OXIDE MINERAL INCLUSIONS IN CR-PYROPES FROM THE ALDANSKAYA LAMPROPHYRE DYKE, YAKUTIA

Rezvukhin D.I.¹, Nikolenko E.I.¹, Sharygin I.S.¹, Malkovets V.G.¹

¹Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk 630090, Russia

m.rezvukhin@igm.nsc.ru

Kimberlite and lamproite/lamprophyre magmas sample a wide variety of xenoliths and xenocrysts from the subcontinental lithospheric mantle (SCLM). Cr-rich pyrope, along with chromite and picroilmenite, is common kimberlite indicator mineral. Xenocrysts of Cr-pyrope from kimberlites and other deep-seated magmatic rocks have been widely used by geochemists in recent decades in order to obtain information about composition and structure of the SCLM. Oxide inclusions within pyropes are of particular interest. Mineralogical studies have shown that pyrope may contain uncommon Ti-rich oxides, such as rutile, picroilmenite, armalcolite, srilankite, carmichaelite, crichtonite group minerals, and other varieties (Varlamov et al., 1996; Wang et al., 1999; Vrana, 2008; Alifirova et al., 2012; Ziberna et al., 2013; Rezvukhin et al., 2016a, 2016b; Malkovets et al., 2016). These inclusions are commonly enriched in rare and incompatible elements and represent composition, which is not typical to depleted peridotites of the lithospheric mantle. Metasomatic origin of Cr-pyrope in the SCLM of ancient cratons is widely discussed in literature on the basis of both mineralogical and geochemical criteria (Hoal et al., 1994; Griffin et al., 1999; Stachel et al., 2004; Malkovets et al., 2007, 2012; Agashev et al., 2013; O'Reilly, Griffin, 2013). Further detailed studies will shed light on the features of pyrope genesis in deep areas of the earth's upper mantle. Here we report the result of investigation of twenty six chrome-rich pyropes with oxide mineral inclusions derived from the eluvium of the Aldanskaya lamprophyre dyke, Aldan province of alkaline magmatism, southeast of the Siberian craton.

Size of studied pyrope grains ranges from 2 to 4 mm. Crystals were implanted in epoxy mounts and polished to bring individual inclusions to the surface. All studied inclusions are primary and are not associated with cracks. Pyrope garnets are predominantly of lherzolitic paragenesis with Cr_2O_3 content from 2.1 to 6.5 wt%. Four Ti- and/or Cr-rich phases have been investigated as inclusions in pyropes: rutile, picroilmenite, chromite and crichtonite group minerals. Inclusions of Ti-oxides are commonly needle- or blade-like, with round or polygonal cross-sections. Laths and tablets are less abundant. Chromite is presented as isometric inclusions, either octahedral or round. Both elongated blades and isometric inclusions are commonly black and opaque, although thin needles of rutile are more brownish. Sometimes needle-like inclusions are strictly oriented in the host pyrope along the certain crystallographic directions. Diameter of studied needle-like inclusions ranges from 5 to 50 μ m and size of isometric chromite inclusions is up to 300 μ m. In studied samples oxide inclusions are in association with silicates (namely olivine, ortho- and clinopyroxene). Oxides may form intergrowths and composite inclusions with each other or with silicates; rutile commonly forms intergrowths with Mg-ilmenite.

Chemical composition of studied inclusions in terms of main constituent components is shown on Fig. 1 (a, b). Composition of inclusions is uniform in a single pyrope host, but varies among different pyrope crystals; however, the scatter is not broad and compositional fields for each mineral are clearly constrained. Similar to host pyrope, inclusions are commonly Cr-rich. There is a positive correlation between Cr content in Ti-oxide inclusions and host garnet. Similar correlations have been recorded previously between Ti-oxide inclusions and host garnets from the Internatsionalnaya pipe (Rezvukhin et al., 2016a, 2016b), as well as in the same mineral association from the ultrabasic diatreme of the Garnet Ridge cluster, Arizona, USA (Wang et al., 1999). Chromite inclusions contain 45.4-58.7 wt% Cr₂O₃. It is interesting to note the significant decrease of Cr₂O₃ content up to 1.5 wt% in host pyrope in thin domains just around the large chromite inclusions. Cr is also the most abundant substituting component in members of the high-Ti association (rutile, picroilmenite, crichtonite group minerals). Cr₂O₃ content in rutile ranges from 2.3 to 7.4 wt%, in picroilmenite from 0.7 to 3.6 wt%.

In chromite inclusions MgO varies from 8.2 to 10.4 wt%, FeO from 22.4 to 26.6 wt%, Al_2O_3 from 8.2 to 20.2 wt%. Chromite also contains up to 1.5 wt% TiO₂. In rutile inclusions TiO₂ content ranges from 89.0 to 98.0 wt%. Except elevated amounts of Cr, rutile contains 0.8-3.3 wt% FeO and up to 0.6 wt% ZrO₂. Mg-ilmenite contains 51.3-57.4 wt% TiO₂, 8.3-13.6 wt% MgO, 25.7-35.5 wt% FeO.

Crichtonite group minerals are rare oxides (titanates) with general formula $ABC_{18}T_2O_{38}$. Crichtonite group minerals are of particular interest due to enrichment in wide variety of incompatible elements, which occupy all four structural positions. Main constituent elements, which fill mostly C and T sites, are in typical range for crichtonite group minerals stable in the lithospheric mantle. TiO_2 is 54.2-67.4 wt%, Cr₂O₃ is 6.9-19.8 wt%, FeO is 7.7-11.6 wt%, and MgO is 1.6-4.1 wt%. Within the group the minerals are distinguished on the basis of dominant cations in A, B, C and T sites. The most important is A site, where large cation of incompatible element is stored. In studied grains 7 cations (Ba, Sr, Na, K, Ca, La, Ce) in A site are presented in different proportions. The dominant cations (at%) are Ca and Ba. B site is occupied by Zr (1.5-5.9 wt% ZrO₂) and Fe. Thus studied crichtonite group minerals are similar to either loveringite (Ca-dominant member of the group) or LIMA series (lindsleyite-mathiasite, Ba and K members of the group, respectively), widely reported from the kimberlites of South Africa (Haggerty et al., 1983; Haggerty, 1991; Konzett et al., 2013). On Fig. 2 the occupancy of A site in different crichtonite group minerals is shown. LIMA series is Ba or K rich, while hitherto reported inclusions in pyropes contain more Ca, Na, LREE or Sr, and the little overlap between fields is presented. Crichtonite group minerals in pyropes from the Aldanskaya dyke somewhat differ in terms of A site occupancy from grains investigated in pyropes from other localities. Compositional points fall in both fields and comprise intermediate trend between LIMA series and Ca/Na/LREE/Sr-rich minerals in pyropes from other localities. However, lindsleyite and mathiasite in kimberlites from the Kaapvaal craton are commonly Al-poor (<1 wt% of Al₂O₃), while inclusions in pyropes are Al-rich (>1 wt% Al_2O_3), including studied grains in pyropes from the Aldanskava dyke, which contain 1-2 wt% Al₂O₃.

The genesis of studied inclusions is debatable. Oxide needles in garnet may result from exsolution processes, or they could be syngenetic or even protogenetic in relation to the host pyrope. It is assumed that Ti-oxides tend to form oriented elongated inclusions in pyrope matrix even if their formation is related to fluid/melt phase. The diameter of studied grains is relatively big; we suggest that formation of large oxide inclusions (especially inclusions of crichtonite group minerals) via exsolution is highly unlikely and they are probably syngenetic with the host pyrope. Nevertheless, Ti-rich mineral association enriched in incompatible elements (Fe, Ti, Ba, Zr and others) in pyropes indicates that these pyropes in the lithospheric mantle underneath the Aldanskaya dyke have metasomatic origin. Incompatible elements were introduced by metasomatic fluid/melt phase, while high chromium content in both pyropes and inclusions was inherited from Cr-rich peridotite protolith, where Cr is concentrated mainly in chromite and subcalcic harzburgitic or dunitic garnet.

Described above mineral association represent conventional set of high-Ti and/or Cr oxides, which is typical for Cr-pyropes from several localities described in literature (Varlamov et al., 1996; Wang et al., 1999; Vrana, 2008; Rezvukhin et al., 2016a, 2016b). However, variations in composition of oxide inclusions in studied pyropes and in other pyropes reported elsewhere indicate on a different composition of metasomatic agent. If compositional features of inclusions reflect the peculiarities of metasomatic phase, then by studying both pyropes and inclusions it is possible to reconstruct geochemical features of parental fluids/melts. Rutile and crichtonite group minerals are important storage sites of incompatible elements in the SCLM. Rutile in metasomatised mantle associations, and as inclusions in pyropes, is often enriched in HFSE, particularly in Nb₂O₅ (Jones et al., 1982; Tollo, Haggerty, 1987; Schulze, 1990; Wang et al., 1999; Konzett et al., 2013; Rezvukhin et al., 2016b). However, neither rutile nor crichtonite group minerals in pyropes from the Aldanskava dyke contain significant Nb or Ta. Crichtonite group minerals in pyropes from the Aldanskaya dyke represent more Ba- and K-rich compositions in comparison with inclusions of these minerals in other pyropes, and several grains almost coincide with LIMA by composition. However, LIMA series from South Africa is lower in Al, and may contain up to 1.5 wt% Nb₂O₅ (Konzett et al., 2013). What is especially notable is that minerals of LIMA series commonly occur in garnet-free phlogopite-K-richterite peridotites (Erlank et al., 1987).

We note finally that pyropes from the Aldanskaya dyke and other lamprophyres of the Chompolo field contain complex association of inclusions: oxides, silicates, sulfides, and composite assemblages consisting of above-mentioned minerals + carbonates and hydrous phases. Thereby metasomatism in the SCLM underneath the Aldan shield is manifold in its occurrences and may be multistage. Further geochemical investigations are required to clarify its exact nature.

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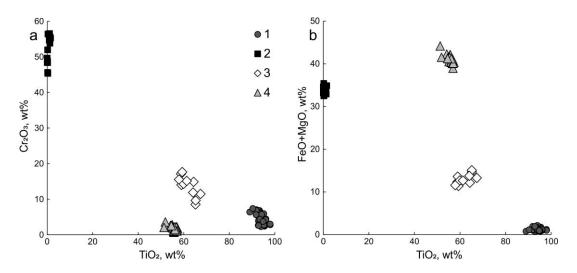


Fig. 1. Composition of oxide mineral inclusions in Cr-pyropes from the Aldanskaya dyke on TiO_2 -Cr₂O₃ (a) and TiO_2 -FeO_{total}+MgO (b) plots. 1 – rutile; 2 – chromite; 3 – crichtonite group minerals; 4 – picroilmenite.

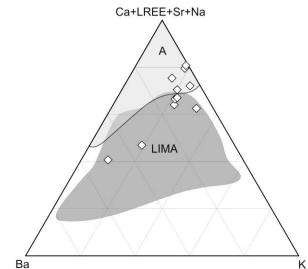


Fig. 2. Composition of inclusions of crichtonite group minerals in Cr-pyropes from the Aldanskaya dyke on the ternary diagram Ba – K – Ca+LREE+Sr+Na (A-site occupancy, at%). Outlined fields: (A) – inclusions in Cr-pyropes from other localities (Wang et al., 1999; Vrana, 2008; Rezvukhin et al., 2016a); (LIMA) – minerals of lindsleyite-mathiasite series from South African kimberlites (Haggerty et al., 1983; Haggerty, 1991; Konzett et al., 2013).

Lindsleyite

Mathiasite

Table1. EMP analyses of crichtonite group minerals in pyropes from the Aldanskaya dyke

Grain	ALD-1	ALD-2	ALD-3	ALD-4	ALD-5	ALD-6	ALD-7	ALD-8	ALD-9	ALD-10	ALD-11
SiO ₂	0.08	0.06	0.10	0.14	0.23	0.10	0.13	0.13	0.16	0.07	0.02
TiO ₂	58.80	58.98	59.32	65.19	64.34	67.40	59.90	61.30	65.21	57.90	64.10
Al_2O_3	1.57	1.42	1.58	1.28	1.43	1.09	1.28	1.47	1.39	1.48	1.02
MgO	2.96	3.11	3.31	3.68	3.59	3.92	3.20	3.46	4.07	3.25	3.80
Cr_2O_3	17.12	13.99	17.63	8.49	14.87	11.47	14.30	15.13	9.62	15.53	11.87
FeO^*	9.32	10.48	8.07	10.99	8.56	9.36	9.47	9.18	11.00	8.32	9.95
BaO	0.88	3.06	1.18	0.32	0.19	0.32	0.64	1.08	0.78	5.07	1.00
SrO	0.50	0.32	0.23	0.51	0.34	0.39	0.60	0.56	0.58	0.25	0.57
Na ₂ O	0.20	0.09	0.21	0.31	0.55	0.61	0.18	0.22	0.26	0.04	0.55
K ₂ O	0.64	0.57	0.65	0.69	0.50	0.54	0.87	0.65	0.63	0.30	0.46
CaO	1.51	0.85	1.47	1.51	1.66	1.59	1.37	1.56	1.67	0.69	1.39
La_2O_3	0.01	0.04	0.05	0.11	n.d.	0.08	0.01	n.d.	0.04	n.d.	n.d.
Ce_2O_3	0.67	1.34	0.65	0.67	0.33	0.40	0.51	0.66	0.68	1.91	0.50
ZrO ₂	4.02	4.65	3.89	4.52	2.27	1.76	5.21	3.37	1.64	4.93	3.00
NiO	0.04	0.03	0.04	0.06	0.02	0.07	0.05	0.06	0.07	0.04	0.07
V_2O_3	0.65	0.91	0.55	0.88	0.60	0.53	0.81	0.70	0.60	0.76	0.47
MnO	0.12	0.10	0.11	0.17	0.16	0.17	0.13	0.14	0.17	0.09	0.13
Nb ₂ O ₅	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HfO ₂	0.06	0.19	0.23	0.18	0.06	n.d.	0.13	0.12	0.07	0.14	0.12
Total	99.14	100.18	99.26	99.69	99.71	99.80	98.78	99.80	98.64	100.78	99.00

n.d. - not determined, *total Fe as FeO.

References:

Agashev AM, Ionov DA, Pokhilenko NP, Golovin AV, Cherepanova Y, Sharygin IS (2013) Metasomatism in lithospheric mantle roots: Constraints from whole-rock and mineral chemical composition of deformed peridotite xenoliths from kimberlite pipe Udachnaya. Lithos 160-161: 201-215.

Alifirova TA, Pokhilenko LN, Ovchinnikov YI, Donnelly CL, Riches AJV, Taylor LA (2012) Petrologic origin of exsolution textures in mantle minerals: evidence in pyroxenitic xenoliths from Yakutia kimberlites. International Geology Review 54(9): 1071-1092.

Erlank A, Waters F, Hawkesworth C, Haggerty S, Allsopp H, Rickard R, Menzies M (1987) Evidence for mantle metasomatism in peridotite nodules from the Kimberley pipes, South Africa. In: Mantle metasomatism, pp. 221-311.

Griffin WL, Shee SR, Ryan CG, Win TT, Wyatt BA (1999) Harzburgite to lherzolite and back again: metasomatic processes in ultramafic xenoliths from the Wesselton kimberlite, Kimberley, South Africa. Contributions to Mineralogy and Petrology 134: 232-250.

Haggerty SE (1991) Oxide mineralogy of the upper mantle. In: Lindsley DH (ed) Oxide Minerals: Petrologic and Magnetic Significance, Vol. 25, pp. 355-416.

Haggerty SE, Smyth JR, Erlank AJ, Rickard RS, Danchin RV (1983) Lindsleyite (Ba) and mathiasite (K): two new chromium-titanates in the crichtonite series from the upper mantle. American Mineralogist 68: 494-505.

Hoal K, Hoal B, Erlank A, Shimizu N (1994) Metasomatism of the mantle lithosphere recorded by rare earth elements in garnets. Earth and Planetary Science Letters 126: 303-313.

Jones AP, Smith JV, Dawson JB (1982) Mantle metasomatism in 14 veined peridotites from Bultfontein mine, South Africa. The Journal of Geology 90(4): 435-453.

Konzett J, Wirth R, Hauzenberger C, Whitehouse M (2013) Two episodes of fluid migration in the Kaapvaal Craton lithospheric mantle associated with Cretaceous kimberlite activity: evidence from a harzburgite containing a unique assemblage of metasomatic zirconium-phases. Lithos 182-183:165-184.

Malkovets VG, Griffin WL, O'Reilly SY, Wood BJ (2007) Diamond, subcalcic garnet, and mantle metasomatism: Kimberlite sampling patterns define the link. Geology 35(4): 339-342.

Malkovets VG, Griffin WL, Pearson NJ, Rezvukhin DI, O'Reilly SY, Pokhilenko NP, Garanin VK, Spetsius ZV, Litasov KD (2012) Late metasomatic addition of garnet to the SCLM: Os-isotope evidence. 10th International Kimberlite Conference, Long Abstract №10IKC-173.

Malkovets VG, Rezvukhin DI, Belousova EA, Griffin WL, Sharygin IS, Tretiakova IG, Gibsher AA, O'Reilly SY, Kuzmin DV, Litasov KD (2016). Cr-rich rutile: A powerful tool for diamond exploration. Lithos 265:304-311.

O'Reilly SY, Griffin WL (2013) Mantle metasomatism. In: Metasomatism and the chemical transformation of rock, Springer, pp. 471-533.

Rezvukhin DI, Malkovets VG, Sharygin IS, Kuzmin DV, Gibsher AA, Litasov KD, Pokhilenko NP, Sobolev NV (2016) Inclusions of crichtonite group minerals in pyropes from the Internationalnaya kimberlite pipe, Yakutia. Doklady Earth Sciences 466(2): 206-209.

Rezvukhin DI, Malkovets VG, Sharygin IS, Kuzmin DV, Litasov KD, Gibsher AA, Pokhilenko NP, Sobolev NV (2016) Inclusions of Cr-and Cr–Nb-Rutile in pyropes from the Internatsionalnaya kimberlite pipe, Yakutia. Doklady Earth Sciences 466(2): 173-176.

Schulze DJ (1990). Silicate-bearing rutile-dominated nodules from South African kimberlites: Metasomatized cumulates. American Mineralogist 75: 97-104.

Stachel T, Aulbach S, Brey GP, Harris JW, Leost I, Tappert R, Viljoen KF (2004) The trace element composition of silicate inclusions in diamonds: a review. Lithos 77(1): 1-19.

Tollo RP, Haggerty SE (1987) Nb-Cr-rutile in the Orapa kimberlite pipe, Botswana. Canadian Mineralogist 25: 251-264.

Varlamov DA, Garanin VK, Kostrovitskiy SI (1996) Exotic high-titanium minerals as inclusions in garnets from lower crustal and mantle xenoliths. Trans Russ Acad Sci Earth Sci 345: 352-355.

Vrana S (2008) Mineral inclusions in pyrope from garnet peridotites, Kolín area, central Czech Republic. Journal of Geosciences 53: 17-30.

Wang L, Essene EJ, Zhang Y (1999) Mineral inclusions in pyrope crystals from Garnet Ridge, Arizona, USA: implications for processes in the upper mantle. Contributions to Mineralogy and Petrology 135: 164-178.

Ziberna L, Nimis P, Zanetti A, Marzoli A, Sobolev NV (2013) Metasomatic processes in the central Siberian cratonic mantle: Evidence from garnet xenocrysts from the Zagadochnaya kimberlite. Journal of Petrology 54(11): 2379-2409.