IOP Conference Series: Earth and Environmental Science

PAPER • OPEN ACCESS

# Mineralogical Features of Ultrahigh Pressure Impact Glasses of the Kara Astrobleme (Pay-Khoy, Russia)

To cite this article: Tatyana Shumilova *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **362** 012041

# Mineralogical Features of Ultrahigh Pressure Impact Glasses of the Kara Astrobleme (Pay-Khoy, Russia)

**Tatyana Shumilova[1], Alexandr Zubov[1], Sergey Isaenko[1], Svetlana Shanina[1]**
[1] Institute of Geology, Komi Scientific Center of Ural Division of Russian Academy of Sciences, Russia; Pervomayskaya st 54, Syktyvkar, 167982, Russia

tg_shumilova@mail.ru

**Abstract**. The behavior of the disordered systems in the conditions of the strong compression attracts particular interest in materials science. Natural impact glasses, being with a metastable state, can keep features of the structure for millions of years, form essential volumes compare to experimentally possible high-pressure products. The complex analysis of geological, mineralogical-petrographic, petrochemical features and degree of crystallinity of tagamites, vein glasses and vitro-clastic formations of the origin type of melt impactites of the Kara astrobleme including their phase state composition have been studied. The melt Kara impactites have dependence on the initial character of the melted sedimentary target and cooling velocity of an impact melt. The lowest order has been described for ultrahigh pressure vein-type glasses which contain silica drops with single crystalline coesite and firstly found melt-crystallized high pressure variety of smectite. The vein melt impactites consist of solidified impact melt presented by totally amorphous alumina silicate glass with augite microcrystallites and ultrahigh pressure silica glass with coesite microcrystals and "drops" of firstly found melt-crystallized high pressure variety of smectite. The boundary between alumina silicate and silica glass is characterized with liquated amorphous Fe-rich drops. The special feature of the studies melt impactites is low alteration in spite of 70 Ma age and high content of water. The large volumes of an impact melt created massive tagamite bodies have longer cooling underwent with the almost complete crystallization. The obtained data indicate the specific nature of melt glasses of vein type and prospects of their further research for fundamental study of amorphous state under ultrahigh pressure and propose new materials.

## 1. Introduction

The disordered substances belong to specific type of materials among which glasses are especially important. However, the structure and features of phase composition of glasses remain insufficiently clear, despite actively conducted studies in materials science [1-7]. At the same time the behavior of the disordered systems in the conditions of the strong compression attracts particular interest in materials science, the numerous studies are carried out. As a rule the experiments are provided at room temperature and under pressure usually reaching 1-2 GPa, only. The high temperature high pressure experimental works are rare and get no more than 1100 °C with pressure 8 GPa [8]. At the same time glasses have quite wide spread occurrences in the nature where the specific importance belongs to impact varieties formed at large astroblemes resulted by large meteorite impact events changing target rocks with ultrahigh pressures (35-90 GPa and more) and very high temperatures getting thousands

Celsius degree [9, 10]. We suppose that natural impact glasses, being in a metastable state, can keep their structural features for million years. They can form rather essential volumes compare to experimentally possible high-pressure products. Thus, the natural impact glasses can be prospectively important to study not only geological problems, such as modeling of astroblemes formation, but also to decide a number of fundamental questions of noncrystalline substances state under extreme conditions, their stability, and also to estimate them as possible materials for hi-tech applications, in particular for different microelectronics and high-energy laser technologies [11-15]. Within this paper we describe some mineralogical features of impact melt impactites with especial attention to recently found ultrahigh pressure vein glasses [16-18].

## 2. Materials and methods

The material was sampled in 2015 and 2017 at the Southern part of the Kara astrobleme (North-Eastern part of the Pay-Hoy ridge, Russia). The ultrahigh pressure high temperature (UHPHT) impact glasses of the vein type were described in natural outcrops in cross-cut position to host suevites. The detailed studies of the UHPHT impact glasses were provided compare to massive melt impactites clastic melt fragments within suevites by a complex of mineralogical studies in the Center of collective use of the Institute of Geology of Komi Scientific Center UB RAS (Syktyvkar, Russia) including Raman spectroscopy, scanning electron microscopy (SEM), electron microprobe analysis (EMPA), X-Ray diffraction (XRD), thermal analysis, fluid chromatography, chemical analysis and others. High resolution transmission electron microscopy (HRTEM) was produced at the National Research Center «Kurchatov Institute» (Moscow, Russia).

## 3. Results

By wait chemical analysis and microprobe studies it was established that the melt impactites of the Kara astrobleme are presented mostly by aluminosilicate content as for bulk melt rock, melt clasts within suevite and for vein UHPHT glasses (Table 1). Also, we have found that the melt varieties have different degree of crystallizing differentiation with elements of UHPHT liquation [16]. The compare analysis of Kara vein, massive melt rock substance and suevitic melt clasts allowed reveal the general regularity in differentiation of impact melts to silicate and aluminosilicate components (Figure 1) within impact melt of vein-like variety with UHPHT differentiation of water-rich aluminosilicate component into crystallized smectite within silica glass with coesite (Figure 1, 2, table 2). The detailed analysis of UHPHT vein impact glasses structure with use of high resolution transmission electron microscopy allowed to prove smectite crystallization directly from impact melt.

The uniform regions of aluminosilicate impact glasses contain in local areas rather evenly the distributed clinopyroxene microcrystals with their possible higher concentration in inhomogeneous regions. Silicate drops are characterized by denser arrangement of coesite in the centers of drops. It is established that the boundary between silicate drops and the aluminosilicate general glass matrix is gradual.

The geochemical specificity of the studied vein UHPHT impact glasses has quite uniform composition (Table 1) forming quite local region on the TAS diagram corresponding to basaltic content compare to massive melt rocks and clusts within suevites having very wide composition [17]. Also, the vain variety has a significant coverage of "forbidden field" for feldspars contents indicates a significant geochemical difference between the impact glasses and condensed crystallized melts of the Kara impactites and volcanic glasses, characterized by a more homogeneous composition for individual volcanic structures and batch eruptions.

**Table 1.** Petrochemical components of vein UHPHT impact glasses

| Component | Chemical composition (wt %) | | | | |
|---|---|---|---|---|---|
| | Kp15-2-15 | Kp15-12-116 | Kp15-12-117 | Kp15-12-119 | Kp15-12-115 |
| $SiO_2$ | 56.56 | 57.25 | 59.68 | 59.16 | 56.18 |
| $TiO_2$ | 0.74 | 0.76 | 0.89 | 0.78 | 0.86 |
| $Al_2O_3$ | 15.17 | 15.00 | 15.00 | 15.64 | 15.07 |
| $Fe_2O_3$ | 7.34 | 6.94 | 6.90 | 6.67 | 6.93 |
| MnO | 0.09 | 0.08 | 0.09 | 0.08 | 0.08 |
| CaO | 3.22 | 3.09 | 2.97 | 2.49 | 3.45 |
| MgO | 5.80 | 4.94 | 5.16 | 4.86 | 4.91 |
| $K_2O$ | 1.64 | 2.19 | 1.36 | 1.91 | 2.45 |
| $Na_2O$ | 2.14 | 2.31 | 2.66 | 2.94 | 2.65 |
| $P_2O_5$ | 0.16 | 0.16 | 0.17 | 0.17 | 0.16 |
| L.O.I | 7.12 | 7.82 | 5.62 | 5.97 | 6.64 |
| Total | 99.98 | 100.54 | 100.5 | 100.67 | 99.38 |
| FeO | 4.23 | 3.21 | 4.33 | 4.30 | 3.29 |
| $H_2O$ | 2.29 | 3.12 | 2.43 | 2.56 | 2.50 |
| $CO_2$ | 0.74 | 0.96 | 0.32 | 0.3 | 0.46 |

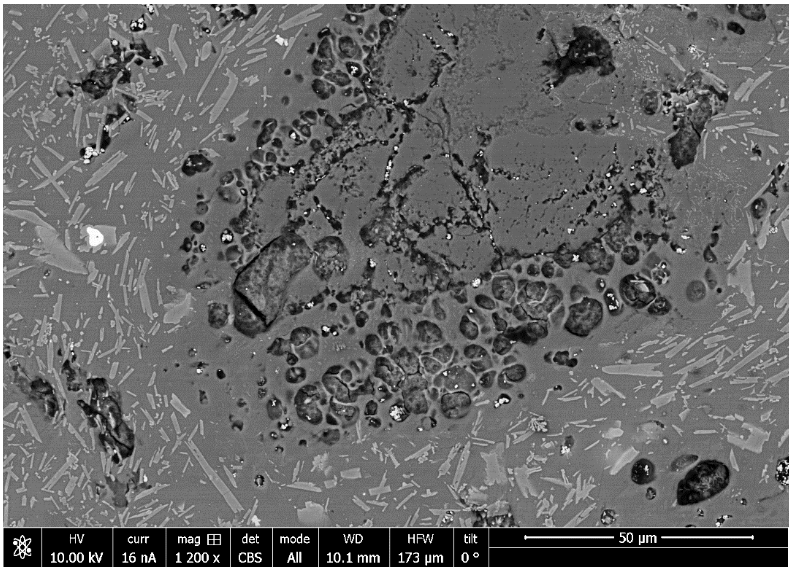


**Figure 1.** SEM image of UHPHT impact vein-like glass (BSE mode) with silica drop (the center part) containing coesite crystals and smectite isolations. The surrounding matrix is presented with alumina silicate glass containing augite microcrystals

Also, it was measured that the vein UHPHT impact glasses have quite high $H_2O$ concentration (Table 1, figure 2) being set generally within glass matrix and partly within melt crystallized smectite (Figure 3) [18]. For some Kara vein glasses specimens, the considerable $H_2$ emanation has been observed above 700 °C.

The detailed studies by means of the high-resolution transmission electron microscopy showed that the coesite microcrystals are located in completely amorphous $SiO_2$ glass. The coesite has single crystalline structure without any deformation defects (Figure 3, table 2). The found twins within coesite have features of their growth mechanism formation (non-martensitic mechanism, diffuse mechanism). Thus, it is possible to conclude that the coesite within the ultrahigh pressure glasses was crystallized from an impact melt that confirms our hypothesis of the high pressure nature of the studied Kara vein impact melt glasses.

X-Ray diffraction patterns of UHPHT vein-like glass, massive melt rocks and clastogenic melt fragments from suevites were decomposed to crystal and X-Ray amorphous components (Figure 4) for calculation of a level ordering by the method described in [19] with use of the ratio of integrated counts of crystalline component to the total area above the linear background (summarized amorphous and crystalline components). Relative crystallinity (RC) has been calculated by the formula (1):

$$RC = CS_C/L_C = C_C/(C_C+A_C)(\%), \quad (1)$$

where $CS_C$ and $L_C$ are the integrated counts above the cubic spline and linear backgrounds, respectively, and $A_C$ and $C_C$ are the counts associated with the amorphous and crystalline components, respectively [19].

On the basis of X-ray diffraction studies it is established that the ultrahigh pressure vein glasses of the Kara astrobleme have the lowest degree of crystallization in comparison to other condensed impact melts – tagamites and vitro-clasts of suevite (Table 3). Thus, tagamites are characterized by high degree of crystallinity – up to 90%. Clastic type has divided into two varieties – containing up to 10% of an amorphous component and its total absence. The vein glasses has the largest content of an amorphous component can get up to 95% according to X-ray diffraction measurements.

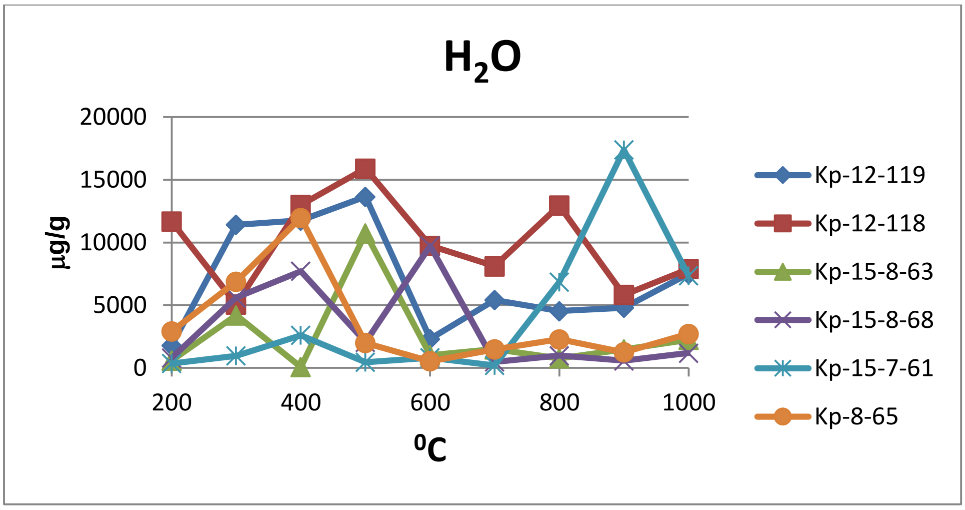


**Figure 2**. Fluid chromatography data of $H_2O$ component within melt impactites: vein-like UHPHT glasses – Kp15-12-118, Kp15-12-119, bulk melt rock - Kp15-8-63, Kp15-8-65, melt clasts- Kp15-7-61, Kp15-8-68

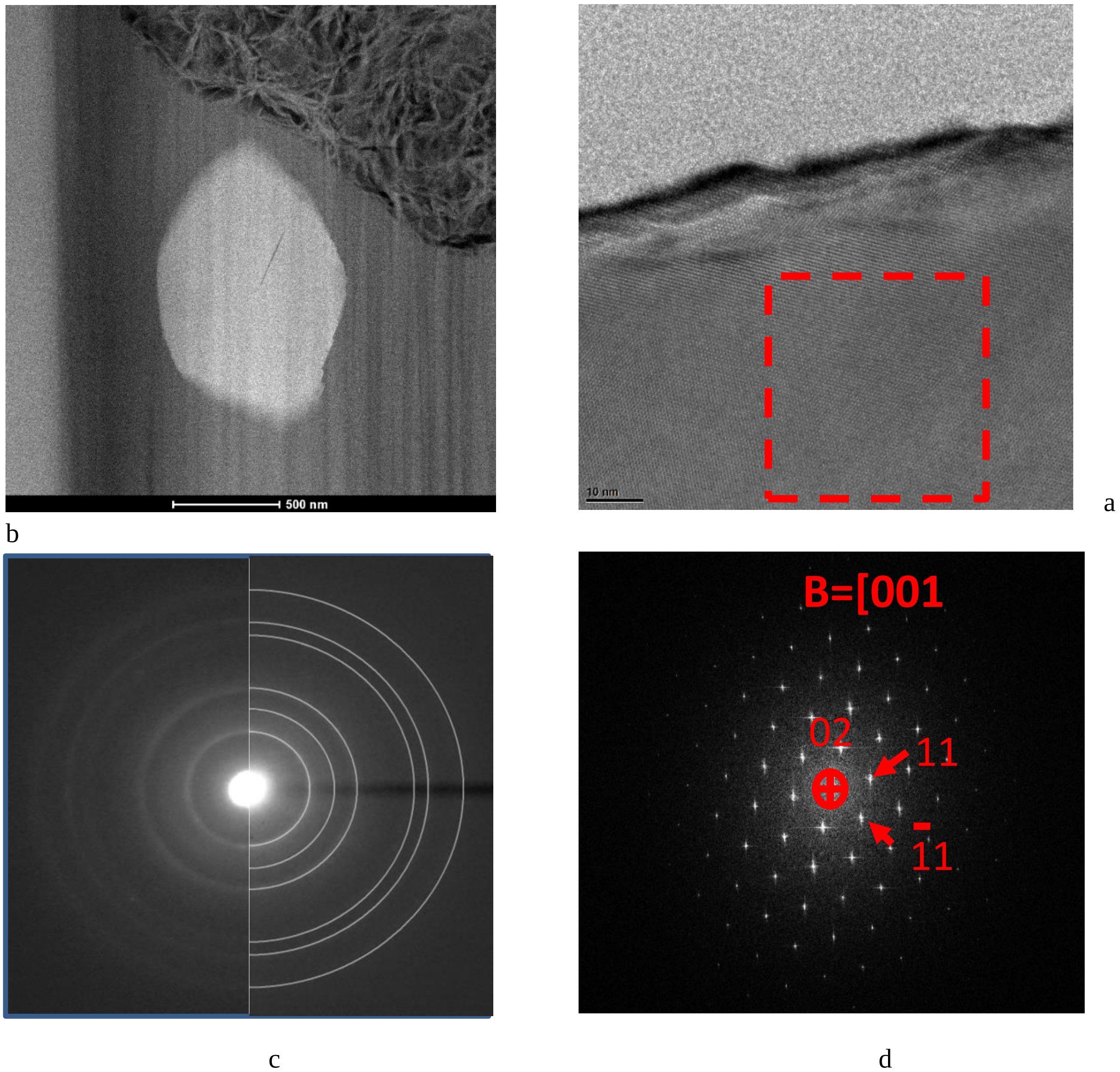


**Figure 3.** TEM data of silica UHPHT glass with coesite single crystal inclusion (light grey. İmage middle) and smectite aggregate (fibbrous pattern, upper part of the image): a – bright field (BF) image; b – HRTEM image with marked regoin for Fourier transformation; c – electron diffraction pattern of smectite with the corresponding distances – 0.437; 0.313; 0.248; 0.163; 0.151 and 0.126 nm; d – Fourier transformation of coesite lattice on the BF image; structural paramters of coesite

**Table 2.** Structural parameters of single crystalline coesite (to the figure 3a) within UHPHT impact glass of vein-type

| Parameter | Experimental | Standard |
|---|---|---|
| $d_{020}$ | 0,614 nm | 0,6165 nm |
| $d_{110}$ | 0,555 nm | 0,555 nm |
| $d_{1-10}$ | 0,555 nm | 0,555 nm |
| Angle((020), (110)) | 63,3° | 63,3° |
| Angle((110), (1-10)) | 53,4° | 53,4° |

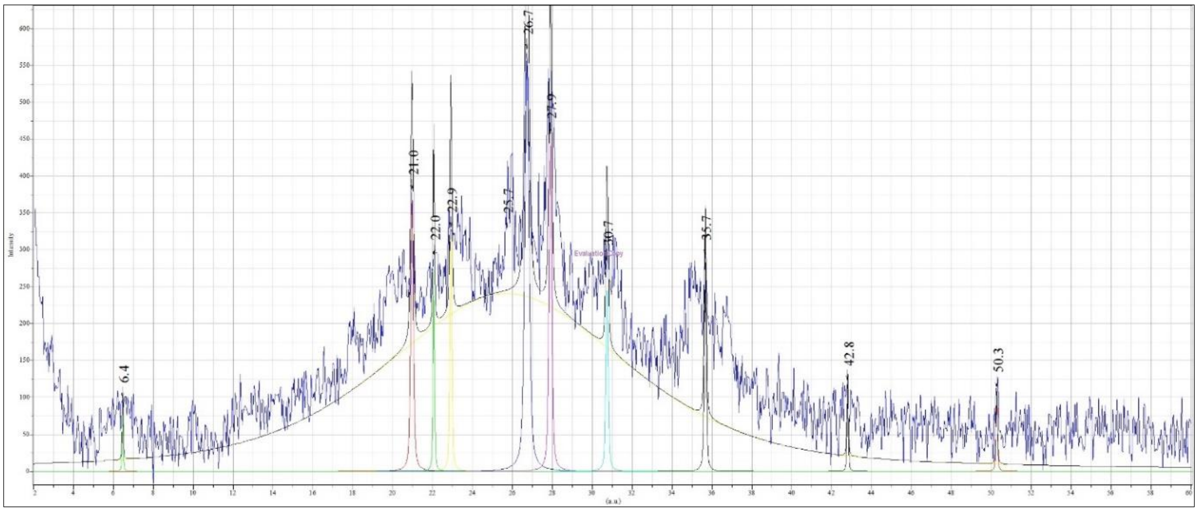


**Figure 4**. X-Ray diffraction pattern of UHPHT vein-like glass, sample Kp15-12-115 (42 % crystallinity)

**Table 3.** Crystallinity level of different melt originated impactites of the Kara astrobleme

| Sample | General characteristics | Crystallinity level, % |
|---|---|---|
| Kp15-8-63 | Massive melt rock | 90 |
| Kp15-8-66 | Massive melt rock | 89 |
| Kp15-7-41 | Vitro-clast of suevite | 90 |
| Kp15-7-58 | Vitro-clast of suevite | 100 |
| Kp15-12-115 | UHPHT impact vein glass | 42 |
| Kp15-12-117 | UHPHT impact vein glass | 47 |
| Kp15-12-118 | UHPHT impact vein glass | 6 |

## 4. Discussion

Nanostructures of UHPHT vein impact glasses of the Kara astrobleme under comparing with low pressure low temperature glasses of natural and artificial origin showed a number of features. The comparative analysis of the impact glasses of incrater impactites, outer crater emissions, volcanic and artificial glasses, including Suprasil standard, showed that the low pressure fast cooled down impact glasses have more uniform $SiO_2$ matrix with smaller amount of impurity in comparison with glasses of volcanic origin and high pressure impact glasses of suevites. In the complex analysis of atomic force microscopy data and microprobe analyses the dependence of the extent of nanostructural heterogeneities of natural glasses from a saturation of their structure by cations modifiers (Al, Na, Ca, Mg) is revealed. The especially strong influence is noticed in connection with Na impurity presence that, most likely, in many respects and defines nanostructural heterogeneity of natural silica-alumina glasses. For rather purer silicate glasses of the studied selection the correlation of a degree of order of structure according to Raman spectroscopy measurements with impurity level is also observed. This allowed conclude that chemical elements impurity is the most significant factor defining nanoheterogeneity of the impact glasses. As for the impurity-less silica glasses (a standard - Suprasil, the Libyan glass) the nanostructure, probably, is defined by statistical density fluctuations of a glass-forming matrix in a melt.

The high content of nonstructured molecular $H_2O$ within the vein UHPHT compare to massive tagamites, vitro-clasts and the sedimentary rock target can be a specific feature of their formation under

UHP conditions. The high level of water concentrations within the glasses can define a high mobility of the UHPHT impact melts and a possibility of residual high pressure significantly more long time what earlier had been described by S.A. Vishnevsky [20] for the Popigai astrobleme. In spite of water-rich specifics the origin amorphous state of the UHPHT vein glasses is low altered with secondary processes and devitrification.

## 5. Conclusion

The complex analysis of geological, mineralogical-petrographic, petrochemical features and degree of crystallinity of tagamites, vein glasses and vitro-clastic formations of the origin type of melt impactites of the Kara astrobleme allowed to establish that the structural and phase states of the melt impactites are defined, first of all, by the initial character of the melted sedimentary target and cooling velocity of an impact melt. The large volumes of an impact melt created massive tagamite bodies have longer cooling underwent with the almost complete crystallization. The obtained data indicate the specific nature of melt glasses of vein type and prospects of their further research.

## Acknowledgments

The authors thank M.A.Tropnikov for SEM and EMPA measurements, I. A. Karateev and L. A. Vasiliev for help in HRTEM studies and smectite identification. The analytical work has been produced in the Center for Collective Use “Geonauka” supported by Project NIR # AAAA-A17-117121270036-7. The study has been provided with financial means of the Russian Science Foundation, Project # 17-17-01080.

## References

[1] Benmore, C. J., Soignard, E., Amin, S.A., Guthrie, M., Shastri, S. D., Lee, P. L., Yarger, J. L. Structural and topological changes in silica glass at pressure. Phys. Rev. B 81, 054105. DOI: 10.1103/PhysRevB.81.054105, 2010.

[2] Brazhkin, V. V., Fomin, Yu. D., Lyapin, A. G., Ryzhov, V. N., Trachenko, K. Two Liquid States of Matter: A Dynamical Line on a Phase Diagram. Phys. Rev. E 85, 031203, 2012.

[3] Brazhkin, V.V., Katayama, Y., Trachenko, K. et al. Nature of Structural Transformations in the B2O3 Glass under High Pressure. Phys. Rev. Lett.101, 035702, 2008.

[4] Deschamps, T., Margueritat, J., Martinet, C., Mermet, A., Champagnon, B. Elastic Moduli of Permanently Densified Silica Glasses. Scientific Reports 4: 7193. DOI: 10.1038/srep07193, 2014.

[5] Kono, Y., Kenney-Bensona, C., Ikutaa, D., Shibazaki, Yu., Wang, Y., Shena, G. Ultrahigh-pressure polyamorphism in GeO2 glass with coordination number >6. PNAS 113 (13), 3436–3441 (2016).

[6] Sato, T., Funamori, N. High-pressure structural transformation of $SiO_2$ glass up to 100 GPa. Phys. Rev. B, 82, 184102, 2010.

[7] Tsiok, O. B., Brazhkin, V. V., Lyapin, A. G., Khvostantsev, L. G. Logarithmic Kinetics of the Amorphous-Amorphous Transformations in $SiO_2$ and $GeO_2$ Glasses under High Pressure. Physical Review Letters, 80(5), 999–1002, 1998.

[8] Guerette, M., Ackerson, M.R., Thomas, J., Yuan, F., Watson, E.B., Walker, D., Huang, L. Structure and Properties of Silica Glass Densified in Cold Compression and Hot Compression 2015 Scientific Reports, 5,15343. DOI: 10.1038/srep15343, 2015.

[9] Stoffler, D. Hamann, C., Metzler, K. Shock metamorphism of planetary silicate rocks and sediments: Proposal for an updated classification system. Invited Review. Meteoritics & Planetary Science, 1–45, 2017.

[10] Stoffer, D., Langenhorst, F. Shock metamorphism of quartz in nature and experiment. I. Basicobservation and theory. Meteoritics, 29, 155–181, 1994.

[11] Bolmatov, D., Brazhkin, V. V., Trachenko, K. Thermodynamic behavior of supercritical matter. Nature Communications 4, Article Number 2331, Doi: 10.1038/ncomms3391, 2013.

[12] Borisova, P. A., Blanter, M. S., Brazhkin, V. V., Somenkov, V. A., Filonenko, V. P. Phase transformations in amorphous fullerite C-60 under high pressure and high temperature. Journal of Physics and Chemistry of Solids, 83,104–108, 2015.
[13] Golubev, Ye. A., Shumilova, T. G., Isaenko, S. I., Makeev, B. A., Utkin, A. A., Suvorova, E. I., Ernstson, K. Nano-heterogeneity of natural impact silica-rich glasses according to atomic force microscopy and spectroscopy. Non-Crystalline Solids 8, 692 3. DOI:10.1038/s41598-018-25037-z, 2018.
[14] Ren, J, Zhang L, Eckert, H. Medium-Range Order in Sol−Gel Prepared $Al_2O_3$−$SiO_2$ Glasses: New Results from Solid-State NMR. J. Phys. Chem. C, 118, 4906−4917, 2014.
[15] Rouxel, T. Elastic Properties and Short-to Medium-Range Order in Glasses. J. Am. Ceram. Soc., 90 (10) 3019–3039, 2007.
[16] Shumilova, T. G., Isaenko, S. I., Makeev,B. A., Zubov, A. A., Shanina,S. N., Tropnikov, Ye. M., Askhabov, A. M. Ultrahigh-Pressure Liquation of an Impact Melt. Doklady Earth Sciences, 480 (1), 595–598. DOI: 10.1134/S1028334X18050070, 2018.
[17] Shumilova, T. G., Lutoev, V. P., Isaenko, S. I., Kovalchuk, N. S., Makeev, B. A., Lysiuk, A. Yu., Zubov, A. A. Spectroscopic features of ultrahigh-pressure impact glasses of the Kara astrobleme. Scientific Reports, 8(1) DOI:10.1038/s41598-018-25037-z, 2018.
[18] Shumilova, T.G., Zubov, A.A., Isaenko, S.I., Karateev, I.A., Vasiliev, A.L. Mysterious long-living ultrahigh pressure or secondary impact crisis? Scientific Reports, submitted, 2019.
[19] Rowe, M. C., Ellis, B. S., and Lindeberg A. Quantifying crystallization and devitrification of rhyolites by means of X-ray diffraction and electron microprobe analysis. American Mineralogist, 97. pp. 1685–1699, 2012.
[20] Vishnevsky, S. A. Popigai astrobleme (Russia): water & diamond potential of impactites-tagamites. 42nd Lunar and Planetary Science Conference, 2011. Abstract 1666, 2011.