Microscopic studies of disordered carbon-rich inclusions in ultra-high pressure glasses from impactites of the Kara astrobleme

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Abstract. The paper presents the results of study of the carbon-containing phase discovered in the impact glass of the Kara astrobleme. We used the following research methods: optical, scanning electron, and atomic force microscopies, as well as Raman spectroscopy. This phase represents carbon-containing inclusions up to several tens of micrometres in size with an amorphous diamond-like structure. At the nanoscale, the studied phase is characterized mainly by a homogeneous structure.

1. Introduction

Diamond-like carbon (DLC) is a general term for various forms of amorphous carbon materials demonstrating the unique properties of natural diamond [1]. DLC is a mixture of sp² and sp³ hybridized carbon atoms. Generally, this material is a diamond-like sp³-matrix with sp²-clusters.

Amorphous diamond-like carbon films and nanocomposites based on them are promising new materials, which determines the relevance of their research [2,3]. The amorphous diamond-like state of carbon is metastable. Therefore, despite the large number of works performed recently on amorphous diamond-like carbon materials, there is a need for further research to determine their properties, structure, and stability limits.

Impact glasses are present among natural objects as a product of impact (shock) transformation of rocks of the Earth's crust [4–8]. Ultra-high-pressure high-temperatures (UHPHT) glasses are particularly interesting, because their formation is caused by the highest pressures (several tens or hundreds of GPa) at temperatures above 3300 K [9-11]. We expect to obtain interesting information from detailed studies of the structure and physical properties of melt impact silicate glasses of the vein type, which have been recently discovered in the impactites of the Kara astrobleme (Pay-Khoy, Russia) [12] formed about 70 Ma. These glasses form ribbon-like subparallel vein bodies, secant suevites, and are characterized by multilevel liquation structures with relic coesite [12]. Detailed results of studying the structure of this impactite by spectroscopic methods showed [13, 14] that it generally consisted of amorphous feldspar material and contained small drops of coesite-containing quartz glass with a low degree of polymerization of the silicate carcass. At that, the spectroscopy indicated the presence of an amorphous
carbon phase in these impactites [13]. The discovery and study of the carbon particles with an amorphous structure in natural impact glasses is of great interest.

This paper reports on the discovery of an amorphous carbon matter in UHPHT glasses of the Kara astrobleme and on the results of the study of this matter by atomic force and scanning electron microscopies.

2. Experimental

For the studies, we used natural UHPHT vein-bodied impact glasses from the Kara astrobleme (Pay-Khoy, Russia). The material was sampled by T.G. Shumilova in 2015 at the right bank of the Kara River.

We studied the polished surface of the sample. It was covered with a gold layer with a thickness about 0.5 nm by magnetron sputtering, and then elemental mapping was performed. Then the gold layer was removed together with the upper layer of the surface to the depth about 0.5 µm by a grinding machine using aluminium oxide powder, and atomic force microscopy (AFM) studies of the selected objects were carried out. The objects on the surface of the sample after AFM study were additionally diagnosed by energy-dispersive X-ray spectroscopy (EDS) mapping and local elemental analysis.

Initially, the samples have been observed with optical microscopy (microscope POLAM-312 and Nikon Eclipse E400 Pol equipped with a camera DCMOS14000KPA). Raman spectroscopy tests were provided by a spectrometer LabRam HR800 instrument (Horiba, JobinYvon) equipped by a He-Ne laser (632.8 nm, 2 mW), an optical microscope Olympus BX41, and a Si-based CCD detector. Spectra were obtained in the 100–4000 cm⁻¹. Zero position, spectra background correction, and individual bands deconvolution have been provided with a curve-fitting procedure from the LabSpec 5.39 software.

The chemical composition has been analysed using a scanning electron microscope (SEM) Tescan MIRA3 equipped by an X-ray energy-dispersive spectrometer.

The topography has been examined with AFM in a tapping and phase-contrast modes using an Integra Prima (NT-MDT, Russia) by super sharp silicon cantilevers SSS-NCH (Nanosensors) with the resonant frequency 330 kHz, the radius at the tip 2-4 nm, and the stiffness constant about 35 N/m. The images have been recorded with resolution of 512 × 512 pixels at a scan frequency 0.9-1 Hz. The sample surfaces were grounded by a silver paste to avoid the influence of static electricity.

![Figure 1. General view of the microstructure of the impact Kara glass: optical image in reflected light. 1 – aluminosilicate glass; 2 – inclusions of carbonaceous matter; 3 – separate inclusions of mixed-layer aluminosilicates.](image-url)
3. Results
Vein UHPHT glass has a fluid microstructure with an aluminosilicate matrix and silicate inclusions of hundreds of micrometres in size [15] (Fig. 1). In addition, numerous rounded inclusions of mixed-layer aluminosilicates are present. They are elongated and often curved according to the matrix texture.

The aluminosilicate glass has a variable composition with a significant presence of iron, calcium, and magnesium (Table 1). Silicate inclusions are chemically homogeneous shapeless areas without contrasting boundaries with the surrounding feldspar glass [15]. The carbon inclusions are presented primarily in the silicate regions. These inclusions have a vitreous luster, rounded shapes, in a longitudinal section similar to beans (Fig. 1). The sizes of the inclusions are from 1 to 10 microns, and thickness is below 2 microns (Fig. 2). The composition of these inclusions cannot be determined correctly by EDS method because of their small thickness. The electron beam penetrates through the carbon inclusion, and the final analysis includes elements being a part of the surrounding matter. First of all, it is silicon, oxygen, and aluminium. Therefore, the carbon content measured in the inclusions using EDS cannot be considered reliable; it likely exceeds this value significantly.

Table 1. The content of rock-forming oxides in basic phases of impact glass of the Kara astrobleme (in at.%).

| Phases            | SiO₂ | MgO  | Al₂O₃ | Na₂O | K₂O   | CaO   | TiO₂ | Fe₂O₃ | C     |
|-------------------|------|------|-------|------|-------|-------|------|-------|-------|
| Aluminosilicate   | 61–78| 2–4  | 12–25 | 0.3–2| 1.75–2.5| 1.5–2.5| 0.1–0.3| 2.5–5  | n.d.  |
| matrix            |      |      |       |      |       |       |      |       |       |
| Silicate          | 90–93| 0.5–1| 0.5–1.5| 0.5–1| 0.5   | n.d.  | 0.1  | 0.5   | n.d.  |
| inclusions        |      |      |       |      |       |       |      |       |       |
| Carbon-rich       | 41–43*| 3–4*| 6.5–7*| 0.75*| 0.75* | 1*    | 0.3–0.6*| 2–3*  | 36–39 |
| inclusions        |      |      |       |      |       |       |      |       |       |

n.d. – not detected, * – probably from the host glass matrix.

Figure 2. SEM image of a cut of amorphous carbon grain.
Figure 3. Raman spectrum of carbon inclusion in the aluminosilicate glass matrix. Typical Raman spectrum of the carbon inclusion and its decomposition into two Gaussian components with maxima near 1368 and 1559 cm$^{-1}$ and FWHM values 300 and 156 cm$^{-1}$, respectively. The solid curve is a sum of two Gaussian components, dashed lines show individual components.

The Raman spectrum of carbon inclusions (Fig. 3) has two wide intersecting bands that correspond to position to D and G bands. The maximum of G-band lies in the range from 1558 to 1568 cm$^{-1}$, the maximum of D-band varies over a wider range from 1360 to 1380 cm$^{-1}$. FWHM values are from 150 to 170 cm$^{-1}$ for G-band and about 300 cm$^{-1}$ for D-band. The ratio of D and G bands maxima values is about 0.7 and the ratio of the integrals ranges from 1.8 to 1.9. A wide band of water in 3200-3500 cm$^{-1}$, which is present in silicate and aluminosilicate glasses [15], is absent in the carbon matter.

Scanning electron and atomic force microscopies show the predominant morphological homogeneity of the carbon inclusion. SEM images allowed revealing that the cleavage surface is broken by sinuous isolated fractures into partially isolated rounded blocks 50-200 nm in size with serrated edges. According to AFM data, the amorphous carbon inclusions are mainly homogeneous and composed of films up to 500 nm long and 50-150 nm wide (Fig. 4).

4. Discussion
Raman spectroscopy is the best method to obtain the bonding structure of DLC materials in details. In the Raman spectra of amorphous carbon with mixed sp$^2$–sp$^3$ hybridization, even a small content of sp$^2$-
bound carbon atoms determines their predominant contribution to the spectra, overlapping the component associated with sp$^2$-hybridized carbon atoms [1]. This phenomenon is well known and is related to the fact that in the visible range the capture cross-section for sp$^2$-bound carbon atoms is much larger, since π-state has a lower energy and is much more polarized than π-state, which gives ten times difference in the spectrum intensity [1]. Therefore, even if the proportion of sp$^2$ bond in the carbon matter is 10-15%, it will dominate in the intensity of the bands in the Raman spectrum.

The shift of G band from the standard graphite 1580 cm$^{-1}$ to 1560 cm$^{-1}$ is probably conditioned by the presence of sp$^2$ bond [1]. The abnormally broadened reflections D and G show a strong distortion of interplanar spacings. This shift, a large band width, and a small ratio of band intensities confirm a significant disorder of the bonds due to increasing sp$^2$-bond formation.

The atomic force and scanning electron microscopies have shown that amorphous diamond-like carbon of geological origin has a more homogeneous structure at the nanoscale, in contrast to natural and synthetic glasses and glassy carbon [16].

Pressure-temperature conditions for the formation of diamond-like films in the laboratory are significantly softer than the impact conditions (pressure less than 200 kPa and temperature less than 2000 K). Diamond-like carbon is formed after rapid cooling of scattered carbon atoms and annealing on relatively cold surfaces at high energy. Nevertheless, there is evidence of the formation of amorphous diamond-like carbon from glassy carbon at high (up to 100 GPa) pressures [18] and amorphous carbon glass under “stellar” (7000-13000 K, 40 GPa) conditions [19]. Therefore, the formation of amorphous diamond-like carbon upon impact of a meteorite into rocks is quite probable. Organic objects (trees, coal, bitumen of different degrees of transformation) could act as precursors.

5. Conclusion
Unusual natural carbon matter was found in UHPHT impact glasses of Kara astrobleme using EDS. It presents the isolated inclusions up to several tens of micrometres in size. Raman spectra allowed comparing structure of studied matter to amorphous diamond-like carbon. The atomic force and scanning electron microscopies were used to study the nanoheterogeneous structure of the amorphous carbon matter. Microscopy showed a predominantly homogeneous layered structure of carbonaceous matter at the nanoscale. However, it looks like it is not the pure carbon, but rather a carbon-containing composite. Additional high-resolution study is required to clarify this point.

Acknowledgements
The study was supported by Russian Science Foundation (project 17-17-01080). The studies were conducted with the help of scientific equipment at the Centre for collective use “Geonauka” at the Institute of Geology of Komi SC of Uralian Branch of RAS supported by NIR # AAAA-A17-117121270036-7 and at the Syktyvkar State University (Syktyvkar, Russia).

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