

Oxygen Regime of Granulite Metamorphism: Modeling by the Method of Gibbs Free Energy Minimization

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Abstract—Using a new version of the Selektor-C program package for the minimization of Gibbs free energy, physicochemical modeling was conducted for real mineral assemblages from the rocks of the Okhotsk and Chogar complexes and the Larba block, which crystallized under granulite-facies conditions. Considering a two-reservoir fluid–rock system, model assemblages of metapelites and metabasites adequate to natural assemblages were reconstructed by the method of Gibbs potential minimization. The P - T parameters of crystallization, oxygen potential, and the composition of the deep fluid that produced the assemblages were estimated. It was shown that the character of oxygen behavior can be dual under granulite-facies metamorphic conditions: inert behavior in rocks enriched in magnetite and (or) hemoilmenite and perfectly mobile behavior (after D.S. Korzhinskii) in rocks devoid of these minerals. It was shown that the oxygen regime is controlled by the degree of complete or partial leveling of oxygen potential between the deep reduced fluid and the rock in agreement with their oxygen capacities.

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INTRODUCTION

The fluid regime is crucial for the understanding of the petrogenesis of metamorphic rocks. This study addresses the solution of the inverse problem: determining pressure, temperature, and activities of water, carbon dioxide, and oxygen, as the major components of fluid controlling the parameters of mineral assemblages, from the compositions of minerals. In the theory of metamorphism, oxygen conditions are of fundamental significance because of the high (often critical) sensitivity of the phase and mineral compositions of assemblages to variations in oxygen fugacity (f_{O_2}). Most investigators accept the fluid model assuming that the potentials of water and carbon dioxide in metamorphic rocks are identical to those in the deep fluid that produces the rocks, and this is related to the perfectly mobile regime of these major fluid components. As to oxygen potential, it is commonly assumed that it is buffered (imposed) by the chemical composition of the rock, which implies its inert behavior.

Of special importance for the fluid model are the concepts of D.S. Korzhinskii on open systems with “differential mobility of components” (Korzhinskii, 1994). According to his hypothesis, the equilibrium of rock with the environment is attained owing to the exchange of chemical potentials of “perfectly mobile” components at constant potentials of less mobile “inert” components. As to the oxygen regime, Korzhinskii suggested that the paragenetic analysis of minerals indicates a notable inertness of oxygen dur-

ing metamorphic, magmatic, and hydrothermal processes; the activity of oxygen at metamorphic processes depends to a large extent on the initial composition of the protolith and is independent of the participation of vadose waters and waters buried in the proto-rocks (Korzhinskii, 1945, 1994; pp. 6–28, 159–167). According to this hypothesis, the dependence of oxygen activity on the alkalinity of the rock or the environment supports the inference that oxygen activity is not a parameter of the external medium but depends on other factors of equilibrium in mineral systems, and this hypothesis has found extensive support in metasomatic systems but is still not clear for normal metamorphic processes (Korzhinskii, 1994, pp. 163–164).

Fonarev (1987) paid special attention to the oxygen regime (specific behavior of oxygen) in the discussion of the evolution of redox conditions during the metamorphism of Precambrian iron formations. He concluded that there is a close relation of the primary banding and structure of rock and the composition of the assemblage with the inert behavior of oxygen. It was claimed that the inert regime of oxygen (locally dependent) is predominant for most regional metamorphic complexes of the Precambrian iron formation up to the highest metamorphic grades. The inert behavior of oxygen during the formation of rocks containing magnetite and hematite was interpreted by him as equilibrium at the dominance of rock over fluid by mass (its buffer capacity). The perfectly mobile regime was described by Fonarev as a continuous input of

Table 1. Compositions of metamorphic rocks selected for modeling¹⁾

Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O ⁺	H ₂ O ⁻	L.O.I.	Total
10v	45.60	0.25	9.81	3.45	24.84	0.80	8.66	2.16	0.81	0.67	0.06	—	0.22	—	97.33
143	72.88	0.25	9.73	4.71	2.80	0.05	5.94	0.34	0.25	1.00	0.12	—	—	1.53	99.60
73v	64.60	0.22	7.16	0.65	17.94	0.17	6.00	0.31	0.05	0.53	0.26	—	0.06	0.08	98.03
1159/2-a	68.95	0.56	15.56	0.86	3.90	0.08	3.36	1.90	2.45	1.34	0.07	—	0.06	0.64	99.73
127-g	65.78	0.55	18.13	3.16	2.46	0.22	2.95	1.46	1.88	1.55	0.11	1.42	0.14	—	99.81
136-e	47.96	1.26	14.84	5.54	9.65	0.27	5.61	10.25	2.58	0.46	0.15	—	—	1.24	99.81
SCh-9/129	46.30	2.25	12.56	6.85	11.00	0.29	6.58	10.51	2.08	0.28	0.33	0.07	—	0.25	99.42
SCh-5/58	44.35	1.47	15.17	5.62	10.81	0.16	8.16	11.09	1.55	0.43	0.19	0.01	—	0.88	99.93
39-e	47.62	0.57	9.28	15.20	15.84	0.56	3.37	2.54	0.74	1.07	0.10	—	0.24	1.64	98.77
A-138	48.71	0.6	8.64	19.03	13.6	0.47	3.59	2.34	0.7	0.99	0.16	—	0.13	1.00	99.96

Note: ¹⁾ The mineral assemblages of the rock samples: 10v, *Grt + Opx + Pl + Bt + Qtz*; 143, *Grt + Opx + Pl + Bt + Crd + Qtz + Rt*; 73v, *Grt + Opx + Kfs + Bt + Qtz*; 1159/2a, *Grt + Pl + Bt + Sil + Kfs + Qtz + Ilm + Rt*; 127-g, *Grt + Pl + Bt + Sil + Qtz*; 136-e, *Grt + Opx + Cpx + Hbl + Pl + Qtz + Mag + Ilm*; SCh-9/129, *Grt + Opx + Cpx + Hbl + Pl + Mag + Ilm*; SCh-5/58, *Grt + Cpx + Hbl + Pl + Mag + Ilm*; 39-e, *Grt + Opx + Kfs + Pl + Qtz + Mag + Ilm*; and A-138, *Grt + Opx + Kfs + Bt + Hbl + Pl + Qtz + Ilm + Mag*.

considerable masses of fluids into the rock sequence, when oxygen fugacity controlled by its composition is independent of the composition of major minerals of the rock and is imposed for the whole sequence (Fonarev, 1987; pp. 265–266). This statement was illustrated by Fonarev (1987; Table 52, Fig. 101) as an increase in the Fe/(Fe + Mg) ratio of orthopyroxene and cummingtonite (at increasing *T* and *P*) accompanied by a distinct decrease in f_{O_2} determined from mineral assemblages, practically up to the CCO buffer. In our opinion, in such a case, a transition to the perfectly mobile behavior of oxygen occurs in magnetite-free (i.e., “ f_{O_2} -mute”) rocks of the quartz–silicate (clinopyroxene–orthopyroxene ± cummingtonite)–carbonate subfacies (Canyon Mount Reed region, Canada) containing graphite. The similar analysis of oxygen behavior (internal control of oxygen potential) was discussed by Labotka et al. (1982) and Frost (1982).

Perchuk (1973, 1986) estimated the potentials of H₂O, CO₂, and O₂ at different stages of the development of the Earth’s crust. He used the reactions (for approximately 200 mineral assemblages) of oxidation–reduction, hydration–dehydration, and carbonation–decarbonation. It was shown that, in the P_{tot} – f_{O_2} coordinates, log f_{O_2} decreases with increasing depth along a hyperbole from –10 at the surface to –19 at 10–12 kbar. Perchuk (1977) argued that the behavior of oxygen was perfectly mobile during the regional metamorphism of metapelites.

Perchuk and Ryabchikov (1976) evaluated the fluid regime of metamorphism by the method of phase correspondence assuming a priori that the oxygen activity calculated from the analyses of mineral assemblages corresponds to the oxygen activity in the deep fluid

responsible for metamorphism. This statement requires additional consideration, especially because all statements concerning the fluid regime are qualitative due to the lack of information on the deep fluid. This study focuses on the evaluation of the regime of oxygen (perfectly mobile or inert) in the processes of granulite metamorphism by the method of Gibbs potential minimization.

OBJECTS

Several granulite-facies metamorphic rocks from the Okhotsk and Chogar complexes and the Larba block were selected for modeling. The chemical analyses of these rocks, the compositions of their minerals, the phase compositions of mineral assemblages, and the *P*–*T* conditions of their formation were reported by Avchenko (1977, 1990). The rocks are low-calcium garnet–orthopyroxene, garnet–cordierite, and garnet–biotite–sillimanite gneisses, gneissic quartzites, and granulites (metapelites), as well as high-calcium garnet–amphibole–two-pyroxene schists (metabasites). The compositions of these rocks and their mineral assemblages are given in Table 1. The rocks are assigned to a single metamorphic stage. However, zoning was observed in the minerals. This is related to the high sensitivity of mineral assemblages (especially metapelitic) to retrograde processes terminating the main metamorphic stage. The zoning of these minerals was described by Avchenko (1977, 1990), and the chemical zoning of garnets was investigated by Avchenko (1982). We used only those mineral assemblages that were not destroyed during the retrograde stage. Special attention was given to mineral zoning; its investigation was aimed at the paragenetic analysis of minerals and obtaining data for the determination of the local parameters of chemical equilibrium under the conditions of the main metamorphic stage.

PROGRAM PACKAGE SELEKTOR-C

The method of the minimization of thermodynamic potentials (Karpov, 1981; Chudnenko, 2007) was used in this study for the estimation of the fluid regime of metamorphism. The Selektor-C program package implementing a convex programming approach for the calculation of equilibria in heterogeneous systems by the minimization of thermodynamic potentials contains all the necessary structures of data and algorithms combined in a common integrated system running in the Microsoft Windows environment. The Selektor-C code can be used to calculate complex chemical equilibria in isobaric–isothermal, isochoric, and adiabatic conditions in multisystems containing an aqueous electrolyte solution, a gas mixture, liquid and solid hydrocarbons, and minerals, including solid solutions and single-component phases. The use of Selektor-C allows one to tackle some problems of the formation of metamorphic mineral assemblages that cannot be solved by the classical method of paragenetic analysis. Among such problems are the modeling of multicomponent and multiphase nonequilibrium megasystems, the proof of the principle of local equilibrium, and the estimation of the formation conditions of nonequilibrium associations. Selektor-C is efficient for the estimation of the level of the oxidation potential of fluid even in mineral assemblages free of magnetite, ilmenite, or graphite. The principle of duality implemented in Selektor-C deserves special attention. This principle is a mathematical tool for the elucidation of the thermodynamic essence of Lagrangian multipliers, which are used in the theory of convex programming. This principle provides a basis for the calculation of the chemical potentials of all independent components of model mineral assemblages (Chudnenko, 2007). The thermodynamic parameters of mineral solid solutions play a key role in Selektor-C. The introduction of solid solutions was necessary for the creation of models for real assemblages and, consequently, the quantitative description of the fluid regime of rocks (Avchenko and Chudnenko, 2005). The principles, methods, and the results of the application of the Selektor-C program package for the analysis of granulite- and amphibolite-grade rocks were discussed in detail by Avchenko et al. (2010). In addition, as will be shown in this paper, the method of minimization allows the evaluation of oxygen behavior.

The models include 70 observed or possible major minerals (end-members) of metamorphic rocks: quartz, plagioclase, K–Na feldspar, biotite, orthopyroxene, clinopyroxene, garnet, cordierite, olivine, hornblende, sillimanite, kyanite, andalusite, ilmenite, magnetite, corundum, sapphirine, graphite, native iron, and rutile. In order to support the uniqueness of the model solution for associations, the following minerals of the amphibolite facies were included: muscovite, epidote, staurolite, zoisite, clinozoisite, and titanite. The thermodynamic properties of the

end-members of solid solution series were calculated using the database of Holland and Powell (1990), and the thermodynamic properties of gas components were taken from the database of Reed et al. (1982).

METHOD OF MODELING

The model consists of two reservoirs. The first reservoir (external fluid of the C–O–H system) contains variable amounts of H₂O, CO, O₂, CO₂, H₂, CH₄, and carbon. Varying the amounts and composition of fluid in the first reservoir, the potentials of fluid components (including O₂) can be imposed in the second reservoir, which contains rock. The composition of fluid is gradually changed to produce a model mineral assemblage in the second reservoir approaching the real assemblage (model solution). The model solution includes the compositions of minerals, their volume proportions, *P*-*T* conditions, and fluid composition. Hence, in contrast to paragenetic analysis, our approach provides information on the composition of external fluid and its O₂ activity. In most (though not in all) cases, the same mineral assemblages can be produced by reducing the external water–carbon dioxide fluid by not only carbon or carbon monoxide, but also by hydrogen, methane, and their mixtures (in very small amounts). The oxygen potential in the external fluid in the models with different variants of component composition remains the same, and the criterion for fluid composition is the close agreement between the model and real compositions of minerals. The attainment of this agreement has to be emphasized, because the model assemblage (composition and amounts of minerals) is rather stringently controlled by the external equilibrium factors: pressure, temperature, potentials of the major components of the external fluid (H₂O and CO₂), *f*_{O₂}, and fluid/rock ratio. This implies that, for the majority of real assemblages, an almost unique solution can be found for the external parameters of the model assemblage.

The reduced fluid formed under specified *P*-*T* conditions in the first reservoir is transferred into the second reservoir with the real composition of metamorphic rock specified by the molar amounts of independent components: SiO₂, TiO₂, Al₂O₃, Fe₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, and H₂O (using total iron content in each sample given in Table 1). The fluid/rock mass ratio varied considerably in the models from 0.25 to 0.005. Temperature and pressure were determined using the PET program (Dachs, 1988), which contains the equations of 25 geothermometers and 16 geobarometers. Simultaneously, pressure and temperature were empirically adjusted during the construction of the model, and the resulting values were practically identical (within 10–20°C and 500–1000 bar) with those obtained by the PET program. The completeness of mineral assemblages, the volume proportions of minerals, the Fe/(Fe + Mg) ratio of sili-

Table 2. Comparison of the (1) real and (2) model compositions of minerals for the assemblages studied

Sample no.	X_{Fe}^{Grt}		X_{Fe}^{Opx}		X_{Fe}^{Bt}		X_{An}^{Pl}		X_{Ca}^{Grt}		X_{Fe}^{Cpx}		X_{Fe}^{Hbl}	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10v	0.82	0.81	0.63	0.61	0.58	0.53	0.40	0.40	0.11	0.12	—	—	—	—
143	0.57	0.56	0.30	0.35	0.27	0.27	0.27	0.30	0.04	0.02	—	—	—	—
73v	0.78	0.76	0.60	0.56	0.50	0.47	—	—	0.013	0.028	—	—	—	—
1159/2-a	0.53– 0.57	0.56	—	—	0.18– 0.24	0.27	0.29	0.29	0.025– 0.027	0.027	—	—	—	—
127-g	0.73	0.70	—	—	0.35	0.37	0.30	0.28	0.06	0.04	—	—	—	—
SCh-9/129	0.80	0.80	0.53	0.56	—	—	0.35	0.35	0.18	0.18	0.44	0.40	*	0.36
SCh-5/58	0.57	0.59	—	—	—	—	0.35	0.35	0.18	0.21	0.31	0.23	*	0.41
136-e	0.80	0.80	0.51	0.57	—	—	0.49	0.48	0.20	0.27	0.42	0.41	0.59	0.53
39-e	0.81	0.82	0.65	0.60	—	—	0.35	0.35	0.16	0.19	—	—	—	—
A-138	0.80	0.79	0.16	0.12	0.43– 0.57	0.43	0.44– 0.49	0.47	0.16	0.12	—	—	0.46	0.50

Note: X_{Fe}^{Grt} , X_{Fe}^{Opx} , X_{Fe}^{Bt} , X_{Fe}^{Cpx} , and X_{Fe}^{Hbl} are the Fe/(Fe + Mg) ratios of garnet, orthopyroxene, biotite, clinopyroxene, and hornblende, respectively; X_{An}^{Pl} is the anorthite mole fraction of plagioclase; and X_{Ca}^{Grt} is the Ca/(Ca + Mg + Fe + Mn) ratio of garnet. An asterisk denotes that the mineral not analyzed, and a dash means that the mineral is absent in the assemblage.

cates, the composition of plagioclases, and Fe and Ca contents in garnets were the main parameters for the verification of an adequate model solution. It was found that the oxidation potential of external fluid plays a key role in the successful modeling. In addition, the formation of a model assemblage adequate to the observed assemblage was strongly affected by the water/rock ratio (W/R) and relative amounts of H₂O and CO₂ controlling the stability of hydrous silicates and assemblages in general.

The modeling was based on the chemical compositions of rocks assuming the inert behavior of all components of the system. It is usually assumed that the composition of deep fluids corresponds to the C–O–H system, and it was previously demonstrated that the fluids of the granulite facies is strongly reduced (Avchenko et al., 1998, 2009). This allows us to use a reduced compressed gas as a proxy for the external fluid. The contribution of the water component of the fluid to the solubility of the major components of rocks (Mg, Fe, etc.) can be considered insignificant (Avchenko et al., 1998; Khudolozhkin, 2007). There are several reasons for the use of a reduced compressed gas rather than an aqueous fluid.

(1) The Selektor-C code employs the modified Debye–Huckel equation. It is valid for aqueous fluids with ionic strengths from 0.1 to 1.0, and its use is limited to temperatures up to ~500°C and pressures up to ~4–5 kbar. Outside these ranges, there are significant deviations of calculations from experimental or natural data (Khudolozhkin, 2007).

(2) If the fluid phase contains a complex electrolyte, the potentials of all components, including oxygen, are uniform in model solutions (in the fluid–mineral assemblage pair) under the conditions of thermodynamic equilibrium. Of course, in the model solutions, equilibrium with respect to oxygen potential is retained also at the elimination of electrolyte from the model, which allows us to use a reduced compressed gas and obtain more accurate results.

(3) Owing to the small amount of fluid (fluid/rock ratio is much less than 1), the effect of dissolution on the composition of the mineral assemblage is very limited and concerns mainly quartz, to a lesser extent K–Na feldspars, and almost negligibly Fe–Mg silicates. The results of modeling showed that Ca, Fe, and Mg were almost lacking in the water–carbon dioxide fluid, and the compositions of minerals remained undisturbed (Avchenko et al., 2010, pp. 173–175; Khudolozhkin, 2007).

RESULTS AND DISCUSSION

The results of the modeling of mineral assemblages are compared with natural observations in Table 2. The table illustrates the degree of agreement between the model solution and natural assemblages. The calculated oxygen fugacity values under given *P–T* conditions in the external and local fluid in the mineral assemblages are given for several model solutions ($f_{O_2}^{I-IV}$) in Table 3. Some discrepancies between the calculated and observed assemblages are related to the imperfection of solid solution models implemented in

Table 3. (1) Observed and (2) model mineral assemblages under given P - T conditions and calculated oxygen fugacity values, $f_{\text{O}_2}^{\text{I-IV}}$

Sample no.	No.	Mineral assemblage	P_s , bar	T , °C	$\log f_{\text{O}_2}^{\text{I}}$	$\log f_{\text{O}_2}^{\text{II}}$	$\log f_{\text{O}_2}^{\text{III}}$	$\log f_{\text{O}_2}^{\text{IV}}$
10v	1	$\text{Grt} + \text{Opx} + \text{Pl} + \text{Bt} + \text{Qtz}$	6200	740	-16.9	-17	-12.7	-17
	2	$\text{Grt}_{22} + \text{Opx}_{52} + \text{Pl}_{16} + \text{Bt}_{7.8} + \text{Qtz}_{1.1} + \text{Ilm}_{0.3}$						
143	1	$\text{Grt} + \text{Opx} + \text{Pl} + \text{Bt} + \text{Crd} + \text{Qtz} + \text{Rt}$	5200	740	-16.7	-17.2	-11.4	-17.2
	2	$\text{Grt}_{14} + \text{Opx}_4 + \text{Pl}_{3.4} + \text{Bt}_{9.3} + \text{Crd}_9 + \text{Qtz}_{59.9} + \text{Rt}_{0.2}$						
73v	1	$\text{Grt} + \text{Opx} + \text{Kfs} + \text{Bt} + \text{Qtz}$	5000	700	-17.8	-18	-14	-18
	2	$\text{Grt}_{21.9} + \text{Opx}_{22.9} + \text{Kfs}_{1.0} + \text{Bt}_{4.9} + \text{Qtz}_{49} + \text{Ilm}_{0.3}$						
1159/2-a	1	$\text{Grt} + \text{Pl} + \text{Bt} + \text{Sil} + \text{Kfs} + \text{Qtz} + \text{Ilm} + \text{Rt}$	7000	750	-16.4	-16.7	-11.6	-16.7
	2	$\text{Grt}_{7.7} + \text{Pl}_{31.4} + \text{Sil}_{4.8} + \text{Kfs}_{0.5} + \text{Bt}_{11.9} + \text{Qtz}_{43} + \text{Rt}_{0.4} + \text{Grt}$						
127-g	1	$\text{Grt} + \text{Pl} + \text{Bt} + \text{Sil} + \text{Qtz}$	6800	700	-17.5	-17.7	-11.1	-17.8
	2	$\text{Grt}_{7.5} + \text{Pl}_{24.7} + \text{Bt}_{14.5} + \text{Sil}_{10.5} + \text{Qtz}_{42.5} + \text{Rt}_{0.1}$						
SCh-9/129	1	$\text{Grt} + \text{Opx} + \text{Cpx} + \text{Hbl} + \text{Pl} + \text{Mag} + \text{Ilm}$	7500	750	-14.9	-15.6	-11.8	-16.7
	2	$\text{Grt}_{19.8} + \text{Opx}_{10} + \text{Cpx}_{24.7} + \text{Hbl}_{13.5} + \text{Pl}_{28} + \text{Ilm}_{3.4}$						
SCh-5/58	1	$\text{Grt} + \text{Cpx} + \text{Hbl} + \text{Pl} + \text{Mag} + \text{Ilm}$	12000	900	-9.9	-12.5	-7.7	-13.6
	2	$\text{Grt}_{40} + \text{Cpx}_{22.7} + \text{Hbl}_{16} + \text{Pl}_{18.6} + \text{Ilm}_{2.5}$						
39-e	1	$\text{Grt} + \text{Opx} + \text{Kfs} + \text{Pl} + \text{Qtz} + \text{Mag} + \text{Ilm}$	6500	710	-13.7	-16.7	-13	-16.7
	2	$\text{Grt}_{31.5} + \text{Opx}_{15.6} + \text{Kfs}_{17.6} + \text{Pl}_{0.03} + \text{Qtz}_{24.8} + \text{Mag}_{9.6} + \text{Ilm}_{0.8}$						
136-e	1	$\text{Grt} + \text{Opx} + \text{Cpx} + \text{Hbl} + \text{Pl} + \text{Qtz} + \text{Mag} + \text{Ilm}$	6000	750	-12.6	-16.1	-12.1	-16.8
	2	$\text{Grt}_{6.7} + \text{Opx}_{3.1} + \text{Cpx}_{1.3} + \text{Hbl}_{48.3} + \text{Pl}_{37.6} + \text{Qtz}_{1.4} + \text{Mag}_{0.2} + \text{Ilm}_{1.2}$						
A-138	1	$\text{Grt} + \text{Opx} + \text{Kfs} + \text{Bt} + \text{Hbl} + \text{Pl} + \text{Qtz} + \text{Ilm} + \text{Mag}$	6400	740	-13.2	-16.3	-12.5	-16.7
	2	$\text{Grt}_{5.1} + \text{Opx}_{2.7} + \text{Kfs}_{0.1} + \text{Bt}_{4.6} + \text{Hbl}_{11} + \text{Pl}_{31} + \text{Qtz}_{44} + \text{Ilm}_{3.5} + \text{Mag}_{1.2}$						

Note: $\log f_{\text{O}_2}^{\text{I}}$ is the oxygen fugacity in a model mineral assemblage adequate to the real assemblage in equilibrium with external fluid (model solution, reservoir no. 2); $\log f_{\text{O}_2}^{\text{II}}$ is the oxygen fugacity of external fluid without its interaction with rock in the solution variant (reservoir no. 1); $\log f_{\text{O}_2}^{\text{III}}$ is the intrinsic oxygen fugacity of the rock calculated at an infinitesimally small amount of fluid (reservoir no. 2); $\log f_{\text{O}_2}^{\text{IV}}$ is the oxygen fugacity of fluid in the C–O–H system under the conditions of its saturation with respect to graphite and under given P - T conditions; and the numerical subscripts show the volume percentages of minerals obtained in the model solution.

Selektor-C and, primarily, the lack of Ti end-members in model *Opx*, *Bt*, and *Hbl*. As a result, the excess Ti content in the models produces hemoilmenite instead of magnetite. The volume fractions of minerals in each model assemblage (Table 3) are similar to visual estimates for the real assemblages (not shown because of their low accuracy).

Two results presented in Table 3 are important for the understanding of the formation of the oxygen regime. First, after a satisfactory model solution is obtained, the oxygen fugacity of fluid (from the first reservoir) producing the assemblage can be considered as the potential of the external fluid, $f_{\text{O}_2}^{\text{II}}$. Second, the model of rock interaction with a negligible amount of external fluid entering from the first reservoir allows us to estimate the intrinsic oxygen potential ($f_{\text{O}_2}^{\text{III}}$), which could be imposed by the rock itself (more precisely the mineral assemblage) without the participation of an

external fluid under given P - T parameters. The calculated compositions of minerals in such model assemblages are, of course, different from the observed characteristics. It is assumed that this potential formally corresponds to the redox state of the rock and its local intrinsic (pore) fluid. In these models, the intrinsic oxidation potential ($f_{\text{O}_2}^{\text{III}}$, Table 3) is significantly higher than that obtained in the model solutions. The reason is that the model assemblage is in equilibrium with a negligible amount of fluid and manifests its own oxygen buffer capacity. When the rock is equilibrated with the necessary amount of reduced fluid producing the real assemblage, lower $f_{\text{O}_2}^{\text{I}}$ values are established. Using this feature, it is possible to estimate the contributions of oxygen potentials (capacities) of the rock and fluid necessary for the formation of the real fluid–rock equilibrium.

A comparison of $f_{\text{O}_2}^{\text{I}}$ and $f_{\text{O}_2}^{\text{II}}$ values for the samples discussed here allows us to divide them into two groups on the basis of the redox response of the rock to the influence of the reduced external fluid. Two variants of model solutions were obtained.

(1) The oxygen fugacity of external fluid from the first reservoir, $f_{\text{O}_2}^{\text{II}}$, is buffered by the rock in the second reservoir at $f_{\text{O}_2}^{\text{I}}$. The equilibrium values of oxygen fugacity in the second reservoir are higher, sometimes by several orders of magnitude, than the values in the first reservoir. In such a case, the model solution characterizes the inert behavior of oxygen (samples SCh-5/58, 39-e, 136-e, and A-138 in Table 3). Such an oxygen regime is established in the metabasites whose mineral assemblages include magnetite and (or) hemoilmenite. The appearance of oxide minerals in these rocks, their amounts, and the composition of solid solutions are consequences of the approach to equilibrium of the two reservoirs. The oxide minerals are indicators of the prevalence of the oxygen buffer capacity of the mineral assemblage over the capacity of the deep reduced fluid. It is reasonable to suppose that an increase in the mass of metamorphic fluid (for instance, owing to an increase in rock permeability) can transform the oxygen regime into a perfectly mobile state (changing the mineral assemblage). During modeling, an increase in the Fe/(Fe + Mg) ratio of silicates, the attainment of its maximum for the given composition of rock, and a decrease in the amount of oxide minerals up to their complete disappearance can be used as formal indicators for such a transition. In this connection, it is noteworthy that Korzhinskii suggested as early as 1937 that the behavior of oxygen during metamorphism can be transitional between perfectly mobile and inert (Korzhinskii, 1937).

(2) The oxygen fugacity of external fluid from the first reservoir imposes the same potential in the rock reservoir. Such an oxygen regime appeared to be typical of metapelites whose assemblages were free of magnetite and (or) hemoilmenite (samples 10v, 143, 73v, 1159/2-a, 127-g, and SCh-9/129 in Table 3). These model solutions correspond to the perfectly mobile oxygen regime, when the reducing capacity of fluid at given metamorphic P - T conditions dominates the capacity of the rock assemblage. The perfectly mobile behavior of oxygen can also be observed when the intrinsic oxygen fugacity is initially similar or identical to the oxygen fugacity of external fluid, for instance, in the presence of carbon in the rock (sample 1159/2-a in Table 3).

The use of the method of minimization for the modeling of “mute” (with respect to f_{O_2}) rocks free of oxide minerals (samples 10v, 143, 73v, 127-g in Table 3) allowed us to constrain f_{O_2} (at any model of external fluid) by the calculation of the boundaries of magne-

tite and (or) hemoilmenite disappearance (or appearance) in the mineral assemblage. For instance, the complete association of sample 127-g at $T = 700^\circ\text{C}$ and $P = 6.8$ kbar cannot be produced at $\log f_{\text{O}_2} = -16$ (contains magnetite), but can be formed at lower values, for instance, $\log f_{\text{O}_2} = -18.5$. In the model solution, the assemblage adequate to the natural one appears at $\log f_{\text{O}_2} = -17.5$ (Table 3). Thus, important information can be gained by the method of thermodynamic potential minimization for rocks containing a mute mineral assemblage.

It should be pointed out that the model solutions do not provide distinct correlations between the oxygen regime, P - T conditions, bulk iron content in the rock, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and rock/fluid ratio. This is related to the simultaneous dependence of the buffer capacity of an assemblage on pressure, temperature, phase composition, and the compositions of minerals, as well as the amount, component composition, and f_{O_2} of the deep fluid forming the assemblage.

It is interesting that the oxygen fugacity values obtained for metamorphic rocks by chromatographic and electrochemical investigations are close to the CCO buffer (Avchenko et al., 1998, 2009), which is consistent with the results of modeling for the estimation of the degree of external fluid oxidation. It is conceivable that, on a regional scale, the geochemical profile of the external metamorphic fluid of the Okhotsk and Sutam complexes is characterized by a reducing regime at an oxygen fugacity level close to or lower than CCO.

CONCLUSIONS

(1) Using the method of thermodynamic potential minimization for a series of granulite-grade metamorphic rocks (metapelites and metabasites), a dual regime of oxygen behavior was established, perfectly mobile and inert, depending on the presence or absence of magnetite and (or) hemoilmenite in the assemblage. It was concluded that the oxygen regime of a natural assemblage is controlled by the degree of complete or partial leveling of oxygen potential between the deep reduced fluid and the rock in accordance with their oxygen capacities.

(2) The obtained results demonstrated that oxygen fugacity values obtained by the methods of phase correspondence for the natural assemblages of granulites containing magnetite and ilmenite, i.e., crystallizing at an inert oxygen regime, may correspond to a local fluid in equilibrium with the mineral assemblage rather than to an external (regional) fluid.

(3) The use of the minimization method for metamorphic rocks free of oxide minerals allows constraining the upper boundary of oxygen fugacity for the “mute” mineral assemblage.

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