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GEOCHEMISTRY

Experience of Modeling the Garnet + Orthopyroxene + Spinel + Plagioclase Reaction by the Method of Thermodynamic Potential Minimization

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Relative to the method of phase correspondence, physicochemical modeling of mineral associations based on the method of thermodynamic potential minimization and consideration of solid solutions offers new opportunities [1]. Although the thermodynamic database of end members and the models of mineral solid solutions are not sufficiently accurate, the high potential of the method based on minimization for the solution of several petrological issues is evident. The present paper shows an implication of this method for thermodynamic analysis of the garnet reaction structure, for which oxygen pressure and fugacity cannot be estimated by conventional thermobarometry.

Solid inclusions in alkaline basalts of the Konfetka paleovolcano in Primorye [2] contain fragments of fractured garnet crystals replaced by orthopyroxene–spinel–plagioclase symplectite along fractures and the periphery (figure). Bright orange stilpnomelane is developed locally in the reaction rim. The symplectite has a specific composition (Table 1). Orthopyroxene shows appreciable variations in the Al_2O_3 content: a lower concentration (2.9–3.4 wt %) at the contact with garnet than at the contact with spinel and plagioclase (9.5–10.3 wt %). Plagioclase is also heterogeneous. Its composition varies from An_{84} to An_{60}. At the same time, the Fe mole fraction of orthopyroxene and spinel is nearly constant. However, the spinel composition is characterized by a lower degree of oxidation ($Fe^{3+}/\Sigma Fe$ = 8.1–11.8 at %, Table 1). The compositional heterogeneity of minerals emphasizes the nonequilibrium state of the symplectite rim, at least, with respect to the Al_2O_3 potential.

Elucidation of *PT* constraints of the garnet replacement by the orthopyroxene–spinel–plagioclase symplectite can provide insight into the genesis of garnet inclusions. The equilibrium temperature of the orthopyroxene–spinel system can be estimated approximately by the Liermann–Ganguly method [3]:

$$T(\mathrm{K}) = \frac{1373(\pm 165) + 12.1P(\mathrm{kbar}) + 2558(\pm 180)X_{\mathrm{Cr}}^{\mathrm{Sp}}}{\ln K_D + 0.55(\pm 0.13)},$$

where $K_D = \frac{(\mathrm{Fe}^{2+}/\mathrm{Mg})^{\mathrm{Sp}}}{(\mathrm{Fe}^{2+}/\mathrm{Mg})^{\mathrm{Opx}}}$ and $X_{\mathrm{Cr}}^{\mathrm{Sp}}$ is the Cr mole fraction of spinel.

Since this equation is valid for high-Cr systems, the temperature calculated for the equilibrium of orthopyroxene and low-Cr spinel in the reaction rim (1100–1150°C) may be slightly overestimated. It is impossible to obtain a more or less precise estimate of the garnet decomposition pressure because of the absence of reliable geobarometers and chemical nonequilibrium (with respect to the Al_2O_3 potential) of coexisting minerals for the Opx–Pl–Sp association.

We shall attempt to elucidate constraints of the symplectite structure formation using the minimization method based on the Selektor-S software package. The principles of this method are given in [4, 5]. Let us emphasize only that the modeling was based on internally consistent thermodynamic data [6] taking into account the solid solution models for garnet, orthopyroxene, clinopyroxene, cordierite, amphibole, olivine, spinel, staurolite, and ilmenite. The thermodynamic properties of mineral solid solutions were mainly adopted from the Holland and Powell models [7, 8]. The SiO_2–TiO_2–Al_2O_3–Fe_2O_3–FeO–MnO–MgO–CaO–

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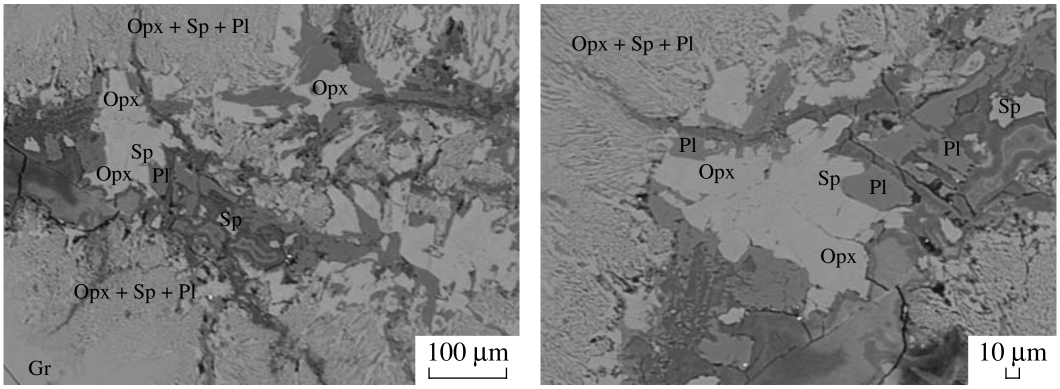

Structure of reaction veinlets in garnet. JXA-8100 microanalyzer. (Gr) Garnet; (Opx) orthopyroxene; (Sp) spinel; (Pl) plagioclase.

Na_2O–K_2O–H_2O–CO_2 system calculated by the Selektor-S program included 50 components, which compose the main observed (or possible) minerals of the granulite-facies (quartz, plagioclase, orthopyroxene, clinopyroxene, garnet, cordierite, amphibole, olivine, magnetite, hematite, spinel, native iron, graphite, corundum, sillimanite, kyanite, and andalusite). Amphibolite-facies minerals (epidote, zoisite, and clinozoisite) were included to constrain the solution. Fluid was modeled by a simple gas system consisting of six components (H_2O, CO_2, CH_4, CO, H_2, O_2). The standard fluid used at the first stage of investigation con-

Table 1. Chemical compositions (wt %) and crystallochemical formulas of garnet and minerals of the reaction structure

Mineral	Gr		Sp			Pl			Opx			
	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	39.19	39.24	–	–	–	47.69	50.23	51.38	50.02	47.09	45.78	46.36
Al_2O_3	21.60	21.31	58.91	59.73	59.18	33.01	32.33	31.36	2.93	9.75	10.34	10.32
Cr_2O_3	–	–	0.12	0.35	0.25	–	–	–	–	–	–	–
Fe_2O_3	–	–	3.90	3.29	3.55	–	–	–	–	–	–	–
FeO	22.62	22.54	26.13	26.41	26.97	0.94	1.25	0.77	28.29	28.16	27.06	26.84
MnO	0.92	0.88	0.52	0.45	0.49	–	–	–	1.14	1.14	1.10	0.97
MgO	9.65	9.37	9.17	9.39	8.89	–	–	–	16.35	14.54	15.04	15.04
CaO	5.96	5.79	–	–	–	16.22	14.92	12.26	0.87	0.69	0.62	0.76
Na_2O	–	–	–	–	–	1.43	1.44	4.07	–	–	–	–
K_2O	–	–	–	–	–	0.35	0.60	0.33	–	–	–	–
Total	99.94	99.13	98.75	99.62	99.33	99.63	100.77	100.77	99.59	101.36	99.93	100.28
Si	2.996	3.021	–	–	–	2.209	2.306	2.334	1.936	1.786	1.752	1.767
Al	1.945	1.993	1.918	1.932	1.926	1.801	1.749	1.678	0.134	0.436	0.466	0.463
Fe^{2+}	1.443	1.449	0.610	0.606	0.623	0.036	0.048	0.029	0.914	0.892	0.864	0.854
Fe^{3+}	-	-	0.082	0.068	0.074	–	–	–	–	–	–	–
Mn	0.059	0.057	0.012	0.01	0.011	–	–	–	0.037	0.036	0.036	0.031
Mg	1.099	1.075	0.378	0.384	0.366	–	–	–	0.943	0.822	0.857	0.854
Ca	0.488	0.478	–	–	–	0.805	0.733	0.596	0.036	0.028	0.025	0.031
Na	–	–	–	–	–	0.128	0.128	0.358	–	–	–	–
K	–	–	–	–	–	0.021	0.035	0.019	–	–	–	–
f, X_{An}	56.77	57.42	61.7	61.2	63	0.84	0.82	0.60	49.23	52.04	50.20	50.00

Note: Mineral abbreviations in Tables 1, 2, and 4: (Gr) Garnet, (Sp) spinel, (Pl) plagioclase, (Opx) orthopyroxene, (Ol) olivine. $f = Fe^{+2}/Fe^{+2} + Mg$ at %; (X_{An}) anorthite content in Pl. The Fe_2O_3 content in spinels is adjusted to stoichiometry. (–) Below the detection limit. Minerals were analyzed with a JXA-8100 microprobe at the Far East Geological Institute, Vladivostok (A.A. Karabtsov, analyst).

Table 2. Chemical compositions (wt %), volumetric ratios of minerals, and $\log f_{O_2}$ value in models 1 and 2 at $P = 4$ kbar and $T = 1000°C$

Component	Model 1			Model 2			
	Sp	Opx	Pl	Sp	Opx	Ol	Pl
SiO_2	–	49.93	46.83	–	49.85	33.59	46.83
Al_2O_3	53.89	4.36	34.19	58.80	3.98	–	34.19
Fe_2O_3	10.73	–	–	4.18	–	–	–
FeO	25.93	27.81	–	29.05	29.17	48.61	–
MgO	9.45	17.89	–	7.97	17.00	17.80	–
CaO	–	–	17.28		–	–	17.28
Na_2O	–	–	1.68		–	–	1.68
Total	100	99.99	99.98	100	100	100	99.98
f, X_{An}	61	47	0.85	67	49	60.5	0.85
vol %	15	43	42	12.7	36.4	8.7	42.1
$\log f_{O_2}$	–9.14			–10.27			

sisted of CO_2, C, and H_2O concentrations equal to 0.001, 0.01, and 0.004 mol/100 g rock. This approach made it possible to obtain a fluid/rock ratio of approximately 1 : 30, which corresponded to conditions of fluid buffering by the rock. At the subsequent stages, the amounts of carbon and oxygen were changed slightly to obtain a mineral association closest to the observed one at the output of the system.

Since we assumed that appearance of the Opx–Pl–Sp reaction paragenesis is mainly related to the decay of garnet, garnet corresponding to analysis 1 (Table 1) was taken as the initial chemical composition of the rock (vector B). A small amount of sodium oxide (0.59 wt) was added, because the reaction rim included plagioclase. Sodium oxide can be present as a minor component in high-pressure garnets. In addition, the primary paragenesis could contain a small amount of jadeite-rich pyroxene and plagioclase before the reaction.

We used two models to solve the problem. In the first model, the reaction rim was supposed to form at 1000°C, which is rather close to the temperature based on the orthopyroxene–spinel geothermometer [3]. The pressure needed for the formation of the Opx–Pl–Sp paragenesis due to vector B was found for each specified temperature. In the second model, we determined the two-element vector of temperature and pressure $\theta^T = (T, P)$ for the specified T, P field. At the same time, we solved the inverse problem of convex programming; i.e., we calculated the optimal θ value, which would minimize the specific criterion function—the sum of standard deviations of known (specified) and calculated (at different *TP* values) mole fractions of phases in the system. In other words, we attempted to find simultaneously *TP* values at which vector B can produce the Opx–Pl–Sp paragenesis closest to the observed association in terms of the mole fractions of phases. The T, P field was specified within a sufficiently wide range (800–1100°C and 3–8 kbar, respectively).

Mineral and fluid compositions based on the first model (Tables 2, 3) show that the Opx–Pl–Sp association is produced from garnet at $P = 4$ kbar. Moreover, only this triple association is formed at a $\log f_{O_2}$ value equal to –9.14 (Table 2, model 1). If the $\log f_{O_2}$ value is higher (–10.3), the Opx–Pl–Sp association is supplemented with a small amount of olivine (Table 2, model 2). It is evident from Tables 1 and 2 that the Fe mole fraction of spinel and orthopyroxene and the Ca mole fraction of plagioclase virtually coincide with actual compositions of these minerals. However, the spinel in model 2 is more oxidized than the real spinel. In model 2, the spinel is close to the real one in terms of the degree of oxidation (Tables 1, 2). If we neglect the minor amount of olivine, the calculated paragenesis turns out to be identical with the real one. Table 4 shows grading of the garnet paragenesis into the Opx–Pl–Sp association with decrease in pressure along the 1000°C isotherm.

In model 2, the Opx–Pl–Sp paragenesis with a small amount of olivine appeared at $T = 4$–4.5 kbar and $T = 800$–$950°C$. Variations in *PT* values were related to different degrees of the specified oxidation of the system. The best approximation to real compositions were achieved at $T = 845°C$, $P = 4.5$ kbar, and $\log f_{O_2}$ equal

Table 3. Chemical composition and logarithm of oxygen fugacity in models 1 and 2 at $P = 4$ kbar and $T = 1000°C$

Model	CO_2	CO	H_2	H_2O	$\log f_{O_2}$
1	30.5	0.06	0.01	69.43	–9.14
2	32.38	0.23	0.03	67.36	–10.27

Table 4. Quantitative ratios of mineral phases (vol %) and $\log f_{O_2}$ value at pressure variation from 4 to 14 kbar (T = 1000°C) in model 2

P, kbar	Sp	Opx	Pl	Gr	Cpx	Ol	$\log f_{O_2}$
4	12.7	36.4	42.1	–	–	8.7	–10.2
6	10.5	29.4	39.4	11.2	–	9.5	–10.1
8	3.3	–	16	73.2	–	7.5	–10.2
10	5	–	2	81	12	–	–10.3
12	3.9	–	0.1	85.2	10.8	–	–9.6
14	3.9	–	–	85.6	10.5	–	–9.7

to –12.4. The appearance of a small amount of olivine in the calculated models can be explained differently. For example, a small amount of stilpnomelane could be formed in the rim due to the replacement of olivine. According to the alternative assumption, the above phenomenon could be provoked by some inaccuracies in the thermodynamic model of the spinel solid solution or the initial composition of vector B. In addition, the structure itself also bears distinct signs of nonequilibrium. Therefore, the calculated association cannot be identical with the observed one. However, the results of the modeling undoubtedly show that the triple Opx–Pl–Sp association is really produced by garnet (with a composition similar to that of analysis 1 in Table 1) at relatively low pressures (<6 kbar). Such Mg- and Ca-rich garnets are relatively high-pressure minerals. At pressure higher than 10–12 kbar, they can enter the eclogite paragenesis (Table 4). Therefore, we can assume that the garnet xenoliths entered the magma at high pressures. Consequently, they were rapidly transported to the intermediate chamber formed at the level of 4–5 kbar. The magma was exhumed after its short-term residence at this level.

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