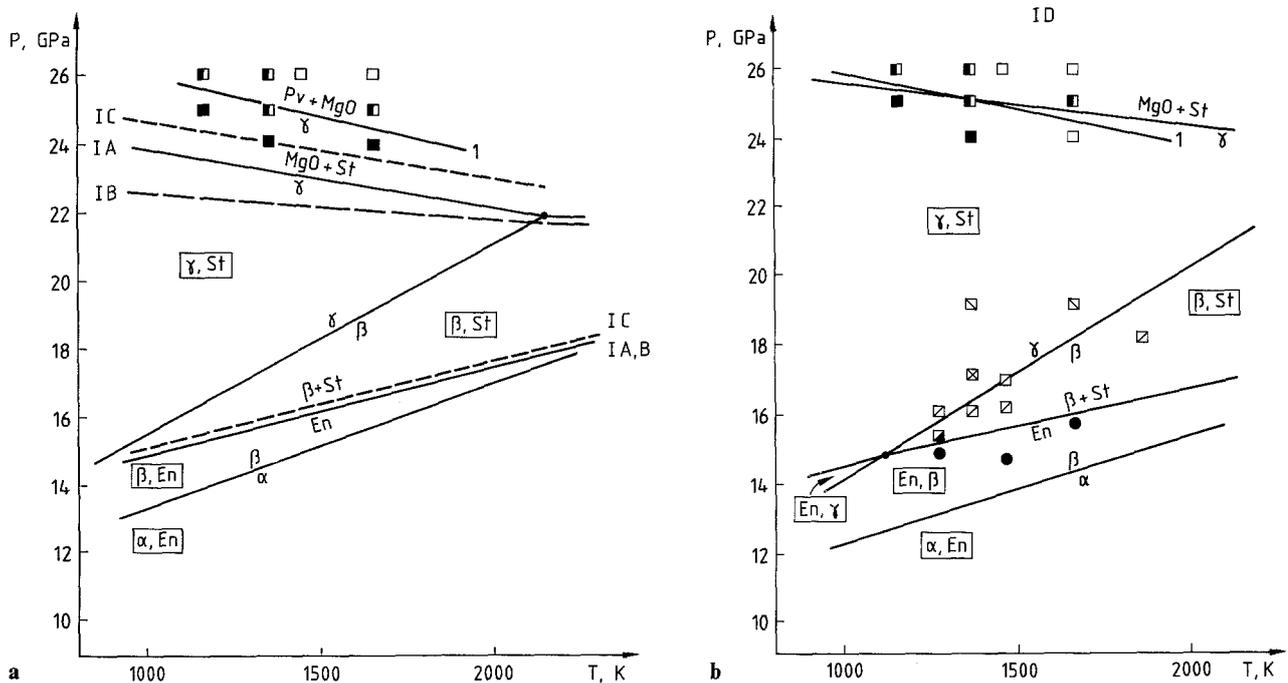


Fig. 4a, b. Topology of the simplified part of the phase diagram for the MgO–SiO₂ system according to the data of Table 4. (a) Basic equilibria $\alpha=\beta$ and $\beta=\gamma$, common for variants IA, B, C are denoted by solid lines. Variant IA: $2 \text{ En}=\beta+\text{St}$ and $\gamma=2 \text{ MgO}+\text{St}$ are shown by solid lines. Variant IB: $2 \text{ En}=\beta+\text{St}$ is the same line as in IA, $\gamma=2 \text{ MgO}+\text{St}$ is shown by dashes and dots. Variant IC: $2 \text{ En}=\beta+\text{St}$ and $\gamma=2 \text{ MgO}+\text{St}$ are shown by dashes. (b) Variant ID: 1-equilibria $\gamma=\text{Pv}+\text{MgO}$ and $\text{Ilm}=\text{Pv}$ according to Ito and Yamada (1982). Symbols are experimental points of Ito and Yamada (1982): \blacksquare – γ ; \square – γ , Pv, MgO; \square –Pv, MgO and Ito and Navrotsky (1985): \bullet –En, \square – $\beta+\text{St}$, \square – $\gamma+\text{St}$, \square –En + $\beta+\text{St}$, \square – $\beta+\gamma+\text{St}$

at 1000–2000° C. At 1000° C the transition pressure for $\beta=\gamma$ according to Sawamoto (1986) is 1.3 GPa below those in previous determinations (Suito 1977, Yagi et al. 1979, Oh-tani 1979). The phase transition $\alpha=\beta$ also takes place at lower pressures compared to the values reported by Suito (1977), Table 1. According to Table 1, the pressure of the basic equilibrium $\alpha=\beta$ was adopted as equal to 13 GPa at 1000° C, the slope of the curve was determined with the

help of equations of state and $\Delta S_{1000}^0(\alpha=\beta)=-11.72 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$ as calculated by Akaogi et al. (1984) on Kieffer's model (1980), Table 4. The values of ΔH_T^0 calculated from the basic equilibria for the transitions $\alpha=\beta$ and $\beta=\gamma$ are in agreement with Akaogi et al. (1984) (see Table 4) within the uncertainty of the calculations and calorimetric determinations.

In the variant 1-D (Fig. 4b) the pressure of γ -spinel de-

Table 5. Results of varying equilibrium $P-T$ parameters for $\text{Ilm}=\text{Pv}$ and $\gamma=\text{Pv}+\text{MgO}$

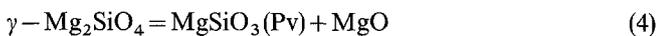
Variant	Ilm=Pv (1) $\gamma=\text{Pv}+\text{MgO}$ (2) $P(T)$ of the transformations P , GPa, T , K	ΔG_r^0 , $\text{J}\cdot\text{mol}^{-1}$	$\gamma+\text{St}=2\text{Ilm}$ dP/dT , $\text{GPa}\cdot\text{K}^{-1}\cdot 10^4$
IIA	(1) $26.11-2\cdot 10^{-3}T$	$47279-6.32T$	-15
	(2) $26.04-1.6\cdot 10^{-3}T$	$91671-12.18T$	
IIB	(1) $26.27-2\cdot 10^{-3}T$	$47740-6.31T$	70
	(2) $25.27-1\cdot 10^{-3}T$	$89790-10.71T$	
IIC	(1) $26.0-2\cdot 10^{-3}T$	$47360-6.38T$	225
	(2) $24.0-0.0T$	$86570-8.16T$	
IIIA	(1) $24.75-1\cdot 10^{-3}T$	$45190-4.78T$	-144
	(2) $26.55-2\cdot 10^{-3}T$	$93420-13.58T$	
IIIB	(1) $26.02-2\cdot 10^{-3}T$	$47360-6.36T$	-210
	(2) $27.82-3\cdot 10^{-3}T$	$97070-16.44T$	
IIIC	(1) $25.85-1.8\cdot 10^{-3}T$	$47150-6.11T$	-84
	(2) $26.55-2\cdot 10^{-3}T$	$93420-13.58T$	

composition into a mixture of oxides is a maximum and amounts to 25.4 GPa at 1273 K, somewhat above that for the reaction $\gamma=\text{Pv}+\text{MgO}$. For the equilibrium $2\text{En}=\beta+\text{St}$ we have $P=15$ GPa at 1273 K, in agreement with experiments (Ito and Navrotsky 1985), but about 1.5–2.0 GPa below previous determinations due to Akaogi and Akimoto (1977) and Liu (1979). The equilibrium $\alpha=\text{En}+\text{MgO}$ discovered by Logvinov (1983) is metastable in the calculated phase diagram.

Thus, the internally consistent variant 1-D of the $P-T$ diagram for the simplified part of the $\text{MgO}-\text{SiO}_2$ system satisfies the whole of experimental data at 1273 K and can form the basis for calculation of the complete phase diagram.

Model of the Complete Phase Diagram

To calculate the complete phase diagram of the $\text{MgO}-\text{SiO}_2$ system, the input information for the variant 1-D is to be supplemented by equations of state for two new modifications of MgSiO_3 in the structures of ilmenite and perovskite² and the data on $P-T$ parameters of basic equilibria involving these phases:



Computation shows that if the pressure of the reaction $\gamma+\text{St}=2\text{Ilm}$ is taken to be $P=20$ GPa (Ito and Yamada 1982; Ito and Navrotsky 1985), and $P=25.3$ GPa at 1000°C for $\gamma=\text{Pv}+\text{MgO}$ (Ito and Yamada 1982) (Table 1), then the experimental sequence of phase transformations $\gamma+\text{St}=2\text{Ilm}$, $\text{Ilm}=\text{Pv}$, $\gamma=\text{Pv}+\text{MgO}$ breaks with increasing pressure since the pressure of the $\text{Ilm}=\text{Pv}$ transition

becomes higher than for $\gamma=\text{Pv}+\text{MgO}$. At the same time, a decrease in the pressure³ of the phase boundary $\gamma=\text{Pv}+\text{MgO}$ by 1.3 GPa produces a transformation sequence that is consistent with experiment. Variation of the pressure of the equilibrium $\gamma+\text{St}=2\text{Ilm}$ within the uncertainty has little effect on the pressure transition of $\text{Ilm}=\text{Pv}$.

In modeling phase relations two variants of the position of the invariant point (γ , Pv, Ilm, MgO) have been considered, this point being outside the limits of the temperature range 1173–1673 K studied experimentally by Ito and Yamada (1982). Changes in the slopes of basic equilibria (3) and (4) within the range 0 to $-3\cdot 10^{-3}\text{GPa}\cdot\text{K}^{-1}$ with intervals of $0.25\cdot 10^{-3}\text{GPa}\cdot\text{K}^{-1}$ give rise to many variants that have been reduced to six topologically inequivalent types (see Table 5 and Fig. 5). The variants marked IIB and IIC of the phase diagram are topologically equivalent to those constructed previously (Kuskov and Galimzyanov 1986; Kuskov et al. 1983a).

Phase Equilibria with MgSiO_3 (Garnet). For the range of temperatures adjacent to the solidus one should take into account a polymorphic modification of MgSiO_3 having garnet structure (Sawamoto and Kohzaki 1985). The calculations are based on experimental data relating to the stability boundary of $\beta+\text{Ilm}$ and $\beta+\text{Gr}$ associations obtained by Sawamoto and Kohzaki (1985) and Kato and Kumazawa (1986). The slope of the $\text{En}=\text{Gr}$ equilibrium curve is chosen in such a way that the low-temperature part of the diagram might not be altered by the appearance of Gr. The slope of the equilibrium is adopted as positive in accordance with

³ This is related to the method of pressure calibration in experiments (Ito and Yamada 1982) based on the $P-T$ parameters of the decomposition reactions of MgAl_2O_4 and $\gamma-\text{Ni}_2\text{SiO}_4$ into oxides. It follows from thermodynamical analysis that the equilibrium pressures must be lowered by 1–1.5 GPa (Kuskov and Galimzyanov 1984, 1986).

² The phase of MgSiO_3 having garnet structure will be considered below.

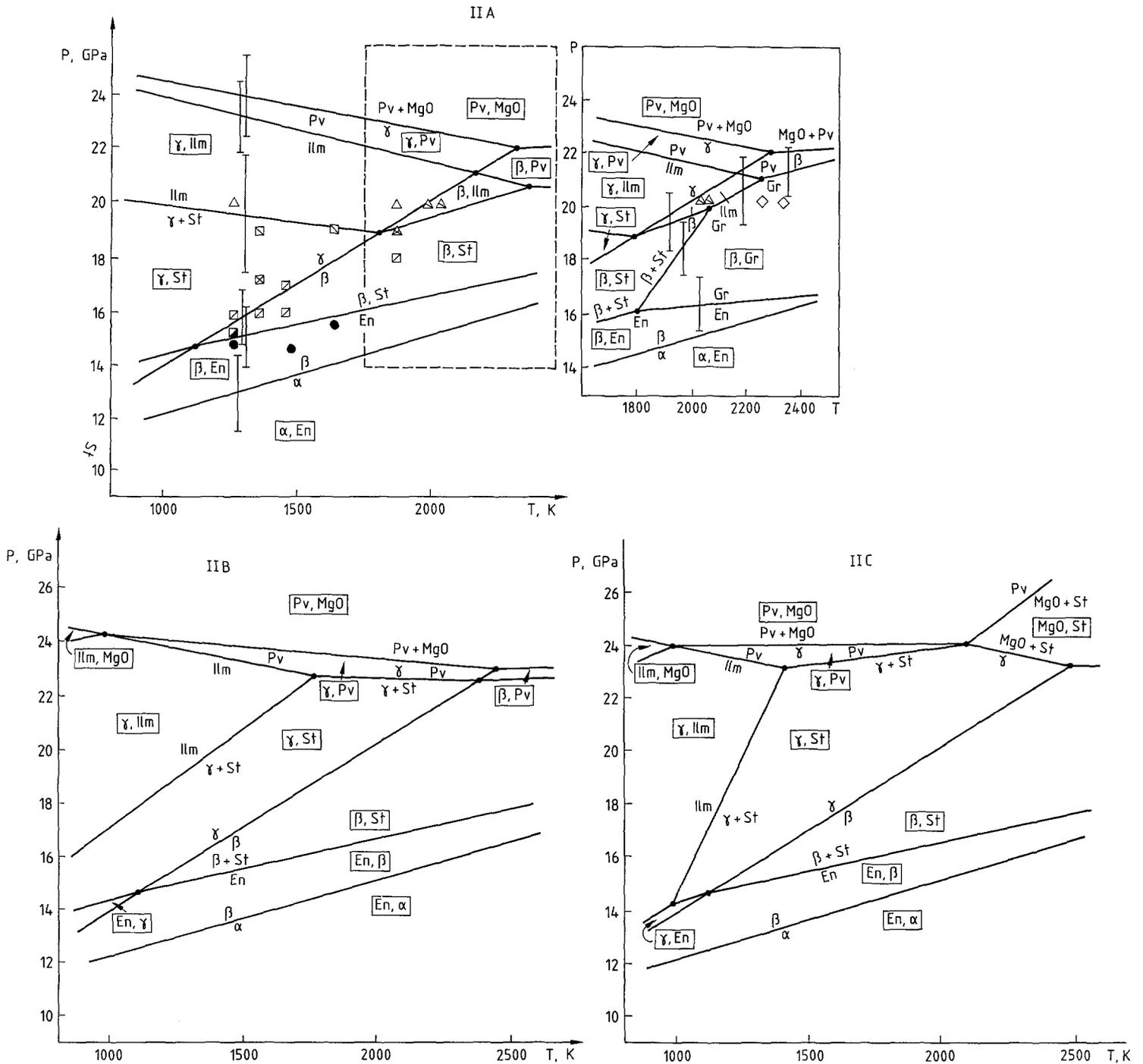


Fig. 5. Topologies of the complete phase diagram for the MgO–SiO₂ system according to the data of Table 5. Symbols are the same as in Figure 4: Δ -Ilm, Δ -Ilm + β + γ + St by Ito and Navrotsky (1985); Δ - β + Ilm, \diamond - β + Gr by Kato and Kumazawa (1986). The uncertainties of phase boundaries due to the errors of input parameters are calculated by error propagation formula (see Kuskov and Galimzyanov 1986) and indicated by error bars. The insets show the high-temperature part of the diagram taking into account the MgSiO₃(Gr) phase. The P - T dependence $P(\text{GPa}) = 14.34 + 1.10 \cdot 10^{-3} T$ for transformation En=Gr is used in calculations; $\Delta G_{\text{En}=\text{Gr}}^0 = 28736 + 12.97 T J \cdot \text{mol}^{-1}$

data of Akaogi and Akimoto (1977) and Irifune (1987). The variants of the extended diagram shown in insets in Figure 5 are tentative because of lack of experimental information.

Discussion

The robustness and stability analysis of a phase diagram as a whole requires calculation of a large number of variants

for the entire uncertainty region of input parameters and consists of the following: (1) construction and fitting of a set of phase diagram variants; (2) reduction of some set of the variants to a single topological equivalent; (3) finding the unique topological configuration of the phase diagram.

According to our calculations, the sequence of phase transformations for a composition intermediate between forsterite and enstatite is identical with increasing pressure

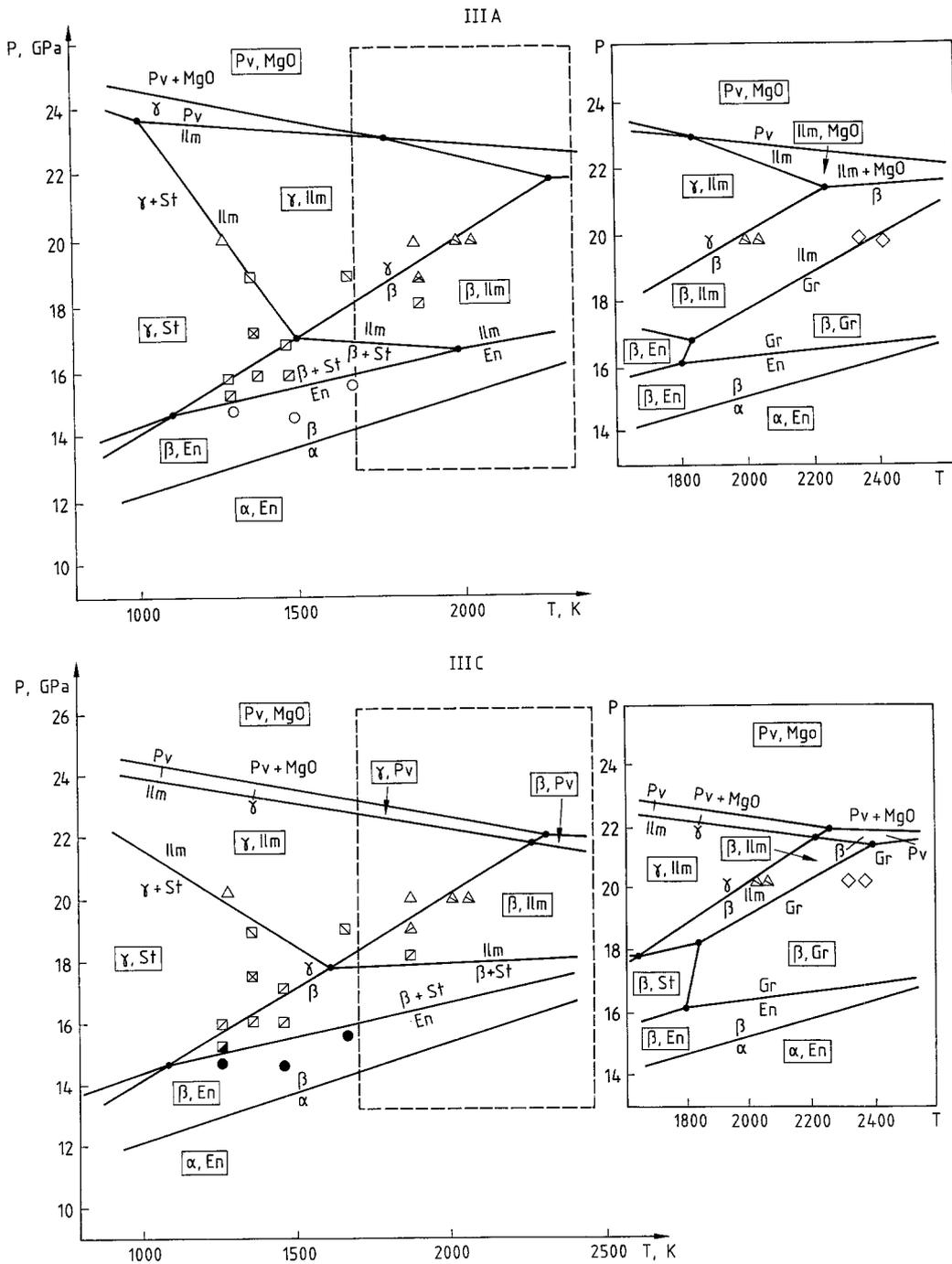
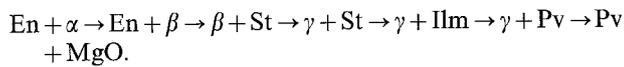
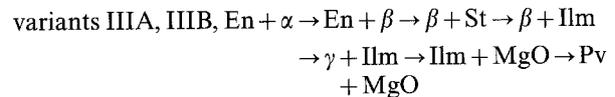
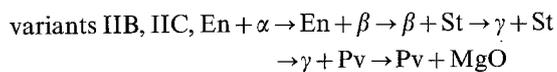
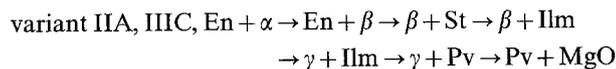


Fig. 5

at 1273 K for all the six variants of phase diagram (see Fig. 5):



As the pressure increases along the 2000 K isotherm, the following sequence of phase associations will take place:



Variants IIA and IIB have identical sequences of phase transformations within the range 298–1800 K but are different above 1800 K, while variants IIB and IIC are identical along the 1800 and 2000 K isotherms. The variants IIB and IIC are at variance with the experiments of Kato and Kumazawa (1986), according to which the phase association $\beta + \text{Ilm}$ is stable at 20 GPa and 2000 K. Variants IIIA and IIIB are equivalent within the range 1000–2500 K (variant IIIB is not shown in Fig. 5) below 1000 K they differ in

Table 6. Internally consistent data base of free energies of phase transformations and recommended values of standard free energies of formation from oxides for minerals in the MgO–SiO₂ system (Variant IIA) at 1000–2000 K

Mineral	Basic equilibria $P(\text{GPa}) = A + B T(\text{K})$	$\Delta G_T^0 \text{ J} \cdot \text{mol}^{-1}$ for phase transitions	$\Delta G_{fT}^0 \text{ J} \cdot \text{mol}^{-1}$
$\alpha\text{-Mg}_2\text{SiO}_4$	–	–	$-60856 + 2.97 T$
En–MgSiO ₃	–	–	$-35230 + 2.68 T$
$\beta\text{-Mg}_2\text{SiO}_4$	$\alpha = \beta\text{-Mg}_2\text{SiO}_4$ $9.16 + 3 \cdot 10^{-3} T$	$24418 + 11.72 T$	$-36438 + 14.69 T$
$\gamma\text{-Mg}_2\text{SiO}_4$	$\beta = \gamma\text{-Mg}_2\text{SiO}_4$ $7.9 + 6.1 \cdot 10^{-3} T$	$6410 + 6.49 T$	$-30028 + 21.18 T$
Pv–MgSiO ₃	$\gamma\text{-Mg}_2\text{SiO}_4 = \text{Pv} + \text{MgO}$ $26.04 - 1.6 \cdot 10^{-3} T$	$91663 - 12.18 T$	$61635 + 9.0 T$
Ilm–MgSiO ₃	$\text{Ilm} = \text{Pv} - \text{MgSiO}_3$ $26.11 - 2 \cdot 10^{-3} T$	$47280 - 6.32 T$	$14355 + 15.32 T$
Gr–MgSiO ₃	$\text{En} = \text{Gr} - \text{MgSiO}_3$ $14.34 + 1.10^{-3} T$	$28736 + 12.97 T$	$-6494 + 15.65 T$
Coes-SiO ₂	$\alpha\text{-quartz} = \text{Coes}$ $1.8 + 1 \cdot 10^{-3} T$	$1590 + 4.9 T$	$1590 + 4.9 T$
St–SiO ₂	$\text{Coes} = \text{St}$ $6.88 + 2.1 \cdot 10^{-3} T$	$43438 + 9.08 T$	$45028 + 13.98 T$

phase sequences. Variant IIIB has the invariant point $\gamma + \text{Pv} + \text{MgO} + \text{St}$ at 25.4 GPa and 800 K (Table 5), but in the region of low temperatures the slow kinetics of the reactions seems to prevent experimental tests of the equilibria $\gamma + \text{St} = 2 \text{Pv}$, $\gamma = 2 \text{MgO} + \text{St}$, and $\text{MgO} + \text{St} = \text{Pv}$. Variant IIIC differs from IIIA in sequences of phase associations at temperatures above 1800 K.

Thus, we have come to three basic variants IIA, IIIA and IIIC of the phase diagram to be subjected to further experimental testing.

For the stability analysis of phase-diagram variants, the most important is the equilibrium $\gamma + \text{St} = 2 \text{Ilm}$ which is very sensitive to changes in the P – T parameters of basic equilibria (3) and (4). Because the volume effect of the transformation $\gamma + \text{St} = 2 \text{Ilm}$ is very small ($\Delta V = -0.93 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 1273 K and 20 GPa) a change within the uncertainty of the slope for basic equilibria causes a drastic change in the slope of the equilibrium under consideration (Table 5), from highly positive (variant IIC) to highly negative (variants IIIA, IIIC).

Calculations (Fig. 5, Table 5) show that the greater the absolute value of the slope of $\text{Ilm} = \text{Pv}$ compared with $\gamma = \text{Pv} + \text{MgO}$, the greater is the positive value of the slope of the phase boundary for $\gamma + \text{St} = 2 \text{Ilm}$; as the difference in the slopes of basic equilibria decreases, the slope of $\gamma + \text{St} = 2 \text{Ilm}$ becomes equal to zero or negative.

We adopted variant IIA as the “best” one, being consistent with the totality of phase equilibria data. Variant IIA is consistent with the experimental synthesis data of Ito and Navrotsky (1985) for the transition $\gamma + \text{St} = 2 \text{Ilm}$ with a slightly negative dP/dT^4 and with experiments at higher temperature than 1800 K of Sawamoto and Kohzaki (1985) for MgSiO₃ composition and Kato and Kumazawa (1986) for MgSiO₃ composition and mixture forsterite + enstatite. In variant IIA the invariant point $\beta + \gamma + \text{Ilm} + \text{St}$ is stable at 19 GPa and 1800 K, the invariant point $\text{Gr} + \text{Ilm} + \text{Pv}$ is stable at 21.6 GPa and 2270 K.

Conclusion

Thermodynamic and basic phase equilibria data are available for construction of the topologies of the complete phase diagram in the MgO–SiO₂ system, but they are not yet sufficient for determination of the single variant of the phase diagram.

Nevertheless the topology of variant IIA satisfies all experimental data over a wide range of pressures (up to 25 GPa) and temperatures (up to 2500 K). A thermodynamic data base for minerals in variant IIA of the MgO–SiO₂ system is established by supplementing the calorimetric data for low pressure phases and equations of state for low and high pressure phases with data calculated from high pressure synthesis experiments. A refined set of standard free energies of formation and phase transformations in the MgO–SiO₂ system is presented in Table 6.

The main result of imitation modeling is that we are able: a) to reveal topologically stable variants of phase diagram and yield internally consistent recommendation for thermodynamic properties and P – T parameters for all equilibria; b) to point out inconsistencies and deficiencies in the experimental data and thus facilitate future experimental research. A refined data base is useful for planning of new experiments at high pressures and temperatures and in generating phase diagrams of mantle compositions.

Acknowledgements. The authors are grateful to Lin-gun Liu for discussion on high-pressure phase transitions in the MgO–SiO₂ system.

Note added in proof. While this paper was in press Sawamoto (1987) published his parameters of the triple point, $\text{Ilm} + \text{Gr} + \text{Pv}$, in pure MgSiO₃ as $P = 22.8 \text{ GPa}$ and $T = 2330 \text{ K}$, which are in very good agreement with the present results.

⁴ Ito and Navrotsky (1985) have obtained a highly negative slope for this equilibrium in their calculations

References

- Akaogi M, Akimoto S (1977) Pyroxene-garnet solid solution equilibria in the system $Mg_4Si_4O_{12}-Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}-Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures. *Phys Earth Planet Inter* 15:90-106
- Akaogi M, Ross NL, McMillan P, Navrotsky A (1984) The Mg_2SiO_4 polymorphs (olivine, modified spinel and spinel) thermodynamic properties from oxide melt solution calorimetry, phase relations and models of lattice vibrations. *Am Mineral* 69:499-512
- Akimoto S, Matsui Y, Syono Y (1976) High pressure crystal chemistry in orthosilicates and formation of the mantle transition zone. In: Strens RGJ (ed) *The Physics and Chemistry of Minerals and Rocks*. John Wiley, London, pp 327-363
- Anderson OL (1980) An experimental high-temperature thermal equation of state by passing the Grüneisen parameter. *Phys Earth Planet Inter* 22:173-185
- Ashida T, Miyamoto Y, Kume S (1985) Heat Capacity, Compressibility and Thermal Expansion Coefficient of Ilmenite-Type $MgGeO_3$. *Phys Chem Minerals* 12:129-131
- Babuska V, Fiala J, Kumazawa M, Ohno I, Sumino Y (1978) Elastic properties of garnet solid-solution series. *Phys Earth Planet Inter* 16:157-176
- Brousse C, Newton RC, Kleppa OJ (1984) Enthalpy of formation of forsterite, enstatite, akermanite, monticellite and merwinite at 1.073 K determined by alkali borate solution calorimetry. *Geochim Cosmochim Acta* 48:1081-1088
- Charlu TW, Newton RC, Kleppa OJ (1975) Enthalpies of formation at 970 K of compounds in the system $MgO-Al_2O_3-SiO_2$ by high temperature solution calorimetry. *Geochim Cosmochim Acta* 39:1487-1497
- Chatillon-Colinet C, Newton RC, Perkins D, Kleppa OJ (1983) Thermochemistry of $(Fe^{2+}, Mg)SiO_3$ orthopyroxene. *Geochim Cosmochim Acta* 47:1597-1603
- Fei Y, Saxena SK (1986) A Thermochemical Data Base for Phase Equilibria in the System $Fe-Mg-Si-O$ at High Pressure and Temperature. *Phys Chem Minerals* 13:311-324
- Galimzyanov RF, Kuskov OL (1988) Imitation modeling of phase diagrams of mineral systems. *Geokhimiya* 3:424-436 [in Russian]
- Gasparik T, Newton RC (1984) The reversed alumina contents of spinel and forsterite in the system $MgO-Al_2O_3-SiO_2$. *Contrib Mineral Petrol* 85:186-196
- Irifune T (1987) An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle. *Phys Earth Planet Inter* 45:324-336
- Ito E, Matsui Y (1977) Silicate ilmenites and the post-spinel transformations. In: Manghnani MH, Akimoto S (eds) *High-Pressure Research. Application to Geophysics*. Academic Press, New York p 193-208
- Ito E, Navrotsky A (1985) $MgSiO_3$ ilmenite: calorimetry, phase equilibria and decomposition at atmospheric pressure. *Am Mineral* 70:1020-1026
- Ito E, Yamada H (1982) Stability relations of silicate spinels, ilmenites and perovskites. In: Akimoto S, Manghnani MH (eds) *High-pressure research in geophysics*. Center for Academic Publication Japan, Tokyo, pp 405-419
- Kato T, Kumazawa M (1986) Melting of $Mg_2SiO_4-MgSiO_3$ system at 20 GPa. *J Geophys Res* 91:9351-9355
- Kawada K (1977) System $Mg_2SiO_4-Fe_2SiO_4$ at high pressures and temperatures and the Earth's interior. Ph D Thesis Univ of Tokyo, Tokyo, 187 p
- Kieffer SW (1980) Thermodynamics and lattice vibrations of minerals, 4, Application to chain and sheet silicates and orthosilicates. *Rev Geophys Space Phys* 18:862-866
- King EG, Barany R, Weller WW (1967) Thermodynamic properties of forsterite and serpentine. US Bur of Mines Rept Invest 6962
- Kiseleva IA, Ogorodova LP, Topor ND, Chigareva OG (1979) Thermochemical studies of the $CaO-MgO-SiO_2$ system. *Geokhimiya* 12:1811-1825 [in Russian]
- Knittle E, Jeanloz R (1987) Synthesis and equation of state of $(Mg, Fe)SiO_3$ perovskite to over 100 Gigapascals. *Science* 235:668-670
- Knittle E, Jeanloz E, Smith G (1986) Thermal expansion of silicate perovskite and stratification of the Earth's mantle. *Nature* 319:214-216
- Kudoh Y, Ito E, Takeda H (1987) Effect of Pressure on the Crystal Structure of Perovskite-Type $MgSiO_3$. *Phys Chem Mineral* 14:350-354
- Kuskov OL, Galimzyanov RF, Khitarov NI, Urusov VS (1983a) Phase relations in the $MgO-SiO_2$ system at $P-T$ conditions of the mantle transition zone. *Geokhimiya* 8:1075-1091 [in Russian]
- Kuskov OL, Fabrichanaya OB (1987) The SiO_2 polymorphs: The equations of state and thermodynamic properties of phase transformations. *Phys Chem Minerals* 14:58-66
- Kuskov OL, Galimzyanov RF (1984) Calculation of equilibrium $MgAl_2O_4-MgO+Al_2O_3$ taking into account the cation disordering of spinel, compressibility and thermal expansion of phases. *Geokhimiya* 1:101-106 [in Russian]
- Kuskov OL, Galimzyanov RF, Truskinovsky LM, Pilchenko VA (1983b) Reliability of thermodynamic calculations of chemical and phase equilibria at superhigh pressures. *Geokhimiya* 6:849-871 [in Russian]
- Kuskov OL, Galimzyanov RF (1986) Thermodynamics of stable mineral assemblages of the mantle transition zone. In: Saxena SK (ed) *Chemistry and Physics of Terrestrial Planets. Advances in Physical Geochemistry*, v 6. Springer-Verlag, New York, pp 310-361
- Liu L (1976a) The high pressure phases of $MgSiO_3$. *Earth Planet Sci Lett* 31:200-208
- Liu L (1976b) The post-spinel phase of forsterite. *Nature* 262:770-772
- Liu L (1979) Calculations of high pressure phase transitions in the system $MgO-SiO_2$ and implications for mantle discontinuities. *Phys Earth Planet Inter* 19:319-330
- Logvinov VM (1983) Phase transformations at high pressures in metasilicates, orthosilicates and carbonates of elements of II group of Mendeleev's system. Ph D Thesis Inst of Geology and Geophysics Novosibirsk 151 pp [in Russian]
- Malinovsky I Yu, Godovikov AA, Run EN, Logvinov VM (1981) Investigation of silicate systems and development of ultra-high pressure apparatus: Application to mantle petrology and genesis of diamond. In: Godovikov AA et al. (eds) *Experimental petrology at high pressures*. Inst of Geology and Geophysics Novosibirsk:4-31 [in Russian]
- Matsui M, Akaogi M, Matsumoto T (1987) Computational Model of the Structural and Elastic Properties of the Ilmenite and Perovskite Phases of $MgSiO_3$. *Phys Chem Mineral* 14:101-106
- Mohr RE, Stout JH (1980) Multisystem nets for systems of $n+3$ phases. *Am J Sci* 280:143-172
- Ohtani E (1979) Melting relation of Fe_2SiO_4 up to about 200 kbar. *J Phys Earth* 27:189-208
- Ostrovsky IA, Doroshev AM, Logvinov VM (1986) A comparison of extrapolative and experimental variants $P-T$ diagram of phase equilibria in the system $MgO-SiO_2$. *Izv AN SSSR ser geol* 1:12-17 [in Russian]
- Ringwood AE (1975) *Composition and Petrology of the Earth's Mantle*. McGraw-Hill, New York
- Robinson GR, Haas JL, Schafer CM, Haselton HT (1982) Thermophysical properties of selected phases in the $MgO-SiO_2-H_2O-CO_2$, $CaO-Al_2O_3-SiO_2-H_2O-CO_2$ and $Fe-FeO-Fe_2O_3-SiO_2$ chemical systems, with special emphasis on the properties of basalts and their mineral components. USA Open Report 83-79 429 p
- Sawamoto H, Kohzaki M (1985) Garnet-like $MgSiO_3$ and constitution of the upper mantle. In: *The First USSR-Japan Symposium on Phase Transformations at High Pressures and High Temperatures*. Listvyanka-on-Baikal, 48-50
- Sawamoto H (1986) Single Crystal Growth of the Modified Spinel

- (β) and Spinel (γ) Phases of $(\text{Mg, Fe})_2\text{SiO}_4$ and Some Geophysical Implications. *Phys Chem Minerals* 13:1–10
- Sawamoto H (1987) Phase diagram of MgSiO_3 at pressures up to 24 GPa and temperatures up to 2200° C: phase stability and properties of tetragonal garnet. In: Manghnani MH and Syono Y (eds) High-pressure research in mineral physics. The Akimoto volume. *Geophys monograph*, 39. Mineral physics, 2. TERRA-PUB, Tokyo, pp 209–219
- Suito K (1977) Phase relations of pure Mg_2SiO_4 up to 200 kilobars. In: Manghnani MH, Akimoto S (eds) High pressure research Acad Press, New York, pp 255–266
- Suzuki I (1975) Thermal expansion of periclase and olivine and their anharmonic properties. *J Phys Earth* 23:145–150
- Watanabe H (1982) Thermochemical properties of synthetic high-pressure compounds relevant to the earth's mantle. In: Akimoto S, Manghnani MH (eds) High-pressure research in geophysics. Center for Academic Publications Japan, Tokyo, pp 441–464
- Weidner DJ, Ito E (1985) Elasticity of MgSiO_3 in the ilmenite phase. *Phys Earth Planet Inter* 40:65–70
- Weidner JJ, Sawamoto H, Sasaki S, Kumazawa M (1984) Single-crystal elastic properties of the spinel phase of Mg_2SiO_4 . *J Geophys Res* 89:7852–7860
- Wood BJ, Holloway JR (1984) A thermodynamic model for solidus equilibria in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. *Geochim Cosmochim Acta* 48:159–176
- Yagi T, Bell PM, Mao HK (1979) Phase relations in the system $\text{MgO}-\text{FeO}-\text{SiO}_2$ between 150 and 700 kbar at 1000° C. *Carnegie Inst Washington* 78:614–618

Received December 31, 1987