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GEOCHEMISTRY

Estimation of Formation Conditions of Mineral Megasystems from Thermodynamic Modeling

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The temperature and pressure of the formation of mineral assemblages and composition of fluid are currently estimated largely with the method of phase correspondence [1, 2]. This method consists in calculation (on a thermodynamic or experimental basis) of a certain stoichiometric mineral reaction, end member relationship, or a complex of certain reactions that determine the *PT* parameters and fugacity of volatile components.

At the same time, geothermobarometric problems can be solved by a principally different method based on search for the minimum Gibbs free energy of a given physicochemical system with a set of constraints [3]. The development of the method of minimization of the thermodynamic potential for geothermobarometric purposes promoted the formulation of the geothermobarometric problem in a nonequilibrium set of mineral systems with (or without) participation of fluid as an inverse problem of convex programming [4]. An implication of the proposed approach for the modeling of mineral assemblages of granulite-facies metamorphic rocks has been outlined in [5]. The results of the investigation have demonstrated the possibility to find a redox potential in mineral assemblages, for which it is impossible or difficult to find oxygen fugacity by the method of phase correspondence. In this communication, we develop the method of minimization in the geothermobarometric setting [4] for a set of samples from intercalating rocks of different compositions reliably formed at close temperatures and pressures. The incorporation of several samples of intercalating rocks of different compositions with various mineral assemblages formed under similar *PT* conditions provides the most reliable estimates of temperature and pressure.

Thus, the geothermobarometer may be presented in the general form as a multireservoir model that consists of k systems ($k \in K$), where K is a finite set of the systems (samples) under consideration. Each system contains d^k—a known (observed or experimentally determined) vector of molar amounts of phases of the kth system. In other words, vector d^k is the quantitative mineral composition of rocks. Element d^k_α of vector (d^k) is a molar amount of phase with index α:

$$d^k_\alpha, \quad \alpha \in \Phi_k, \quad k \in K,$$

where Φ_k is the totality of phases of the kth system.

Let us define the temperature and pressure region, which includes the sought values of temperature $\hat{T}$ and pressure $\hat{P}$. Let us denote $\theta^T = (T, P)$ as a two-element vector of temperature and pressure. Then, the defined region may be a priori denoted as $D^0_\theta = \{\theta/\theta^- \le \theta \le \theta^+\}$, where $\theta^- = (T^-, P^-)^T$ and $\theta^+ = (T^+, P^+)^T$ are the lower and upper limits, respectively, of the defined intervals by temperature and pressure. Let us denote the finite choice of vectors θ from D^0_θ as $D_\theta \subset D^0_\theta$.

The search for an optimal value of vector θ requires the solution of the inverse problem of convex programming, i.e., the determination of temperature and pressure that minimize a criterion function—the sum of squares of deviation of the known (defined) and calculated (at different temperatures and pressures) molar amounts of phases in the system:

$$f(x^k_\theta) = \sum_k \sum_\theta \omega^k (d^k - x^k_\theta)^2, \quad k \in K, \quad \theta \in D_\theta, \quad (1)$$

where x^k_θ is the vector of molar amounts of phases determined as a result of the solution of the θth direct problem of the vortex programming of the minimiza-

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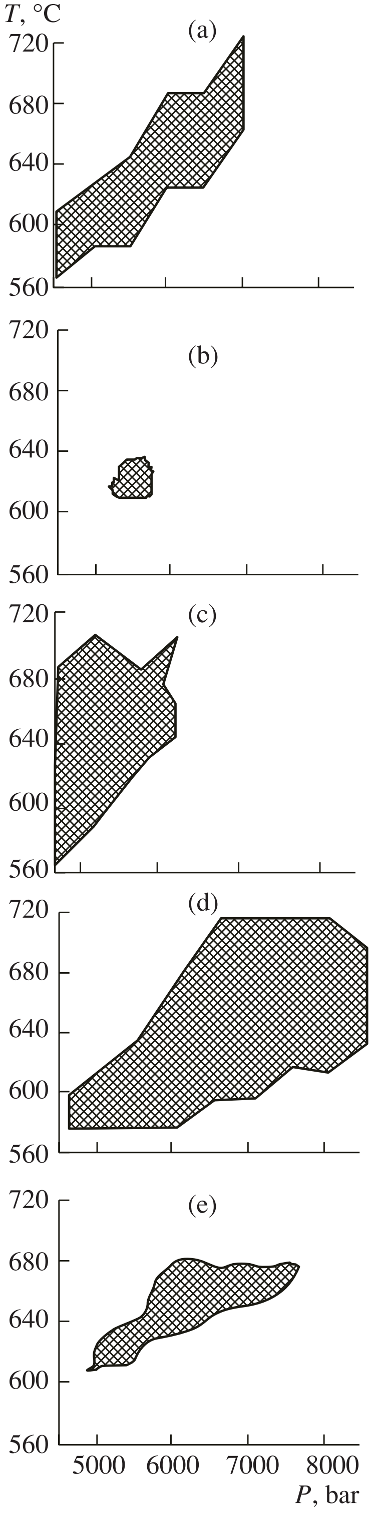
tion of the adjusted isobaric–isothermal potential $G(x_\theta^k)$ of the kth system with a fixed $\theta \in D_\theta$ and ω^k is the vector of normalizing coefficients of the kth system. An element of vector ω^k is determined as $d_\alpha^k : \omega_\alpha^k$, $\alpha \in \Phi$, $k \in K$. The vector of normalizing coefficients allows us to take into account the influence of the criterion function of various-rank molar amounts of phases in the systems (their difference may reach a few orders of magnitude) by specifying the respective weight factors to all phases. We assume that ω_k is always >0.

Thus, the solution of the inverse problem is reduced to the solution of a series of direct problems presented in parametric form, which makes it possible to identify the parameters (temperature and pressure) that minimize the sought criterion function on a finite sample array of optimal x_θ^k values induced by a finite sample array of parameters $\theta \in D_\theta$. In a chosen point of the *PT* region, we calculate the equilibrium composition of all rocks of the considered nonequilibrium megasystem. According to the principle of local equilibrium, a specific minimum of the Gibbs free energy corresponds to each megasystem. The integral criterion function (1) is calculated on the basis of these computations. The search for a minimum of the criterion function is carried out with the method of the golden section. The high reliability and economy of this method for the solution of deterministic problems should be noted.

From the viewpoint of computation, there is no guarantee that the obtained optimal solution $\hat{x}_\theta^k$ will be unique relative to the vector of parameter θ. This is especially characteristic of systems with a rather wide *PT* stability region of a certain mineral assemblage (figure). Therefore, it is extremely important to consider at once several mineral systems in a single segment of the metamorphic sequence composed of the rocks with different assemblages of coexisting minerals. In this case, the determination of the optimal value of the criterion function will represent a minimum of the total value of computation functions over all k systems. Taking into account the integral character of the criterion function, the more diverse the composition of rocks (systems), the higher the probability to obtain a unique solution by temperature and pressure.

Let us demonstrate the possibility of the method based on a thoroughly studied exposure of metamorphic rocks on the right bank of the Gilyui River, where we observed an intercalation of volcanosedimentary rocks metamorphosed under conditions of amphibolite facies. These rocks pertain to the Ilikan Group (Stanovoi metamorphic complex) of the Ilikan lithotectonic zone in the central Dzhugdzhur–Stanovoi Block. According to indirect evidence, the age of metamorphism in this region is estimated at 1.9 Ga [6].

The studied samples are composed of amphibole–biotite and garnet–biotite gneisses, amphibolites, and garnet amphibolites (Table 1). The thickness of sepa-



Stability fields of mineral assemblages in metamorphic rocks from exposure OG-6 in *PT* coordinates: (a) sample 6-8, (b) sample 6-5, (c) sample 6-6, (d) sample 6-2, and (e) sample 6. The mineral assemblage of metapelitic gneiss (sample 6-5) is stable within a small *PT* region in comparison with mineral assemblages of amphibolites (sample 6-2 and others).

Table 1. Mineral assemblages in metamorphic rocks from exposure OG-6

Sample	Rock	Mineral assemblage	Remark
OG-6	Garnet amphibolite	Gr + Hb + Pl + Q + Ilm	Very small amount of secondary Bi; Ap and Zr are present
OG-6-2	Amphibolite	Hb + Pl + Q + Ilm	Sph, Ap, and Chl are present
OG-6-5	Biotite gneiss	Gr + Bi + Pl + Q + Ilm	Ap, Ot, Mz, and late-stage Kfs are present
OG-6-6	Garnet–biotite gneiss	Gr + Hb + Bi + Pl + Q + Ilm	Ap, Ot, Zr, and late Kfs are present
OG-6-8	Garnet amphibolite	Gr + Hb + Pl + Q + Ilm	Ap and very small amounts of apparently late Bi and KFs, Chl, and Py are present

Note: (Gr) garnet; (Hb) amphibole; (Pl) plagioclase; (Bi) biotite; (Q) quartz; (Ilm) ilmenite; (Ap) apatite; (Zr) zircon; Sph (sphene); Chl (chlorite); (Kfs) potassium feldspar; (Ot) orthite; (Py) pyrrhotite; (Mz) monazite.

Table 2. Chemical compositions, wt % of metamorphic rocks from exposure OG-6 on the right bank of the Gilyui River

Sample	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	H_2O^-	L.O.I.	P_2O_5	Total
OG-6	51.81	0.67	15.00	9.08	2.10	0.00	8.48	8.99	1.72	0.61	0.88	0.35	0.19	99.88
OG-6-2	50.14	0.84	13.98	10.11	3.06	0.45	6.65	10.21	1.98	0.99	0.04	1.00	0.19	99.64
OG-6-5	61.08	0.91	17.25	6.25	0.57	0.10	2.85	2.82	3.33	2.53	–	0.77	1.33	99.79
OG-6-6	65.09	0.42	15.52	3.76	–	0.04	2.52	6.09	4.02	0.73	–	0.14	1.08	99.41
OG-6-8	50.69	0.89	15.62	10.17	2.37	0.16	6.88	9.03	1.91	0.54	–	0.15	1.57	99.98

Note: Analyses were performed at the Far East Geological Institute, Far East Division, Russian Academy of Sciences (L.V. Nedashkovskaya, analyst).

rate beds with different mineral assemblages varies from a few meters to tens of centimeters. Table 2 shows the chemical compositions of rocks. All mineral assemblages were studied with a JEOL-8100 microprobe at the Far East Geological Institute in Vladivostok (I.A. Aleksandrov, analyst). The chemical analyses of minerals are available upon request. The Ca-rich amphibolites and garnet amphibolites comprise four rock varieties (Tables 1, 2), while low-Ca rocks are represented by one sample of garnet–biotite gneiss (Tables 1, 2, sample OG-6-5). The problem was formulated in the following way: find probable *PT* estimates in the considered nonequilibrium megasystem of metamorphic mineral assemblages formed at close *PT* values, if approximate molar (volumetric) amounts of minerals in each assemblage are known. At the input, we specified the chemical composition of rocks (Table 2), molar amounts of minerals in each rock, and the *PT* range for which we should find optimal *PT* values, given that these values are close or similar in each mineral assemblage.

The computation was performed with the Selector-S software package. The ranges of the sought parameters were 500–720°C and 4000–8000 bar. The final solution with Selector-S comprises the composition of minerals, their volumetric amounts, *PT* parameters, and fluid composition. The computed thermodynamic system consisted of 61 components that make up the major observed (or probable minerals) in metamorphic rocks formed under conditions of granulite and amphibolite facies: quartz, plagioclase, K–Na feldspar, orthopyroxene, clinopyroxene, garnet, cordierite, biotite, olivine, amphibole, muscovite, ilmenite, magnetite, hematite, native iron, corundum, graphite, sillimanite, kyanite, andalusite, epidote, zoisite, clinozoisite, rutile, spinel, titanite, staurolite, calcite, and dolomite. The modeling was based on an internally consistent thermodynamic data set [8] with consideration of models of solid solutions for minerals, largely after [9, 10]. The fluid was specified as a simple gas system consisting of six components (H_2O, CO_2, CH_4, CO, H_2, and O_2). In the first solution, we introduced the standard fluid consisting of CO_2, C, and H_2O (molar amounts equal to 0.001, 0.01, and 0.004 per 100 g of rock, respectively). The resultant amount of fluid was equal to the fluid/rock ratio of 1/30, corresponding to conditions of fluid buffering by the rock. In the subsequent solutions, we slightly changed the amounts of carbon and oxygen in order to obtain the experimental mineral assemblages that would be closest to those specified in rock samples. Tables 3 and 4 present two versions of the solution. As can be seen, the real mineral assemblages are in good agreement with those obtained with Selektor-S. The calculated and real Fe mole fractions of coexisting minerals, plagioclase numbers, and Ca mole fraction Ca/(Ca + Fe^{2+} + Mg) of garnet are also very similar. The modeling results show only two minor inaccuracies: a small amount of kyanite (<1 vol %) appears in sample OG-6-5, and the Ca mole fraction of garnet shows a small systematic underestimation (Table 3). These inaccuracies are caused by

Table 3. Comparison of compositional parameters of minerals in (1) real and (A, B) model assemblages. CO_2 content in fluid is up to 15% in model A and up to 60% in model B

Sample	$X_{\mathrm{Fe}}^{\mathrm{Gr}}$			$X_{\mathrm{An}}^{\mathrm{Pl}}$			$X_{\mathrm{Ca}}^{\mathrm{Gr}}$			$X_{\mathrm{Fe}}^{\mathrm{Hb}}$			$X_{\mathrm{Fe}}^{\mathrm{Bi}}$		
	1	A	B	1	A	B	1	A	B	1	A	B	1	A	B
OG-6	0.73	0.71	0.73	0.46	0.48	0.49	0.12	0.07	0.07	0.33	0.33	0.31	–	–	
OG-6-2	–	–	–	0.46–0.39	0.49	0.48	–	–	–	0.48	0.49	47	–	–	–
OG-6-5	0.83–0.86	0.83	–	0.31	0.31	–	0.06	0.05	–	–	–	–	0.51	0.51	–
OG-6-6	0.76	0.80	0.78	0.39	0.34	0.34	0.14	0.06	0.06	0.39	0.41	0.40	0.40	0.46	0.44
OG-6-8	0.75	0.76	0.76	0.42	0.49	0.51	0.14	0.09	0.09	0.38	0.40	0.35	0.39	–	–

Note: ($X_{\mathrm{Fe}}^{\mathrm{Gr}}$, $X_{\mathrm{Fe}}^{\mathrm{Bi}}$, $X_{\mathrm{Fe}}^{\mathrm{Hb}}$) Iron mole fraction, $Fe^{2+}/(Fe^{2+} + Mg)$ of garnet (Gr), biotite (Bi) and hornblende (Hb), respectively; ($X_{\mathrm{An}}^{\mathrm{Pl}}$) plagioclase number; ($X_{\mathrm{Ca}}^{\mathrm{Gr}}$) Ca mole fraction, $Ca/(Ca + F^{2+} + Mg)$ of garnet.

Table 4. Comparison of amounts of minerals (vol. %) in the (1) mineral assemblages and (A, B) model assemblages

Sample	Hb			Bi			Gr			Pl			Q			Ilm		
	1	A	B	1	A	B	1	A	B	1	A	B	1	A	B	1	A	B
OG-6	70	60.5	57	–	–	–	1.5	9	11	17.5	20	22	11	9.5	10	<1	1	1
OG-6-2	76	64	63	–	–	–	–	–	–	11	28	29	13	6	6	<1	2	2
OG-6-5	–	–	–	23	23	–	7	2	–	50	45	–	20	28	–	<1	1	–
OG-6-6	15	18	18	10	2	0.8	0.1	0.1	0.2	45	54	54	30	26	26	<1	0.5	0.5
OG-6-8	65	55	50	<2	–	–	5	10	12	15	26	30	13	8	7	<1	1	1

imperfect models of solid solutions for hornblende and biotite.

The model values of temperature and pressure for five intercalating metamorphic rocks are equal to 615°C (±30°) and 5.5 (±1) kbar. The calculated *PT* conditions correspond to amphibolite facies and are rather close to the *PT* estimates based on known thermobarometers [11, 12]. The calculation of temperature based on the garnet–biotite thermometer [11] and the model of the garnet solid solution [13] yield 600–650°C for all samples. The pressure estimates obtained with the garnet–hornblende–plagioclase barometer [12] are 8 kbar for sample OG-6-5 and 6.2–6.9 kbar for samples OG-6-6 and OG-6-8. The redox potential or oxygen fugacity was determined for all samples with a sufficient accuracy. This parameter turned out to be close to the CCO buffer. Thus, the observed mineral assemblages are appreciably reduced. Let us note that oxygen fugacity cannot be estimated in these assemblages by the method of phase correspondence. At the same time, the CO_2/H_2O ratio in Ca-rich rocks remains uncertain, because the mineral assemblages under consideration are insufficiently sensitive to the variation of this ratio. The agreement between mineral assemblages obtained by the minimization of free energy and the natural ones indicates that the observed mineral assemblages are close to the thermodynamic equilibrium state with respect to the set of minerals and their compositions. This fact is based on the basic principle of local equilibrium and confirms not only the sufficient reliability of the accepted model but also the postulated constancy of *PT* conditions with the rock outcrop.

In practice, we can markedly constrict the initial *PT* region by computation of the stability of mineral assemblages of the megasystem in *T* and *P* coordinates (figure). The boundary values of stability fields may be used as corrected *P* and *T* ranges for minimization of the $f(x_\theta^k)$ function.

The proposed method is an alternative one for the determination of *PT* parameters in each rock and the subsequent estimation of the formal weighted mean value, leading to the summation of all errors at each step of modeling. The accuracy of estimation of the sought parameters is limited only by fulfillment of conditions of local equilibrium, the completeness of mineralogical and chemical-analytical data, the reliability and consistence of the used models of solid solutions, and the thermodynamic properties of end members that make up minerals of metamorphic rocks.

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