

THE ROLE OF fO_2 REGIME IN EVOLUTION OF MANTLE METASOMATISM AND DIAMOND FORMATION.

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The relationship between metasomatism and general metamorphism in deep-seated xenoliths from the Udachnaya pipe makes it possible to recognize two major metasomatism stages. Metasomatic associations texturally equilibrated with the primary minerals belong to the early stage: graphite + phlogopite + sulfides (Galimov et al., 1989), phlogopite + apatite (Solovjeva et al., 1994), phlogopite + ilmenite. Metasomatic associations develop among the primary mineral grains and also as streaky segregations and veinlets. In the first case metasomatic and primary minerals form an integral granoblastic fabric and relatively large mica flakes (0.2 - 2 mm) are usually deformed. Metasomatizing fluids seem to be introduced in subcontinental lithosphere during the entire rock metamorphism.

The primary and metasomatic mineral composition of this stage for two characterizing samples are given in table 1. One margin in common type granular spinel lherzolite xenolith (218 / 87) is fringed by mica plates (0.2 - 1 mm) and fine ilmenite grains developed at 1 cm of the margin. O_2 from intergrowth with phlogopite significantly more ferruginous compared to O_1 in xenolith that indicate the absence of total chemical equilibrium during the metasomatism. Sp_1 from lherzolite and Ilm from selvage are poorly oxidized. Narrow dark rims on phlogopite plates (Phl₂) and submicroscopic Ti-magnetite grains (Sp_2) enclosed in them are already belonging to later metasomatic stages. Blocks (0.8 - 3 cm) of orthopyroxene deformed megacryst in the sample 68 / 83 are healed by fine-grained granoblastic aggregate from diopside, mica and apatite also filling two thin veinlets. The former small melting areas composed by submicroscopic serpentine, calcite and magnetite material are related to phlogopite and apatite. Exsolved pyroxene megacrystals are healed by garnet, pyroxene, mica and graphite granoblastic aggregate in two garnet pyroxenites from the Udachnaya pipe, described by Galimov et al., (1989).

Table 1

Sample	(218 / 87) Spinel lherzolite with a Phl - Ilm selvage									(68 / 83) Pyroxenite with Phl , Ap		
Oxide, wt.%	Ol ₁	Ol ₂	Opx	Cpx	Sp ₁	Sp ₂	Phl ₁	Phl ₂	Ilm	Opx	Cpx	Phl
SiO ₂	40.62	40.25	55.88	54.31	-	-	41.65	38.30	0.02	55.76	52.52	40.90
TiO ₂	-	0.01	-	-	-	17.0	3.05	3.45	57.20	0.03	0.19	4.36
Al ₂ O ₃	-	-	3.79	3.39	46.32	4.0	11.14	14.95	0.13	3.47	4.69	14.74
Cr ₂ O ₃	-	0.01	0.65	0.82	22.72	1.0	0.74	0.79	1.06	0.47	0.83	1.12
Fe ₂ O ₃	-	-	-	-	1.03	-	-	-	2.16	-	-	-
FeO	7.44	11.53	4.86	1.68	10.92	63.0*	4.89	4.91	23.55	6.25	2.16	2.75
MnO	0.04	0.14	0.11	0.02	0.24	-	-	-	0.39	0.11	0.06	-
MgO	51.93	48.06	34.11	16.78	18.34	15.0	23.54	22.70	15.75	33.74	14.56	19.99
CaO	-	0.04	0.40	22.20	-	-	-	-	0.13	0.15	22.24	-
Na ₂ O	-	-	0.02	1.01	-	-	0.31	0.13	-	-	1.47	0.29
K ₂ O	-	-	-	0.02	-	-	9.72	9.90	-	-	-	9.62
NiO	0.37	0.28	0.07	0.02	0.16	-	0.16	0.09	0.08	0.10	0.05	0.24
total	100.4	100.32	99.89	100.25	99.73	100.0	95.20	95.22	100.47	100.08	98.77	94.01
(557 / 80) Garnet-olivine websterite with metasomatic phlogopite and chromite						(233 / 82) Garnet harzburgite (lherzolite ?) with primary chromite and graphite						
	Gnt	Opx	Cpx	Chr	Phl	Ol	Gnt	Opx	Chr	Sp	Phl	
SiO ₂	42.15	58.35	55.96	0.44	43.75	41.77	40.78	58.69	-	0.10	39.99	
TiO ₂	0.01	0.02	0.10	0.85	0.26	-	-	-	-	0.44	1.82	
Al ₂ O ₃	18.54	0.39	2.76	3.38	11.72	-	17.08	0.32	7.26	34.43	13.58	
Cr ₂ O ₃	6.94	0.30	4.91	57.62	0.62	0.02	8.96	0.22	65.69	29.75	2.18	
Fe ₂ O ₃	-	-	-	-	-	-	0.23	-	-	6.39	-	
FeO	7.90	5.34	3.10	23.32*	3.64	7.22	6.91	4.58	14.92	10.91	3.96	
MnO	0.46	0.11	0.09	0.66	0.03	0.10	0.52	0.07	0.55	0.45	0.01	
MgO	20.05	35.17	14.01	9.08	24.33	50.32	19.23	36.71	11.44	16.81	23.28	
CaO	5.09	0.32	15.64	-	0.01	0.02	6.05	0.26	-	-	0.02	
Na ₂ O	-	-	4.38	-	0.20	-	-	0.15	-	-	0.24	
K ₂ O	-	-	0.02	-	11.26	-	-	-	-	-	9.74	
NiO	-	-	-	0.04	0.06	0.36	-	-	-	0.12	0.11	
total	101.14	100.00	100.97	95.39	95.88	99.81	99.76	101.00	99.86	99.40	94.93	

* total iron as FeO

The late metasomatism is pervasive in deep-seated xenoliths of various lithology, it is largely examined in kimberlites elsewhere in the world and is usually believed to be a precursor of kimberlite magmatism. Two subsequent processes can be revealed. At early step metasomatic phlogopite and titanous chromite replace the primary garnet and the clinopyroxene is recrystallized into chains of fine Cr-diopside grains. Reactional phlogopite, chromite and Cr-diopside form irregular areas, "ponds". The chromite composition ($0.7 - 2.2\% \text{ TiO}_2$; $3.1 - 5.6\% \text{ Al}_2\text{O}_3$; $57.6 - 58.8\% \text{ Cr}_2\text{O}_3$; $0.88 - 0.93 \text{ Cr}/(\text{Cr}+\text{Al})$; $0.54 - 0.59 \text{ fm}$) approaches to least chromian chromites of diamondiferous peridotitic paragenesis that possibly due to high reduced fluid regime of the prekimberlite metasomatism initial stage. The primary (Ol, Opx, Gnt) and syngenetic (Phl, Chr, Cr-Di) mineral compositions from garnet olivine websterite (557 / 80) are listed in table 1. The next stage of this metasomatic process is represented by characteristic reactional rims on primary and early stage metasomatic minerals. Reactional rims on garnet include Al-pyroxenes, mica, inhomogenous spinel (from Cr-spinel to magnetite), amphibole. Orthopyroxene is replaced on margins by acicular amphibole, the submicroscopic clinopyroxene, spinel, magnetite grains. Primary sulfides are replaced by djerfisherite. Rare ilmenite can be identified in this stage products. Spinel composition related to late metasomatism exhibit continuous series from titanous chromites through Cr-spinel to magnetites (Sp_2 in 218 / 87), that seem to be testified the fluid change from reduced at the beginning of metasomatic cycle to oxidized one at the end. The late metasomatism is sometimes followed by partial rocks melting. This process results in rounded, composed by polycrystalline submicroscopic aggregates which include Ti-amphibole, Ti-phlogopite, spinelids, calcite, rare zone olivine and oxidized ilmenite, isotropic serpentine.

The primary and metasomatic mineral compositions from garnet harzburgite (Iherzolite?) with discrete chromite grains and single graphite plates (233 / 82) belonging to the primary assemblage are given as example. Chromite chemistry is similar to that of chromites from diamond inclusions and diamondiferous peridotites, and it practically does not contain ferric iron. The late submicroscopic oxidized Cr-spinel and fine-flaked phlogopite form narrow external kelyphitic rims on garnet and intergrained segregations.

In order to evaluate the fluid $\lg f\text{O}_2$ of late prekimberlite metasomatic stage we used Spenser's and Lidzley's method (1981) for estimation of coexisting spinel-ilmenite pairs from the following associations:

1. Former melting areas in reactional rims on primary minerals of enstatite eclogite (88/85);
2. Polycrystalline submicroscopic inclusions (Ti-Phl, Cc, Ilm, Sp, Serp) in Cr-poor garnet megacryst (C-52);
3. Polycrystalline submicroscopic inclusions of the same composition in Cr-poor garnet megacryst from deformed peridotite (UV-303);
4. Fine-grained ilmenite-phlogopite MARID-type orthopyroxenite (195 / 82).

Estimated $\lg f\text{O}_2$ values are plotted on and above the FMQ curve (Fig.1). The points corresponding to Ilm-Sp inclusions in compositionally heterogeneous ($0.4-0.6\% \text{ TiO}_2$; $3.3-5.5\% \text{ Cr}_2\text{O}_3$; $12.5-13.3\% \text{ FeO}$; $7.7-10.5\% \text{ CaO}$) Ca-rich garnet megacryst from the Udachnaya pipe chemically similar to some megacrysts reveal analogous position but at higher temperatures. These data together with high $\lg f\text{O}_2$ values obtained by Haggerty and Tompkins (1983) for ilmenite megacrysts suggest that prekimberlite asthenosphere derived fluids have been strongly oxidized. On the contrary, the starting of the late metasomatic process took place under reduced conditions that propose asthenospheric fluid $f\text{O}_2$ inversion in the range of entire diamond and kimberlite-forming cycle, discussed in the proposed model (Fig.2)

The model consists of two stages: (I) the subcontinental lithosphere plate (L) with incorporated ancient cratons is geodynamically compressed preventing heat and magma escape. A change of the convective heat flow in the asthenosphere (A) by the conductive one in the lithosphere causes a temperature rise of $300-400^\circ\text{C}$ under the lithosphere base resulting in the appearance of a discontinuous melt layer. The asthenospheric melting layer is a membrana which mainly allows passage of mobile hydrogen and noble gases. The hydrogen flow involves a series of gas reaction: $2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_4 + \text{C} + 4\text{H}_2\text{O}$; $2\text{CO} + 4\text{H}_2 \rightarrow \text{CH}_4 + \text{C} + 2\text{H}_2\text{O}$; $3\text{NO} + 6\text{H}_2 \rightarrow 2\text{NH}_3 + \text{N} + 3\text{H}_2\text{O}$. This leads to diamond (D) crystallization in the upper boiling melt layer, redox-metasomatism (IW), diamond growth in the deepest lithosphere ($> 150 \text{ km}$), as well as to Green and Taylor's "redox-melting" with the formation of "eclogite" melts. On the contrary, deeper horizons of the asthenospheric melt layer are inversely more oxidized (FMQ). Melt layer is a barrier for the asthenospheric diapirs.

(II) Removal of geodynamic vice, loosening of the lithosphere plate and rifting. As a consequence, flowing of asthenospheric melts up into the rift and their partial freezing to uplifted parts of the lithosphere base (cumulus of crystals -C) take place. When the weakened zone of the plate sliding along the asthenosphere, happens to occur directly above the ascending convective stream (Cs), the

asthenospheric diapirs (D) with entrained diamond-bearing substance rush through the lithosphere. Kimberlitic liquids separate in the upper part of rising diapirs due to their partial melting.

References

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Fig.1 T - lg fO₂ relations for coexisting Ilm - Sp pairs from late metasomatic products and melting areas in deep-seated xenoliths, megacrysts and ilmenite-phlogopite orthopyroxenite of MARID-type, the Udachnaya and Mir (C-52) pipes (crosses); for Ilm -Sp pairs, included in Ca-rich garnet megacryst, the Udachnaya pipe (closed circles); Ilm -Sp pairs in ilmenite megacrysts from West Africa (open circles) and buffers MnO - Mn₃O₄, FMQ, MW, IW from Haggerty and Tompkins (1983).

Fig.2 The model of diamond formation. Dashed line gr-di is the graphite-diamond boundary.

