Structure of natural impact glasses by microscopic data

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Abstract. Newly found impact vein-bodied ultrahigh pressure high temperature (UHPHT) glasses from Kara astrobleme (Russia) and impact drop-shaped glasses from Ries crater suevites (Germany) have been investigated. The nanostructure of the glasses has been analysed using atomic force microscopy (AFM) supported by a complex of optical microscopy, scanning electron microscopy (SEM) combined with EDS analysis, and Raman spectroscopy. The received data demonstrate the different levels of impact melt differentiation through partial crystallization and polymerization; the amorphous substance is presented by similar 60-80 nm globular nanostructural composition.

1. Introduction
Glasses are the most important materials among disordered substances. However, the structure and features of phase composition of glasses remain not quite clear, in spite of actively provided studies in materials science. The behaviour of the disordered systems under strong compression attracts a special interest for fundamental understanding and application needs [1-4]. To the date, numerous studies have been carried out mostly at room temperature in microvolume output within diamond anvil cells under pressure of up to 100 GPa. At the same time, the natural glasses from impact craters can have a specific importance being formed with hyperpressures (35-90 GPa and above) and high temperatures (up to 3000°C). In comparison to experimentally possible high-pressure products, the natural impact glasses form rather essential volumes and can keep structural features for many millions of years, which allows using them not only for the geological tasks and modelling of astroblemes formation, but also for fundamental studies of noncrystalline substances under extreme conditions, to analyse their stability, and also to estimate them as possible materials for hi-tech applications, in particular for high-energy laser technologies and microelectronics [5,6].

The impact glasses have specific structural composition and physical features [3,4]. However, so far the essential attention to natural impact glasses as to a possible new type of high pressure materials is not fully studied. Due to the above specified points, the detailed study of nanostructure of the natural impact glasses, especially for UHPHT varieties, is urgent and very actual both for fundamental problem of disordered substance behaviour at extreme conditions and its subsequent relaxation, and for the applications.
2. Objects and methods
For the studies, we used natural glasses from drop-shaped impact glasses from suevites of the Ries crater (Bavaria, Germany) and UHPHT vein-bodied impact glasses from the Kara astrobleme (Pay-Khoy, Russia). The samples were provided by T.G. Shumilova during expeditions in 2013 and 2015 years, correspondently.

At the present study, the impact glass samples have been analysed using atomic force microscopy (AFM) supported by a complex of optical microscopy, scanning electron microscopy (SEM) combined with microprobe analysis, and Raman spectroscopy.

Initially, the impact glass samples have been observed with optical microscopy in transparent light with and without polarizer for selecting amorphous matter. For this purpose, a microscope POLAM-312 and Nikon Eclipse E400 Pol equipped with a camera DCMOS14000KPA were used.

Raman spectroscopy measurements were provided at room temperature by the spectrometer LabRam HR800 instrument (Horiba, Jobin Yvon) equipped with the He-Ne laser (632.8 nm, 2 mW), the optical microscope Olympus BX41, and the Si-based CCD detector. Spectra were received in the range of 100-4000 cm\(^{-1}\) with grating of 600 g/mm, a slit 100 μm, and a confocal hole size 300 μm. Zero position, spectra background correction, and individual bands deconvolution have been provided with a curve-fitting procedure from the LabSpec 5.36 software.

The chemical composition of the glasses has been analysed for cleaved surfaces of the samples using a Tescan Vega LMH scanning electron microscope equipped by an X-ray energy-dispersive spectrometer (EDS) accompanied with AZTEC software (Oxford Instruments) processing.

The nanostructure has been studied here with AFM analysis by surface morphology analysis in a semicontact mode using an Integra Prima (NT-MDT, Russia) by super sharp silicon cantilevers SSS-NCH (Nanosensors) with the resonant frequency 330 kHz, the radius of the tip 2-4 nm, and the stiffness constant about 35 N/m. To avoid the effect of static electricity, the sample surfaces were grounded by a silver paste. The technique of sizes measure was described in detail in Refs. [4,7].

3. Results
The studied impact glasses are presented with preferably amorphous substance that is evidently observed on the optical images in transparent polarized light (Fig. 1). Both the Kara and Ries glasses demonstrate well seen or partially present fluidal texture contrasted with different iron oxide presence illustrated by brown and yellow colours of varied density depending on iron oxidation/reduction level and its concentrations.

According to microprobe measurements, the analysed impact glasses are presented by aluminosilicate type having varying silica content with different concentrations of cation modifiers of the glass network with the biggest variation of Na\(_2\)O and Fe\(_2\)O\(_3\). The SiO\(_2\) content corresponds to intermediate (andesite) level. In Table 1, the rock-forming oxides contents are presented for the samples studied by AFM. In addition to the listed components, quite large content of H\(_2\)O has been detected within the Kara UHPHT impact glasses counting up to several percent.

| Sample | Impact object | SiO\(_2\) | MgO | Al\(_2\)O\(_3\) | Na\(_2\)O | K\(_2\)O | CaO | TiO\(_2\) | Fe\(_2\)O\(_3\) |
|--------|---------------|----------|-----|----------------|---------|-------|-----|---------|-------------|
| KR-2-15 | Kara astrobleme | 71.8     | 4.0 | 16.1           | 5.1     | 1.6   | 1.1 | 0.3     | 0.5         |
| R-13-5/1 | Ries crater    | 67.6     | 2.6 | 16.5           | 2.7     | 2.1   | 3.2 | 0.6     | 4.0         |
| R-13-8a | Ries crater    | 58.0     | 2.6 | 14.6           | 1.6     | 2.9   | 2.2 | 0.9     | 3.7         |
Figure 1. Optical images of the impact glasses in transparent polarized light: (a,b) Kara glass, KR-2-15; (c,d) Ries glass, R-13-5/1; (e,f) Ries glass, R-13-8a; (a,c,e) parallel polarizers; (b,d,f) crossed polarizers. The scale bar 50 μm.

The Raman spectroscopy supports an amorphous state of the studied glasses for the both impact varieties. At the same time, the spectra allow observing the difference in structural ordering of the glasses and partial impact melt crystallization. Thus, we can evidently obtain specific Raman characteristics both for the glasses of the impact craters and for the different samples within the same crater that demonstrate quite wide variety of the structural features.
The low-frequency range 400-700 cm\(^{-1}\) is associated with a level of glass polymerization toward the Raman shift increasing. Glasses usually have general spectral characteristics corresponding to their structural features in the range 800-1200 cm\(^{-1}\) of Raman spectra [8,9]. The band around 800-850 cm\(^{-1}\) is explained by isolated SiO\(_4\) tetrahedra vibrations, where oxygen atoms have non-bridging state (Q\(^0\)). The maxima at 900 cm\(^{-1}\) and 950-980 cm\(^{-1}\) are associated with terminal groups in SiO\(_4\) tetrahedra, with three and two non-bridging oxygen atoms (Q\(^1\) and Q\(^2\), correspondently). Spectral range 1050-1200 cm\(^{-1}\) is described by non-bridging bonds in SiO\(_4\) tetrahedra with unbridged oxygen atoms presence (Q\(^3\)).

The studied impact glasses have mixed distributions with Q\(^0\) (Fig. 2), where n is the number of bridging oxygen per a tetrahedrally coordinated cation. The Ries impact glass has the most three-dimensionally ordered structure with the largest statistical output of the Q\(^{32}\) and Q\(^{33}\) units (Fig. 2). The Kara UHPHT glass with coesite (KR-2-15) has the dominant structural unit Q\(^0\) corresponding to the lowest order compared with the shortest tetrahedral chains to the other glasses [4]. In spite of high water presence within the impact glasses, according to the provided Raman spectroscopy and other studies [3,4], it rather has free molecular state without chemical bonding with the glass structural networks. The Q\(^{13}\)/Q\(^0\) ratio shows that the most ordered (with a high degree of polymerization) glass is present in the sample R-13-8a.

**Figure 2.** Raman spectra of the studied impact glasses: R13-5/1 and R13-8a – the Ries crater glasses; KR-115 – the Kara astrobleme UHPHT glass, KR-2-15 – the Kara astrobleme UHPHT glass with coesite bands.
Figure 3. Typical SEM images in secondary electron mode of the glass surfaces: (a) KR-2-15; (b) R-13-8a; (c) R-13-5/1.

Table 2. Silica states of the Kara and Ries impact glasses by the data of Raman spectroscopy.

| Sample    | \(Q^9\) Position, cm\(^{-1}\) | \(Q^9\) FWHM, cm\(^{-1}\) | \(Q^{22}\) Position, cm\(^{-1}\) | \(Q^{22}\) FWHM, cm\(^{-1}\) | \(Q^{23}\) Position, cm\(^{-1}\) | \(Q^{23}\) FWHM, cm\(^{-1}\) | \(Q^{33}\) Position, cm\(^{-1}\) | \(Q^{33}\) FWHM, cm\(^{-1}\) | \(Q^{33}/Q^9\) |
|-----------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|
| R13-5/1   | 802                           | 81                          | 969                           | 80                          | 1065                          | 67                          | 1206                          | 100                          | 0.44                        |
| R13-8a    | 821                           | 38                          | 976                           | 90                          | 1078                          | 98                          | 1196                          | 100                          | 1.38                        |
| KR-115    | –                             | –                           | 1002                          | 22                          | 1093                          | 137                         | –                             | –                           | –                           |
| KR-2-15   | 801                           | 88                          | 948                           | 113                         | 1081                          | 300                         | –                             | –                           | 0                           |

SEM images show a complicated surface relief (Fig. 3). The surface of the sample R-13-8a presents globules with diameter of about 80 nm and rod-shaped morphological elements about 500 nm in length and 60-100 nm in thick. These elements are set in disorder; the elongated morphological elements are reoriented. The surface of the sample R-13-5/1 shows a hilly relief with short flakes about 50-80 nm in thick that are often released from the hillocks. The relief of the surface of the KR-2-15 sample is more flat, having the characteristic surface of a shell-like fracture of a cleavage surface.

Numerous experiments indicate that the glasses are heterogeneous at the scale of a few nanometers [11]. This heterogeneity can be associated with density fluctuations in pure silica glasses or with chemical composition fluctuations in glasses. This heterogeneity is well manifested on the cleavage surface and is detected by AFM, which is actively used to study the nano-heterogeneity of natural and artificial glasses [4, 11, 12].

Typical AFM images of the samples KR-2-15 and R-13-5/1 show the initial surface roughness as elongated rounded hillocks (Fig. 4), with diameter of 60-70 nm and height of several nanometres. The hillocks are general morphological elements of the glass surface in presence of micro-islands and cracks. Usually, the hillocks are observed being separated from each other with a slight contrast at the images. Moreover, the surface of the sample KR-2-15 is more homogeneous at the microscopic level than the sample R-13-5/1.

The cleavage surface of the sample R-13-8a is more complicated. It consists of islands with diameter about 1 \(\mu\)m and height about 100 nm, which are covered with elongated hillocks about 60-70 nm in diameter. There are numerous rod-like nanocrystals on the surface. Many of them grow directly from the surface, which indicates that they are not debris formed during cleavage. These crystals make it difficult to access the surface to estimate roughness and measure the size of the hillocks. However, in general, the nanoscale surface roughness was also detected for this sample (Fig. 5 – inset).
Figure 4. Typical AFM-images of the samples KR-2-15 (top) and R-13-5/1 (bottom).

Figure 5. AFM images of surfaces of the R-13-8a sample.
According to the EDS results, the studied samples are multicomponent aluminosilicate glasses with impurities of sodium and magnesium. For similar multicomponent synthetic melts, the manifestation of phase separation as a nanoscale roughness is shown in Ref. [12]. The studied samples looked quite homogeneous on the EDS-images, but their elemental inhomogeneity could occur at a nanoscale level that was beyond the sensitivity of the EDS analysis. In our case, the phase separation manifested itself as the surface nanoscale roughness.

Unlike in "pure" silicate impact glasses (as described in Ref. [4]), nanocrystallites and larger morphological elements of the surface occur in multicomponent impact glasses. Morphological elements uniformly cover the surface and are densely packed. If these elements are associated with the distribution of impurities in the melt, it can be assumed that the distribution of impurities in the solidified melts of the impact glasses studied was fairly uniform.

4. Conclusion

We have studied natural glasses solidified from silica-rich melts formed under UHP shock metamorphism from Kara astrobleme (Russia) and Ries crater suevites (Germany). Rounded and elongated morphological nano-elements (60-80 nm in size) of the impact glass surface are observed by AFM and SEM. They cover the surface uniformly and are densely packed. We attribute the roughness and its changing to nanoscale compositional and structural variations within the glass microstructure. With the help of microscopy, nanocrystallites were found in the sample R-13-8a, which was the most ordered according to Raman spectroscopy.

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