10IKC-028

THE ALKALINE MINERALS FROM THE MANTLE XENOLITHS OF KIMBERLITE PIPES OF YAKUTIA

L.N. Pokhilenko and T.A. Alifirova

V.S. Sobolev Institute of Geology and Mineralogy SB RAS, 3Koptyuga ave., Novosibirsk, 630090, Russia

Introduction

Lately Cl-, F-, P- and alkaline minerals found in kimberlite, mantle xenoliths and diamonds attract attention of specialists.

Fig.1. Salt xenolith in the the fresh nonserpentinized kimberlite of the Udachnaya pipe (Yakutia). The picture was taken immediately after crushing of the enormous blok of a very dense kimberlite. July 2011.

Phlogopite, apatite, sodalite, potassium feldspar, tetraferryphlogopite, galite, sylvite, alkaline carbonates and sulfates were discovered among the accessory minerals of mantle xenoliths from unchanged kimberlite of Udachnaya pipe (Yakutia) (Golovin et al., 2007, Kamenetsky et al., 2007, Pokhilenko, 2009, Pokhilenko and Pokhilenko, 2010). Besides, sulfides of different composition, including the K-Cl-bearing sulfide - djerfisherite $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$ (Golovin et al., 2008, Sharygin et al., 2008, Pokhilenko et al., 2010) and Cl-free K-sulfide, were found in the interstices, micro-cracks and matrix of main minerals of those xenoliths (Pokhilenko et al., 2011).

We devote this paper to a discussion of the deep metasomatic origin of such minerals uncovered in micro-cracks, inclusions, compound reaction rims around the garnets from the phlogopite-bearing pyroxenites and phlogopite-ilmenite-bearing ultrabasite of the kimberlite pipe Udachnaya. The findings of alkaline minerals were also noted for the exsolution structures in garnets of websterite and pyroxenite from kimberlite pipes Mir and Udachnaya and exsolution lamellae in clinopyroxene of eclogite from Obnazhennaya pipe.

Garnet-orthopyroxenites

Samples UV-92/03, UV-46/92 (Udachnaya pipe) represent partially recrystallized enstatite megacrystals. Large enstatite domains with isometric or elongated garnet (for both samples), graphite and phlogopite grains (for UV-92/03) are the essentials of the sample (Fig. 2).

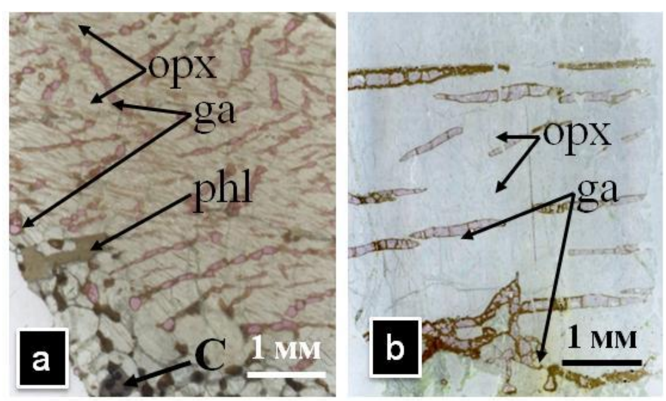


Fig.2 UV-92/03 (a), UV-46/92 (b).

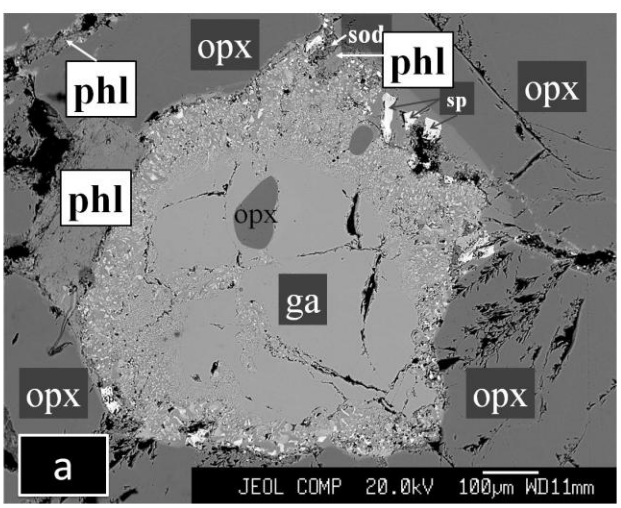
Garnet occurs as oriented vermicular intergrowths, chains of small grains between orthopyroxene blocks and isometric grains beyond orthopyroxene. Garnet isolations are surrounded by reaction rims, which mainly consist of nonequilibrium pyroxenes with varying degree of alumina and highly alumina spinel, sodalite, potassium feldspar, apatite and phlogopite. The many kinds of accessory minerals were also found in the orthopyroxene matrix, interstices, microcracks.

Table-1 demonstrates total mineral compositions of the xenoliths.

Table-1. **Mineral compositions of the xenoliths UV92/03, UV46/92. Opx – orthopyroxene, Cpx – clinopyroxene, Ga – garnet, Phl – phlogopite, Ol – olivine, Sp – spinelide, Gr – graphite, Ap – apatite, Sod – sodalite, K-fls – potassium feldspar, Su – sulfide. Щелочные минералы выделены курсивом.**

Sample	Main minerals	Minerals from the garnet rim	Minerals from the opx-matrix, interstices, micro-cracks
UV92/03	Opx, Ga, *Phl*	Al-Opx, Al-Cpx, Al-Sp, *Phl*, *Sod*, *Ap*, *K-fls*	Gr, Ol, *Phl*, Cpx, *Sod*, *K-fls*, *Ap*, Cr-Ti-Sp, *$CaCO_3$*, *KCl*, Fe-Ni and *K-Su*
UV46/92	Opx, Ga	Al-Opx, Al-Cpx, Al-Sp, *K-fls*, *Phl* placed around the garnet rim	Ol, Cpx, *Phl*, Cr-Ti-Sp, *Ap*, *$CaCO_3$*

Phlogopite is presented in both samples as big grains in orthopyroxene matrix, ingrowths, small grains or fine-grain masses in the intergrain space or cracks, mineral of garnet rims. Last is distinguished by the elevated TiO_2, Al_2O_3, Cr_2O_3, Na_2O and FeO content and reduced SiO_2, MgO content as compared to the phlogopite from the orthopyroxene matrix (Fig.3a). Apatite, potassium feldspar, sodalite were found among the minerals of the rims around garnet (Fig. 3b). Sylvite was discovered in interstice between the orthopyroxene, phlogopite and minerals of the garnet rim of sample UV92/03. K-sulfides isolations were situated in the micro cracks together with phlogopite, tetraferry-phlogopite, and Ca-carbonate (Fig. 3c), rarely high Mg# and Si# olivine and high Mg# clinopyroxene intergrowth.



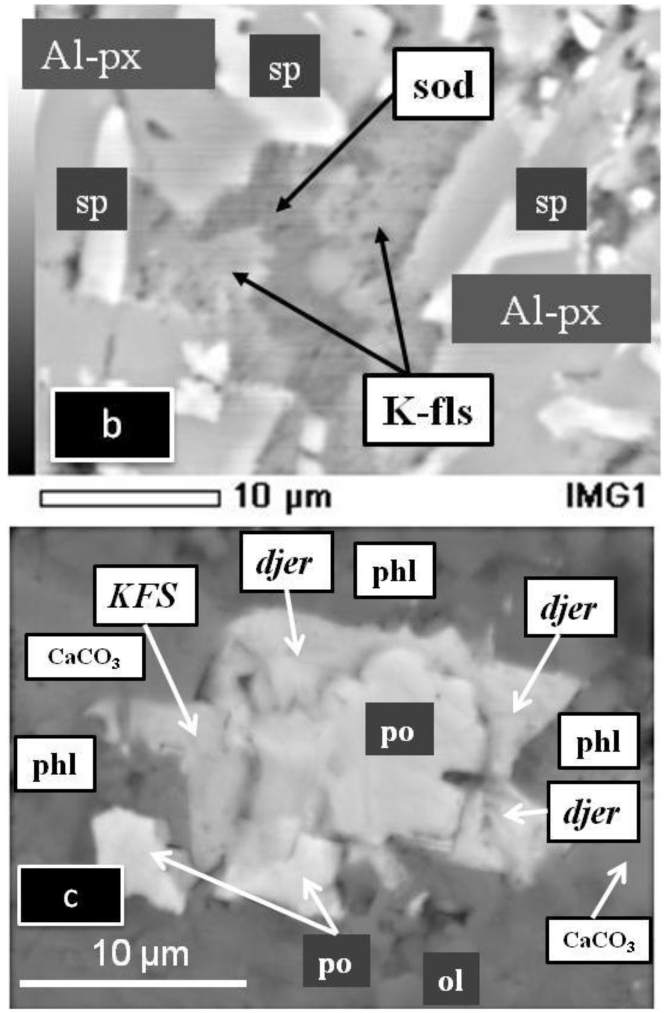


Fig. 3. a – phlogopite as a rockforming mineral, as a mineral of garnet rim and as a mineral filling up the microcrack, b – sodalite and potassium feldspar among the minerals of garnet rim, c – pyrrhotite (po) and K-sulfides (djer – djerfisherite and KFS – Cl-free K-su) among the minerals filling up the mickrocrack.

Ilmenite ultrabasite

Ilmenite ultrabasite UV-162/09 (Fig. 4) was studied with the help of an electron scanning microscopy, x-ray microprobe analysis. The following mineral phases have been found and analyzed: olivine (two generations), ilmenite (two generations), orthopyroxene, garnet (two generations), clinopyroxene, phlogopite (two or more generations), Ca-carbonate, Ti-magnetite, spinel (zoned), tetraferryphlogopite, sodalite, Fe-Ni-Cu-sulfides (with exsolution structures), djerfisherite (changing composition), barite, galite, apatite, perovskite. Many kinds of the alkaline minerals of this rock is shown in Fig.5.

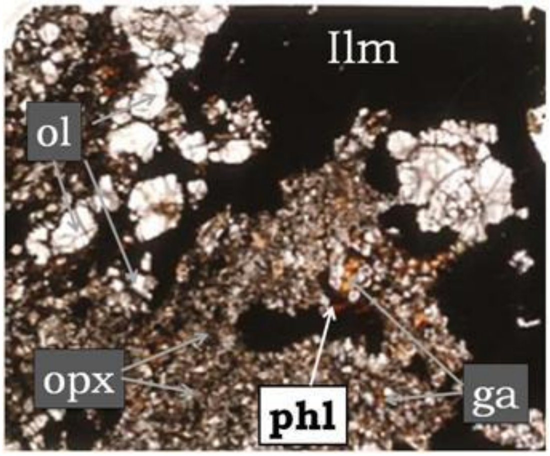
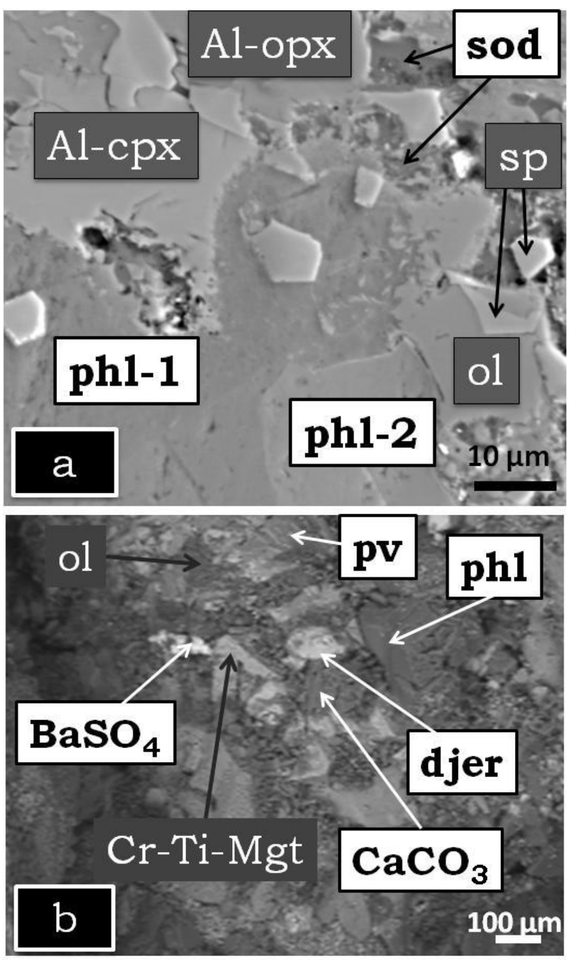


Fig. 4. Main minerals of Ilmenite ultrabasite UV-162/09

Phlogopite displays wide variations of its composition in TiO_2 (0.4-3.2 wt.%), Cr_2O_3 (0.05-1.2 wt.%), FeO (2.5-6.9 wt.%). Also tetraferryphlogopite has a variable composition at FeO (11-15 wt.%).



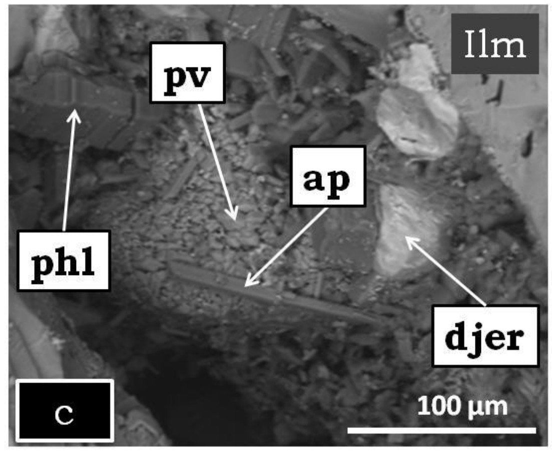


Fig. 5. a – two generation of phlogopite, sodalite among the minerals of Ilm ultrabasite UV162/09; b,c – minerals filling the pinholes in the sample: pv – perovskite, phl – phlogopite, ap – apatite, djer – djerfisherite, $BaSO_4$ - barite, $CaCO_3$.

Exsolution structures

Oriented prisms of F-apatite (wt %: CaO 54.7, P_2O_5 41.9, FeO 0.42, F 2.7, Cl 0.74) with a thickness up to 40–50 µm and a length up to 400 µm parallel to rutile and ilmenite lamellae were observed in garnet of phlogopite-garnet orthopyroxenite UV70/03 from the Udachnaya pipe (Fig. 6). This allowed us to assume the exsolution nature of apatite and consider its origin to be synchronous to other minerals exsolved from host garnet, i.e., Ti minerals, namely rutile and ilmenite.

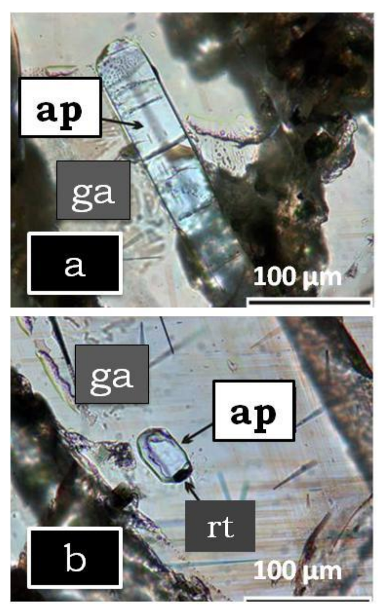


Fig. 6. Transmitted light image of apatite (ap) in garnet (ga): a – large oriented apatite plate; b – diphase inclusion of apatite (ap) and rutile (rt) together with thin lamellae of rutile and ilmenite.

The processes of cpx decomposition in eclogite O-160 (Obnazhennaya pipe, Yakutia) are complex and multifarious. In addition to garnet, corundum, kyanite lamellae there is a phase with cryptocrystalline structure in clinopyroxene matrix. The oxide proportion in this phase allowed us to look upon it as anortite (Fig.7).

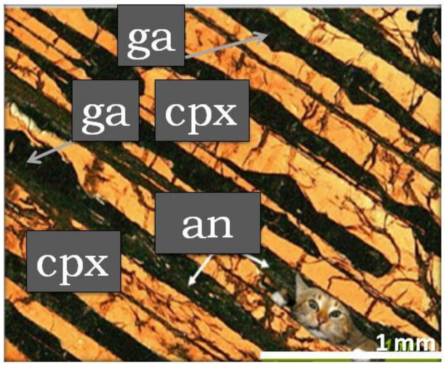
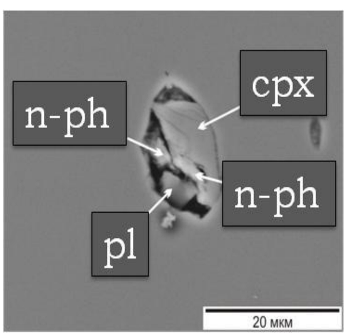


Fig. 7. Transmitted light image of polyphase lamellae garnet+anortite in the clinopyroxene of eclogite O-160 from the Obnazhennaya pipe.

The compound lamella (cpx + Na-Plagioclase + 2 nonequilibrium complex phases) was found in the garnet of phlogopite-bearing websterite M5/01 (Mir pipe) together with lamellae of rutile, ilmenite, clino- and orthopyroxenes (Fig. 8). We suppose that plagioclase is not immediate product of exsolution of the initial garnet. It was formed at the expense of clinopyroxene lamella exsolution.



	Cpx	Pl	Initial Cpx
SiO_2	56,8	71,6	56,1
TiO_2	0,45	0,00	0,00
Al_2O_3	4,88	15,9	4,06
Cr_2O_3	0,80	0,00	3,88
FeO	1,21	0,00	2,50
MnO	0,00	0,00	0,00
MgO	13,70	0,00	13,51
CaO	19,0	1,18	15,2
Na_2O	3,25	10,5	4,82
K_2O	0,00	0,87	0,00
Sum	100,0	100,0	100,0

Fig. 8. Back scattered electron image of polyphase lamella of clinopyroxene (cpx), plagioclase (pl), and nonequilibrium phases (n-ph) in garnet (cross section). Chemical compositions (wt %) of clinopyroxene and Na-plagioclase lamellae in garnet from olivine websterite M5/01: composition of clinopyroxene from complex lamella in garnet obtained on a scanning electron microscope; reconstructed composition of primary clinopyroxene lamella (Initial cpx) before exsolution of plagioclase and nonequilibrium phases from it.

Discussion

The appearance of Cl-bearing and alkaline minerals in the mantle xenoliths is conditioned probably by their secondary enrichment in the deep mantle horizons, which was caused by the general preparation of substrate to kimberlite formation.

At that time hot melts containing aggressive fluids accumulated in the mantle areas adjacent to our rocks. This stage is related to large phlogopite grains in opx-matrix of UV92/03. Next stages of mantle metasomatism connect with the beginning of the formation of reaction rims around garnet, which are mainly made of ortho-, clinopyroxenes of different aluminum content and enlarged and zonal spinel at the rim periphery. UV92/03 garnet rim also contains phlogopite enriched in Ti, Al, Cr as compared to the matrix phlogopite. UV46/92 phlogopite, which edges the rim, is also enriched in these components. This fact can points to discrete or stepwise nature of metasomatic effect. During the capture of the studied rocks by alkali enriched kimberlite melt and transport to the surface they underwent further transformations. Probably the transportation didn't occur immediately but with short stop somewhere at the crust boundary. Potassium feldspar, cryptocrystalline phlogopite of different composition (enriched in K and Si), which contains apatite and clinopyroxene and sometimes calcium carbonate in the cracks point to the fact. UV92/03 was recovered from the block of fresh kimberlite, which didn't subject to serpentinizatoion and other changes. Variety of alkaline minerals supports this fact. Thus sodalite (Na-enrichment) occurs in the garnet rim at this stage and sylvite was found in the interstitial space between opx blocks, large phlogopite grain and garnet rim. Small grains of K-containing sulfides (first microns) djerfisherite and Cl-free KFe-sulfide were noted in the micro cracks.

Interesting finds of Ca, F, P, and alkali bearing minerals in the exsolution structures in minerals of mantle xenoliths also provide evidence for the multistage nature and heterogeneity of mantle enrichment and the important role of these components in the formation and deep transformations of rocks.

Anorthite lamella appeared in the pyroxene matrix of eclogite O-160 (Obnazhennaya pipe, Yakutia) can be interpreted as a final stage of decomposition of cooling pyroxenes, because according to the experimental data it is stable in this system up to P = 2.5-2.7 Gpa and T = 1100-1200^{o}C. The equations reflecting the process of orthopyroxene matrix breakup could be written like

$CaAl_2SiO_6 + Al_2SiO_5 \rightarrow CaAl_2Si_2O_8$(anortite)$+Al_2O_3$;

$2CaAl_2SiO_6+2Ca_{0.5}AlSi_2O_6 \rightarrow 3CaAl_2Si_2O_8$(anortite).

To explain the exsolution of plagioclase ftom cpx-lamella of phlogopite-bearing websterite M5/01 (Mir pipe) with such a composition (Fig. 8), we should mention that (1) the main endmembers in the reconstructed composition of initial pyroxene from complex lamella are jadeite ($NaAlSi_2O_6$) and juriite ($NaCrSi_2O_6$) (16.9 mol % of the jadeitic endmember, 10.8 mol % of the juriitic endmember, and 5.2 mol % of the aegirine endmember), whereas newly formed pyroxene is characterized by a high portion of the aegirine ($NaFeSi_2O_6$ endmember (12.3 mol %), significantly lower jadeite content (11.4 mol %), and absence of juriite; (2) the complex lamella contains two nonequilibrium phases with a high chromium concentration (these phases are most likely represented by thin intergrowths of minerals, presumably chromite and silicate). Based on the above mentioned facts, we suggest the following reaction of plagioclase formation:

$(NaAlSi_2O_6 + 2NaCrSi_2O_6 + 3FeSiO3)$(Na-C-Al-pyroxene) $+1/2O_2 \rightarrow NaAlSi_3O_8$(albite)+2NaFeSi2O6(Na-Fe-pyroxene) $+(FeCr_2O_4 + 2SiO_2)$ (nonequilibrium phase?, intergrowths?).

It is necessary to mention the prevailing role of Na at a definite stage of the formation of this phlogopite bearing rock, i.e., high potassic rock. Most likely there was stepwise rock enrichment first in Na and Ti (during crystallization of the primary garnet) and then in K (during the formation of phlogopite).

Conclusion

Presence of the alkaline minerals in the deep-seated mantle xenoliths could be explained by 1) the influence of kimberlite melt (Sharygin et al., 2008), or 2) metasomatic treatment of the rock before its keeping by kimberlite (Egorov et al., 2004, Pokhilenko, 2009, Pokhilenko et. al., 2010). In any case there was multistage mantle process, where alkalies (Na, K, Ca) and Cl, F, P played an appreciable part.

Finds of phlogopite, apatite, carbonates, K-sulfides in the diamond (Logvinova et al., 2008) confirm the deep-seating of the process. A very wide range of PT-condition of examined samples, several generation of phlogopite and presence of water-containing phlogopite and water-soluble sylvite in the same place of one sample suggest the multistep process. (Pokhilenko, 2009).

Metasomatic enrichment (introducing the Ti, Ca, Na, P, F) of initial garnets from the websterite M5/01 and the phl-orhtopyroxenite UV70/03 had an effect on the composition of exsolution phases, wich were formed as a result of changing P-T-fO_2-conditions.

References

Egorov, K.N, Solov'eva, L.V and Simakin, S.G (2004) Megacrystalline Cataclastic Lherzolite from the Udachnaya Pipe: Mineralogy, Geochemistry, and Genesis // Dokl. Akad. Nauk, 397 (1), 88–92 [Dokl. Earth Sci. 397, 698].

Golovin, A.V, Sharygin, V.V and Pokhilenko N.P (2007) Melt inclusions in olivine phenocrysts in unaltered kimberlites from the Udachnaya-East pipe, Yakutia: Some aspects of kimberlite magma evolution during late crystallization stages. // Petrologiya 15 (2), 178–195 [Petrology 15, 168].

Golovin, A.V., Sharygin, I.S, Korsakov, A.V, Kamenetsky, V.S and Pokhilenko N.P (2008) Alkali- and Cl- enriched carbonate-silicate melt inclusions in sheared lherzolite xenoliths from unaltered kimberlites of the Udachnaya-East pipe (Yakutia) // 9th International Kimberlite Conference, Frankfurt, Germany, Extended Abstract No 9IKC-A-00061.

Kamenetsky, V.S, Kamenetskaya, M.B, Sharygin, V.V, Golovin, A.V (2007) Carbonate-chloride enrichment in fresh kimberlites of the Udachnaya-East pipe, Siberia: a clue to physical properties of kimberlite magmas? // Geophys. Res. Lett., v. 34, pp. 9316-9321.

Kamenetsky, V.S, Sharygin, V.V, Kamenetskaya, M.B and Golovin, A.V (2006) Chloride-carbonate nodules in kimberlites from the Udachnaya pipe: alternative approach to the evolution of kimberlite magmas. Geochem. Int., v. 44 (9), pp. 935-940.

Logvinova A.M., Wirth R., Fedorova E.N., Sobolev N.V (2008). Nanometre-sized mineral and uid inclusions in cloudy Siberian diamonds: new insights on diamond formation // Eur. J. Miner., v. 20, p. 317—331.

Pokhilenko, L.N (2009) On mineralogy of deep-seated xenoliths – sample UV92/03: rock transformation // in Proc. of the IX Intern. Seminar "Deep Seated Magmatism, Its Sources and Plumes" (Miass, 2009), No. 1, pp. 239–256 [in Russian].

Pokhilenko, L.N and Pokhilenko N.P (2010) Ilmenite Ultrabasite UV162/09: The Role of Deep Metasomatism in the Rock Formation. Goldschmidt Conf. Abstrs, A822.

Pokhilenko, L.N, Pokhilenko N.P and Vladykin N.V (2010) Garnet orthopyroxenites from the Udachnaya kimberlite pipe (Yakutia); features of their composition and origin // in Proc. of the X Intern. Seminar "Deep Seated Magmatism, Its Sources and Plumes" (Sudak, 2010), No. 1, pp. 126-143.

Pokhilenko, L.N, Golovin, A.V., Sharygin, I.S and Pokhilenko N.P (2011) The accessory minerals of the mantle xenoliths: the first finding of Cl-free K-Fe sulphide // Doklady Earth Sciences, 2011, Vol. 440, Part 2, pp. 1404–1409.

Sharygin, V.V, Kamenetsky, V.S, Kamenetskaya, M.B (2008) Potassium sulfides in kimberlite-hosted chloride-"nyerereite" and chloride clasts of Udachnaya-East pipe, Yakutia, Russia. Can Mineral, 46(4): 1079 - 1095.

Sharygin, I.S, Golovin, A.V and Pokhilenko N.P (2008) Melt pockets in sheared garnet lherzolite xenoliths from the Udachnaya-East kimberlite pipe (Yakutia, Russia). XI Intern. Kimberlite Conf. Extended Abstr. 9IKC-A-00213.