Mineralogy and genesis of kimberlite-hosted chloride-containing nodules from Udachnaya-East pipe, Yakutia, Russia

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Abundant chloride-bearing nodules have been recently described in the diamondiferous Udachnaya-East pipe in Yakutia (Kamenetsky *et al*., 2006; 2007a). They occur in the deep levels of the pipe (> 350 m) in exceptionally fresh kimberlites (Marshintsev *et al.*, 1976). The lack of secondary, alteration-related minerals in these Udachnaya-East kimberlites (UEK) is associated with an essentially carbonate-chloride groundmass and the presence of chloride-bearing nodules (Kamenetsky *et al*., 2004, 2006, 2007a; Sharygin *et al*., 2007b). The shapes and sizes of chloride-bearing nodules and segregations are variable, from spherical and round to angular and from 0.5 to 30 cm in diameter, rarely up to 1 m. The contacts of the nodules with the host kimberlite are sharp (< 1 mm), without evidence of thermometamorphic effects. In some cases, the contact zone is composed of a breccia-like aggregate of olivine, calcite, Na-Ca carbonates, sodalite, phlogopite–tetraferriphlogopite, humite–clinohumite, perovskite, apatite, Fe-Ti oxides, djerfisherite and alkali sulfates set in a matrix of chlorides (Kamenetsky *et al.,* 2006, 2007a).

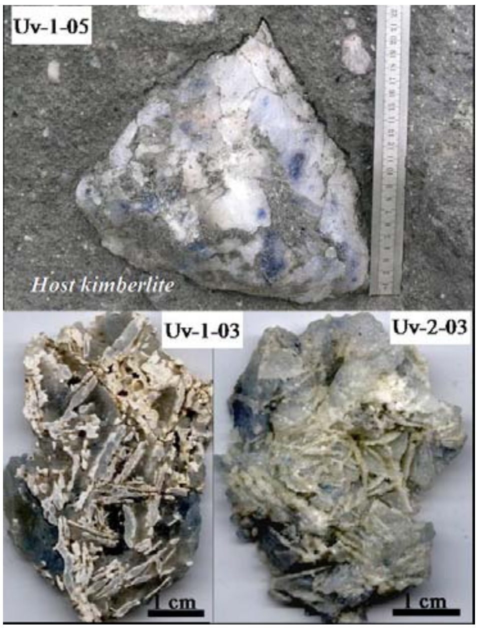

Fig. 1. Chloride (Uv-1-05), chloride-“nyerereite” (Uv-1-03) and chloride-shortite-northupite-calcite (Uv-2-03) varieties of nodules.

The mineral assemblage of the nodules is dominated by chlorides, and the chloride-rich (>90-95% NaCl+KCl) varieties are most common. Chloride-carbonate (~50% NaCl+KCl), chloride-carbonate-silicate (50-70% NaCl+KCl), and carbonate-rich species (<10% NaCl+KCl) are less common (Fig. 1, Kamenetsky *et al.,* 2006, 2007a). Halite is predominated over sylvite. The latter mineral is commonly localized as amoeboid blebs in halite or as individual grains among halite grains. Rarely halite occurs as blebs in sylvite grains (Fig. 2).

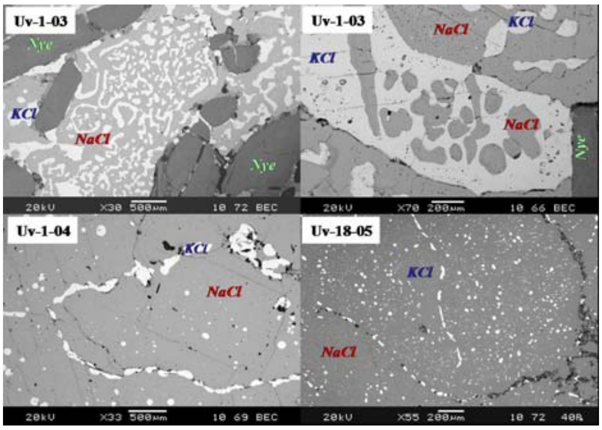

Fig. 2. Distribution of chlorides in chloride-“nyerereite” (Uv-1-03) and chloride (Uv-1-04, Uv-18-05) varieties of nodules. Nye - “nyerereite”. BSE images.

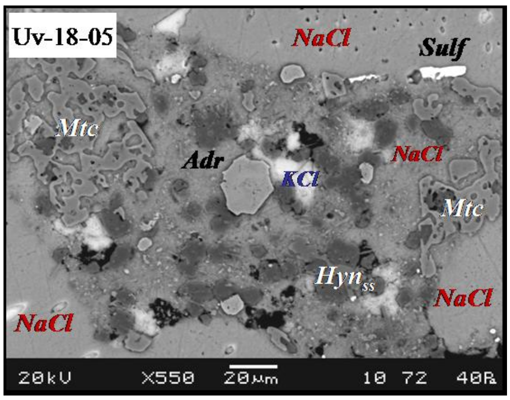

Fig. 3. Fine-grained interstitial aggregate in a chloride nodule. Sulf - sulfides (pyrrhotite+djerfisherite), Mtc - monticellite, Adr - Ti-andradite; Hyn_{ss} - haüyne solid solution. BSE image.

In addition to chloride and carbonate components, the presence of fine-grained aggregate of chlorides, silicates, carbonates and sulfates ± sulfides (1-5 vol.%, rarely - up to 30 vol.% in chloride-carbonate-silicate species) is typical of the nodules. In individual samples of essentially chloride species such aggregates vary from chloride-sulfate-silicate to chloride-carbonate-silicate in composition, and are commonly localized among chloride grains (Fig. 3). Minerals found in the nodules are listed in Table 1 in comparison with kimberlite groundmass and olivine-hosted melt inclusions. It should be noted that mineral species in chloride-bearing nodules occur wider than in host kimberlites and melt inclusions in olivine. The findings of wollastonite, diopside, Ti-andradite, monticellite and haüyne in essentially chloride nodules indicate their high-temperature origin.

The chloride-carbonate nodules are most remarkable, as they are composed of "nyerereite" (Na-K-Ca-S carbonate) and shortite-northupite-calcite varieties. Halite, sylvite, zoned "nyerereite", shortite, aphthitalite and rasvumite are the main minerals in the chloride-"nyerereite" nodules. Zoned "nyerereite" crystals (up to 5 cm) have spongy rims consisting of shortite, aphthitalite and calcite (Fig. 4). The central part of these crystals is a Na-K-Ca-S-carbonate resembling nyerereite and zemkorite, but having distinct a XRD pattern.

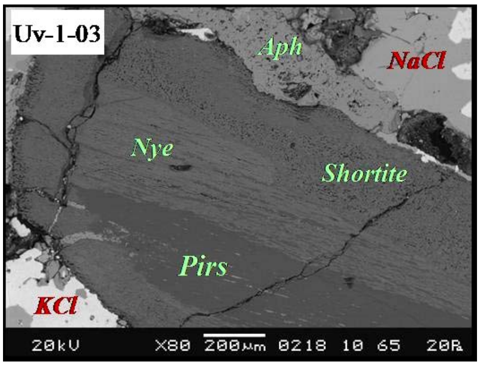

Fig. 4. Zoned "nyerereite" crystal with shortite-rich rim and partial replacement of "nyerereite" by pirssonite, chloride-"nyerereite" nodule. Aph - aphthitalite, Pirs - pirssonite.

Chloride-shortite-northupite-calcite nodules contain different minor phases, which are localized on the contact of chlorides and carbonates or as crystal inclusions in carbonates. These phases are aphthitalite, phlogopite–tetraferriphlogopite, apatite, djerfisherite, Na-sulfates, Ca-Ba-Sr-sulfates and carbonates (alstonite-paralstonite, olekminskite, barite, celestine), galena, Cu-sulfides and bradleyite.

The minerals of the nodules are prone to alteration, with complete degradation observed under surface conditions. The water-soluble chlorides and alkali sulfates are dissolved, whereas alkali carbonates are replaced by pirssonite, $Na_2Ca(CO_3)_2{\cdot}2H_2O$, and other H_2O-bearing carbonates (up to trona), and a Fe-rich oxidized coating is developed on the surface of the K-sulfides. Similar alteration has been described as typical of the Oldoinyo Lengai natrocarbonatites (Mitchell, 2006; Zaitsev, Keller, 2006).

Table 1. Comprehensive data for the Udachnaya-East minerals found in chloride-bearing nodules (ND), kimberlite groundmass (KG) and melt inclusions in kimberlite olivines (MI).

Mineral	Formula	ND	KG	MI
Sulfides				
Pyrrhotite	$Fe_{1-x}S$	x	x	x
Pentlandite	$(Fe,Ni)_9S_8$		*	
Chalcopyrite	$CuFeS_2$	*	*	
Djerfisherite	$K_6Na_{0-1}(Fe,Ni,Cu)_{24}S_{26}Cl$	x	x	X
Rasvumite	KFe_2S_3	X	x	
Galena	PbS	*		
Sphalerite	ZnS	*	*	
Chlorides				
Halite	$NaCl$	X	x	X
Sylvite	KCl	X	x	X
Carbonates				
Calcite	$CaCO_3$	X	X	X
Dolomite	$CaMg(CO_3)_2$		*	*
Siderite - Magnesite	$FeCO_3$ - $MgCO_3$			*
Shortite	$Na_2Ca_2(CO_3)_3$	X	x	x
Zemkorite-Nyerereite	$(Na,K)_2Ca(CO_3)_2$	X	x	X
Northupite	$Na_3Mg(CO_3)_2Cl$	X		x
Alstonite - Paralstonite	$BaCa(CO_3)_2$	x		
Olekminskite	$Sr(Sr,Ca,Ba)(CO_3)_2$	*		
Nahcolite	$NaHCO_3$			*
Pirssonite	$Na_2Ca(CO_3)_2{\cdot}2H_2O$	x	x	*
Gaylussite	$Na_2Ca(CO_3)_2{\cdot}5H_2O$	*	*	
Trona	$Na_3(CO_3)(HCO_3){\cdot}2H_2O$	x		
Sulfates				
Aphthitalite	$NaK_3(SO_4)_2$	X	*	X
Schairerite	$Na_{21}(SO_4)_7F_6Cl$	x		
Barite	$BaSO_4$	x		
Celestine	$SrSO_4$	*		
Anhydrite	$CaSO_4$	*		
Syngenite	$K_2Ca(SO_4)_2{\cdot}H_2O$	*		*
Phosphates				
Apatite	$Ca_5(PO_4)_3(F,OH)$	x	x	*
Bradleyite	$Na_3Mg(PO_4)(CO_3)$	*		
Oxides				
Rutile	TiO_2		x	
Perovskite	$CaTiO_3$	*	X	*
Chromite	$(Fe,Mg)(Cr,Al)_2O_4$	*	X	*
Ti-magnetite	$(Fe,Mg)(Fe,Ti)_2O_4$	*	X	*
Magnetite	$FeFe_2O_4$	x	X	X
Ilmenite - Pyrophanite	$(Fe,Mn,Mg)TiO_3$	x	x	x
SiO_2 polymorph	SiO_2	*		
Brucite	$Mg(OH)_2$	*		
Silicates				
Phlogopite	$KMg_3AlSi_3O_{10}(F,OH)_2$	x	X	X
Tetraferripholopite	$KMg_3FeSi_3O_{10}(OH)_2$	*	*	X
Diopside-Hedenbergite	$Ca(Mg,Fe)Si_2O_6$	*	*	*
Wollastonite	$CaSiO_3$	*		
Humite-Clinohumite	$(Mg,Fe)_7(SiO_4)_3(F,OH)_2$	x		x
Ti-garnet	$Ca_3(Fe,Ti,Al)_2(SiO_4)_3$	*		
Cuspidine	$Ca_4Si_2O_7F_2$	*		
Sodalite-Haüyne$_{ss}$	$Na_8Al_6Si_6O_{24}Cl_2$	*	*	*
Olivine	$(Mg,Fe)_2SiO_4$	x	X	x
Monticellite	$Ca(Mg,Fe)SiO_4$	*	*	*

Note: X - main; x - minor (1-5%); * - accessory. New author's data and data from Egorov *et al.* (1988), Kornilova et al. (1998), Golovin *et al.* (2007), Sharygin *et al.* (2007a-b), Kamenetsky *et al.* (2004, 2006, 2007a).

Origin of chloride-bearing nodules

Chloride minerals and chloride-bearing nodules in the UEK groundmass represent a petrological oddity, the origin of which can be important in understanding petrogenesis and emplacement of kimberlite magmas. In the first paper describing chlorides in the Siberian kimberlites their origin was *a priori* ascribed to post-magmatic crystallization from the platform brines (Pavlov, Ilupin 1973). The weakness of such idea is that platform brines cause strong alteration in kimberlites, whereas the studied UEK samples have no serpentine or other low-temperature hydrous silicates. In contrast, the UEK chloride and chloride-carbonate nodules are essentially water-free, and their mineral assemblage (e.g., presence of "nyerereite", phlogopite, olivine, Ca-silicates and K-sulfides; see Table 1) strongly supports high-temperature crystallization (Kamenetsky *et al.,* 2004, 2006, 2007a-b; Golovin *et al.,* 2007; Sharygin *et al.,* 2007a-b). Another model considered contamination of the kimberlite magma by platform brines during emplacement (Egorov *et al.,* 1988; Kornilova *et al.*, 1998). However, such process should inevitably result in formation of abundant H_2O-rich minerals and further autometasomatic reactions. The UEK and chloride-bearing nodules contain one potentially H_2O-bearing mineral, phlogopite, but its abundance is low (<5 vol.%).

Two other scenarios can be responsible for high-temperature origin of chlorides in the UEK. The chloride-bearing nodules may represent fragments of evaporites entrapped by and reacted with the kimberlite magma. Such mechanism is possible for some kimberlite pipes from the southern Siberian craton (e.g. Mir and Internatsional'naya pipes), where evaporites (halite and dolomite lithologies) are dominant among country rocks. This is not the case for the sedimentary sequence around the Udachnaya pipe (Zinchuk, 2000), even at significant depths (up to 2000 m). Small lenses of halite (5-10 cm) were recorded in large carbonate blocks within the UEK (N.P. Pokhilenko, pers. comm.), but these cannot be taken as ample evidence of wider occurrence of chlorides in local sediments. Moreover, our samples lack borate minerals and bitumen (or products of their pyrolysis) that are typical of the Siberian evaporites.

Our preferred model considers the formation of chloride-bearing assemblages at the latest evolutionary stages of the kimberlite magma (Golovin *et al.,* 2007; Kamenetsky *et al.,* 2004, 2006, 2007a-b; Sharygin *et al.*, 2007a-b) and mantle origin of chlorine in the UEK (Maas *et al.,* 2005). Earlier crystallization of olivine drives the residual melt towards essentially "dry" and non-silicate compositions, as recorded by melt inclusions in the UEK olivine (Golovin *et al.,* 2007; Kamenetsky *et al.,* 2004, 2007a), that crystallize calcite, alkali carbonates, chlorides, sulfates and potassium sulfides at temperatures <800^{o}C.

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