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GEOCHEMISTRY

The Oldest Volcanic Glass in the Early Paleoproterozoic Boninite-type Lavas, Karelian Craton: Results of Instrumental Investigations

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Since Early Precambrian volcanic rocks are typically strongly altered by superimposed processes, they retain primary composition and texture only in exceptional cases. Such a case is observed in the Early Paleoproterozoic volcanic rocks of the Vetrenyi Belt Formation of the synonymous riftogenic structure in southeastern Karelia, where volcanic glass is locally preserved [1–3]. The Sm–Nd, Re–Os, and U–Pb (zircon) ages of volcanic rocks of this formation range from 2.5 Ga in the lower parts to 2.41 Ga in the upper parts of the sequence [1–3].

Zolotykh and Ladygin [4, 5] also confirmed the presence of volcanic glass in these rocks. During short-term field works in 2000, we collected additional samples in the southeastern termination of the graben-shaped Vetrenyi Belt, where the least altered rocks were preserved. The samples were mainly treated at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry.

In previous works, the volcanic glass in these rocks was determined by petrographic methods, but its reliable identification requires the use of modern physical techniques.

General data on geology and rock composition of the Vetrenyi Belt. During the Early Paleoproterozoic (2.5–2.3 Ga ago), the large magmatic province of siliceous high-Mg (boninite-type) series formed in the eastern Baltic Shield [6]. It consists of the layered mafic–ultramafic intrusions, dike swarms, and volcanosedimentary complexes in graben-shaped structures, including the Vetrenyi Belt (Fig. 1). In terms of geology and abundance, this province approximates large plume-related Phanerozoic magmatic provinces, such as Siberian traps, but sharply differs from them in rock composition. During Svecofennian tectonic activity (2.0–1.9 Ga ago), the rocks of the province were unevenly affected by dynamometamorphism [7]. The rocks of the Vetrenyi Belt suffered the least alteration and, in places, preserved a nearly fresh appearance.

We studied rocks from the upper section of the Vetrenyi Belt Formation near Myandukha Mountain at the southeastern termination of the structure. The volcanic edifice in this area consists of seven low-angle basaltic flows with a total thickness of 200 m. The presence of pillow lavas and hyaloclastites suggests subaqueous conditions of their formation. During subsequent transformations, the rocks were unevenly affected by low-temperature alterations with appearance of fibrous actinolite, chlorite, serpentine, and other minerals. However, very fresh rock types which retained primary magmatic minerals and volcanic glass are occasionally found here.

The rocks have a typical porphyraceous texture with olivine and less common pyroxene phenocrysts and chromite microphenocrysts. The groundmass is characterized by a microspinifex-type texture with acicular, long-prismatic, radial, and paniculate aggregates of clinopyroxene and rarer plagioclase, as well as skeletal olivine and pyroxene among the volcanic glass. The most crystallized rocks contain calcic plagioclase. The rock compositions are given in the table.

Fresh olivine both in spinifex aggregates and in phenocrysts ranges from Fo_{80} to Fo_{63}. Clinopyroxene corresponds to high-Al augite $Wo_{45–47}En_{40–41}Fs_{11–14}$ with 7.2–7.5 wt % Al_2O_3, pigeonite $Wo_{11}En_{60}Fs_{29}$ with Al_2O_3 4.8 wt %, and pigeonite–augite $Wo_{32–38}En_{48–54}Fs_{14–15}$ with 1.5–2.0 wt % Al_2O_3. The Cr-spinel is represented by Al-chromite with 43.5–45.1 wt % Cr_2O_3, while plagioclase corresponds to $Or_{0.7–0.8}Ab_{35.6–36.8}An_{62.5–63.6}$. Such mineral compositions are typical of high-Ca bon-

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inite lavas, in particular, of those found in Late Cretaceous Bassit ophiolites in Syria [8].

The *volcanic glass* is brown in plane-polarized light and isotropic in cross-polarized light. It shows a fluidal–banded structure in hyaloclastites and composes a matrix between olivine, pyroxene, and plagioclase in basalts. The glass has a spotty appearance in back-scattered electron images (Fig. 2). According to microprobe determinations, its chemical composition ranges from basalt (SiO_2 50–54 wt %) to andesite (SiO_2 56–60 wt %) (table, analyses 4–9). Results of its electron microscopic study are shown below.

Experimental technique. Zones (areas) of spotty volcanic glass were mechanically extracted from a thin section and treated to obtain the suspension specimens for electron microscopic study. Particles of the glass and crystalline inclusions therein were identified on a JEM-100C transmission electron microscope equipped with an EDS Kevex-5100 allowing the determination of elements from Na to U. The tilting of the specimen with a goniometer made it possible to reveal crystalline phases among predominant glass particles based on extinction contours appearing over the crystal. Such a feature of crystalline compounds allowed a complete identification of all phases in the specimen. The back-scattered electron images, electron diffraction patterns, and EDS spectra were recorded from particles. Minerals were reliably identified using the structural and chemical data obtained.

Results. The electron microscopic study of suspension specimens of the glass from two samples revealed ultrafine crystals giving Si, Ca, Fe (and possibly, Al) peaks in the EDS spectra among the numerous amorphous SiO_2 particles (with K impurity). The glass particles in suspension specimen consist of two morphologically different types. Type 1 consist of thick, often wedge-shaped, structurally uniform amorphous SiO_2 particles with acute margins (Fig. 2). Their EDS spectra show significant K impurity, with Si/K peak height ratio of ~ 4/1. They occasionally include amorphous SiO_2 particles with a clumpy, less compact structure and Ca impurity. Type 2 is composed of amorphous filmy (or platy) SiO_2 particles with traces of Al, K, and Ca. The plates have a fine-porous structure (about 10 Å) owing to the nanometer size of SiO_2 particles.

For exact determination of the composition of amorphous SiO_2 phases, the suspension specimens prepared for transmission electron microscopy were investigated with a scanning electron microscope equipped with LINK ISIS. The data are listed in the table (analyses 10–14). Since secondary electron images differ from TEM images, their direct comparison is impossible. Therefore, the listed compositions are presumably ascribed to both phases characterized above. It should be also noted that the TEM study was performed on thin foils, rather than massive polished samples. Therefore, compositions were normalized and the results are semi-quantitative data that only give insight into chemical variations.

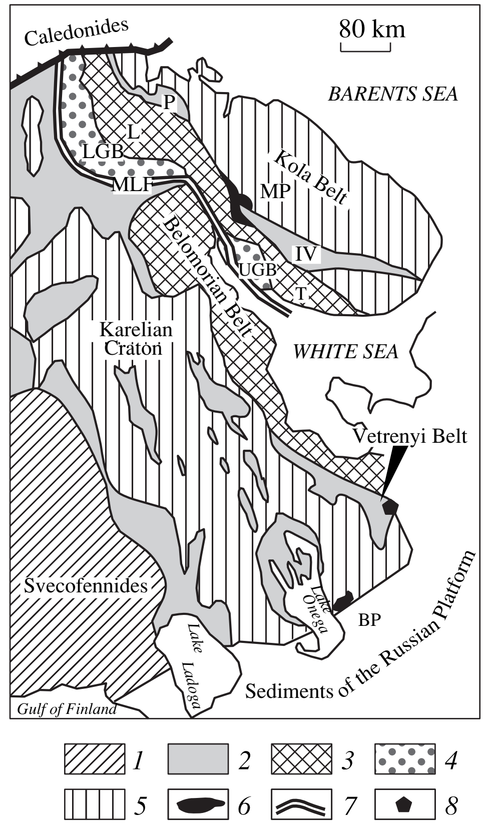

Fig. 1. Schematic geological structure of the eastern Baltic Shield. (*1*) Svecofennian block; (*2*) Paleoproterozoic volcanosedimentary belts: (P) Pechenga, (IV) Imandra–Varzuga; (*3*) Belomorian and other mobile belts: (T) Tersk, (L) Lottinsk; (*4*) Lapland–Umba granulite belt: (LGB) Lapland fragment, (UGB) Umba fragment); (*5*) Archean cratons; (*6*) Early Proterozoic layered massifs: (MP) Monchegorsk pluton, (BP) Burakovka Pluton; (*7*) Main Lapland Fault (MLF); (*8*) Myandukha Mountain.

All amorphous SiO_2 phases often show no significant rings of intensity, though some of them yield electron diffraction patterns with a weak and wide diffuse reflection, indicating certain structural ordering of these aggregates.

Scarce crystalline phases are found among amorphous SiO_2 particles. Based on diffraction data, they are mainly identified as clinoamphiboles with insignificant compositional variations suggested by peak height variations of elements in the Kevex spectra. However, individual diffraction patterns indicate that the sample also contains orthopyroxene. Taking into account the extinction of reflections, the unit cell parameters of these crystals at the same elemental composition (Si, Al, and Fe) should be approximately equal, i.e., $a = 18$ and $c = 5.04$.

We also found scarce epidote with a composition corresponding to $Al_2Si_3Ca_{4.5}Fe_{1.5}$ (the numbers indicate only the relative peak height of elements). α-quartz is a rare mineral. It is normally free of impurities and occurs in close intergrowths with potassium glass. The

Composition of basalts and volcanic glass therein (Vetrenyi Belt Formation, Myandukha Mountain)

An. no.	Sample no.	Rock	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3	P_2O_5	Total
1	303	Bulk	51.75	0.59	12.60	10.64	0.18	11.20	8.48	2.05	0.69	0.09	0.09	98.36
2	VB33	″	51.83	0.68	9.94	11.30	0.18	14.74	9.27	1.56	0.38		0.06	99.94
3	VB100	″	51.97	0.72	10.70	11.48	0.19	13.13	9.43	1.93	0.36		0.08	99.99
4	303	glass (l)	50.54	0.82	11.91	11.35	0.20	11.25	11.72	2.58	0.09	0.18		100.64
5	″	glass (d)	54.20	1.00	16.82	5.97		5.47	10.10	6.48				100.04
6	VB33	glass (l)	60.33	0.62	20.60	3.18		1.33	7.21	6.26				99.53
7	″	glass (d)	58.50	0.50	18.88	5.73		2.84	7.93	4.84				99.22
8	VB100	glass	59.77	0.50	19.03	6.74	0.09	0.91	7.67	5.85	0.08			100.64
9	323	″	59.05	0.72	17.46	8.09	0.14	1.86	8.66	3.73	0.35			100.06
10	303	″	84.30		4.58			0.53	0.26	5.81	4.32			99.80
11	″	″	85.29		4.89	0.31		0.37	0.24	4.23	4.67			100.00
12	″	″	83.84		4.46			0.63	0.31	6.17	4.81			100.22
13	″	″	87.92		9.11				1.92		1.79			100.74
14	″	″	90.63		8.17						2.73			101.53

Note: Analyses (4–9) were performed using a microprobe; analyses (10–14) were performed using a LINK ISIS spectrometer. The compositions of light (l) and dark (d) glasses are shown (Fig. 2a). The absence of data indicates the contents below detection limit. The total iron is given as FeO.

phase boundary in the intergrowths is often rounded and sharp.

In one case, we found intergrowth of glass, amphibole, and regularly oriented pseudohexagonal microcrystals of a high-temperature SiO_2 polymorph, i.e., tridymite (Fig. 2). Tridymite is a stable phase at 867–1470°C and may be preserved in a metastable state under rapid cooling. Two amphibole crystals in the intergrowth are differently oriented. Evidently, this indicates crystallization from different centers at rapid cooling of the melt.

We also discovered single grains of halite (NaCl) and nanometer-sized TiO_2 polymorph (anatase) as microinclusions in the glass.

Layer silicates often occur as micrometer-sized platy crystals. They cannot be reliably identified because of the absence of spatial reflections along the *c* axis, which allows the unambiguous determination of unit cell parameters. Taking into account the elemental composition of particles, these phases may be identified as kaolin, chlorite, and biotite. We also detected lamellar crystals with silicate composition (Mg, Si and Fe), and unit cell parameters ($a \sim 5.2$, $b \sim 9.0$) and basal reflection $d_{002} \sim 9.2$ Å (×2 = 18.4) presumably corresponding to talc.

In addition, we found aggregates of ultrafine crystals consisting of Al and Cu. They yield ring diffraction patterns corresponding to a cubic lattice with $a \sim 4.28$ Å. This phase presumably corresponds to Al-bearing cuprite (Cu_2O) rather than the independent Al phase.

Thus, our study first showed that the Early Paleoproterozoic lavas of boninite-type series indeed contain volcanic glass. It consists of amorphous SiO_2 particles (with traces of K and occasional Ca) and very fine (micrometer- and nanometer-sized) aggregates of amphiboles, tridymites, α-quartz, orthopyroxene, epidote, layer silicates, talc, and others) halite, anatase, and cuprite. These phases are unevenly distributed over the glass, thus providing its spotty appearance and variable chemical composition. It is interesting that their composition sharply differs from that of macrocrystals in the same lavas, where they are mainly represented by olivine, high-Al pyroxene, chromite, and plagioclase. Moreover, it was established that micro(nanometer) crystals predominantly consist of hydrous phases (amphiboles and layer silicates), which occasionally occur in intergrowths with high-temperature metastable phases, (e.g., tridymite), thus indicating that their origin was not related to glass devitrification.

These microinclusions are irregularly distributed over the volcanic glass, presumably providing its spotty color and significant compositional differences within a single sample. They have no certain orientation, thus suggesting that their distribution was not related to sec-

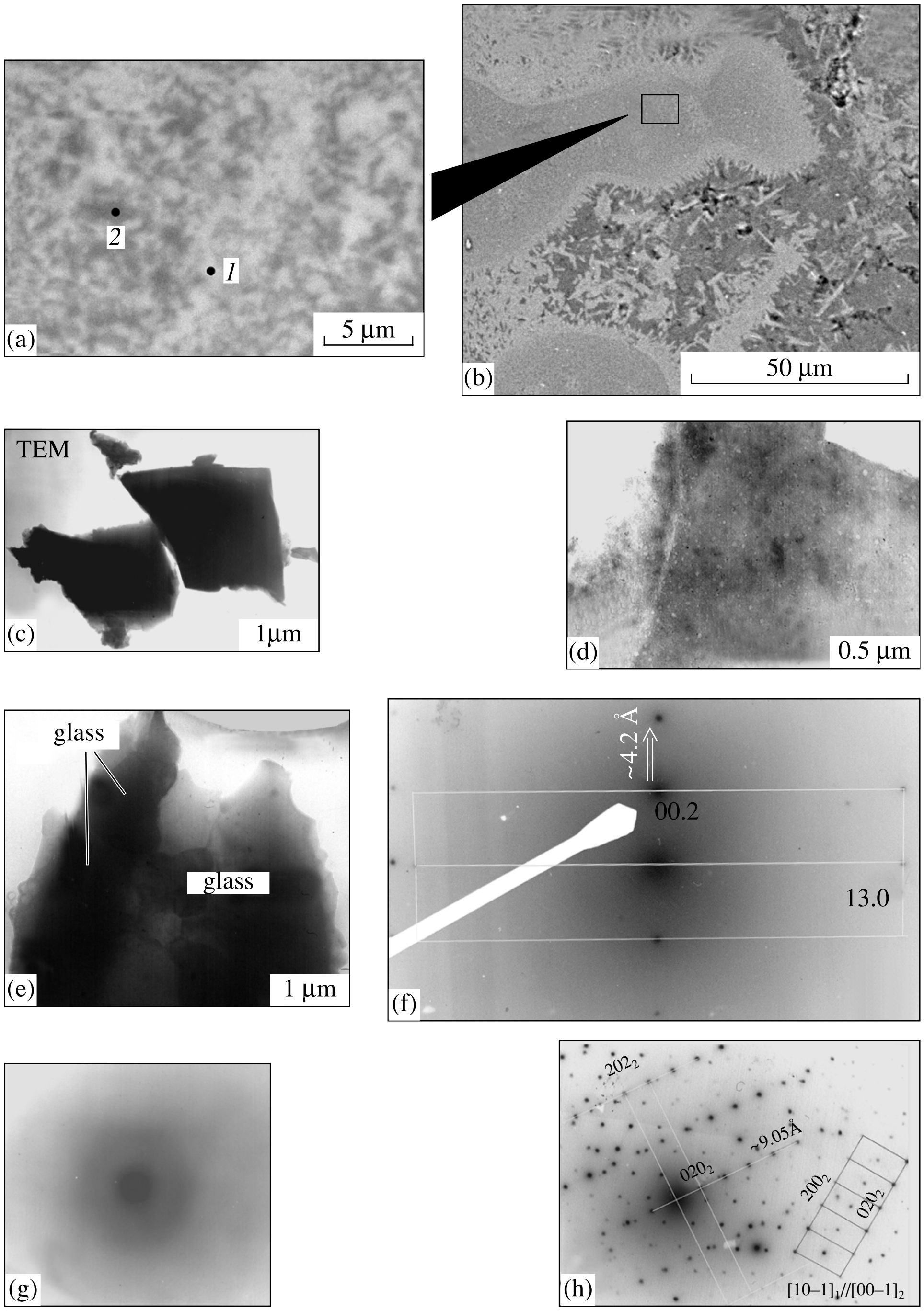

Fig. 2. Volcanic glass from basalts of Myandukha Mountain (Sample 303). (a) Back-scattered electron image of glass: (*1*) light phase, (*2*) dark phase (table, and analyses 4–7); (b) back-scattered electrons image of semivitreous basalt; (c, d) SEM images of amorphous SiO_2: ((c) dark glass particles, (d) dense aggregates of disperse grains); (e) intergrowth of two randomly oriented amphibole crystals, regularly oriented pseudohexagonal tridymite (crystals in center) and quartz glass; diffraction patterns (f) tridymite; (g) quartz glass, (h) ampbibole.

ondary processes, but reflects the primary heterogeneity of melt preserved owing to rapid cooling.

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