

Melt and fluid inclusions in diamonds and minerals of mantle xenoliths as a source of information on mantle fluids

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1. Introduction

Composition of fluids and the redox conditions of deep-seated geological processes related to the nucleation and growth of diamond still remains a subject of considerable discussion.

Diamond and its inclusions bear information about the petrogenesis and geochemistry of the Earth's interior. The strength of the diamond and its low reactivity in a silicate environment ensure that the trapped substances remain shielded from their changing environment (Roedder, 1984).

This report presents results of cryometric, chromatographic, micro-Raman, micro-Infrared, electron and ion microprobe studies of fluid and melt inclusions in synthetic and natural diamond, garnet, clinopyroxene, olivine and coesite crystals.

2. Experimental and analytical procedures

Synthetic diamond, garnet, clinopyroxene and coesite crystals were grown in the high-pressure split-sphere apparatus known in the literature as the "BARS" apparatus (Pal'yanov et al., 1990).

Micro-Raman analyses were carried out on the multi-channel Raman spectrometer OMARS 89 (DILOR), equipped with 1100-channel detector LN/CCD-1100 PB and an Ar laser. Infrared spectra were recorded on the FT-IR spectrometers equipped with an IR microscope ("Bruker", Germany).

The microthermometric studies in the temperature range from -196 to +1400°C were carried out on the freezing and heating stage. Gases were analyzed in the gas chromatographic complex (Sokol et al., 2000).

The major and REE element composition of melt inclusions and host minerals were determined using electron and ion microprobe.

3. Results

3.1. Fluid and melt inclusions in synthetic diamond

The presence of fluid in the form of a separate free phase, and the entrapment of this phase in crystals of diamond was demonstrated for the first time for synthetic diamonds grown in metal-carbon systems at 60 kbar and 1350-1400°C (Fig. 1).

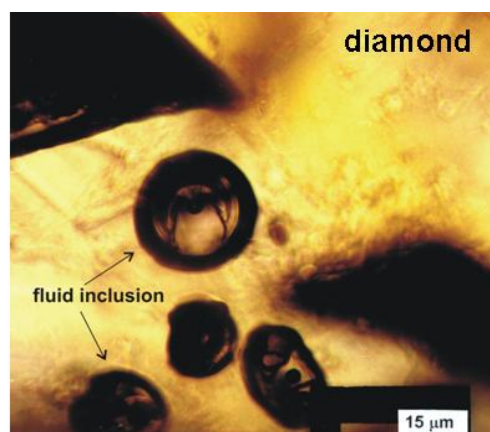


Fig.1. Micrograph of fluid inclusions in synthetic diamond, grown in Fe-Ni-C system.

Further studies demonstrated that primary high dense fluid inclusions in these diamonds contain methane and other high molecular hydrocarbons (Tomilenko et al., 1998). Besides, primary inclusions in diamond contain graphite, which covers the walls of inclusions as an opaque film.

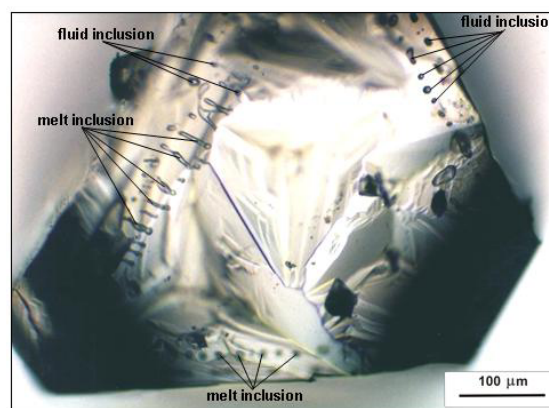


Fig.2. Micrograph of fluid and melt inclusions in synthetic diamond, grown in carbonate-carbon system.

Primary high dense fluid inclusions and syngenetic melt inclusions are peculiar to the diamonds grown in carbonate-carbon systems at 70 kbar and 1700-1750°C (Fig. 2). The study of fluid inclusions by Raman spectrometry has revealed that inclusions contain carbon dioxide (1384 cm^{-1}) (Fig. 3) and water.

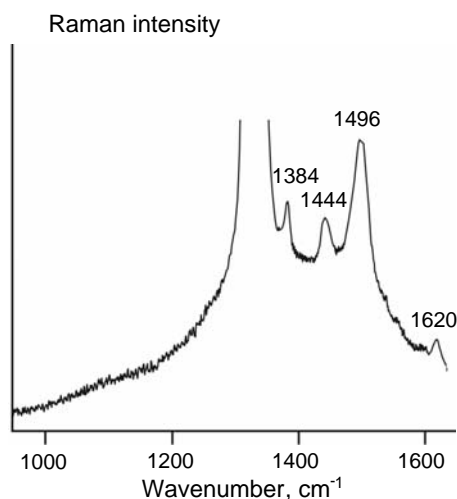


Fig.3. Raman spectrum of fluid inclusion in diamond crystal, grown in carbonate-carbon system.

Besides, some inclusions have been found to contain amorphous carbon clusters possessing sp^3 bonds, which apparently originated from fluid phase upon cooling of the system (1444 and 1496 cm^{-1}). It has been found that the composition of melt inclusions matches that of the starting carbonates. The obtained data suggest that diamond crystallized in alkaline-carbonaceous melts in the presence of volatiles, such as water and carbon dioxide.

3.2. Fluid and melt inclusions in synthetic garnet, clinopyroxene and coesite crystals

Primary water-carbon acid fluid inclusions and syngenetic inclusions of carbonate and silicate-carbonate melts have been also found in garnet, clinopyroxene and coesite crystals obtained in the experiments with carbonate-carbon and carbonate-silicate systems at 1400-1700°C and 60-70 kbar (Fig. 4,5).

The garnets synthesized in experiments with dolomite marble and garnet-pyroxene rock of the Kokchetav Massif, Northern Kazakhstan, contain single melt inclusions up to 80-100 micrometers in size (Fig. 4). Melt inclusions are also present in pyroxene and newly formed coesite. The melt inclusions represent fine-grained aggregates of recrystallized carbonatite melt. In addition, some garnets contained single-melt inclusions as well as melt inclusions containing diamond (Fig. 4). According to data of chromatographic analysis the gaseous phase in a crystallization ampoule is composed chiefly of water and CO_2 . The content of gaseous phase in this case is one and a half orders of magnitudes higher than in the experiment with garnet-pyroxene

rock.

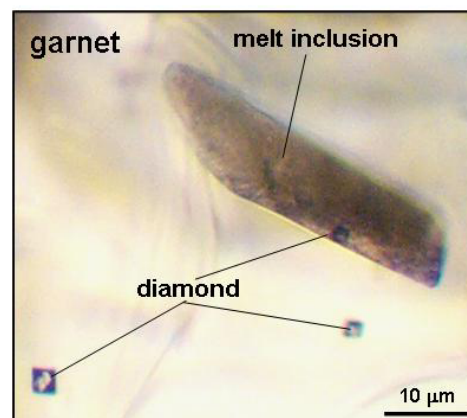


Fig.4. Micrograph of melt inclusion with diamond in synthetic garnet, synthesized in experiment with dolomite marble. The diamond inclusions in garnet were identified by Raman spectroscopy.

Primary fluid inclusions and syngenetic inclusions of silicate-carbonate melts have been found in coesite crystals obtained in the experiments with carbonate-silicate system ($\text{MgCO}_3\text{-(SiO}_2\text{+Al}_2\text{O}_3\text{)}$) at 1200-1800°C and 5.2-7.5 kbar (Fig. 5).

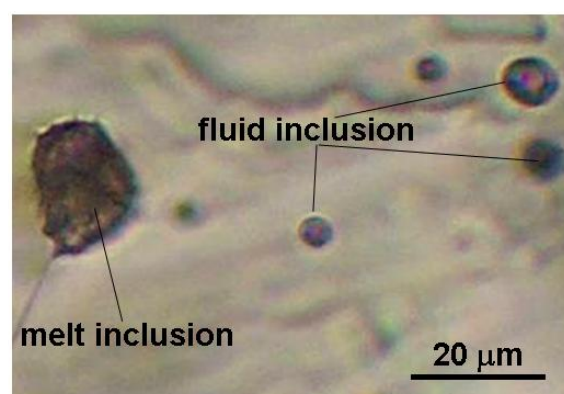


Fig.5. Micrograph fluid and melt inclusions in synthetic coesite, synthesized in experiment with carbonate-silicate system ($\text{MgCO}_3\text{-(SiO}_2\text{+Al}_2\text{O}_3\text{)}$).

The formation of coesite in the interaction between MgCO_3 , SiO_2 , and Al_2O_3 occurred in the presence of fluid and insignificant amount of melt. This is evidenced by the observation of fluid and melt inclusions in coesite (Fig. 5), as well as by the presence of quenching phases in the samples. Raman spectrometric examination of fluid inclusions in a coesite immediately after the experiment detected a peak at 1384 cm^{-1} corresponding to CO_2 . This agrees well with the gas chromatography data. The decrepitation of the fluid inclusions during next several days after the experiments indicates that the fluid in inclusions was under very high pressure.

3.3. Fluid inclusions in natural diamond and garnet crystals from mantle xenoliths

Fluid inclusions have also been found in natural diamonds from placers of Yakutia (Russia). The studied diamonds are defined as sharp-edge curve-faced crystals of the form, transitional between octahedron and dodecahedron. The crystals are mosaic with divergent structure and consist of elongated sub individuals that develop from the centre and are somewhat rotated relative to one another (Tomilenko et al., 2001). The fluid inclusions are substantially flattened, and in plan view they have close - to - isometric form with elements of octahedral symmetry. According the cryometric, Raman and IR-spectroscopic studies, two types of high dense fluid inclusions can be distinguished: water-nitrogen-carbon acid and water-nitrogen-hydrocarbon (Fig. 6).

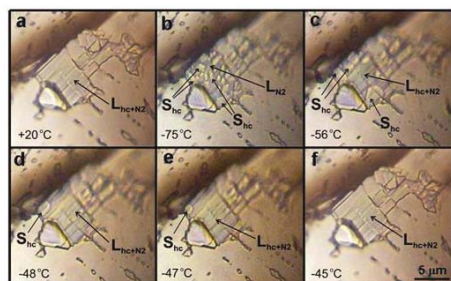


Fig.6. Micrographs of fluid inclusion in natural diamond from Yakutia, illustrating phase transformations in the essentially hydrocarbonic inclusion on cooling in the freezing stage to -75°C and further heating to -45°C. L_{hc} - liquid phase; S_{hc} - solid phase of hydrocarbons.

The water-nitrogen-carbon acid inclusions are usually located close to the centre of crystals whereas the water-nitrogen-hydrocarbon inclusions - on the periphery. This suggests the change of the fluid composition from water-carbon acid (CO₂-rich) to hydrocarbon (CH₄-rich) during crystallization of diamond monocystal.

Primary (syngenetic) crystalline and fluid inclusions have been found in the garnets from diamondiferous eclogites from Mir and Udachnaya kimberlite pipes. On the basis of crystal morphology studies, coupled with microprobe analyses and Raman-spectrometry, the crystalline inclusions are paramorphs of α -quartz after coesite. Importantly, Raman bands of 206 and 464 cm⁻¹, characteristic of α -quartz under normal conditions, are shifted by toward a higher-frequency area (to 234 and 476 cm⁻¹, respectively). This effect is caused, most likely, by high pressure under which crystalline inclusions occur in garnet. Along with crystalline inclusions garnets host syngenetic primary fluid inclusions. All fluid inclusions have experienced partial decrepitation, revealed by a halo of tiny daughter inclusions surrounding them. Upon freezing of the liquid phase of inclusions, the formed solid phases melt at -40°C, and the last solid phase

disappears at -33°C (Fig. 7). IR spectroscopy of inclusion fill reveals strong absorption bands at 2857, 2870, 2925, and 2950 cm⁻¹, corresponding to hydrocarbons. These results suggest the presence in fluid inclusions of a mixture of liquid hydrocarbons "heavier" than methane.

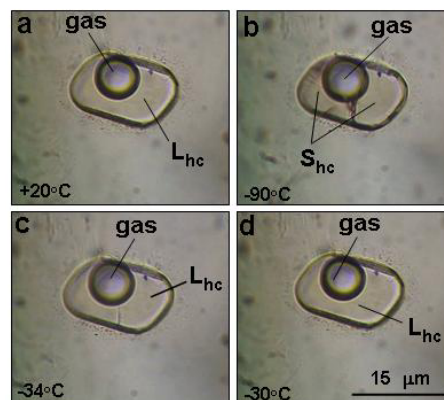


Fig.7. Micrographs of fluid inclusion in garnet from xenoliths eclogite, illustrating phase transformations in the essentially hydrocarbonic inclusion on cooling in the freezing stage to -90 °C and further heating to -30°C. L_{hc} - liquid phase; S_{hc} - solid phase of hydrocarbons.

4. Conclusions

It is found experimentally that diamond, garnet, clinopyroxene and coesite trap melt and fluid inclusions during crystallization at high temperatures and pressures of the upper mantle. The content of the inclusions reliably represents the properties of the source where they have been nucleated and grown. The obtained data suggest that methane and other hydrocarbons can dominate in the fluid composition of some areas of the mantle whereas carbon acid and water, in other areas.

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This study was funded by the RFFI (№ 06-05-64727)