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Uranium Retention in Silica-Rich Natural Glasses: Nuclear Waste Disposal Aspect

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Abstract: Uranium-containing glass samples with an age of 140–145 million years were collected within the volcanic rocks of the largest volcanic-related uranium ore deposit in the world. Main features of their composition are high concentrations of silica and uranium, the largest for the rocks of this type. In contrast to this, the ages of fresh (unaltered) low-silica natural glasses of a basic composition (basalts) usually do not exceed a few million years. The volcanic low-silica glass is unstable at longer times and in older ancient rocks is transformed into a crystalline mass. The geochemistry of uranium including the behavior in solids and solutions is similar to that of long-lived transuranic actinides such as radioactive Np and Pu from high-level radioactive waste. This allows uranium to be used as a simulant of these long-lived hazardous radionuclides both at the synthesis and for the study of various nuclear wasteforms: glasses, glass crystalline materials and crystalline ceramics. The data obtained on long-term behavior of natural glasses are of importance for prognosis and validation of stability of nuclear wasteforms disposed of in geological disposal facilities (GDF).

Keywords: volcanic glasses; nuclear waste; uranium retention

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1. Introduction

Glasses are solids quenched from liquids without phase separation, which can be avoided using enough rapid cooling rates. For example, metallic glasses are produced using fast cooling whereas silicate glasses are formed on the natural cooling of melts because crystallization in such systems proceeds at very low cooling rates. Upon heating, glasses continuously change their properties to those of a liquid-like state (melt) in contrast to crystals, where such changes occur abruptly at the melting point, T_m. The ranges of solid-like and liquid-like behavior of amorphous materials are divided by glass transition temperature, T_g. Whether a material behaves either as a liquid or a solid depends on the connectivity between its elementary building blocks—atoms, molecules, or clusters. Solids are characterized by a high degree of connectivity whereas structural blocks in melts have a lower connectivity. There is a threshold connectivity determining the T_g in each actual system being a function of composition and logarithmically dependent on cooling rate [1,2]. Being solid-state solutions, glasses are highly tolerant to compositional changes. Properties of glasses change continuously with variation of composition. The high chemical durability and tolerance of glasses to compositional variations as well as the ease of their production by cooling of molten mixtures of substances have determined vitrification to be an effective method of nuclear waste immobilization. Indeed, nuclear waste vitrification provided a high degree of retention of radionuclides and significantly contributed to the increased safety of the storage, transportation and final disposal of high-level nuclear waste, which is a dangerous by-product of the peaceful use of nuclear energy [3–5]. Several countries have operated vitrification facilities for decades, significantly reducing the hazard of environmental contamination arising from highly radioactive liquid waste generated at spent nuclear fuel reprocessing (Table 1).

Table 1. Data on industrial vitrification of high-level nuclear waste [6].

Country, Facilities	Performance Data
France, R7/T7, AVM	8252 tonnes, 291·10^6 TBq to 2019
USA, DWPF, WVDP, WTP	7870 tonnes, 2.7·10^6 TBq to 2012
Russia, EP-500	6200 tonnes, 23.8·10^6 TBq to 2010
UK, WVP	2200 tonnes, 33·10^6 TBq to 2012
Belgium, Pamela	500 tonnes, 0.5·10^6 TBq. Completed.
Japan, Tokai	70 tonnes, 14.8·10^3 TBq to 2007
Germany, Karlsruhe	55 tonnes, 0.8·10^6 TBq. Completed.
India, WIP (1), AVS, WIP (2)	28 tonnes, 9.62·10^3 TBq to 2012
Slovakia, Bohunice	1.53 m^3 to 2012

Silicate glasses have been generically selected as the most reliable wasteform to immobilize high-level nuclear waste (HLW) apart from Russia, which uses phosphate glass and partially the joint Belgium–Germany vitrification program Pamela (Table 2).

Table 2. Composition of HLW glasses, wt% [7].

Country	Plant	Glass Composition
Belgium	Pamela	$70.7P_2O_5\cdot 7.1Al_2O_3\cdot 22.2Fe_2O_3$ and $52.7SiO_2\cdot 13.2B_2O_3\cdot 2.7Al_2O_3\cdot 4.6CaO\cdot 2.2MgO\cdot 5.9Na_2O\cdot 18.7$ Misc. [1]
France	AVM	$46.6SiO_2\cdot 14.2B_2O_3\cdot 5.0Al_2O_3\cdot 2.9Fe_2O_3\cdot 4.1CaO\cdot 10.0Na_2O\cdot 17.2$ Misc.
France	R7/T7	$54.9SiO_2\cdot 16.9B_2O_3\cdot 5.9Al_2O_3\cdot 4.9CaO\cdot 11.9Na_2O\cdot 5.5$ Mis.
Germany	Karlsruhe	$60.0SiO_2\cdot 17.6B_2O_3\cdot 3.1Al_2O_3\cdot 5.3CaO\cdot 7.1Na_2O\cdot 6.9$ Mis.
India	WIP	$30.0SiO_2\cdot 20.0B_2O_3\cdot 25.0PbO\cdot 5.0Na_2O\cdot 20.0$ Mis.
India	AVS	$34.1SiO_2\cdot 6.4B_2O_3\cdot 6.2TiO_2\cdot 0.2Na_2O\cdot 9.3MnO\cdot 43.8$ Mis.
Japan	Tokai	$46.7SiO_2\cdot 14.3B_2O_3\cdot 5.0Al_2O_3\cdot 3.0CaO\cdot 9.6Na_2O\cdot 21.4$ Mis.
Russia	EP500	$53.3P_2O_5\cdot 15.8Al_2O_3\cdot 1.6Fe_2O_3\cdot 23.5Na_2O\cdot 5.8$ Misc.
UK	WVP	$47.2SiO_2\cdot 16.9B_2O_3\cdot 4.8Al_2O_3\cdot 5.3MgO\cdot 8.4Na_2O\cdot 17.4$ Misc.
US	DWPF	$49.8SiO_2\cdot 8.0B_2O_3\cdot 4.0Al_2O_3\cdot 1.0CaO\cdot 1.4MgO\cdot 8.7Na_2O\cdot 27.1$ Misc.
US	WVDP	$45.8SiO_2\cdot 8.4B_2O_3\cdot 6.1Al_2O_3\cdot 11.4Fe_2O_3\cdot 1.4MgO\cdot 9.1Na_2O\cdot 17.8$ Mis.
US	WTP	$50.0SiO_2\cdot 20.0B_2O_3\cdot 5.0Al_2O_3\cdot 25.0Na_2O$

[1] Miscellaneous, including oxides of radioactive waste.

Nuclear waste management is a mature internationally regulated industry that deals with all aspects of nuclear waste generated as dangerous by-products of the application of nuclear energy. Although there are not unresolved problems with controlling and handling nuclear waste, many scientific areas related to nuclear waste management focus the attention of experts. These activities include the analysis of long-term behavior of vitrified nuclear waste in deep geological facilities (GDF) after its disposal [8]. Natural glass-like materials can therefore be useful as analogues of vitrified nuclear waste in extrapolating short-term experiments to longer time frames and projections about the long-term safety of disposal [9,10]. Natural glasses to a certain degree similar in composition to that of the HLW glasses (Table 2) are found in nature and have been subjected to conditions similar to that expected if the GDF is becoming flooded with water and the canisters are breached, allowing groundwater to react with the glassy wasteform. The study of natural glasses with ages of millions of years can provide the necessary link between theoretical models on the long-term vitreous nuclear waste stability, study of historical vitrified material with ages of up to 1800 years [11,12] and laboratory tests aiming to provide information on the long-term durability of a glassy wasteform [13].

Volcanic rocks such as those with a silica-rich (rhyolites, obsidians) or low silica content (basalts) composition are usually used as natural analogues for borosilicate (B-Si) vitreous nuclear wasteforms to predict their alteration in a long-time perspective [9,14]. Studies are devoted to the analysis of their alteration from the mineralogical point of view and mechanical stability. Investigations were also performed on the geochemistry of U, Th and rare earth elements (REE) in the rocks, but these studies are mainly connected with the problem of the source of uranium of deposits [15–17]; for example, for uranium ores of Transbaikalia, Russia [18,19]. The common oxidation states of uranium in nature are +4 and +6, whilst in synthetic ceramics and glasses, three valent forms of uranium are observed: +4, +5 and +6, which are also typical for Np and Pu [20,21]. Therefore, uranium can serve as a good radioactive simulant for the investigation of behavior of transuranic actinides both at the synthesis and aging of nuclear wasteforms.

It is generally accepted that vitreous basic volcanic rocks (basalts) can be used as natural analogues (counterparts) of borosilicate glass [22–24] due to the similarity in mechanisms of their alterations. Both basaltic and borosilicate glasses are characterized by a decrease in leaching rate with time by three to five orders of magnitude in comparison with the initial rate. An extremely low rate of long-term dissolution for both kinds of glasses is controlled by the very slow diffusion through the altered layer. Basaltic glasses have low concentrations of uranium, usually at the order of a few ppm (10^{-4} wt%), thus the analysis of its behavior is rather difficult. For this reason, only some silica-rich (acid) volcanic rocks with uranium content up to 140 ppm [25,26] are of special interest for characterization of uranium behavior in natural glasses as analogues of synthetic vitreous materials, including wasteforms for actinide-containing waste. The description of such uranium-rich glasses is given below.

2. Natural Radioactive Glasses

The rocks investigated were formed from melts that naturally and rapidly cooled enough to form glasses rather than forming crystalline rocks. The high chemical resistance of silicate glasses allows them to remain stable and almost unaltered in the environment for many millions of years. For example, the highly siliceous volcanic glass found in the Novogodnee deposit (the U-glass) with an age of 135–145 million years (My) contains uranium at concentrations ranging from tens to 140 ppm [18,19,25,26] that is an order of magnitude superior to the average concentration of this element in such rocks.

The Novogodnee deposit is situated within a reducing geochemical environment of the volcano-sedimentary cover of a volcano caldera in the southern part of the Streltsovska uranium ore field (Figure 1).

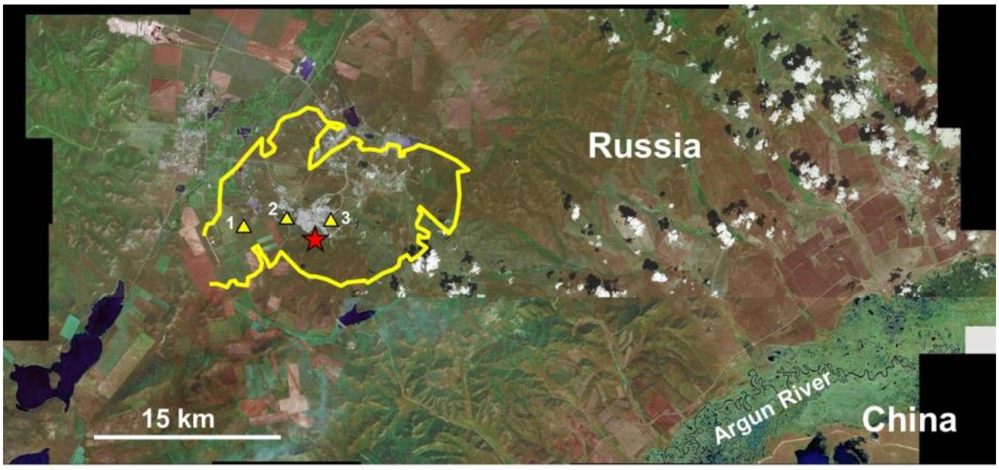

Figure 1. Novogodnee deposit (shown by the red star) is located in the central part of the Streltsovka ore field within the Streltsovka caldera (within the yellow contour) with three paleovolcanoes: 1—South-Western, 2—Krasniy Kamen and 3—Maliy Tulukuiy (see details in [25,26]).

The volcanic caldera of Jurassic–Cretaceous age (145–140 Ma) has a diameter of about 20 km and a total area of 180 km^2 comprising 20 uranium deposits. The host rocks are up to 1.4 km thick of volcano-sedimentary accumulation within the caldera lying on a granitic Proterozoic–Paleozoic basement. Ore concentrates of U (thousands ppm) are observed within veins, as sub-vertical stockworks and along stratiform layers in the volcanic and sedimentary units. The mineral phases of U present are oxide (pitchblende), silicates (coffinite) and titanate (brannerite). The total resources are about 280 ktU with average uranium content in ore equal to 0.2 wt%.

The uranium deposits can serve as natural analogues of currently deployed deep geological disposal facilities (GDF) in stable geological conditions [27–31]. Indeed, features, events and processes (FEPs), which occurred during previous periods of time of such deposits, can be analyzed so that by reversing the time, one can appraise the most probable scenario of GDF evolution [32]. A sheetlike body of highly preserved rhyolite–rhyodacite glass of an obsidian–perlite type rich in U was found in the Novogodnee deposit at a depth of 300 m from the surface of the Earth. Data on the behavior of glasses with uranium at the Novogodnee deposit are essential to investigations of actinide migration paths, mobilization, retardation, redistribution and accumulation under existing redox conditions.

The unaltered volcanic high-silica glass in this field was found to contain abnormally high concentrations of uranium detected by *f*-radiography (XRF). Uranium retardation can be caused by sorption. This factor, together with the deformational alteration and partial devitrification of volcanic glass, is of particular significance at the Novogodnee deposit [26]. The local reducing barriers are formed along the periphery of a sheetlike body of obsidian–perlites near mineralized and open fractures and in intensely altered cataclastic zones. The results of detailed micro-studies indicate an intensive redistribution of uranium with the accumulation of its ultra-high contents up to 500–1000 ppm. Such local favorable conditions within the sheetlike body are formed in the presence of sorption-intensive mineral phases (leucoxene–hematite aggregate) and a higher degree of fracturing of glasses. Here, the ability of the sorption-intensive phases to retard uranium was fully manifested.

3. Bulk Characterization of the Natural Uranium Volcanic Glass

The sheetlike body of rhyolite–rhyodacite volcanic glass has a zonal structure with unaltered massive and fluidal obsidian–perlites (U-glasses) in the core, surrounded by the zone with volcanic bombs and rock fragments developed in the central part (Figure 2 and Tables 3 and 4).

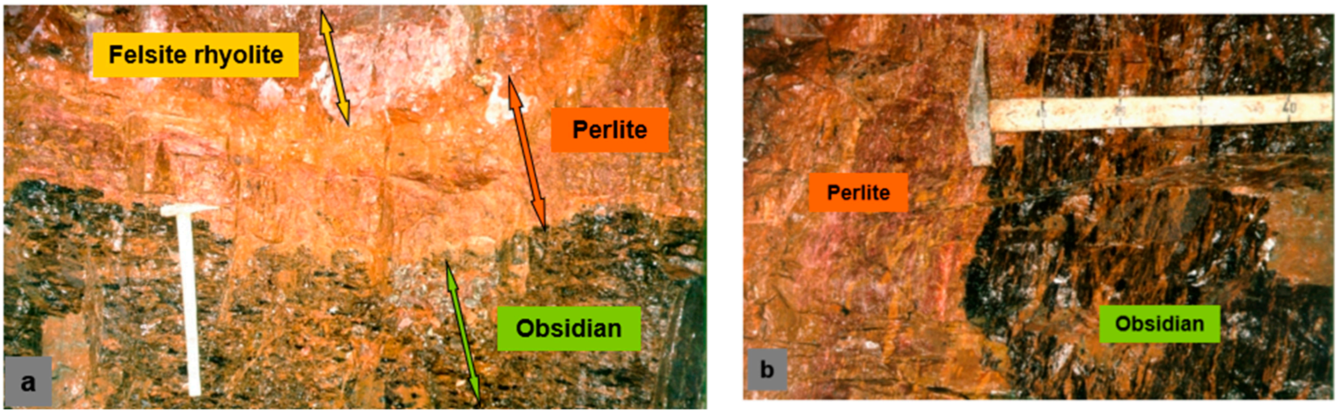

Figure 2. *Cont.*

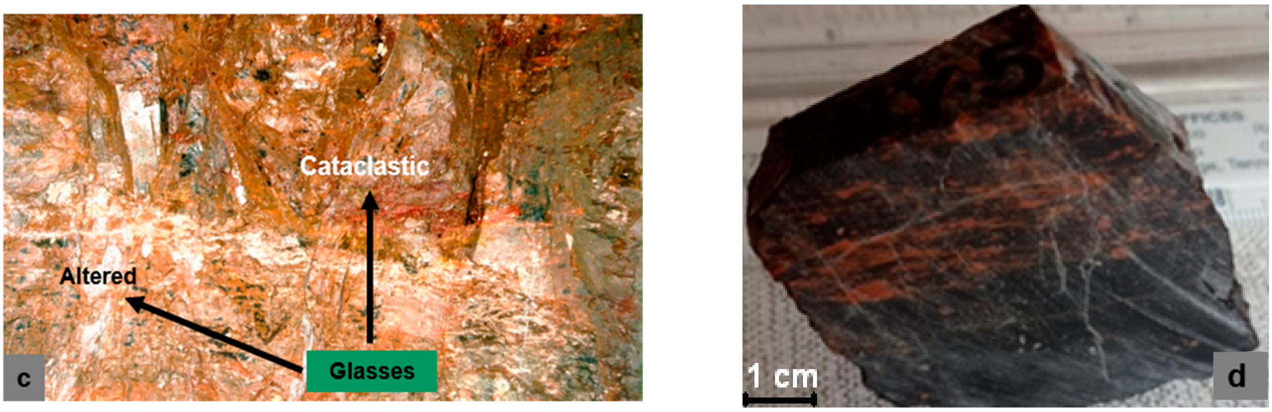

Figure 2. Samples and position of volcanic glass bed-like body in felsite rhyolite layer: (**a**) the top of the fresh obsidian–perlite volcanic glasses bed; (**b**) well-preserved obsidian–perlite glasses; (**c**) bottom of the cataclastic and altered glasses bed; and (**d**) sample of U-glass NY5 from depth of 300 m.

Chemical analyses of the rock samples were performed in the Centre for Collective Use of Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry Russian Academy of Sciences—Analitika using an X-ray fluorescence analysis and Axios mAX&PAN analytical spectrometer for rock-forming elements as well as ICP mass spectrometry, Nexion 2000 c for rare elements (Tables 3 and 4).

Table 3. Compositions of glasses (rock-forming elements, wt%), description in the text.

No.	SiO_2	TiO_2	Al_2O_3	ΣFeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	F	LOI [1]
NY1	70.77	0.12	11.51	1.26	0.081	0.18	0.75	4.16	4.24	0.01	0.03	0.32	6.04
NY5-1	71.38	0.13	11.23	1.29	0.085	0.06	0.44	5.83	2.55	<0.01	<0.01	-	6.59
NY5-2	71.78	0.17	11.41	1.37	0.041	0.29	1.80	2.58	5.24	0.02	<0.01	-	5.05
NY5-3	71.76	0.12	11.30	1.24	0.071	0.16	0.84	4.33	3.66	<0.01	0.03	0.07	6.22
NY22-1	71.50	0.12	11.20	1.23	0.085	0.11	0.49	5.66	2.49	<0.01	<0.01	0.05	6.63
NY22-2	71.51	0.12	11.32	1.26	0.072	0.19	0.95	3.96	3.78	<0.01	<0.01	0.05	6.44
NY19-2	66.81	0.13	0.13	1.30	0.062	0.24	2.42	2.81	3.26	0.02	0.06	0.29	10.48
NY15	61.60	0.14	0.14	2.43	0.194	3.93	2.27	1.32	1.92	0.02	0.14	0.53	12.05
NY17	62.76	0.15	0.15	1.89	0.536	1.24	2.65	1.05	2.72	0.01	0.06	0.25	12.64
NY18	64.57	0.14	0.14	2.29	0.226	1.37	2.31	1.41	1.99	0.02	0.06	0.33	12.02
NY12	59.59	0.14	0.14	1.53	0.207	4.03	2.55	0.55	2.30	0.01	0.09	0.83	14.90
NY7-2	66.80	0.14	0.14	1.42	0.259	1.01	2.15	1.58	3.78	0.02	0.03	0.45	9.41

[1] LOI—loss on ignition. Dash (-): the element was not determined.

Table 4. Compositions of glasses (description in the text) for rare and radioactive elements [1], ppm.

No.	Li	Rb	Sr	Cs	Co	Zr	Nb	Mo	Ba	Ta	Pb	Th	U
NY1	96.9	808.9	173.4	933.6	2.5	197.1	55.0	5.2	23.1	4.7	42.6	45.9	25.8
NY5-1	89.9	752.5	33.2	291.9	0.3	189.8	51.6	7.9	6.5	4.5	28.9	44.6	19.1
NY5-2	245.4	410.5	343.1	758.3	0.9	195.1	56.6	6.6	71.2	4.4	35.8	56.7	23.5
NY5-3	132.6	790.5	155.2	753.4	0.4	199.7	55.3	7.9	18.9	4.7	38.5	53.6	23.7
NY22-1	94.4	913.1	56.8	605.3	0.2	196.8	49.1	6.5	5.3	2.7	30.3	32.4	17.8
NY22-2	127.2	666.3	149.3	827.7	0.3	198.7	51.7	5.7	10.8	3.9	28.2	15.9	12.8
NY19-2	63.7	179.2	680.6	1201.7	17.1	183.6	48.9	3.8	36.2	12.3	23.3	36.3	18.4
NY15	77.4	152.7	493.9	1485.2	402.1	205.3	47.5	2.5	237.5	4.6	57.0	52.1	9.7
NY17	134.2	186.9	3244.2	744.6	3.9	228.5	62.2	-	137.3	5.9	81.1	70.7	15.6
NY18	87.6	182.2	595.8	1715.8	59.4	212.5	118.1	-	186.4	1032.4	17.8	65.8	14.2
NY12	538.7	140.9	443.5	273.2	69.7	211.3	59.0	2.9	102.3	5.5	49.3	53.5	15.3
NY7-2	172.9	238.8	1057.8	966.3	4.8	195.6	53.2	0.6	61.4	4.5	45.4	45.3	15.2

[1] Dash (-): the element was not determined.

Volcanic rock samples NY1, NY5 and NY22 are seen as glasses being relatively fresh and unaltered whereas samples NY19-2, NY15, NY17 and NY18 are characterized as intensively altered and devitrified glasses. Samples NY18 and NY19-2 are cataclastic and altered glasses. The fresh obsidian–perlites NY5 (such as shown below in Figure 2) and NY22 were divided into three groups: NY5-1 and NY22-1 (obsidian), NY5-2 and NY22-2 (perlite) and NY5-3 (interbedding of obsidian and perlite).

Devitrification of the glass led to the formation of crystallites within glasses such as hair trichites, globulites and aggregates of scopulites. At terminal stages of crystallization, spherulites and microlites were formed (Figure 3, see also [26]).

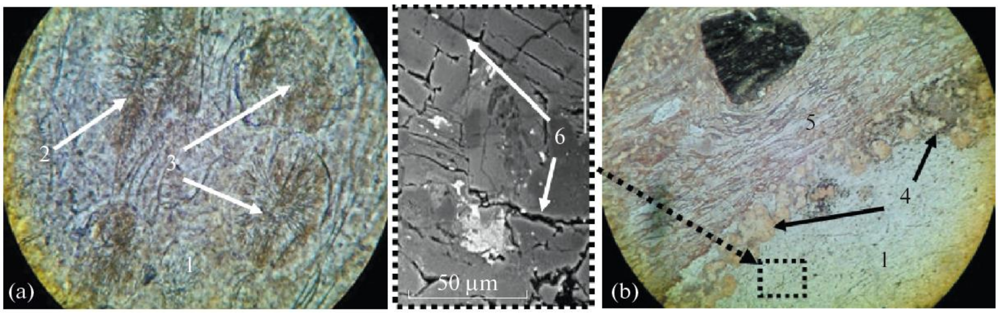

Figure 3. Massive (1) and fluidal (5) glasses of Novogodnee deposit with successive devitrification stages: hair trichites, (**a**)—globulites; (3)—scopulite aggregates; (2)—spherulites; and (4)—crystallites. The long side of thin section is 1.09 mm (**a**) or 2.78 mm (**b**), parallel nicols; The BSE image is shown in the center of the figure.

Volcanic glasses of the Novogodnee deposit, although being significantly older than a hundred million years, still contain uranium at relatively high concentrations, retaining it both in the glassy and crystalline phases. The distribution of uranium in volcanic glasses was studied with *f*-radiography using polished thin sections covered by film of special track detectors, which were irradiated by thermal neutrons [26]. The *f*-radiography method is based on the fission of uranium nuclei in a nuclear reactor under irradiation by neutrons and allows, with high sensitivity and accuracy (mass sensitivity threshold of the order of $\cdot 10^{-10}$) detecting the distribution of uranium, as well as determining local and total concentrations. The fundamental possibility of determining the uranium content is based on the fact that fragments of the spontaneous or forced fission of nuclei of heavy elements leave destruction areas (tracks) in the environment, which can be detected under a microscope after the chemical etching of the surface. Qualitative assessments of uranium distribution and calculation of its contents were performed by analyzing micro-images from lavsan detectors, following the methods and software developed at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry Russian Academy of Sciences. Polished thin sections of the samples mounted on quartz glasses and covered by lavsan track detectors were irradiated at the National Research Nuclear University (MEPhI) Atomic Center with a thermal neutrons fluence of 3×10^{16} neutrons/cm^2 for low (1–3 ppm) uranium contents, and 3×10^{14} and 4×10^{13} neutrons/cm^2 for high (>3–5 ppm) and very high (>500–1000 ppm) contents, respectively. Relatively high content of uranium is hence characteristic for both unaltered and altered volcanic rocks of the Novogodnee deposit including partly devitrified glasses (Table 5).

Table 5. Distribution of uranium in volcanic glasses.

Samples	Number of Sites Studied	Content of U, ppm		Variation Coefficient
		Average	Range	
		Relatively unaltered massive and fluidal glasses [1]		
Fresh glass (NY22-1)	8	25.26	23.97–27.47	5.31
Fresh glass (NY5-1)	9	19.30	18.17–21.03	4.97
Initial devitrified I (NY22-1)	9	17.85	17.30–19.11	3.59
Initial devitrified II (NY5-1)	9	14.12	12.54–15.18	6.94
		Altered and devitrified glasses		
Altered I glass (NY23-1)	9	14.75	13.12–17.75	10.78
Altered II glass (NY0-1)	9	11.42	9.49–12.19	8.06
Altered III glass (NY2-1)	9	5.34	5.06–6.62	10.86
Altered IV glass (NY26-1)	9	1.72	1.60–2.69	26.16
Area with HEM (NY26-1) [2]	5	39.55	32.12–55.33	22.66

[1] The term fluidal glass denotes a glass where the direction of melt flow that occurred before its vitrification is revealed from the image of glass. [2] Areas uniformly impregnated with sorption-capacious hematite (HEM) were identified in brown volcanic glass (perlite) with elevated uranium content detected.

4. Discussion

Two aspects of the geochemical and mineralogical studies of natural glasses are of particular interest. The first one is related to their study as a potential source of useful elements, e.g., U, in the uranium ore deposits in volcanic-related mineral systems. The second direction concerns the use of volcanic rocks as analogues of vitreous actinide wasteforms used for HLW immobilization in assessing their long-term stability under underground disposal conditions. Data revealed through such type analyses can be a significant addition to existing short-term testing protocols used in laboratories [33].

Silicate glasses have been used for some five decades to immobilize HLW radionuclides including residual uranium and plutonium isotopes remnant from spent nuclear fuel reprocessing [3–6,12,34]. They were also proposed for the immobilization of nuclear fuel containing lava, which resulted from the Chernobyl catastrophe [35]. HLW glasses used in practice are characterized by a high content of crystalline phases within their vitreous body [3,5,36]; moreover, there is a technological trend to increase the content of crystalline phases [37], accounting for advantages offered by glass-crystalline wasteforms [38–40]. Volcanic glasses investigated do also contain crystalline phases, which could be either initially formed at magmatic melt (volcanic lava) solidification or be products of glass devitrification. The most important structural feature of them would then be the speciation of uranium within glass and the crystalline phase's structure. Although uranium can exist in the oxidation states U^{6+}, U^{5+} and U^{4+} in alkali borosilicate glasses, most of the uranium (~90%) occurs as U^{6+} with a small amount of U^{5+} under standard melting conditions using the air atmosphere. Moreover, U^{4+} is not observed, with the exception of strongly reducing conditions. The U^{6+} occurs in the form of the uranyl species $UO_2{}^{2+}$ with an additional four or five equatorial oxygens coordinating to the uranium cation [41–44]. It is supposed that uranium acts essentially as a glass intermediate within the alkali silicate glass following the rearrangements [44]:

$$UO_3 + 4Si\left(O^-\right)\left(O_{\frac{1}{2}}\right)_3 + 4M^+ \rightarrow U^{6+}(=O)_2\left(O_{\frac{1}{2}}\right)_6 + 4Si\left(O_{\frac{1}{2}}\right)_4 + 4M^+, \quad (1)$$

where M^+ is the alkali ion. Each mole of UO_3 thus requires two moles of alkali for charge balance, which results in little structural rearrangement of the glass where uranium occupies sites in the interstices of the glass network related to the alkali channels [44]. This allows for the high solubility of UO_3 in silicate glasses, which is in a borosilicate glass above 40 wt% under an atmosphere of air, whereas under reducing conditions it is only about 10 wt% [4,41,42]. The authors of [43] have shown that two distinct first neighbor distances occur for the U–O correlations, the first being at 1.8 ± 0.05 Å having 1.9 ± 0.2 oxygens and the second at 2.2 ± 0.05 Å with 3.7 ± 0.2 oxygen atoms. They have observed significant second neighbor atomic pair correlations between uranium and the network formers (*Si*, B) and the modifiers such as Na, concluding that uranium ions take part in the network forming, and that this may be the reason for the observed good stability of uranium containing silicate glasses and their high hydrolytic resistance. It is supposed that uranium atoms in the borosilicate glass are connected through an oxygen atom with the network former and modifier atoms, forming a network structure that consists of mixed tetrahedral made of SiO_4, units, tetrahedral made of BO_4 units and BO_3 trigonal units, which are partly connected by uranium atoms [43,44]. Obtained data and the similarity in the U^{6+} environments in layered alkali uranates and in silicate glasses have allowed the authors of [44] to suggest the possible structural model for silicate glasses containing uranium where the uranyl ions sit in the alkali channels of the modified random network of silicate glasses (see e.g., [2]).

Radiation from decaying radionuclides gradually alters the glass structure, leading to changes in its properties including valence states and migration potential of radionuclides [7,45,46]. Although the content of uranium in the above-described glasses is considered anomalously high for natural volcanic samples, their radioactivity is much lower than that of high-level waste [3–5] when radiation-induced effects are evident [7,47]. The direct determination of uranium valent states in volcanic glasses thus remains a key challenge and its complexity is partly caused by both its content, which is about tens of ppm, and complex composition that are complicating the characterization. This will assist in resolving the unique and scientifically most difficult aspect of nuclear waste management, aiming to extrapolate wasteform short-term laboratory testing results to the long-time periods ranging from thousands to millions of years [48].

Migration of uranium is initiated by glass corrosion in contact with groundwater. Silicate glasses corrode in water via two main processes—(a) diffusion-controlled ion exchange and (b) hydrolysis [5]. The ion exchange mechanism involves the mutual diffusion and exchange of a cation in glass with a proton (probably in the form of H_3O^+) from water via the reaction:

$$(\equiv\text{Si-O-M})_{\text{glass}} + H_2O \leftrightarrow (\equiv\text{Si-O-H})_{\text{glass}} + \text{M-OH}, \tag{2}$$

In dilute near-neutral solutions, the ion exchange controls the initial release of cations and at relatively low temperatures and not very high pH it can dominate over hydrolysis for many hundreds or even thousands of years [49]. Ion exchange reactions cause selective leaching of cations and are characterized by the normalized leaching rate given by:

$$NR_{xi} = \rho(D_i/\pi t)^{1/2} = \rho 10^{-pH/2}[\kappa D_{0H}/C_i(0)\ \pi t]^{1/2}\exp(-E_{di}/2RT), \tag{3}$$

where ρ (g/cm^3) is the glass density, D_i (cm^2/day) is the effective interdiffusion coefficient, E_{di} (J/mol) is the interdiffusion activation energy (e.g., British magnox waste glass has E_{di} = 36 kJ/mol [49]), R is the universal gas constant R = 8.314 J/mol, T (K) is the temperature, D_{0H} (cm^2/day) is the pre-exponential coefficient in the diffusion coefficient of protons (hydronium ions) in glass, $C_i(0)$ (mol/L) is the concentration of cations at the surface of the glass and κ is a constant that relates the concentration of protons in glass to the concentration of protons in water, i.e., to the pH of the solution. The leaching rate decreases with time t, as $t^{-1/2,}$ and the lower the pH of the contacting solution, the higher the $NR_{X,i}$. Hydrolysis, which is a near-surface reaction of hydroxyl ions with the glass network, destroys it, and this leads to congruent dissolution of all glass components into contacting water and subsequent deposition of silica gel layers as secondary products on the surface of glass. Hydrolysis occurs through the reaction [5]:

$$(\equiv\text{Si-O-Si}\equiv)_{\text{glass}} + H_2O \leftrightarrow 2(\equiv\text{Si-O-H}). \tag{4}$$

This leads to the complete dissolution of the glass network (disordered glass lattice) and the formation of ortho-silicic acid, H_4SiO_4. Glass hydrolysis is characterized by a normalized dissolution rate [5]:

$$NR_{xi} = \rho r_c = \rho k a^{-\eta}[1 - (Q/K)^{\sigma}]\exp(-E_a/RT), \tag{5}$$

where r_c is the normalized rate of dissolution measured in unit cm/day, k is the characteristic rate constant, a is the activity of hydrogen ions (protons), η is the pH-dependent exponent (typically η ~ 0.5), E_a is the activation energy of hydrolysis (e.g., British magnox waste glass has E_a = 60 kJ/mol [49]), Q is the product of the ionic activity of the rate control reaction, K is the equilibrium constant of this reaction and σ is the order of the reaction. The rate of hydrolytic dissolution does not depend on time. The higher the pH of the contacting water, the higher the NR_H.

The total corrosion rate NR_i (normalized with respect to the content of component labelled (i)) is determined by the sum of the contributions from (a) ion exchange, (b) hydrolysis and (c) very rapid (so-called instantaneous) dissolution of radionuclides from the glass surface, i.e., surface contaminants [5,49]:

$$NR_i = NR_{X,i} + NR_H + N\Phi_{si}, \tag{6}$$

where the factor $N\Phi_{si}$ accounts for instantaneous dissolution. When the pH changes, the ion exchange rate ($NR_{X,i}$) changes as $10^{-pH/2}$, while the hydrolysis rate (NR_H) is proportional to $10^{pH/2}$, so the dependence of the glass corrosion rate (NR_i) on pH appears as a U-shaped curve with a minimum for neutral solutions [50]. In saturated solutions, Q → K, which is typical for glasses in a geological environment such as volcanic glasses in a volcano caldera or vitrified HLW in a GDF; therefore $NR_H \to 0$. That is, in this case, the corrosion of the glass is determined by diffusion-controlled ion exchange. In dilute aqueous solutions, ion exchange is characteristic for the initial stages of corrosion, and hydrolysis for the later stages. The time it takes to transition from one mechanism to another depends on the composition of the glass and environmental conditions such as pH and temperature. The higher the temperature, the shorter the transition time [49]. The newly formed glass surfaces, due to the cracking of large glass blocks, will follow this pattern of transition of corrosion mechanisms from the initial selective corrosion via ion exchange to the late mechanism controlled by hydrolysis; thus, the overall composition of components leached out of glasses is complex. The analysis shows that the typical rate of corrosion via the hydrolysis (r_c) of borosilicate glasses used to immobilize nuclear waste is about 0.1 μm/y [51]. Without contact of glass with water, the radionuclides including uranium will remain retained within the glass body structure.

5. Conclusions

Volcanic-type uranium deposits of the Streltsovskoye ore field provide a unique opportunity to study uranium-bearing volcanic glasses under various redox conditions. Joint geological–structural, mineralogical–geochemical, petrophysical, hydrogeochemical and isotope–geochemical monitoring studies of fracture veins and atmospheric waters have been conducted for more than 20 years and continue at present. It is shown that the rocks of the Novogodnee deposit are unique objects, which can be used for studying the conditions, migration paths, migration mechanisms and accumulation of uranium in different structural settings under varying redox conditions. Despite devitrification processes within the geological time frames, the ancient volcanic rocks within the large Streltsovka uranium ore field were found to contain large-size blocks of natural glasses having the highest content of silica. The silica-rich rocks located in the southern part of the ore field, formed about 140–145 million years ago, have retained uranium for geological time scales, preventing its migration out of its body. Silica-rich volcanic glasses still confine the uranium as a proof of the high reliability of vitreous and glass crystalline wasteforms, based on silicate glasses, used as nuclear waste immobilizing matrices at geological time scales.

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