PYRRHOTITE, PENTLANDITE AND HIBBINGITE FROM METAKIMBERLITES OF UDACHNAYA-VOSTOCHNAYA PIPE, NORTHERN YAKUTIA

Elena L. Sokolova
Fersman Mineralogical museum, RAS, Moscow, mineral@fmm.ru
S.A. Vorob'ev
Faculty of Geology, Lomonosov Moscow State University, mineral@geolo.msu.ru

Kimberlites of numerous pre-trappean pipes and dikes of East Siberia platform have significant amount of lizardite serpentine, which associates with calcite, dolomite, amakinite or brusite, magnetite, goethite, pyrite, quartz, chalcedony, amethyst, smectites, hydrotalcite group minerals, celestine, stroncianite and some ore minerals. This paragenesis witnesses low grade metamorphism of zeolite facies which altered the rocks at various degree. Processes of regional low grade metamorphism usually occur in conditions of high oxidation potential causing formation of hematite and magnetite in metakimberlites. Patches of fresh rock can be found in Udachnaya-Vostochnaya pipe and in some places there is no goethite or magnetite present in very altered rocks. Pyrrhotite and pentlandite occur in abundance instead. Pyrrhotite and pentlandite of the studied samples are closely associated with Cl-containing lizardite and magnesian hibbingite $(Fe^{2+}_{1.55}Mg_{0.42}Mn^{2+}_{0.03})_{2.00}(OH_{2.88}Cl_{0.12})_{3.00}Cl_{1.00}$. Presence of hibbingite confirms our assumption that kimberlite were altered with fluids rich in chlorine. The source of them was chloride brines derived from evaporates that occur in the carbonate-terrigenous sequence hosting Udachnaya-Vostochnaya pipe.
Pyrrhotite composition has high iron content and is very close to FeS, thus the mineral is not magnetic. We need to note that studied metakimberlites do not contain magnetic minerals. Average pentlandite composition corresponds to the formula $(Ni_{4.0}Fe_{4.5}Co_{0.5})_{9.0}S_{8.0}$ with Ni/Co ratio close to the one in primary kimberlite and kimberlitic olivine and is in range from 7.7 to 9.9. Apparently, olivine was the source of Fe, Ni and Co, and sulphur derived from an hydrite-bearing carbonate-terrigenous early Paleozoic host rocks, saturated with bitumen, which often contain sulfur compounds.
3 figures, 2 tables, 16 references.
Keywords: metakimberlite, pyrrhotite, pentlandite, Cl-bearing lizardite, magnesian hibbingite, low grade regional metamorphism, Udachnaya-Vostochnaya pipe.

Kimberlite rocks of numerous pipes and dikes of Siberia platform are always in various degree altered. Practically fresh rock can be adjacent to totally altered patches of rock in the same pipe. Such kimberlites contain significant amount of lizardite serpentine in association with calcite, dolomite, amakinite or brusite, magnetite, goethite, pyrite, quartz, chalcedony, amethyst, smectites, hydrotalcite group minerals, celestine, stroncianite and some ore minerals. Our data confirms that this alteration was caused by hydrothermal metamorphic processes due to post-trappean regional metamorphism of zeolite facies conditions (Sokolova, Spiridonov, 2006; 2007; Sokolova *et al.*, 2010).

The main characteristic of low grade regional metamorphism is irregularity of its manifestations. As it was a fluid-dominated process, parts of the rocks with pores of fractures were the most altered. Metamorphic fluids had as a rule high oxidation potential and their composition was governed by mobile components of country rock and kimberlite itself.

Kimberlites of Udachnaya-Vostochnaya pipe and the host anhydrite bearing early Paleozoic carbonate-terrigenous rocks containing evaporate lenses and sparsely saturated with bitumen, which often contain sulfur compounds, both are very irregularly altered with low grade metamorphism. Fresh kimberlites containing such unstable minerals as shortite can be found near to completely altered rocks.

Size of the altered zones range from tens of centimeters to several tens of meters. Primary olivine phenocrysts were altered into pseudomorphs of carbonate, carbonate-serpentine, saponite, talc-carbonate with phlogopite and tetraferriphlogopite platelets that were altered into chlorite, carbonates, vermiculite and correncite. Cement mass contains sparse ilmenite dissemination, perovskite altered to titanite; individual apatite grains, newly formed ore minerals and so on (Lebedev, 1963; Milashev, 1963; Bobrievich *et al.*, 1964; Franzesson, 1968; Nikishova *et al.*, 1978; Kornilova *et al.*, 1981; Podvysotskiy *et al.*, 1981; Marshintsev *et al.*, 1984; Egorov *et al.*, 1991; Zinchuk, 2000; Sokolova, Spiridonov, 2006; Sokolova *et al.*, 2010). Sulfide minerals form scarce fine dissemination in the volume of altered kimberlite and fill fractures and bunnies in association with carbonates. Iron sulfides dominate: pyrite, pyrrhotite, marcasite, greigite. Some researchers report pyrite concentrations to go up to

Table 1. ***Chemical composition of perovskite (1), ilmenite (2), pycroilmenite (3) and titanomagnetite (4) from metakimberlites of Udachnaya-Vostochnaya pipe***

Component (wt.%)	1	2	3	4
CaO	36.02	–	–	–
MgO	–	–	13.19	10.83
FeO	3.10	44.19	24.35	46.19
MnO	–	2.97	3.38	0.79
Cr_2O_3	–	–	–	25.73
TiO_2	53.12	50.99	55.87	10.20
Al_2O_3	–	–	–	3.19
Nb_2O_5	4.79	0.86	–	–
Total	97.03	99.01	96.79	96.93
Atomic formular coefficients based on total cations				
Ca	0.93	–	–	–
Mg	–	–	0.46	0.55
Fe^{2+}	0.06	0.94	0.47	0.43
Mn	–	0.06	0.07	0.02
Fe^{3+}	–	0.01	0.01	0.91
Cr	–	–	–	0.70
Ti	0.96	0.98	0.99	0.26
Al	–	–	–	0.13
Nb	0.05	0.01	–	–
Total	2	2	2	3

Note: Analyses were done in the laboratory of Fersman Mineralogical museum of the RAS with electron microprobe JEOL JCXA-50A. Analytical conditions: acceleration voltage 20 kV, energy dispersive spectrometer, probe current 20 nA. Standards: ilmenite USNM 96189 (Fe, Ti, Mn), metallic Nb, omphacite USNM 110607 (Ca, Mg, Al), chromite USNM 117075 (Cr). Images were taken with CamScan-4D electron microscope. Analyst A.A. Agakhanov.

1 – 2% in some parts of altered pipes and dikes. Galena, sphalerite, chalcopyrite, pentlandite, millerite, makinavite, tochilinite and other sulfides occur in much smaller amounts. Brief descriptions and single analyses of these minerals are published in some works dedicated to minerals of altered kimberlites (Ilupin, 1962; Ilupin *et al.*, 1990; Zinchuk, 2000), but their origin was not discussed.

We studied drill coresamples from 430 m level, which were taken from the contact of Udachnaya-Vostochnaya kimberlite pipe with host dolomite-bearing rocks. Kimberlite was obviously altered but many small relict pieces of the primary rock can be found in it. Fine grained quenching zone 0.1 – 0.7 mm thick was found along the contact. Phlogopite platelets and long olivine phenocrysts were elongated parallel to the contact in a narrow zone. Olivine was completely altered in the samples studied. Knitted and platy pseudomorphs of lizardite with thin inclusions of dolomite and calcite formed in place of olivine. Fringy saponite aggregate formed around the pseudomorphs (Sokolova *et al.*, 2010). The main mass of the rock is formed by metamorphic calcite, saponite, phlogopite platelets that partially were substituted with corrensite and individual grains of apatite and relicts of Nb-containing perovskite $(Ca_{0.93}Fe^{2+}_{0.06}Nb^{2+}_{0.01})_{1.00}(Ti_{0.96}Nb_{0.04})_{1.00}O_{3.00}$ and Nb-containing ilmenite $(Fe^{2+}_{0.94}Mn_{0.06})_{1.00}(Ti_{0.98}Fe^{3+}_{0.01}Nb_{0.01})_{1.00}O_{3.00}$, pycroilmenite $(Mg_{0.46}Fe^{2+}_{0.47}Mn_{0.07})_{1.00}(Ti_{0.99}Fe^{3+}_{0.01})_{1.00}O_{3.00}$ (table 1), newly formed pyrrhotite and pentlandite.

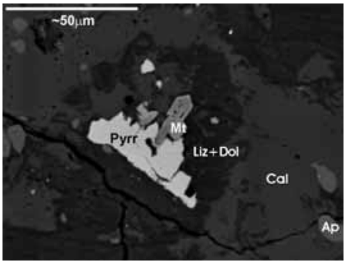
Pyrrhotite rarely forms dissemination in the cementing mass of the metakimberlite (fig. 1). Its composition shown in the table 2 was averaged from analyses of 10 grains. The mineral is quite pure and corresponds to the formula $Fe_{0.982}S_{1.000}$ (до $Fe_{0.984}S_{1.000}$). High iron pyrrhotite associated with mackinawite was discovered in Udachnaya-Zapadnaya pipe (Ilupin *et al.*, 1990).

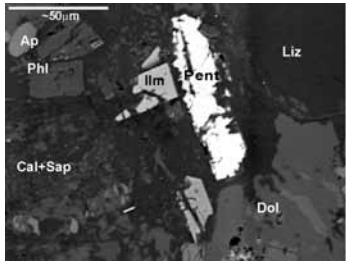
Pyrrhotite with high iron content is practically unmagnetic. Its composition reflects that activity of sulphur, which binds with iron first, was not high in the fluid. Pyrrhotite was found intergrown with primary high chromium magnesian titanomagnetite of the composition $(Mg_{0.55}Fe^{2+}_{0.43}Mn_{0.02})_{1.00}(Cr_{0.70}Al_{0.13}Fe^{3+}_{0.91}Ti_{0.26})_{2.00}O_{4.00}$ (table 1) with iron content f = 56.3. These minerals are in place of olivine phenocrysts totally altered into lizardite-dolomite aggregate.

Pyrrhotite formation could follow the reaction, which involved magmatic calcite. The products of the reaction were pyrrhotite, lizardite and dolomite:

$$20(Mg_{0.9}Fe_{0.1})_2SiO_4 + 6CaCO_3 + 4H_2S + 16H_2O + 6CO_2 = 10Mg_3Si_2O_5(OH)_4 + 4FeS + 6CaMg(CO_3)_2.$$

Pentlandite was found much less quantity in the studies metakimberlites as crystals in cementing mass (figure 2). Composition of pentlandite was measured in 6 grains (table 2). The variation of it was not significant and content of admixtures was below the methods' detection limit. The average pentlandite composition corresponds to the formula $(Ni_{4.0}Fe_{4.5}Co_{0.5})_{9.0}S_{8.0}$, Ni/Co ratio was constantly in the range from 7.7 to 9.9, which is close to the elements' ratio in the primary rock and in olivine from kimberlites (Barmina, Frenkel, 1981). Primary olivine is deemed to be the source of Fe, Ni and Co in pentlandite. These elements were not carried out as they were not mobile and were deposited in situ in newly formed minerals. Anhydrite-bearing early Paleozoic carbonate-terrigenous host





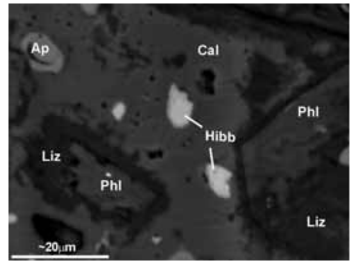


Figure 1. Metamorphic pyrrhotite (Pyrr) in intergrowth with high chromium magnesium titanomagnetite (Mt) in completely altered olivine phenochryst, replaced with lizardite-dolomite aggregate (Liz+Dol) surrounded by calcite (Cal) with individual apatite grains (Ap). Backscattered electron (BSE) image.
Figure 2. Crystal of metamorphic pentlandite (Pent) with calcite (Cal), phlogopite (Phl), ilmenite (Ilm), apatite (Ap) in carbonate-lizardite (Dol, Liz) and calcite-saponite (Cal+Sap) aggregate. Backscattered electron (BSE) image.
Figure 3. Magnesium hibbingite (Hibb) in calcite (Cal) with phlogopite (Phl), lizardite (Liz), apatite (Ap). Backscattered electron (BSE) image.

Table 2. **Chemical composition of pyrrhotite (1-10) and pentlandite (11-16) from metakimberlite of Udachnaya-Vostochnaya pipe**

Components (wt.%)	Fe	Ni	Co	S	Total	Formula	Ni/Co
1	62.16	–	–	36.29	98.45	$Fe_{0.983}S_{1.000}$	–
2	62.69	–	–	36.79	99.48	$Fe_{0.980}S_{1.000}$	–
3	62.53	–	–	36.48	99.01	$Fe_{0.984}S_{1.000}$	–
4	62.33	–	–	36.38	98.71	$Fe_{0.983}S_{1.000}$	–
5	61.78	–	–	36.11	97.89	$Fe_{0.982}S_{1.000}$	–
6	62.56	–	–	36.60	99.16	$Fe_{0.981}S_{1.000}$	–
7	61.71	0.01	–	35.98	97.70	$Fe_{0.905}S_{1.000}$	–
8	62.12	–	–	36.33	98.45	$Fe_{0.981}S_{1.000}$	–
9	61.77	–	–	36.10	97.87	$Fe_{0.982}S_{1.000}$	–
10	62.09	0.01	–	36.28	98.38	$Fe_{0.982}S_{1.000}$	–
11	32.98	31.07	3.18	34.13	101.36	$(Ni_{4.02}Fe_{4.49}Co_{0.41})_{8.92}S_{8.08}$	9.8
12	32.80	30.93	3.20	34.10	101.03	$(Ni_{4.01}Fe_{4.48}Co_{0.41})_{8.90}S_{8.10}$	9.8
13	32.55	30.38	3.96	33.16	100.05	$(Ni_{4.00}Fe_{4.50}Co_{0.52})_{9.02}S_{7.98}$	7.7
14	32.48	30.35	3.87	33.89	100.59	$(Ni_{3.96}Fe_{4.45}Co_{0.50})_{8.91}S_{8.09}$	7.9
15	31.92	31.56	3.43	33.50	100.41	$(Ni_{4.13}Fe_{4.39}Co_{0.45})_{8.97}S_{8.03}$	9.2
16	32.78	30.21	3.11	34.02	100.12	$(Ni_{3.95}Fe_{4.51}Co_{0.40})_{8.86}S_{8.14}$	9.9

Note: Pyrrhotite formulas were calculated for S=1; pentlandite formula were calculated for total of 17 atoms. Analyses were performed in the laboratory of A.Ye. Fersman Mineralogical museum of the RAS with electron microprobe JEOL JCXA-50A. Analytical conditions are the same as for analyses in the table 1. Standards used: ilmenite USNM 96189 (Fe), metallic Co, NiO (Ni), barite (S). Images were taken with CamScan-4D electron microscope. Analyst A.A. Agakhanov.

rocks could be the source of sulphur. They were saturated with bitumen, which often contain sulfur compounds.

Pentlandite-millerite pair can be used as a mineral geothermometer. Lack of millerite in the studied sample indicates temperatures higher than 250°C corresponding to high temperature part of the zeolite facies.

We suppose, that pyrrhotite and pentlandite were deposited from metamorphic fluids with moderate activity of S_2. Lack of magnetite, a typical mineral of altered kimberlites, in the studied rock showed low O_2 activity during its alteration. Sulphur concentration in the fluids was low, otherwise pyrite would be formed. It's important to keep in mind possible lack of magnetic minerals in kimberlite during magnetometric prospecting.

We found elevated chlorine content up to 1.9% was a characteristic feature of lizardite in the metakimberlite (Sokolova *et al.*, 2010). Another chlorine-bearing mineral phase was found during the study: fine grained less than 10 μm formation of magnesium hibbingite composition. Microprobe analysis of it was (in at.%): Fe 30.27, Mg 8.17, Mn 0.62, Cl 21.87, which coincide with formula $(Fe^{2+}_{1.55}\ Mg_{0.42}Mn^{2+}_{0.03})_{2.00}(OH_{2.88}\ Cl_{0.12})_{3.00}Cl_{1.00}$. Presence of the mineral confirms our suggestion that the kimberlite was altered in conditions of low grade regional metamorphism with involvement of high chlorine fluids, which derived from chloride brines. The source of the brines was evaporate lenses in the carbonate-terrigenous formation hosting Udachnaya-Vostochnaya kimberlitic pipe.

The authors are grateful to Atali A. Agakhanov for quality microprobe analyses and Ernst M. Spiridonov for valuable consulting.

The work was supported by Ministry of Education grant # 16.518.11.7101.

References

Barmina G.S., Frenkel, M.Ya. On distribution coefficients of Ni, Cr, Mn, V, Co in olivines and pyroxene // Proceedings of VII Meeting on Geochemistry of Magmatic Rocks. Moscow, **1981**. Moscow, GEOHI AS of the USSR, 1981. P. 10 (in Russian).

Bobrievich, A.P., Ilupin, I.P., Koslov, I.T., et al. Petrography and mineralogy of kimberlitic rocks of Yakutia. Moscow, Nedra, **1964**. 192 pp. (in Russian).

Egorov, K.N., Bogdanov, G.V., Lashkevich, V.V., Medvedeva, T.I., Tikhonova, G.A. Stages in physical-chemical conditions of serpentinization of kimberlites // ZVMO. **1991**. Vol. 120, Issue 6. P. 1 – 12.

Franzesson, E.V. Petrology of kimberlites. Moscow. Nedra. **1968**. 191 pp. (in Russian).

Ilupin, I.P. Distribution and origin of some hydrothermal and hypergene minerals in Yakutian kimberlites // Soviet Geology. **1962**, # 3, pp. 152 – 156 (in Russian).

Ilupin, I.P., Vaganov, V.I., Prokopchuk, B.I. Kimberlites. Moscow, Nedra, **1990**. 258 pp. (in Russian).

Kornilova, V.P., Nikishova, L.V., Nikishov, K.N. Serpentine group minerals in Yakutian kimberlites // Parageneses of minerals in kimberlite rocks. Yakutsk, Yakutsk Department of Siberian Branch of the Academy of Science of the USSR. **1981**. P. 65 – 81 (in Russian).

*Lebedev, A.A.*On hydrothermal stage of serpentinization of kimberlites in connection to discovery of brusite in them // Petrography and mineralogy of primary diamond deposits. Moscow. Publisher of the Academy of Science of the USSR. **1963**. Issue 8. P. 71 – 86 (in Russian).

Marshintsev, V.K., Nikishova, L.V., Gotovtsev, V.V. Serpentine filling needle channels in olivine from Udachnaya-Vostochnaya pipe // DAN – Doklady of the USSR Academy of Science. **1984**. vol. 227. P. 697 – 700 (in Russian).

Milashev, V.A. Paragenetic associations of secondary rock forming minerals in kimberlitic rocks // Geochemistry. **1963**. # 6. P. 557 – 564 (in Russian).

Nikishova, L.V., Altuhova, Z.A., Nikishov, K.N. Electron microscopy study of serpentine from main cementing mass of kimberlitic breccia // NTI. Yakutsk. Publisher of Yakutsk Department of Siberian Branch of the Academy of Science of the USSR. **1978**. P. 25 – 27.

Podvysotskiy, B.T., Vladimirov, B.M., Ivanov, S.I. at al. Serpentinisation of kimberlites // Doklady of the USSR Academy Science. **1981**. Vol. 256. P. 946 – 950 (in Russian).

Sokolova, E.L., Spiridonov, E.M. Association of goethite and lizardite as a typical formation in of zeolite facies metakimberlites and metaperidotites inclusions in them // New Data on Minerals. **2006**. Vol. 41. P. 86 – 90.

Sokolova, E.L., Spiridonov, E.M. Ca-containing stroncianite, barite, dolomite and calcite in metakimberlites of Zarnitsa pipe, Yakutia // New Data on Minerals. **2007**. Vol. 42. P. 158 – 163.

Sokolova, E.L., Spiridonov, E.M., Vorobyiov, S.A. Chlorine-containing lizardite from metakimberlites of Udachnaya-Vostochnaya pipe, North Yakutia // Petrology. **2010**. Vol. 18. # 2. p. 134 – 138 (in Russian).

Zinchuk, N.N. Postmagmatic minerals of kimberlites. Moscow, Nedra. **2000**. 538 pp. (in Russian).