VOLATILE COMPONENTS IN THE UPPER MANTLE
(based on data on fluid inclusion studies)

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Nowadays the composition of volatiles and their role in deep-seated processes are judged mainly from experimental studies in the region of high pressures [Kushiro et al.,1968; Boettcher et al.,1980; Ryabchikov et al.,1980,1982; Falloon et al.,1989; Eggler,1987; Fedorov et al.,1991], thermodynamic calculations [Taylor et al.,1989; Fedorov et al.,1991,1992] and results of mass-spectrometer and chromatographic studies of natural diamonds and satellite-minerals [Melton, Giardini,1974,1981; Roedder, 1984; Bartoshinsky et al.,1987; Tal'nikova et al.,1991; Pokhilenko et al.,1994]. The detection of fluid inclusions in crystals of natural and synthetic diamond and satellite-minerals of diamond and their investigation by non-destructive methods of analysis allows a direct information to be obtained on the composition of volatiles involved in mineral-forming processes under the upper mantle conditions [Tomilenko, Chupin, 1983; Bakumenko et al.,1992; Voznyak et al.,1992; Chepurov et al.,1994; Pal'yanov et al.,1994].

Series of monophase fluid inclusions have been found during careful optical studies of flatly parallel plates made from diamond crystals from the placers of northeastern Siberian Platform. They are located in healed cracks which are not exposed on the crystal's surface. The inclusions are flat and have a shape of isometric plates with facet elements, mainly {111}. They are colorless, isotropic in polarized light and behave as a matrix, given birefringence exists in the crystal. Along with fluid inclusions the cracks contain graphite. Cryometric and Raman-spectroscopic investigations showed that all inclusions in terms of their composition may be divided into three types: carbon dioxide-nitrogen-hydrocarbonic (?) (type I), carbon dioxide-nitrogen (type II) and hydrocarbonic (?) (type III). Precipitation of one or several solid phases occurs (metastable phase transition) in all inclusions on cooling in freezing stage in the range of -50°C to -120°C. In all inclusions of type I commonly two solid phases successively freeze out, which differ in melting temperatures and composition (phase A - solid hydrocarbons (?) with melting temperature about -42°C and phase B - solid carbon dioxide with melting temperature about -66°C). In all second type inclusions on cooling only phase B (solid carbon dioxide) freezes out, and in inclusions of the third type - only one solid phase A (solid hydrocarbons (?) with melting temperature about -36°C). The volume of precipitated solid phases for inclusions of type I is about 30% (phase A about 10% and phase B about 20%), for type II about 20% (only phase B), and for inclusions of type III - about 75-80% (only phase A). Further cooling up to -196°C of the residual liquid does not result in it heterogenization or other changes in every type inclusions. The results of cryometric and Raman-spectroscopic studies suggest that the composition of inclusions of type I is represented by carbon dioxide, nitrogen, and hydrocarbons (?), while type II - mainly by carbon dioxide and nitrogen, and inclusions of type III - basically by hydrocarbons (?). Fluid inclusions of types II and III are typically localized within one healed crack and were most

likely formed as a result of necking down of the first type inclusions. Although the detected fluid inclusions are located in diamonds along cracks, healed inclusions undoubtedly indicate that during preservation of inclusions the conditions (temperature, pressure, composition of medium) necessary for crystallization of substance still existed. The latter is confirmed also by the presence of negative diamond shape in the habit of inclusions, necking down and recrystallization of sites around inclusions in diamond.

Primary fluid and melt inclusions were found in pyropes typical of parageneses of websterite xenoliths from kimberlite pipe "Mir" (Yakutia). The IR-spectra of fluid inclusions have a strong absorption band in the frequency region 3000-2800 cm^{-1}, which is typical of hydrocarbons. Data of thermo- and cryometric studies of fluid in garnets, favor the alkane nature of these hydrocarbons. Judging from homogenization temperatures these inclusions may be represented by n-alkanes not less than C_5-C_{11} (with due regard for critical temperatures of the latter). After freezing of the liquid phase of inclusions, melting of crystals formed is observed at $-20^{\circ}C$ and the last solid phases disappear at $-10^{\circ}C$. In case of n-alkanes this may correspond to mixtures of alkanes with chains of C_{11} type and higher-molecular compounds. In melt inclusions melting of solid phases and solution of fluid bubble is observed at about $965-980^{\circ}C$. However, we failed to homogenize inclusion because at about $1100^{\circ}C$ they usually explode, apparently, due to developing high fluid pressure in inclusions at these temperatures.

The Raman spectroscopy data on the composition of fluid inclusions in synthetic diamond also suggest a principal possibility on the participation of hydrocarbons (alkanes) in crystallization processes of diamond in its stability field. In synthetic diamonds, obtained by the temperature gradient grown method in the system Fe-Ni-C at a high-pressure apparatus of "split sphere" type, monophase liquid inclusions of disc-, pipe-like-lenticular shape or with a facet of negative diamond crystal were found. The Raman-spectra of inclusions display bands in the subregions of spectra 3000-2700, 1475-1450, 1310-1175, 1150-950 cm^{-1}. The absence of a strong line in the frequency region 1600 cm^{-1} indicates the presence of saturated hydrocarbons (alkanes) in inclusions. In the frequency region 3000-2700 cm^{-1}, C-H valency variations occur, which are more or less localized within CH_2 and CH_3 groups. The narrow region 1475-1450 cm^{-1} in Raman-spectrum exhibits a band favored by the position of antisymmetric deformation of CH_3 and scissors-like variations of CH_2. The CH_2 - torsion modes occur in the region 1310-1175 cm^{-1} too. The absence of lines in the region 888- 837 cm^{-1}, peculiar to nonbranched alkanes, suggests that Raman-spectrum registered is most likely a mixture of branched and cyclic alkanes. The Raman-spectrum region in these alkanes is free of lines. As the pressure in fluid inclusions is essentially higher than one atmosphere, the spectra obtained do not coincide with the Raman-spectra of hydrocarbons recorded under normal conditions.

In garnets of eclogites from the kimberlite pipes "Udachnaya" and "Obnazhenaya" (Yakutia) monofase liquid inclusions were found whose composition, according to data of cryometry and Raman-spectroscopy, is represented mainly by liquefied nitrogen. On cooling to $-196^{\circ}C$, the majority of the inclusions display no visible phase inclusions, which

suggests lower than -196°C heterogenization temperatures of preserved solutions and their high density (more than 0.806 g/cm³). Only in separate inclusions, which seem to undergo partial unsealing, heterogenization of inclusions was observed at -196°C (T_{hom} = -188 ÷ -196°C).

On the basis of data of chromatographic analysis of volatiles from garnets and olivines of harzburgites, spinel lherzolites, garnet pyroxenes, diamondiferous dunites, and eclogites from kimberlite pipes "Mir", "Udachnaya" (Yakutia) and "Roberts Victor" (South Africa) and thermodynamic modeling of component composition of fluid for PT-conditions of formation of the rocks considered, calculated using program TEMPACT, it was established that prevailing components for all samples is water, methane, and carbon dioxide. Some samples along with water, carbon dioxide, and methane also contained elevated content of nitrogen. The amount of other components is negligible. The oxygen fugacity at PT - parameters and H/(O+H) values, typical of each rock investigated, was calculated using the data obtained. It was shown that redox conditions of formation of these associations are similar to conditions of buffer reaction WM at 50 kbar. However, the redox conditions of formation of these rocks cannot be judged unambiguously. They might have been formed under more reducing conditions, but the composition of fluid inclusions varied during post-crystallization period and, hence, the possibility that the results of analysis reflect averaged situation from the conditions of rocks prior to their removal to the surface is not ruled out.

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