Raman Spectroscopy of Mineral Inclusions in Diamonds from Yakutia

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Abstract. New data on the study of residual pressure in mineral inclusions in diamonds from kimberlite pipes and placers of Yakutia obtained using Raman Spectroscopy are presented. Calculated values of residual pressure in olivine and coesite inclusions in kimberlite diamonds according to works of Israeli et al [1] and Sobolev et al [2] indicate that the host crystal crystallized at the depth not less than 165 km, at pressure of 4.8-5.0 GPa and temperature T=1200 °C. Comparative analysis of Raman spectra of olivine inclusions in diamonds from placers of Ebelyakh river on inclusions, contained in diamond and then brought to the surface, showed that olivine inclusions are less stressed. The structural orientation of olivine inclusions in diamonds from placers of Ebelyakh river possibly plays a role in these differences of Raman spectra.

1. Introduction
Investigation of mineral inclusions capsulated in diamonds makes it possible to obtain accurate information on the condition of diamond crystallization. In the present study, mineral inclusions in diamonds from kimberlite pipes and alluvial placers of Yakutia have been analysed by Raman Spectroscopy.

2. Materials and methods
Diamonds from kimberlite pipes Aikhal, Udachnaya, Mir are octahedron crystals of Type I according to the of Orlov’s mineralogical classification [3]: Their facets are covered by trigonal and ditrigonal layers with parallel or sheaf-like hatched angles and reversely oriented etching pits (Figure 1). The specimen sizes do not exceed 4 mm by the longer axis. In these diamonds, mineral inclusions are represented by garnet, olivine, graphite, chromite and coesite.

Diamonds from placers of Ebelyakh river are transparent light-brown rounded dodecahedron crystals as described by Ugap’eva et al [4], (Figure 2). Their curved surfaces of dodecahedroids are sometimes complicated by a shagreen microlief, bands of plastic deformation, and etching caverns. Olivine, sulphide inclusions are obtained in this type of diamond. The sizes of studied samples do not exceed 6 mm by the longer axis.
Mineral inclusions were analysed by Raman Spectroscopy using LabRam HR 800 Horiba Yvon spectrometer with a 1024-channel LN/CCD detector at the Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences (analyst S.V. Goryainov). Raman spectra were acquired consecutively for mineral inclusions located within the host diamond and then for inclusions exposed on the surface. The calculation technique of residual pressure estimation followed that published earlier by Sobolev et al. [2].

3. Results and Discussions
Olivine inclusions were investigated in both the diamonds from kimberlite pipes Udachnaya and Aikhal, and the placers of Ebelyakh river. The olivine inclusions in the studied samples from both kimberlite pipes and the placers form groups (Figure 3). The size ranges of inclusions were 20-300 µm in the kimberlite diamonds and about 25 µm in the Ebelyakh placers diamonds. The features of olivine morphology in diamonds were described in the work of Ugap’eva et al. [4].
The most intensive bands of stretching vibrations were SiO$_4$-groups in olivine spectrum observed as a doublet with maximums about 825 and 857 cm$^{-1}$, which has significant shift rate on pressure 2.81±0.09 and 2.69±0.12 cm$^{-1}$/GPa, that is presented as increased values of band frequencies in stressed inclusions (Figure 4a). Analysis of Raman spectra showed that, these bands had a maximum shift on frequency for inclusion in sample from pipe Aikhal: 826.14 and 857.17 cm$^{-1}$. This doublet was used for determination of residual pressure $P_i$ in olivine inclusion, and frequencies for zero pressure were identified experimentally on Raman spectra of inclusion, brought to the surface: ~823.47 and 855.71 cm$^{-1}$. Raman spectra, obtained from the inclusion in the sample, gave maximum shift to each doublet band for value $\Delta \nu = 2.67 \pm 0.2$ and 1.46 ± 0.2 cm$^{-1}$, that corresponds to inner residual pressure in inclusion $P_i = 0.41 \pm 0.05$ GPa calculated from formulas of Izraeli et al. [1] and Yasuzuka [5]. According to Izraeli et al. [1] this residual pressure in inclusion helps in evaluating pressure of diamond crystallization, which, according to the calculations, is at least $P_f = 4.8 \pm 0.5$ GPa at model temperature of its growth 1200 °C.

Comparative analysis of Raman spectra of olivine inclusions in diamonds from placers of Ebelyakh river on inclusions, contained in diamond and then brought to the surface, showed that frequency shifts are insignificant for any band of the doublet $\Delta \nu = \pm 0.3$ cm$^{-1}$ (~822.9 - 823.5 cm$^{-1}$ and 855.4 - 855.7 cm$^{-1}$) and it is impossible to calculate pressure of diamond crystallization in this case (Figure 4b).

In diamond from pipe Mir with couple inclusions of coesite, small inclusion (60 μm – maximum diameter) contained higher internal pressure and was used for microanalysis (Figure 5).
Fig. 5. Raman spectra of stressed coesite inclusion in diamond from pipe Mir compared with free coesite.

Note that the two microfractures were found around this small inclusion in the diamond, which can slightly reduce internal pressure preserved in inclusion. Elastic tangential stresses were observed in diamond around this inclusion, which indicates a high degree of preservation of the tense inclusion. The most intensive band of coesite with 521 cm$^{-1}$ has a significant shear velocity of 2.9 ± 0.1 cm$^{-1}$/GPa. This band is used to measure internal pressure in $P_i$ inclusion. Raman spectra of coesite gave maximum band shear of 521 cm$^{-1}$ for value $\Delta \nu = 9.53 \pm 0.5$ cm$^{-1}$, which corresponds to residual pressure in inclusion $P_i = 3.29 \pm 0.2$ GPa, calculated by the formula inverse to the ratio: $\nu = 521.0 + 2.9 P_i$ (GPa). Using model of mechanic stress calculation in coesite-diamond system, described in the work of Sobolev et al. [2], pressure of diamond crystallization from pipe Mir $P_f = 5.0 \pm 0.5$ GPa at temperature of its growth 1200 °C was calculated.

4. Conclusions
Estimated values of the residual pressure in olivine and coesite inclusions in diamonds from kimberlite pipes indicate that the host crystal has been crystallized at PT-conditions such as 4.8-5.0 GPa at temperature of its growth 1200 °C. There is no doubt that diamonds from placers also crystallized at high P-T parameters, so it is not clear why there are no differences of Raman spectra of olivine inclusions inside the diamond and surfaced after polishing. But it should be noted that the studied olivine inclusions in diamonds from kimberlite pipes of Yakutia were regularly oriented relative to the host crystal, whereas olivines in diamonds from placers were not oriented according to Ugap’eva et al. [4]. Perhaps the structural orientation of mineral inclusions plays a role in these differences of Raman spectra.

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