Scanning probe microscopy in mineralogical studies: about origin of the observed roughness of natural silica-rich glasses

Ye A Golubev[*] and S I Isaenko

Institute of Geology of Komi SC of Uralian Branch of RAS, Syktyvkar, Russia

[*]golubev@geo.komisc.ru

Abstract. We have studied different mineralogical objects: natural glasses of impact (tektites, impactites) and volcanic (obsidians) origin, using atomic force microscopy, X-ray microanalysis, infrared and Raman spectroscopy. The spectroscopy showed the difference in the structure and chemical composition of the glasses of different origin. The analysis of the dependence of nanoscale heterogeneity of the glasses, revealed by the atomic force microscopy, on their structural and chemical features was carried out.

1. Introduction

The study of mineral surfaces by the scanning probe microscopy (SPM) methods began about twenty years ago. This is rather late as compared to the application of these methods in other natural science disciplines – physics, chemistry, biology, etc. Natural glasses were one of the first mineralogical objects to study by SPM.

Glasses are melts that are solidified near the glass transition temperature, when the cooling rate exceeds the maximum cooling rate under the given conditions for crystallization [1]. The main geological processes of glass formation are:

(i) explosive and impact processes resulting in the melting of rocks under the influence of ultrahigh pressures (35–90 GPa and above) and high temperatures (up to 3000 °C) as well as formation of *impactites*;

(ii) ablation and transport of the melted substance over significant distances after explosive and impact processes (*tektites* are thus formed);

(iii) melting of rocks at the contact with magma resulting in *buchites*;

(iv) hardening of igneous melts resulting in *obsidians*.

Structural differences due to PT-conditions of cooling, concentration, and composition of impurities, and water content, contribute to the appearance of nanoscale structural peculiarities of the glasses. Although the main SPM studies were carried out for artificial glasses [2-6], the most common natural glasses were also studied by these methods [7-9]. AFM observations of the cleavage of the glasses show a surface of shallow hillocks, which are usually as large as several tens of nanometers wide and several nanometers high. The surface roughness data are actively used to evaluate the processes of corrosion, fracture, and polishing in glasses. However, the nature of this roughness remains unclear. Many authors believe that the presence of roughness indicates that the glasses, including natural ones, are heterogeneous at the nanometer scale [4]. This heterogeneity can be caused both by density fluctuations in pure silicon dioxide, and by composition fluctuations in

multicomponent glasses [10]. It has been shown in [11] that the size of the hillocks is much larger in those glasses, in which nuclei of nanocrystallites are present. The possibility of interpreting the cleavage surface of the glasses from the point of view of the discovery of their structural and chemical inhomogeneities, allows speaking about the globular or pseudoglobular structure of the glasses; since for many mineralogical samples, the objects, microscopically observed on the surface, are conditioned by supramolecular structural features [12, 13]. Spectroscopic data allow determining the structure and chemical bonds in natural glasses, distinguishing volcanogenic glasses from impact glasses [14]. The purpose of this study is an attempt to connect structural and chemical data on natural glasses to the results of AFM observations of their surface.

2. Objects and methods

The objects of our study were natural impact glasses: *irgizite* from Zhamanshin Crater (Kazakhstan) and *Libyan Desert glass* (Egypt); volcanogenic *obsidians* (from Kamchatka Peninsula, Armenia, and Italy); and *moldavite* related to tektites (Czech Republic).

The chemical and local structure was determined by the methods of infrared (IR) and Raman spectroscopy, the local chemical composition was estimated by X-ray energy-dispersive spectral analysis. Nanoscale structural features were detected by the atomic force microscopy (AFM).

The surface morphology of the samples has been characterized by AFM measurement in tapping mode using Ntegra Prima microscope (NT-MDT SI, Russia) with super sharp silicon cantilevers of model SSS-NCH (Nanosensors). The resonant frequency of cantilevers is about 330 kHz, the radius at the end is 3–5 nm and the stiffness constant is about 35 N/m. The images have been recorded at a scan frequency between 0.8 and 1 Hz for a resolution of 512×512 pixels. To reduce the effect of static electricity on the images, we increased humidity in the room (relative air humidity of about 85%) and grounded the samples. For each sample, we performed at least 5 AFM images with 3–5 different scan areas.
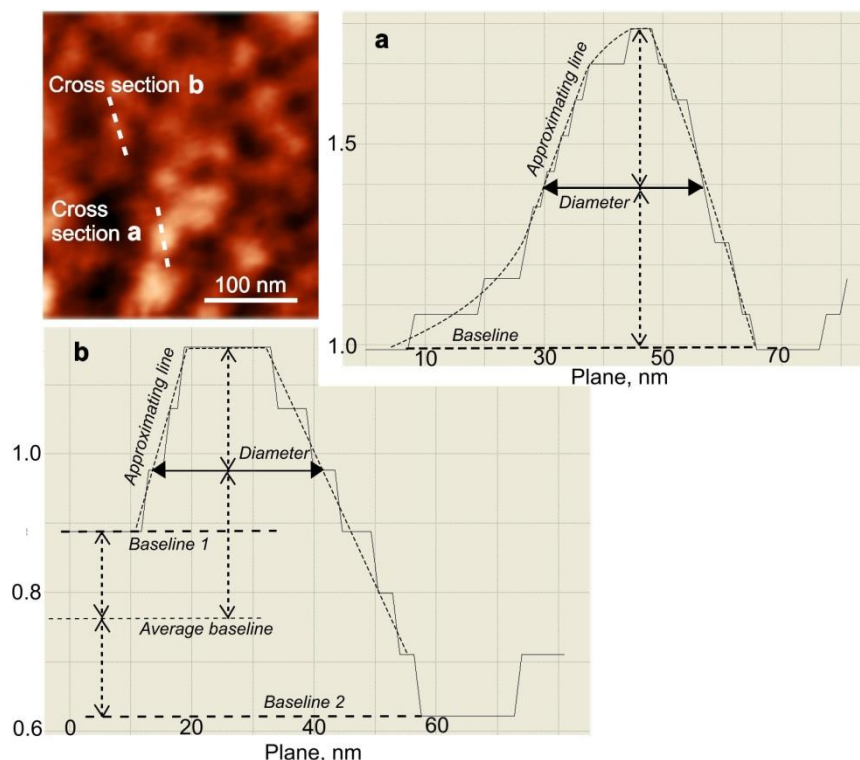

Figure 1. Scheme for measuring of the hillock diameter.

Method for measuring the size of the objects on the surface. In the majority of the works, the surface roughness is used to quantify the objects on AFM images, which is estimated from a standard histogram. In this case, we receive the average height of the hillocks. However, the glasses have a complex surface relief. It can be characterized by roughness of several orders in the image plane: micron-size waves; submicron-size wave; islands of 200–300 nm in diameter, covered by hillocks with diameter of the tens of nanometers. Therefore, the measured roughness always possesses several levels on natural glasses. Moreover, the comparative analysis is complicated by the influence of experimental parameters, such as tip radius, tip-sample force, scan size and pixel resolution. In our work we performed measurements of visible linear sizes (diameter) of the contacting hillocks along the surface profiles (Fig. 1). Due to the complex surface relief, the bases of the hillocks are positioned, as a rule, at the different heights. Therefore, the measurement of diameters was conducted at a half of the hillocks height. The height was measured from the average baseline between baselines of hillock to peak. Such an approach allows decreasing somehow the object broadening effect on the surface by a probe. We measured sizes of 95–120 hillocks for various samples.

The cleaved surfaces of the samples were studied with a Tescan Vega LMH scanning electron microscope with W heated cathode. X-ray energy-dispersive spectrometry (EDS) was used to investigate the chemical composition with AZTEC software (Oxford Instruments) processing.

Raman spectroscopy was carried out with a LabRam HR800 instrument (Horiba, JobinYvon) at room temperature. The system was equipped with an Olympus BX41 optical microscope and a Si-based CCD detector. The spectra were recorded in the 100–4000 cm^{-1} range using a spectrometer grating of 600 g/mm, with a confocal hole of 300 μm and a slit of 100 μm. As an exciting radiation, an external Ar$^+$ laser (514.5 nm; 1.2 mW) was used. After background correction, individual lines were deconvolved using a curve-fitting procedure from the software provided by LabSpec 5.36.

3. Results

The spectroscopic and X-ray spectral studies allowed establishing the composition of the matrix of glasses (Table 1). It can be seen that SiO_2 content increases in sequence: volcanic glasses – tektite – impactites. On the AFM images the microscopic heterogeneity of the glasses is shown as practically isometric rounded hillocks (Fig. 2), which sizes in the image plane are the tens of nanometers. The distribution of the hillocks is narrow in size, having a lognormal-like appearance (Fig. 3). The smallest average hillock diameters are as follows: for Libyan glass – 21 nm, for irgizite – 26 nm; for moldavite – 34 nm. The average hillock diameter for obsidians varies within 55–70 nm. The hillock nature is traditionally associated with the nanocrystalline structural features of glasses [9,11]; however, published images of high-resolution transmission electron microscopy [15,16] show that atomic lattices in natural glasses are disordered, and it is more correctly to explain their appearance by density fluctuations or by chemical heterogeneity. The results of X-ray spectral analysis of the glasses are given in the Table 1. It can be seen that there is a direct correlation between the hillock size and the content of impurities. The more impurities are, the greater the size of the hillocks is.

Table 1. Composition of the glasses (at. %).

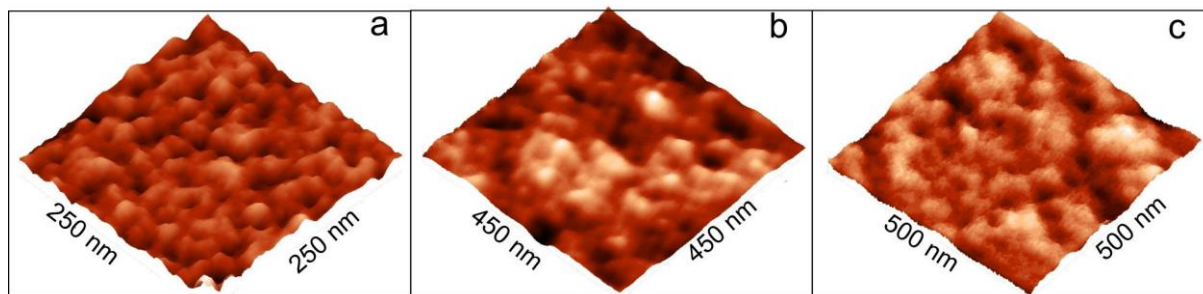|	Libyan glass	Irgizite	Moldavite	Obsidian (Kamchatka)	Obsidian (Italy)	Obsidian (Armenia)
O	66.1	65.5	64.2	61.9	60.9	63.3
Si	33.4	26.5	27.4	24.5	25.5	23.9
Mg	not det.	1.6	1.1	0.9	1.3	0.1
Al	0.3	4.0	3.9	0.8	0.6	6.6
Na	not det.	0.8	0.3	5.8	7.7	2.5
K	–//–	0.8	1.5	0.2	0.2	2.0
Ca	–//–	0.7	1.0	1.9	3.5	0.3
Ti	–//–	0.2	0.1	not det.	not det.	0.1
Fe	0.1	1.4	0.4	0.1	0.1	0.1

Figure 2. Typical AFM images of the surface of natural glasses: (a) Libyan glass; (b) irgizite; (c) obsidian (Italy).
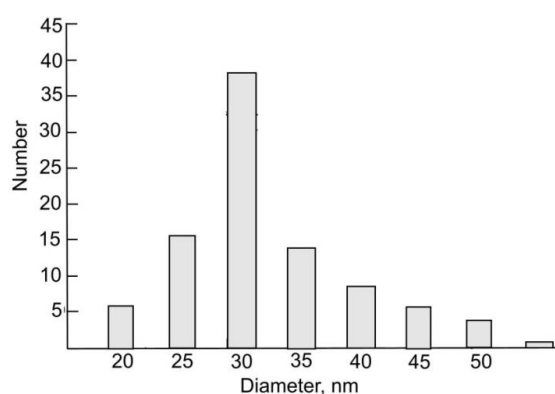

Figure 3. Typical measured distribution of hillocks diameter (for moldavite).

According to IR spectroscopy, three types of vibrations in the SiO_2 molecule were revealed in the glasses. One vibration is associated with crystal structure, in this case with valence vibrations in the quartz molecule. Two others are connected with valence and deformation vibrations in SiO_2 structures.

In our case, a shift of the peak of the valence vibrations of crystalline SiO_2 (900–1100 cm^{-1}) toward smaller angles is observed: in Libyan glass (1102 cm^{-1}), irgizite (1088 cm^{-1}), moldavite (1085 cm^{-1}), and obsidians (1039–1042 cm^{-1}). The absorption bands in this region are typical for all silicate glasses and can be attributed to the valence vibrations of silicon and oxygen atoms in the bridge bonds of the silicon-oxygen tetrahedron. In the spectra of impactites, the absorption band is bifurcated and broadened, which is possibly due to the isomorphous substitution of silicon atoms in the tetrahedron for aluminum atoms. For example, it is known that at the partial replacement of Si^{4+} by Al^{3+}, the valence absorption bands shift to low frequencies. The tetrahedral layer is filled by the principle of the closest packing, so replacing of Si (with ionic radius 0.39 Å) by Al (0.57 Å) or Na (0.92 Å) increases the dimensions of the tetrahedra. Therefore, the shift of this maximum results most likely from the complexity of tektite and volcanic glass. We observe dependence of the diameter of the hillocks on the surface of the glasses on the position of the given maximum in the IR spectrum (Fig. 4). Taking into account the chemical nature of this shift, together with the results of elemental analysis, it is possible to assume the chemical nature of nanoscale heterogeneity of glasses. It can be associated with such a feature of the formation of glasses from melts, as the accumulation of a glass-forming agent (SiO_2) in domains surrounded by a melt with a higher content of cation-modifiers, which are usually elements of the first and second groups [14]. In our samples, there are Na, Ca, Al, and Mg impurities (table), and their content increases from impact glasses to tektites and volcanic glasses. Cations of modifiers are located in free cavities of the structural lattice, compensating excessive negative charge of the complex anion. The strength of the modifier-oxygen bond is much lower than the strength of the glass-to-oxygen bond, so the modifiers do not form strong coordination groups, and when the glass breaks, the bonds break along the clusters of modifier elements.
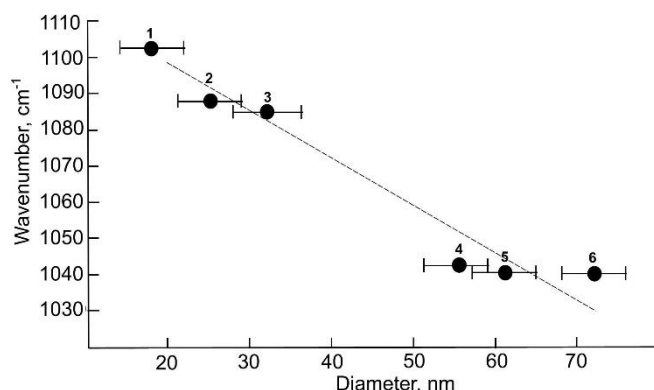
Figure 4. Dependence of the displacement of the ν (SiO$_2$) band about 1100 cm^{-1} on hillocks diameter. 1 – Libyan Desert glass; 2 – irgizite; 3 – moldavite; 4 – obsidian from Kamchatka; 5 – obsidian from Italy; 6 – obsidian from Armenia.

On the Raman spectra, the structural features of glasses are shown, first of all, in the high-frequency region 800–1200 cm^{-1} [14]. The band with a maximum in the region of 800–850 cm^{-1} is related to the valence vibrations of isolated SiO$_4$ tetrahedra, in which all the oxygen atoms are non-bridging (structural units Q^0). The bands with a maximum in the regions 900 cm^{-1} and 950–980 cm^{-1} are conditioned by vibrations of terminal groups in SiO$_4$ tetrahedra, with three and two non-bridging oxygen atoms (structural units Q^1 and Q^2), respectively. The band with a maximum in the range 1050–1200 cm^{-1} is associated with valence vibrations of the non-bridging bonds in SiO$_4$ tetrahedra with one non-bridging oxygen atom (structural units Q^3). In the low-frequency region (400–700 cm^{-1}) there is an intense band, the maximum of which shifts toward higher frequencies with increasing degree of polymerization of the glass.

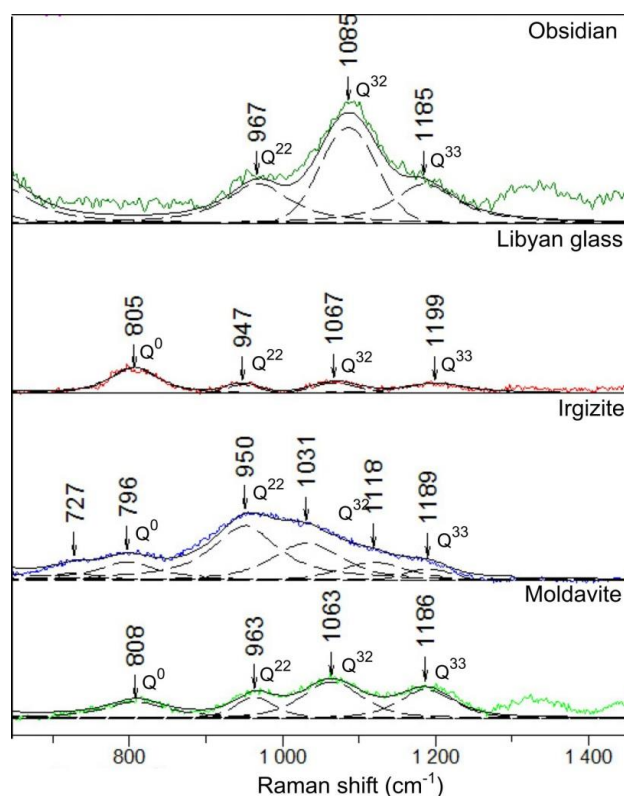**Figure 5.** Raman spectra of glasses.

Our samples show mixed distributions of Q^n, and the obsidian spectrum shows the most 3D-ordered structure (Fig. 5). In their spectra, the largest statistical weight of the structural units Q^{32} and Q^{33} is recorded. In the spectrum of moldavite, as in obsidians, the band, corresponding to the structural unit Q^{32}, is predominant, but this band is not yet so clearly distinguished against the background of the remaining bands. In addition, unlike the obsidians, the bands appear, which correspond to the structural units Q^0, which testifies to the significant number of SiO_4-chain breaks and a relatively more disordered structure. In irgizite, the band of the structural unit Q^{22} becomes the predominant one, while the essential role of the band Q^0 remains, which testifies to the relatively smaller ordering of irgizite in comparison with the moldavite. In Libyan glass, the band of the structural unit Q^0 becomes the dominant band, which testifies to the lowest orderliness of this glass in comparison with the others, in particular, to the shortest chains of tetrahedra.

4. Conclusion

According to the results of elemental X-ray spectral analysis and IR spectroscopy, the impact glasses (impactites and tektites) have more homogeneous silica matrix with fewer impurities than volcanic glasses. The dependence of the saturation degree of the natural glasses structure with cation-modifiers (Al, Na, Ca, Mg) on the dimensions of surface inhomogeneities is revealed. It allows relating IR spectroscopic and X-ray spectroscopic data with nanostructural glass features. There is the correlation between the degree of ordering of the structure (according to the Raman spectroscopy data) and content of the impurities in silica glasses. This fact allows suggesting chemical nature of the glass nanoheterogeneity obtained by AFM. The presence of impurities, partially framing the nanosized regions of the glass-forming matrix, promotes the cleavage along the impurity-containing regions and the formation of a rough cleavage surface.

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