

Thermodynamics of minerals of the mantle transition zone

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Abstract - Although the mineral composition and inner structure of the transition zone of the Earth's mantle has often been examined in the literature, a detailed picture of phase equilibria at pressures over 100 kbar, both in the mantle and in silicate systems modelling its composition, has not yet been clearly outlined. The reason lies in the difficulties of conducting experimental studies at the p-T parameters of the transition zone which increase greatly with the number of phases. Thus, use of numerical computation techniques of chemical thermodynamics becomes indispensable, making it possible to generalize and match the available experimental data on simple systems and, based upon these, to derive phase diagrams of much more complex systems. From a petrologic-geochemical point of view, the final aim of such an approach consists of plotting a p-T diagram of a multicomponent system and modelling the mineral composition of the mantle; from a geophysical point of view, the knowledge of equations of state of minerals and phase diagrams of an adequately common chemical composition enables us to predict seismic anomalies and to determine their intensity. Seismic discontinuities in the mantle can be connected not with just one individual transformation, but with their totality or even with the existence of invariant points in the phase diagrams.

INTRODUCTION

Phase diagrams provide the basis for understanding the distribution and state of Earth materials.

Physicochemical modelling techniques, widely used now in geochemical studies of phase equilibria (Ref. 1-7), are based on the postulates of chemical thermodynamics, according to which spontaneous processes take place that tend to the formation of such substances, and in such amounts, that the total Gibbs free energy of the system is decreased, reaching a minimum in the state of equilibrium. The maximum number of phases coexisting in phase equilibrium is limited by the Gibbs phase rule. Usually, however, a list of minerals potentially able to exist in an equilibrium system greatly exceeds the number determined by the phase rule. In order to evaluate the equilibrium compositions of these so called multisystems, it is, first of all, necessary to find stable assemblages and only then to determine the equilibrium compositions.

This paper presents a new integrated approach to a problem of modelling phase composition and structure of the Earth's mantle, involving the technique of constrained optimization.

In order to calculate the composition of a heterogeneous system at very high pressure and temperature using the available algorithms, the knowledge of thermal equations of state for all phases is necessary; it is this fact which still hampers the thermodynamic analysis of geochemical processes in the mantles of the terrestrial planets.

Building on an earlier developed algorithm for thermal equations of state of solids (Ref. 8), an algorithm for the construction of p-T diagrams of mineral systems in a large p-T range through direct minimization of Gibbs free energy is suggested in the present paper, along with the construction of a model phase diagram of the system MgO-FeO-SiO₂, which is fundamental for the mineralogy of the mantle.

TASK SETTING

Before mathematically formulating the task of computing the p-T diagram of a mineral system at ultrahigh pressures, a list of assumptions should be specified, providing the basis for subsequent constructions.

(1) Only systems of pure substances (i.e., the systems with minerals of constant composition) will be considered in the present study, ignoring the formation of solid solutions. This is the simplest model of actual multicomponent systems but, in view of inadequate data on thermodynamic properties of solid solutions and equations of state, the construction of the model is a first stage in the development of more adequate models.

(2) Phases are presumably isotropic (polycrystalline state) and exist in hydrostatic equilibrium. Pressures in all phases are the same and equal to the total pressure in the system. The most suitable case for the calculation of phase equilibria at high pressures would be the situation when all input data on thermodynamic constants come from thermochemical and ultrasonic testings, as well as from compressibility and thermal expansion measurements, of the same standard samples. But such an ideal situation is never realized in practice, and to derive the equations of state of minerals, as well as phase diagrams of mineral systems, use has to be made of initial thermodynamic constants obtained from different experiments, conducted on different samples, with possible defects in their crystal structures.

(3) The set of phases that can exist in an equilibrium system, as well as their thermodynamic properties at the atmospheric pressure, has presumably been obtained from experiment; this means that, within the scope of this approach, we can predict neither the formation of new phases in the system nor their properties.

The Gibbs free energy G_T^P of a closed system comprising n stable phases can be expressed as follows:

$$G_T^P = \bar{\mu} \bar{x} \quad (1)$$

or, in a more completed form

$$G_T^P(x_1, x_2, \dots, x_n) = \sum_{i=1}^n \mu_i x_i = \sum_{i=1}^n x_i \left(\Delta G_{T,fi}^O + \int_0^p V_i dp \right) \quad (2)$$

where

$\bar{\mu} = (\mu_1, \mu_2, \dots, \mu_n)$ - vector-row of the chemical potentials of the phases;

$\bar{x}^t = (x_1, x_2, \dots, x_n)$ - vector-column of the phase composition of the system;

t - transposition operation;

$\Delta G_{T,fi}^O$ - standard Gibbs free energy of the i-phase formation;

V_i - molar volume of the i-phase at fixed p and T.

Since the objective function (1) and the constraints are linear, the finding of the phase-composition vector \bar{x} of a thermodynamic system at constant p and T which minimizes its free energy G_T^P is a classic task of linear programming. A standard simplex-method can be used to solve it (Ref. 9). By varying p-T intervals and finding a stable phase composition for each point, a complete phase diagram of the system can be obtained in the p-T range of interest.

THE ALGORITHM

Thermodynamic computation of equilibria at ultrahigh pressures is based on standard free energies of formation of minerals, as well as on the equations of state. The analysis of various empiric and semiempiric methods for the construction of the equations of state of solids (Ref. 10) has shown that, among many current approaches, one of the most accurate and physically substantiated is the potential method (Ref. 11, 12) through which various physical characteristics of a substance in a megabar pressure-range can be obtained, with a minimal set of input data. This method has been used by the authors to derive the equations of state for many minerals and to tabulate $\int_0^p V dp$ values for practical thermodynamic calculations of systems at very high pressures (Ref. 8, 10, 12, 13, 14). Seven constants

should be set for each mineral under normal conditions ($p = 1$ atm, $T = 298$ K): adiabatic bulk modulus and its pressure derivative, heat capacity at constant pressure, Debye temperature, density, thermal expansivity, and molecular mass. The values of molar volume, density, $\int_0^p V dp$ values, bulk moduli, thermal expansivity, heat capacity, and other data are tabulated at the output of the program, at the desired p - T intervals.

The $\int_0^p V dp$ values necessary for the calculation of the Gibbs free energy of formation of phases at high pressures and temperatures enter a special disk-file which also stores the data of the standard Gibbs free energy of formation of the phases. The $\int_0^p V dp$ tables of the 6 by 6 format (pressures: 0, 100, 200, 300, 400 and 600 kbar; temperatures: 298, 1000, 1273, 1500, 1800 and 2000 K) are compact enough, easy to check, and provide a rather accurate description (within 0.2 kJ mol^{-1}) when cubic interpolation spline is used (Ref. 15).

The $\int_0^p V dp$ calculation in the megabar pressure range is generally less than one per cent, even for little-known phases (Ref. 10) and does not exceed errors in determining standard thermodynamic functions of minerals. This is due to the fact that the integration procedure partly compensates random errors in defining subintegral functions.

The information file with data on the equations of state, standard Gibbs free energies of formation and stoichiometry of minerals, along with data-processing programs, comprises a data-base for the calculation of the p - T diagram of a multisystem at the pressures and temperatures of the mantle.

The practice of thermodynamic calculations at high pressures often presents such cases when standard thermodynamic functions of high-pressure phases are lacking, but there are reliable experimental data on the p - T parameters of phase equilibria. In these situations it is possible, knowing the equations, of state of phases, to calculate standard Gibbs free energies of formation, since the value of ΔG_T^p for the phase transition on the equilibrium line is equal to zero (Ref. 7):

$$\Delta G_T^p = \Delta G_T^0 + \int_0^{p_{eq}} V dp = 0, \quad (3)$$

where ΔG_T^0 , V and p_{eq} are the change in standard Gibbs free energy, volume and equilibrium pressure of the phase transformation, respectively.

Therefore, the suggested algorithm for the calculation of the p - T diagram of a multisystem is as follows:

- (1) Construction of the thermal equations of state for all phases of the multisystem (Ref. 8).
- (2) Calculation of the missing data of the standard free energies of phase transformations using the previously tabulated equations of state and experimental p - T parameters of equilibrium.
- (3) Calculation of the equilibrium-phase composition \bar{x} of the system at various pressures and temperatures through direct minimization of the Gibbs free energy (1) under the stated constraints. Selection of stable phase assemblages and their transformations.
- (4) Computation of the p - T parameters of the stable phase transformation using the equation of the phase equilibrium (3).

The described algorithm has been used by the authors through a HPDIAG program written in Fortran language for a BESM-6 computer. The computation of the phase composition in 150 points of the p - T plane for a system of 5 components and 38 phases has been accomplished within one minute of machine time.

CONSTRUCTION OF THE PHASE DIAGRAMS

The described technique of modelling the phase diagram of a multisystem comprising phases of constant composition can be demonstrated for the systems $\text{MgO-Al}_2\text{O}_3$ - SiO_2 and MgO-FeO-SiO_2 which are basic for petrology of the mantle. The equations of state of minerals and standard thermodynamic functions of phase transformations have been published by Kuskov and Galimzyanov (Ref. 7).

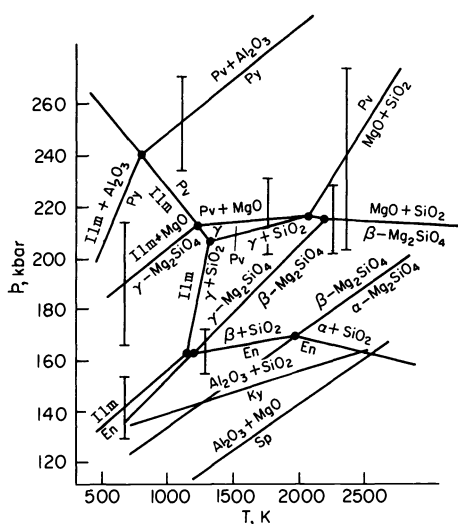


Fig. 1

Fig. 1. p-T diagram of phase relations in the MgO-Al₂O₃-SiO₂ system: Py, pyrope; Pv, MgSiO₃ (perovskite); Ilm, MgSiO₃ (ilmenite); En, enstatite; SiO₂, stishovite; α , β , γ , γ' , polymorphs of Mg₂SiO₄; Ky, kyanite; Sp, MgAl₂O₄. Error bars indicate the uncertainty in the calculated equilibrium pressure.

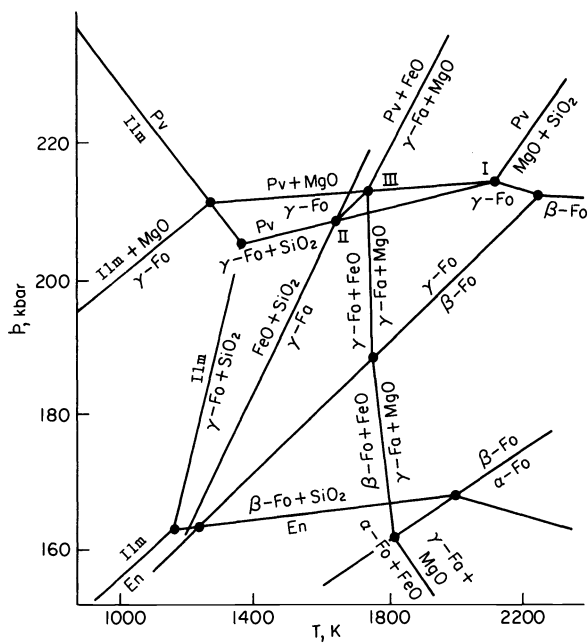


Fig. 2

Fig. 2. p-T diagram of phase relations in the MgO-FeO-SiO₂ system: α -Fo, β -Fo, γ -Fo, polymorphs of Mg₂SiO₄; γ -Fa, Fe₂SiO₄ (spinel).

The results of the modelling are shown in Fig. 1 and Fig. 2. Minimization of the Gibbs free energy of the system for each of the selected points on the p-T plane has been carried out, and the equilibrium phase composition has been determined. The stability domains of the various mineral assemblages have been separated by the univariant curves of stable equilibria.

The calculations of the phase diagrams through direct minimization of the Gibbs free energy at the p-T parameters of the transition zone confirms the trend, which has been discovered by Kuskov et al. (Ref. 6), of invariant points to concentrate within two comparatively narrow p-intervals that perfectly match the pressures in the major geophysical discontinuities of the mantle at the depths of 400 and 670 km. Therefore, an opinion can be expressed that seismic discontinuities in the mantle may be related both to the combination of certain univariant transformations near the invariant point and to the invariant point itself on the phase diagram. Thus, seismic discontinuities at different depths (for instance, 640-720 km) in different regions can be connected not with just one individual transformation, but with their totality or even with the existence of an invariant point in the phase diagram.

Fig. 3 shows a density is profile of a mantle of pyrolite composition calculated on the basis of independent thermodynamic information and consistent with phase diagrams of mineral systems (Ref. 6,7). From the comparison of the "thermodynamic distribution" of density it is seen that the thermodynamic profile reveals a more definite fine density structure within the transition zone and allows one a detailed elucidation of the phase transformation in this area of the mantle. This is explained by the fact that a number of chemical transformations with comparatively small jumps of density are not registered by seismic methods. The thermodynamic profiles of various initial model compositions may serve as a basis for specifying mineral composition and the structure of the transition zone in conjunction with seismic sounding methods.

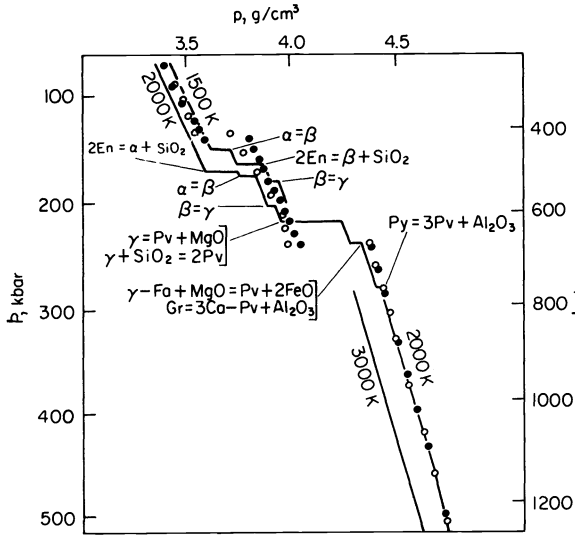


Fig. 3. Density distribution in the transition zone of the mantle. o, from Jordan and Anderson (Ref. 16); ●, from Dziewonski and Anderson (Ref. 17). Solid lines are thermodynamic calculations. Pyrolite composition was used. The density calculations are based on calculated equilibrium assemblages at appropriate p and T, and equations of state of the co-existing phases. The estimated error in the density of perovskite + MgO assemblage is $\pm 0.03 \text{ g.cm}^{-3}$ at 300 kbar.

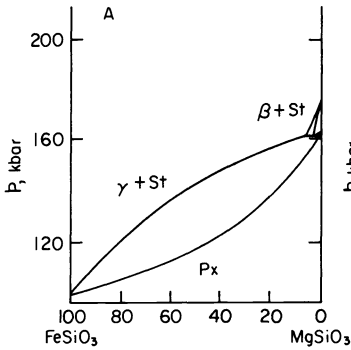


Fig. 4A

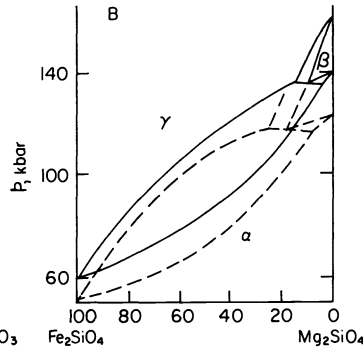


Fig. 4B

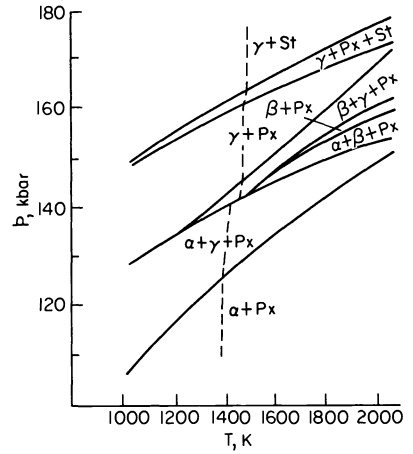


Fig. 5

Fig. 4. p-x diagram of phase relations in the MgO-FeO-SiO₂ system: α, β, γ, polymorphs of Mg₂SiO₄; Px, pyroxene; St, stishovite. A. Calculated phase diagram for the pseudo-binary system at 1500 K. B. Calculated phase diagram for the pseudo-binary system Mg₂SiO₄-Fe₂SiO₄ at 1273 K (solid lines); the dashed line is the experiment conducted by Akimoto et al. (Ref. 18) at 1273 K. The cause of the divergence lies in both the uncertainty with regard to the thermodynamic functions of Fe₂SiO₄ and Mg₂SiO₄ (α, β, γ) and in the calibration method employed in the experiment.

Fig. 5. p-T diagram of phase relations in the MgO-FeO-SiO₂ system with an Fe to Mg+Fe ratio of 0.12. The adiabatic distribution of temperature of the mantle is shown by the dashed line. At 140 kbar, the olivine to β phase transformation is responsible for a sharp 400-420 km discontinuity.

However, to identify a fine structure of the mantle, use should be made of the data on solid solutions. The results of calculations for ideal solid solutions in the MgO-FeO-SiO₂ system are presented in Fig. 4-6 (the method of calculation has been described by Kuskov and Fabrichnaya (Ref. 14)). The algorithm for the calculation of the p-T diagram of the multisystem, which has been suggested in the paper, can be used in principle as a stage in constructing more adequate models, including solid solutions.

The phase diagram reliability analysis requires the evaluation of many different variants to be carried out for the whole area of uncertain input parameters. The error estimate for univariant equilibria pressures is rather inefficient in view of a too strong correlation within both the standard thermodynamic functions and the p-T parameters of equilibria, and therefore cannot track substantial changes in the topology of a diagram at slight fluctuations of input data.

All these problems suggest new requirements in the procedure of a phase diagram computation. The complexity of relevant systems and uncertainty

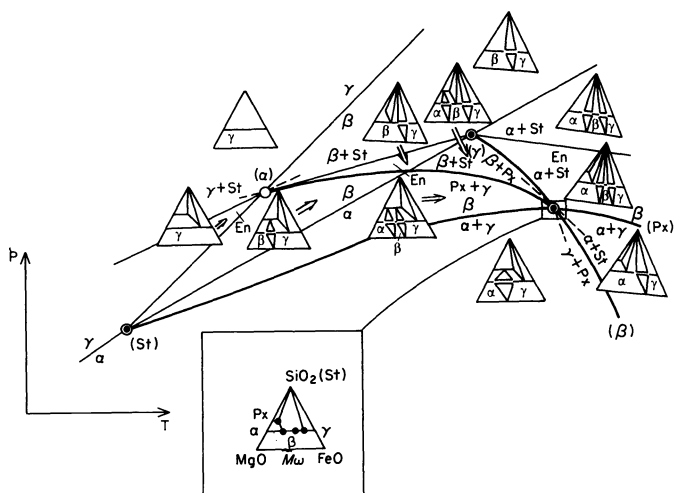


Fig. 6. A qualitative topology of phase diagram at 400 km discontinuity. Fine and coarse lines are univariant lines for the MgO-SiO₂ and MgO-FeO-SiO₂ systems:

$(x_{Mg}^{Px} > x_{Mg}^{\alpha} > x_{Mg}^{\beta} > x_{Mg}^{\gamma})$. α, β, γ , polymorphs of Mg₂SiO₄ or solid solutions in Mg₂SiO₄-Fe₂SiO₄; En, enstatite; St, stishovite; Px solid solutions in MgSiO₃-FeSiO₃.

of input data demand the development of computer-user interactive systems and imitation modelling techniques for a comprehensive analysis of the sensitivity of phase diagrams to fluctuations of input data, and this is immediately connected with the urgent task of achieving consistency between calorimetry and phase equilibria at high pressures.

In conclusion I would like to emphasize that phase diagrams of model systems serve as a basis for the interpretation of the mineral composition of the mantle. Seismological methods, based on the phase diagrams of the constant and variable composition systems, will have a great deal of power and will make it possible to reveal the fine structure of the mantle, and to construct an adequate model of the internal structure of the Earth.

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