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 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 microscopy, as well as Raman spectroscopy. This phase represents carbon-containing inclusions up to several tens of micrometers in size with an amorphous diamond-like structure. At the nanoscale, the studied phase is characterized mainly by a homogeneous structure, which is different from glasses with a heterogeneous structure.

Introduction

Diamond-like carbon (DLC) is general terms by which various forms of amorphous carbon materials are termed that demonstrate some unique properties of natural diamond [1]. DLC is a mixture of sp^2 and sp^3 hybridized carbon atoms. Generally, this material is a diamond-like sp^3– matrix with sp^2 – 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 researches to determine 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], and ultra-high-pressure high-temperatures

(UHPHT) glasses are particularly interesting because their formation is caused by the highest pressures (several tens – hundreds GPa) at temperatures up to 3300 K and above [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 were recently discovered in the impactites of the Kara astrobleme (Pay-Khoy, Russia) [13] formed about 70 Ma. These glasses form ribbon-like subparallel vein bodies, secant suevites, and are characterized by multilevel liquation structures with relic coesite [13]. Detailed results of studying the structure of this impactite by spectroscopic methods showed [12, 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 [12]. The discovery and study of the carbon particles with an amorphous structure in natural impact glasses is greatly interesting.

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 microscopy.

Objects and methods

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 an antistatic layer of gold with a thickness of 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 aluminum 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.

Preliminary 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 with a He-Ne laser (632.8 nm, 2 mW), an optical microscope Olympus BX41 and a Si-based CCD detector. Spectra were received 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 analyzed using a scanning electron microscope (SEM) Tescan MIRA3 equipped by an X-ray energy-dispersive spectrometer.

The nanotopography has been examined with AFM in a tapping and phase-contrast mode 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. To avoid the influence of static electricity the specimens surfaces were grounded by a silver paste.

Results

Vein UHPHT glass has a fluid microstructure with an aluminosilicate matrix and silicate inclusions hundreds of micrometers in size [15] (Fig. 1). In addition, numerous rounded inclusions of mixed-layer aluminosilicates are present that are elongated and often bent according to the matrix texture.

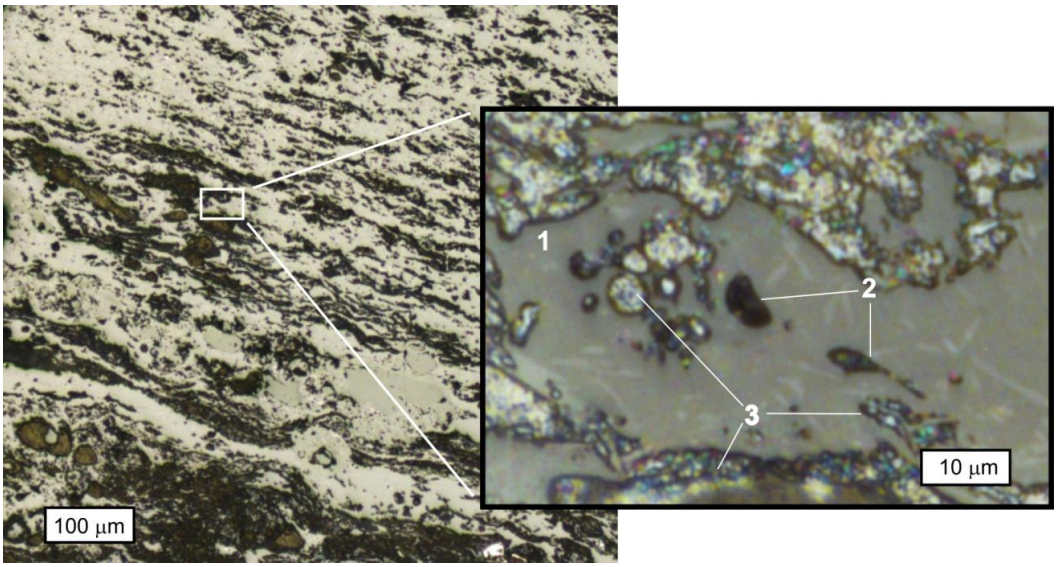

Figure 1. General view of the microstructure of the impact Kara glass: optical image in reflected light. 1 – Aluminosilicate glass; 2 – Inclusions of carbonaceous matter; 3 – Separate inclusions of mixed-layer aluminosilicates.

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

Phases	SiO_2	MgO	Al_2O_3	Na_2O	K_2O	CaO	TiO_2	Fe_2O_3	C
Alumino-silicate matrix	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.
Silicate inclusions	90–93	0.5–1	0.5–1.5	0.5–1	0.5	n.d.	0.1	0.5	n.d.
Carbon-rich inclusions	41–43*	3–4*	6.5–7*	0.75*	0.75*	1*	0.3–0.6*	2–3*	36–39

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

The aluminosilicate glass has a variable composition with a significant presence of iron, calcium and magnesium (Tab. 1). Silicate inclusions are chemically homogeneous shapeless areas without contrasting boundaries with the surrounding feldspar glass [15]. The carbon inclusions are present 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, their thickness does not exceed 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 that are part of the surrounding matter. First of all, it is silicon, oxygen and aluminum. Therefore, the carbon content measured in the inclusions using EDS cannot be considered reliable; it likely exceeds this value significantly.

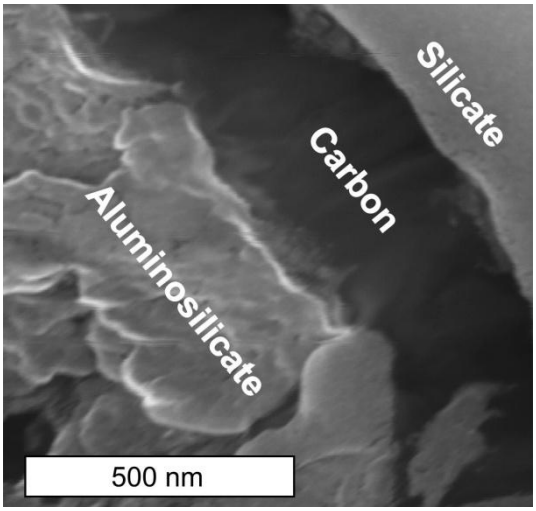

Figure 2. SEM image of a cut of amorphous carbon grain.

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

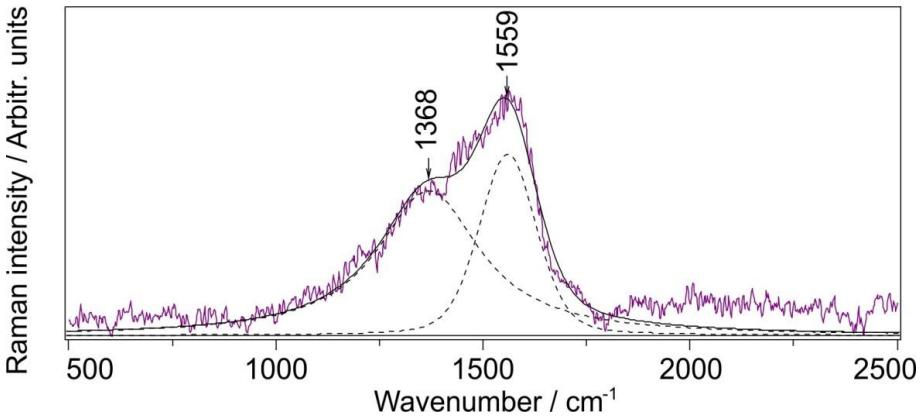

Figure 3. Raman spectrum of carbon inclusion in the aluminosilicate glass matrix. Typical Raman spectrum of the carbon inclusion and its decomposition to two Gaussian components with maxima near 1368 and 1559 cm^{-1} and FWHM values 300 and 156 cm^{-1}, respectively. The solid curve is a sum of two Gaussian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

Scanning electron and atomic force microscopy show the predominant morphological homogeneity of the carbon inclusion. SEM images present 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, composed mainly of films up to 500 nm long and 50–150 nm wide (Fig. 4).

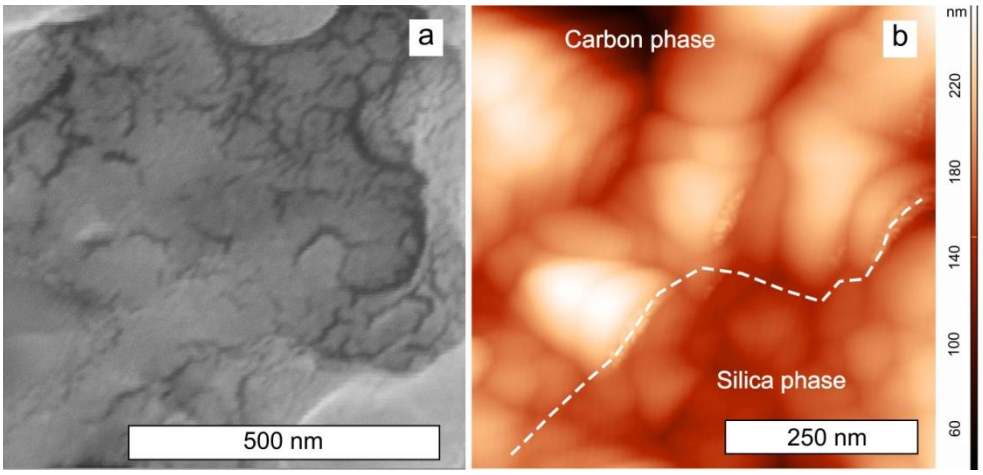

Figure 4. Cleavage surface of carbon inclusion: SEM image (a); AFM image (b).

Discussion

Raman spectroscopy is the best method to obtain the detailed bonding structure of DLC materials. In the Raman spectra of amorphous carbon substances 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^3–hybridized carbon atoms [1]. This phenomenon is well known and 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 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^3 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^3–bond formation.

The results of atomic force and scanning electron microscopy show 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 rapidly cooling 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.

Conclusion

Unusual natural carbon matter was found in UHPHT impact glasses of Kara astrobleme using EDS. It was present as isolated inclusions up to several tens of micrometers in size. Raman spectra allowed comparing structure of studied matter to amorphous diamond-like carbon. The atomic force and scanning electron microscopy 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 is possible not be purely carbon, but rather a carbon-containing composite, but additional high-resolution studies are required to clarify this point.

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References

[1] Robertson J, 2002 Diamond-like amorphous carbon *Materials Science and Engineering R* **37** 129–281.

[2] McKenzie D R, Muller D, Pailthorpe B A, 1991 Compressive-Stress-Induced Formation of Thin-Film Tetrahedral Amorphous Carbon *Physical review letters* **67** 773–776.

[3[Grill A, 1999 Diamond-like carbon: state of the art *Diamond and Related Materials* **8** 428–434.

[4] Impact craters at the turn of the Mesozoic and Cenozoic. Sat Art. / Ed. Masaytis V L, L .: Nauka, 1990. 191 p.

[5] Lyutoev V P, Lysyuk A Yu, 2016 The structure and texture of silica of impactites of the Karsky astrobleme *Vestnik of the IG of the Komi Science Center* **9** 24–32.

[6] French B M, 1998 Traces of Catastrophe: A Handbook of Shock-Metamorphic Effects in Terrestrial Meteorite Impact Structures. LPI Contribution No. 954. Lunar and Planetary Institute, Houston, Texas. 120 pp.

[7] Melosh H J, Impact cratering – A geological process. Oxford Univ. Press, New York 1989.

[8] Robertson P B, Grieve R A F, 1977 Shock attenuation at terrestrial impact structures. In: Roddy D J, Pepin P O, Merill R B. (eds) Impact and explosion cratering. Pergamon Press, New York, pp. 687–702.

[9] Langenhorst F, Deutsch A, 1994 Shock experiments on pre-heated α-and β- quartz: I. Optical and density data *Earth Planet. Science Letters* **125** 407–420.

[10] Schmitt R T, 2000 Shock experiments with the H6 chondrite Kernouvé: pressure calibration of microscopic shock effects *Meteoritics & Planet. Sci* **35** 545–560.

[11. Stöffler D, 1984 Glasses formed by hypervelocity impact. *J. Non-Cryst. Solids* **67** 465–502.

[12] Shumilova T G, Lutoev V P, Isaenko S I, Kovalchuk N S, Makeev B A, Lysiuk A Yu, Zubov A A, Ernstson K 2018 Spectroscopic features of ultrahigh-pressure impact glasses of the Kara astrobleme Scientific Reports **8(1)** 6923.

[13] Shumilova T G, Isaenko S I, Makeev B A, Zubov A A, Shanina S N, Tropnikov Ye M, Askhabov A A, 2018 Ultrahigh-Pressure Liquation of an Impact Melt. Part 1 *Doklady Earth Sciences* 480 595–598.

[14] Shumilova T G, Zubov A A, Isaenko S I, Karateev I A, Vasiliev A L, 2019 Mysteriouslong-living ultrahigh pressure or secondary impact crisis? *Geoscience Frontiers* In press

[15] Golubev Y A, Shumilova T G, Isaenko S I, Radaev V A, Utkin A A, Makeev B A, Ernstson K, Microscopic studies of ultra-high pressure glasses from impactites of the Kara astrobleme *J. Non-Crystalline Solids*. In press.

[16] Golubev Y A, Shumilova T G, Isaenko S I, Utkin A A, Makeev B A, Suvorova E I, Ernstson K, 2018 Nano-heterogeneity of natural impact silica-rich glasses according to atomic force microscopy and spectroscopy data *J. Non-Crystalline Solids*. **500**, 388–400.

[17] Golubev Y A, Shumilova T G, Isaenko S I, 2018 Structure of natural impact glasses on microscopic data *IOP Conf. Series: Mat. Sci. and Eng.* **443** 0120082018.

[18] Lin Y, Zhang L, Mao H K, Chow P, Xiao Y, Baldini M, Shu J, Mao W L, 2011 Amorphous diamond: a high-pressure superhard carbon allotrope *Phys Rev Lett* **107(17)** 175504

[19] Shumilova T G, Tkachev S N, Isaenko S I, Shevchuk S S, Rappenglück M A, Kazakov V A, 2016 A “diamond- like star” in the lab. Diamond-like glass *Carbon* **100** 703–709.