

Volkhovite: A New Type of Tektite-Like Glass

G. T. Skublov^a, Yu. B. Marin^a, V. M. Semikolennykh^a, S. G. Skublov^b, and Yu. N. Tarasenko^a

^aSt. Petersburg State Mining Institute, Vtoraya Liniya 21, St. Petersburg, 199026 Russia

^bInstitute of Precambrian Geology and Geochronology, Russian Academy of Sciences,
nab. Makarova 2, St. Petersburg, 199034 Russia

Received September 1, 2006

Abstract—Volkhovites are tektite-like glasses of mafic and ultramafic composition discovered in the fluvio-glacial drift of the Valdai glaciation (10–60 ka ago) along the right bank of the Volkhov River (59°27' N, 32°01' E). Volkhovite particles are small in size (0.1–3.0 mm) and irregular in shape, with various microtektite aerodynamics (globular, droplike, and dumbbell-like forms). They are perfectly preserved, and, thus, postglacial in age. Sporadic volkhovite grains (up to 20 items per 1 kg of loam) were detected over an area 1.0 × 1.5 km². Some samples from local spots 20 × 30 m² in size are anomalously enriched, up to 1700 volkhovite grains per 1 kg of loam. Tiny Ti–Fe, Fe, and Cu–Au spherules, particles of quenched glass and cinder, and fragments of the Precambrian and Paleozoic rocks are spatially associated with volkhovites. The suggested cryptomagmatic model assumes that the glass and cinder are pre-Holocene in age, whereas volkhovites were formed in the post-glacial time as a result of the outburst of the slag–stone–melt–mud–gas mixture that ascended from the asthenosphere to the surface. Drops of the melt solidified in the air instantaneously to form tektite-like glasses, and the tuffsite-like agglomerate mixed with the fluvio-glacial drift.

DOI: 10.1134/S107570150708003X

INTRODUCTION

Tektites are a type of natural glass that were studied most thoroughly and extensively among the other numerous types, such as obsidians, tachylites, fulgurites, and impact, or tektite-like glasses (O'Keefe, 1976, 1994; *Impactites*..., 1981; Koeberl, 1986, 1994; Feldman, 1990; Barnes, 1990; Scholze, 1990; Vogel, 1992; Marakushev et al., 1993; Boushka et al., 1993; Povenmire, 1997; Heinen, 1998; Heide et al., 2001, 2003), typically occurring as relatively small homogeneous aerodynamic shapes, such as spherules, tear-drops, and pear- or dumbbell-like bodies. The meteoritic sources of tektite material were determined for three fields of scattered tektites (for bediasite and georgiite in North America, moldavite in Central Europe, and ivorite in West Africa), whereas the occurrence of meteoritic craters is only inferred for Australian–Asian tektites (indochinite, australite, zhamanshinite, irgizite, and others). Chemically, tektites are close to obsidian, and their SiO₂ concentration only rarely decreases below 60% and usually ranges from 70 to 75%. Some tektites are richer in Cr, Ni, Co, Mg, and some other elements, which are presumably derived from the material of the extraterrestrial impactor.

Tektite-like impact glasses were found in the craters of Aouelloul in Mauritania, Darwin and Henburn in Australia, Lonar in India, Wabar in Saudi Arabia, and Zhamanshin in Kazakhstan. These glasses show some features notably different from those of tektites,

although it is hard to draw a sharp boundary between them. Glasses from Libya, North Africa, are more distinct from other tektites and can be considered transitional between tektites and impactites themselves (Barrat et al., 1997). Tektite-like urengoite from western Siberia is obviously of the impact genesis, but its source has not been identified (Deutsch et al., 1997).

Along with tektites, the group of natural glasses includes *microtektites*, which occur as small (usually <2 mm) grains of various shape, color, and transparency in three of the four known fields of dispersed tektites (except the Central Asian field) and in rocks marking the C/Tr (Cretaceous–Tertiary) boundary. They play an important part in constraining the boundaries of the fields of scattered tektites and their stratigraphic age and provide information on the relationship between tektites and impact events, location of the craters, etc. (Montanari and Koeberl, 2000; Marini, 2003). Recent studies, including geochemical investigations, have demonstrated that microtektites cannot be regarded as a merely scaled-down version or fragments of tektites, because they could be produced during different stages of the impact process. A type of microtektites principally different from the others is bottle-green tektites, which are characterized by elevated concentrations of Fe, Mg, and siderophile elements and lower contents of silica and alkali metals. The composition of microtektites generally corresponds to that of sedimentary rocks with a minor admixture of meteoritic material (Glass et al., 2004).

Corresponding author G.T. Skublov. E-mail: skublov@land.ru

The Australasian tektite belt, which was first recognized by Izokh (1997), tends to the northwest for more than 10000 km from Australia to the Zhamanshin crater and is the only one in which Muong Nong-type tektites were found. These tektites are characterized by a pseudofluidal structure and occur in vast volumes (billions of tons). A key point in the problem of the relationship between tektites and impactites was the find of tektite-like glasses irgizites in the Zhamanshin crater, which notably differ from zhamanshinites, the impact glasses of this crater (Florensky and Dabizha, 1980). Further studies have demonstrated that the chemistry of tektite-like irgizites and microtektites from the Zhamanshin crater is close to that of similar glasses found elsewhere (Skublov and Tyugai, 2005a, 2005b; Skublov et al., 2005) and that some features of their composition can be explained by the multistage genesis of impact glasses (Skublov and Tyugai, 2004). The age of the tektites related to the Zhamanshin crater remains uncertain as yet. Izokh (1997) argued for a young (~10000 yr) age of the Zhamanshin crater, while Florensky and Dabizha (1980) believed that the age of the silicic glasses is older (750000 yr).

The genesis of tektites and microtektites still remains a matter of discussion. Some researchers believe that tektites are the products of extraterrestrial volcanism that were somehow delivered to Earth (O'Keefe, 1976, 1994; Izokh, 1997). At the same time, other scientists argue that the compositional and textural features of tektites rule out their volcanic genesis and should have been determined by collisions of cosmic bodies with Earth (Koeberl, 1986, 1994; Heide et al., 2001). A comparison of the impact glasses and tektites reveals their significant differences, although all of them could be produced by a single process. Every impact event produces impact glasses, but only occasionally tektites. It is, thus, reasonable to suggest that the genesis of tektites requires some unusual conditions, or that they were slowly destructed after their origin (Heinen, 1998).

RESEARCH METHODS

Our research was carried out issuing from the suggestion that the Australasian tektite belt can continue from the Zhamanshin crater farther northwestward. If continued, this line crosses the Gulf of Finland of the Baltic Sea, whose surroundings are known to include numerous meteoritic craters: 13 in Finland, 6 in Sweden, 5 in Estonia, and 2 in Russia. Some of them are as young as 50 ka. This led us to hope to find a meteoritic crater of the Zhamanshin age (approximately 10 ka) in the European part of Russia. The reason for our hope was the discovery of Holocene microtektites in the Kola Peninsula (Nechaeva, 1982) and sporadic finds of metallic spherules in pan samples (Panova et al., 2004). Another equally important issue is the search for tektite-like glasses as in situ (not displaced) objects. Because of this, the kame and osar complexes are com-

monly preferred to glaciofluvial planes, with less attention paid to alluvial and lacustrine deposits. Therefore, we always thoroughly analyzed satellite images (Landsat) and published geological maps on the scale 1 : 200000.

Fieldwork. We collected 1- to 2-kg samples from Quaternary loose sediments. This amount of material was proven sufficient to draw statistically reliable conclusions about the composition of the loam, sandy clay, loess (1 kg), gravelly sand, and boulder-bearing loam (2 kg). Much attention was focused on examining quarries that mining clay, sand, gravel, and boulder material, as well as natural exposures, cliffs, and artificial cuttings and outcrops (in prospector pits and shallow hand-boring boreholes and wells). We collected about 1000 samples (100 in 2004, 700 in 2005, and 200 in 2006). As a result, we revealed more than 20 microtektite aureoles in southern Karelia, Leningrad oblast, Pskov oblast, and Novgorod oblast, with each of these aureoles including at least one sample with low contents of the glasses (commonly 5–20 grains per kg of the sample material), and three areas with natural cinder. The most interesting find was made near the township of Kirishi. When studying loams in 2005, V.M. Semikolennykh noted tiny gold specks in loose deposits along the right side of the Volkhov River. Subsequent sampling (conducted together with Yu.N. Tarasenko) resulted in revealing various microtektites. A.P. Kazak and M.N. Afanasov (of the All-Russia Research Institute of Geology) confirmed their affiliation with microtektites and drew attention to their amazing similarities with microirgizites from G.T. Skublov's collection. In 2006, we undertook a number of joint prospecting routes, which made it possible to specify the geological setting of the tektite-like glasses and to identify their close relationship with other glasses and cinder.

Sample processing. The initial investigation in the spring of 2006 was centered on the systematic sampling of the tektite aureole. We selected one sample (2012) of the more than 20 sandy loam samples examined under a binocular that contained the highest concentration of tektite grains. The mass of the sample was 1590 g, and it was processed manually to avoid damage of the volkhovite grains. The sample was held for 1 day covered by water until the maximum swelling of the clay material. Clay-silt particles were separated in slowly running water, so that the sample was eventually separated into gravel-sand (605 g) and clay-silt (985 g) fractions, which were dried on a water bath for further examination.

The sandy fraction was then screen through the commonly used set of screens into (i) very coarse-grained (<10 mesh; grain sizes: minimum 1 mm along the short axis, average 3 mm, maximum 6 mm along the long axis), (ii) coarse-grained (10–20 mesh; corresponding grain sizes: 0.7, 1.3, and 3 mm), (iii) medium-grained (20–40 mesh; corresponding grain sizes: 0.4, 0.7, and 1.5 mm), (iv) fine-grained (40–60 mesh; corresponding grain sizes: 0.2, 0.4, and 0.8 mm), and

Table 1. Distribution of volkhovite grains in the sandy fraction of the loam, sample 2012

No.	Size, mesh	Type	Fraction								Total	
			magnetic		EM-1		EM-2		nonmagnetic			
			N_1	P_1	N_2	P_2	N_3	P_3	N_4	P_4	N	P
1	>10	WF	6	0.26	10	0.43	13	0.56	2296	98.25	2325	100
2	10–20	WF	26	0.01	80	0.22	400	1.10	35827	98.61	36333	100
3		V	4	0.01	11	0.03	49	0.13	12	0.03	76	0.21
4	20–40	WF	130	0.05	750	0.27	3300	1.20	271805	98.48	276000	100
5		V	14	0.005	50	0.02	769	0.28	52	0.02	885	0.32
6	40–60	WF	297	0.03	2376	0.24	9504	0.96	978120	98.80	990000	100
7		V	24	0.002	80	0.008	940	0.09	130	0.013	1174	0.12
8	<60	WF	16600	0.01	199200	0.12	1112200	0.67	164672000	99.20	166000000	100
9		V	40	0.00002	70	0.00004	400	0.0002	50	0.00003	560	0.0003
Total		V	82	3	211	8	2158	80	244	9	2695	100

Note: N_i is the number of grains in a given fraction; N is the total number of grains; P_i is the percentage of grains in a given grain-size fraction; WF is the whole fraction, V is volkhovite. Font types correspond to data obtained by examining the fraction under a binocular (boldfaced type), by weighing and further calculating (italics), and by calculating (Roman type). No volkhovites were found in the fraction >10 mesh.

(v) very fine-grained (<60 mesh; corresponding grain sizes: 0.1, 0.2, and 0.5 mm). The masses of the fractions were as follows: (i) 93 g, (ii) 109 g, (iii) 138 g, (iv) 99.5 g, and (v) 166 g. This means that the sandy fraction of the loams is practically unsorted by the fluvioglacial process. The selective counting of grains and their weighing were conducted to determine the average mass of a single grain in each fraction: (i) 40 mg, (ii) 3.3 mg, (iii) 0.5 mg, (iv) 0.1 mg, and (v) 0.01 mg. We were then able to calculate the number of grains in each fraction in sample 2012: (i) 2325, (ii) 36 333, (iii) 276 000, (iv) 990 000, and (v) 166 000 000, which was enough to look for microtektites. Using a MRM-1 hand-held magnet and a steel needle, we separated each size fraction of the sample into magnetic and strongly electromagnetic (EM-1), weakly electromagnetic (EM-2), and nonmagnetic fractions and counted the number of grains in each of them under a binocular. The results (Table 1) indicate that the loam of sample 2012 contains approximately 1700 volkhovite grains per kilogram of the material. The overwhelming majority of these grains is contained in the coarse-, medium-, and fine-grained fractions with average sizes of 1.3, 0.7, and 0.4 mm, respectively, i.e., the average size of the volkhovite grains is 0.7 mm. The least number of volkhovite grains (3, 9, and 8) was detected in the magnetic, nonmagnetic, and strongly electromagnetic fractions, respectively; and a high content (80%) was established in the weakly electromagnetic fractions. The weakly electromagnetic sandy medium-grained fraction contained 3300 grains, 769 of which were volkhovite, whose content is, thus, at a maximum (23%) in this fraction.

For further research, we selected 1000 volkhovite grains with regard to their abundance, grain size, and magnetic properties. These grains were then separated according to their color and grain shape. The grains vary in shape from equant to strongly elongated and irregular in line with variation in color from black volkhovite to honey-yellow and green. This tendency is not as pronounced clearly for brown volkhovite and weakly elongated grains. Then, with regard to the size, magnetic properties, color, and shape of the volkhovite grains, we picked representative samples by hand to prepare polished thin sections for microprobe analysis. We also analyzed fragments of cinder, glasses devoid of traces of aerodynamic shaping, grains of various minerals, and metal spherules. The grains were taken in the following proportions: ~50% volkhovite, 20% glasses and cinders, and ~10% metal spherules. Three polished thin sections were prepared with large ($N = 93$), medium-sized ($N = 182$), and small ($N = 213$) grains. As was revealed by examining the pellets in transmitted and reflected light, all volkhovite grains are transparent or translucent and can be conveniently subdivided into three major groups: (1) honey-yellow; (2) green with transitions to pale green and blackish green; and (3) brown passing to brick-red, chocolate, and black. We managed to observe inclusions of metallic spherules or, more rarely, amygdules and various minerals in volkhovite grains. The greatest number of these inclusions were found in volkhovites of a green color.

After microprobe analyses and the preliminary classification of volkhovites and related glasses, cinder, and metallic spherules, the necessity arose to obtain additional grains of honey-yellow volkhovite, green volkhovite with inclusions, various cinder, metallic

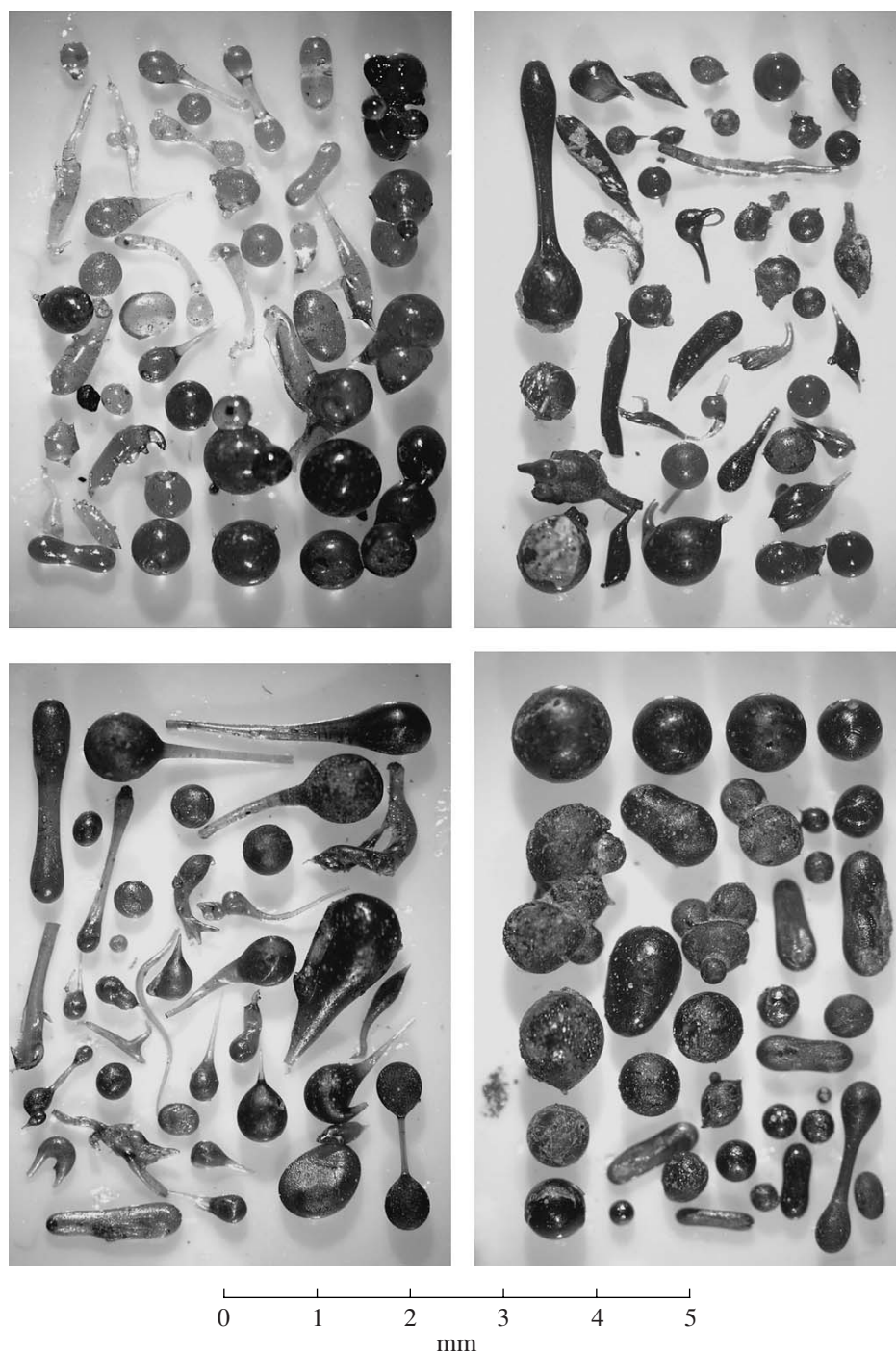


Fig. 1. Volkhovite grains of various shapes and colors.

spherules, and minerals for their closer examination. In the summer of 2006, a 5-kg loam, sample 2035, was taken in compliance with the scheme described above. Three additional glass platelets were prepared of large, medium-sized, and small grains of various compositions, with 71, 154, and 147 grains, respectively, which were used to prepare polished thin sections. In addition, we prepared a demonstration glass platelet with volkhovite grains (Fig. 1).

Analytical procedures. Here, 182 of 860 grains of volkhovites, cinder, spherules, and minerals were glued to six glass platelets and subjected to microprobe analysis. Most of the selected grains were characterized by one or two spot analyses, while the most interesting grains were analyzed at three–five to seventeen spots. As a result, we obtained 373 microprobe analyses. The analyses were carried out on an ABT-55 SEM equipped with a Link AN 10000 analytical system (analyst

M.D. Tolkachev, Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences). We took back-scattered electron (BSE) images of each analyzed grain (Fig. 2). Because of the carbon sputter coating on pellets for microprobe analyses, the impossibility of analyzing carbon and oxygen, and some features of our samples, which contained grains of shungite-like material, metal and silicate phases analyzed simultaneously, as well as the substantial deviation of the analytical totals from 100% in some samples, we proceeded from provisional assumptions.

First, we selected nine samples whose totals were greater than 110%. In sample 212.19, the following concentrations of oxides were determined (wt %): FeO 63.5, SiO₂ 66.2, TiO₂ 16.9, Al₂O₃ 3.5, Cr₂O₃ 0.9, and <1% each of the other oxides (total 152.8%). This composition suggests that the spherule was produced under strongly reducing conditions. We did not explore the possibility of the presence of Fe, Ti, Cr, and Al silicides in this sample, and the latter was not included into the composite sampling for statistical processing. The totals of the other eight analyses ranged from 113 to 120%. All of these samples were ferrous or silicate-ferrous inclusions in various types of volkhovites and likely contained limited amounts of silicides. These analyses were rejected from the sampling for further statistical processing. Second, we rejected analyses with totals lower than 10% (possibly, glassy carbon or shungite), close to 60% (carbonates), and 70–90% (perhaps, carbon-saturated cinder). Analyses with totals of >90% were included in the sampling for statistical processing. Third, the compositions of metallic spherules and some cinders that contain >80% Fe were recalculated using the oxygen-free model. At the same time, analyses of the silicate-ferrous cinder quite often could be satisfactorily recalculated using the oxygen model. Because of this and with the aim of unification, all analyses were normalized to certain coefficients and recalculated to the oxygen model, and the analytical totals were normalized to 100%. These data were further utilized in the statistical calculations.

Statistical processing. The analyses recalculated to 100% were grouped into a database, in which each sample was supplemented with encoded information on its grain size, magnetic properties, color, grain shape, and possible geological setting. We broadly applied various statistical techniques (Davis, 1973), including factor analysis (Belonin et al., 1982). The applications of these techniques were considered in detail in our earlier publications (Marin et al., 1983; Skublov and Tyugai, 2004).

Classification of glasses and cinders. It was most difficult to classify volkhovites and the related glasses and cinders. Considering the final result (Table 2), one can see that the classification is detailed enough and supported by geological, petrographic, and petrochemical data. The principal classification features were the aerodynamic shape of the silicate glasses (volkhovites;

group A); the color of volkhovite grains, which varied from predominantly honey-yellow (Mg-volkhovite) to brown (Ca-volkhovite), and green (Mn-volkhovite); the color of the metallic spherules, which varied from steel gray (D1) to lustrous black (D2) and yellow (Cu–Au spherules); and the clastic shape of glass and cinder fragments, the abundance of fluid inclusions in the Vesicular lustrous silicate glasses (E1), a drastic increase in the magnetization of the cinders with their transition from ferrous-silicate cinders (E2) to ferrous cinders (E4). Our petrographic and microprobe studies allowed us to identify inclusions in volkhovite (group B) and other newly formed phases (group C). A more detailed classification was based on petrochemical data. In certain instances, the differences between the types of the newly formed phases were so significant (A1, A2, and A3) that they were clearly discernible even without statistical criteria, and the application thereof only confirmed the conclusions at a 0.001–1% significance level. The boundaries between the petrochemical types are usually sharp enough (E1, E2, E3), although gradual transitions are also possible (E3, E4). Petrochemical subtypes of the glasses and cinders were distinguished by statistical parameters. Each of the types thus distinguished was tested for the homogeneity of the sampling by the corresponding criteria at the 5–10% significance level. For example, subtypes of various volkhovite types were recognized by their P, Cr, Ni, and Co contents: with medium (subtypes 1, 3, and 5), high (subtypes 2, 4, and 6), and anomalously high (subtype 7) concentrations of these oxides. The most significant petrochemical differences were established between three subtypes of equant inclusions in Mn-volkhovites, which allowed us to classify these spherules into standard, exploded, and high Cr.

During the detailed examination of volkhovites, we noted anomalously high CaO concentrations in the glasses (18–42%), which is atypical of pre-Holocene igneous rocks (Marin et al., 1983), and the amazing distinctive features of three volkhovite types, which are enriched in (1) Mg, Ti, Al, and K; (2) Ca, Na, and SO₃; and (3) Mn, Si, Fe, and Cr. During the second stage, when data on volkhovites were analyzed together with petrochemical data on the inclusions, metallic spherules, glasses, and cinders with the use of a mean concentration matrix (Table 2), we arrived at the conclusion that all of them have a common genesis. During the final stage of our research, the factor analysis of the combined selection of the mean concentrations of glasses, cinders, silicate minerals, and their varieties allowed us to distinguish the following associations of chemical elements: (1) P, Ni, Co, Fe, and S; (2) Cr, Ti, Mn, Mg, and Ca; and (3) K, Si, Na, and Al (Fig. 3). We suggested that the elements of the first group accumulated in the metallosphere (according to Larin, 2005), the second-group elements accumulated in the asthenosphere, and elements of the third group accumulated in the lithosphere. The magmatic chambers developed at the asthenosphere–lithosphere boundary produced

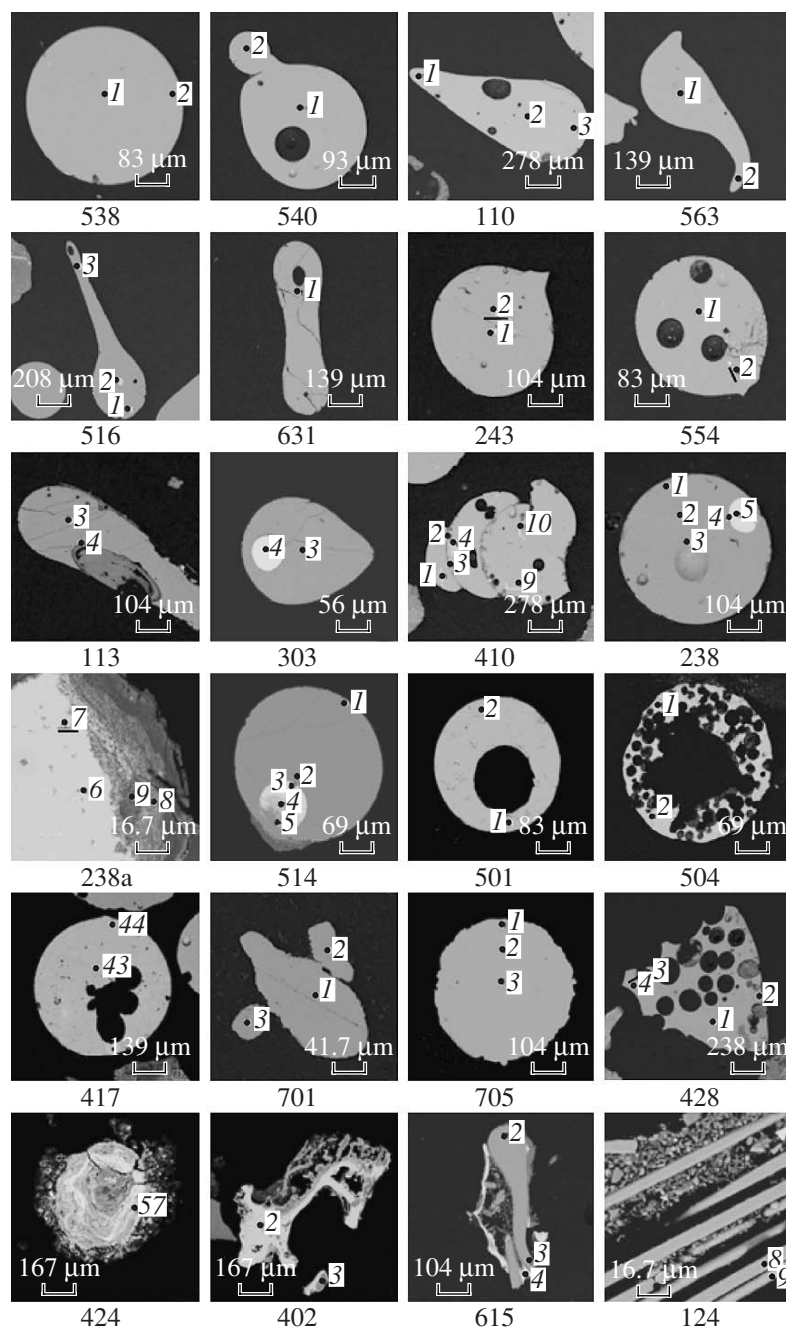


Fig. 2. Secondary-electron images of volkhovites, spherules, glasses, and cinders. Volkhovite: (samples 538, 540) magnesian, (110, 563) calcic, (516, 631) manganoan; inclusions in volkhovites: (243) magnesian, (554) calcic, (113) calcite amygdale in manganoan volkhovite, (303) nondecrepitated spherule, (410) high-Cr inclusions; (238, 514) decrepitated spherules; metallic spherules: (501) ferrous, (504, 417) Ti-Fe, (701, 705) Cu-Au; (428) Vesicular silicate glasses; (424, 402) cinders; (615) inclusions in Fe-tektite; (124) inclusions in a shungite-like aggregate.

volkhovites, while minerals were formed only in the lithosphere.

RESULTS

Geology of the study area. The area where volkhovites were found is situated in the northern part of the Russian Platform and composed of gently dipping Pale-

ozoic sedimentary sequences. In the study area itself, the glacial deposits are underlain by the Upper Ordovician dolomite, which rests on the Middle Ordovician dolomite and limestone (Kegel, Khrevitza, Idavera, and Tallinn units), the Lower Ordovician limestone of the Kunda Unit, glauconite limestone of the Volkhov Unit, glauconite sand of the Leet Unit, and dyctionine shales and oboloid sand of the Pakerort Unit. The thickness of

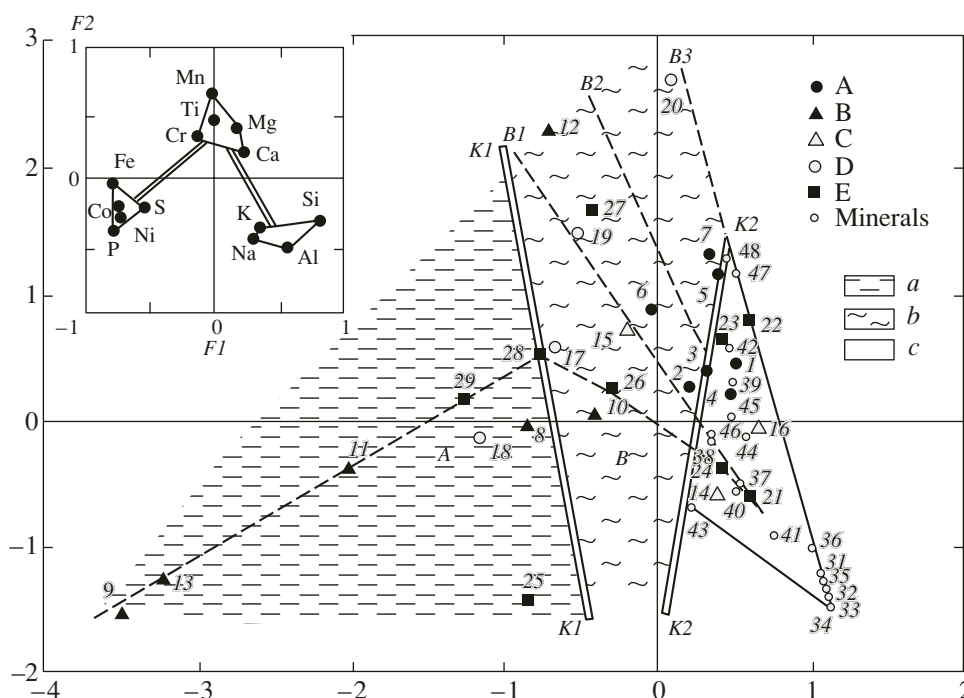


Fig. 3. Petrochemical model of the formation of volkhovites based on the data processed using the method of principal components of the matrix of the mean concentrations of major oxides in the composite sampling of volkhovites, related spherules, glasses, and cinders (Table 2, nos. 1–29) and minerals (nos. 31–48): (31–36) feldspars, (37) biotite, (38, 39) hornblende, (40) glauconite, (41) chlorite, (42) Cr-diopside, (43–46) garnet, and (47, 48) serpentine. The inset at the left-hand top corner is a diagram of the factor loadings on the (*F1*) first and (*F2*) second factors; the factor weights are 27 and 13%, respectively. The diagram in the right-hand bottom corner shows the values of factors *F1* and *F2* for 47 samplings; (*a*) field of the P, Ni, Co, Fe, and S assemblage, (*b*) field of the Cr, Ti, Mn, Mg, and Ca assemblage; (*c*) field of the K, Si, Na, and Al assemblage; *K1* and *K2* are the boundary lines separating the assemblages; *B1*, *B2*, and *B3* are petrochemical trends; A–E are the groups shown in Table 2.

the Ordovician deposits reaches 170 m. They are underlain by the Cambrian clay of the Piratas, Lontovas, and Lomonosov formations 130-m thick. These rocks rest on Neoproterozoic clay with siltstone, sandstone, and gravelstone beds approximately 200-m thick. The platform basement consists of the Archean and Paleoproterozoic granites, gneisses, crystalline schists, and amphibolites.

The loose lacustrine–glacial and fluvioglacial deposits are clays, loams, sandy loams, and sands, which were dated by most researchers at the Holocene and thought to be deposited during the Valdai glaciation at 65–10 ka ago. Based on fossil floral remnants, these deposits are correlated with the Krestets Unit of the Upper Valdai recession moraine unit. Their thickness usually does not exceed 30 m. In the area where volkhovites were found, these are brown, gray, and yellowish brown or, occasionally, bluish loams, usually with up to 7–15% sand fraction. The deposits contain rare well-rounded boulders and pebbles of various Precambrian rocks.

Volkhovite. One of the most conspicuous features of volkhovites is their clearly pronounced aerodynamic shape (Figs. 1 and 2) with a predominance of spherules, slightly elongated egg-, ellipsoid-, and dumbbell-shaped particles; the strongly elongated and irregularly

shaped grains are less frequent. Volkhovites are classified into three groups: magnesian, calcic, and manganoan. As mentioned above, they are characterized by the maximum concentrations of the following elements: (1) Mg, K, Al, and Ti; (2) Ca, Na, and S; and (3) Mn, Cr, Si, and Fe. The concentration ranges of many oxides in these groups do not overlap.

The magnesian volkhovites are dominated by spherical shapes; the predominance of these morphologies in the calcic glasses is pronounced not as conspicuously, and they contain much elongated, droplet-, and irregularly shaped grains; and the manganoan volkhovites consist of approximately equal amounts of isometric, elongated, and irregularly shaped grains. The size of volkhovite grains increases from magnesian (0.3 mm, on average) to calcic (0.4 mm) and further to manganoan (0.5 mm) volkhovites. While the first group only very rarely includes large grains, the manganoan volkhovites are notably dominated by large and medium-sized particles contained in approximately equal amounts.

Color is a good distinguished feature of volkhovites. All grains of magnesian volkhovites have a rich honey-yellow color and are almost always transparent. The calcic glasses are predominantly dark brown and grade into black and brown; they are usually opaque under a

Table 2. Statistical parameters of the distribution of oxides in the major types of volkhovites, glasses, and cinders from the Kirishi structure

No.	Number of samples	Group	Type	Sub-type	SiO ₂		TiO ₂		Al ₂ O ₃		FeO		MnO	
					x	s	x	s	x	s	x	s	x	s
1	12	A. Silicate glasse—volkhovites	A1. Magnesian volkhovites	1	38.96	0.43	0.88	0.13	11.62	0.21	0.61	0.10	0.70	0.06
2	13			2	39.24	0.43	0.98	0.09	11.90	0.27	0.66	0.20	0.66	0.08
3	26			1	36.56	0.84	0.67	0.14	10.73	0.42	1.07	0.43	2.33	0.16
4	5			2	40.69	1.07	0.86	0.68	10.18	1.07	3.73	1.92	0.72	1.39
5	69	B. Inclusions in volkhovites	A3. Manganoan volkhovites	1	49.87	1.50	0.35	0.07	4.93	0.21	9.66	0.98	12.06	0.53
6	13			2	49.64	1.17	0.35	0.07	5.00	0.21	9.85	0.38	11.83	0.56
7	1			3	49.55		0.56		2.71		10.18		13.15	
8	2			1	17.66	3.80	0.27	0.21	6.21	0.91	52.83	9.77	0.19	0.11
9	2	C. Inclusions in other newly formed grains	B2. Calcic	1	1.37	1.05	—	—	0.19	0.10	91.90	2.60	0.12	0.16
10	8			2	38.32	11.16	0.67	0.23	8.38	1.93	30.77	8.22	4.20	3.54
11	5			1	1.21	0.16	0.04	0.04	0.03	0.05	93.46	2.47	0.28	0.20
12	8			3	0.89	0.23	0.22	0.25	3.49	2.13	19.14	13.21	8.35	1.87
13	10	D. Metallic spherules	C1. In Fe-and Ti-spherules	3	2.43	2.07	0.08	0.10	0.14	0.15	72.78	19.99	1.85	2.62
14	3			1	55.67	18.06	1.63	1.54	20.41	6.19	8.99	9.05	0.26	0.21
15	1			1	53.44		0.32		4.96		9.00		11.70	
16	2			1	57.53	0.31	0.02	0.03	16.08	0.08	0.18	0.10	0.04	0.01
17	13	E. Silicate-ferrous glasses and cinders	D1. Ferrous	1	0.44	0.41	0.38	0.76	0.12	0.09	97.78	1.20	0.49	0.37
18	2			2	2.84	0.62	—	—	—	—	92.19	2.20	0.36	0.08
19	8			1	11.33	13.58	21.35	13.65	1.77	0.84	56.86	12.74	6.39	5.15
20	2			2	16.73	0.41	43.50	0.09	7.67	0.28	10.04	0.23	12.08	0.17
21	9	F. Ferrous-silicate cinders	E1. Vesicular silicate glasses	1	56.41	6.92	1.14	0.48	22.85	3.74	8.80	4.15	0.07	0.06
22	2			3	56.28	3.46	0.67	0.31	13.73	1.51	5.88	1.17	15.88	1.97
23	2			3	47.90	4.67	0.51	0.16	8.05	4.23	5.80	5.15	5.94	8.18
24	5			1	40.49	5.37	0.69	0.51	17.50	2.46	31.58	4.73	0.40	0.32
25	1	G. Silicate-ferrous glasses and cinders	E2. Ferrous-silicate cinders	2	35.94		0.56		19.90		30.63		0.21	
26	8			1	17.05	18.00	0.51	0.84	6.99	5.67	70.02	25.48	0.83	1.07
27	1			2	10.73		7.28		3.05		62.03		15.00	
28	28			1	1.51	1.44	0.08	0.26	0.17	0.26	97.14	1.97	0.30	0.25
29	2	H. Ferrous cinders	E4. Ferrous cinders	2	2.02	1.98	0.01	0.02	—	—	96.44	1.97	0.34	0.17

Table 2. (Contd.)

No.	Number of samples	Group	Type	Sub-type	MgO		CaO		Na ₂ O		K ₂ O		P ₂ O ₅	
					x	s	x	s	x	s	x	s	x	s
1	12	A. Silicate glasse—volkhovites	A1. Magnesian volkhovites	1	11.66	0.59	32.80	0.65	0.40	0.15	1.28	0.05	0.040	0.072
2	13			2	12.10	0.38	31.49	0.44	0.38	0.17	1.19	0.06	0.124	0.113
3	26		A2. Calcic volkhovites	1	2.65	0.43	41.89	1.16	0.98	0.15	0.60	0.06	0.018	0.055
4	5			2	2.89	1.01	37.27	1.97	0.65	0.51	2.11	0.98	0.252	0.473
5	69	B. Inclusions in volkhovites	A3. Manganoan volkhovites	1	3.39	0.31	18.00	0.76	0.27	0.16	0.18	0.03	0.046	0.102
6	13			2	3.38	0.29	17.94	0.61	0.27	0.22	0.19	0.03	0.216	0.148
7	1			3	3.03		18.89		—		0.29		—	
8	2		B1. Magnesian	1	8.23	0.68	11.24	3.87	0.41	0.08	0.48	0.18	1.173	0.004
9	2	C. Inclusions in other newly formed grains	B2. Calcic	1	0.18	0.25	1.00	0.06	0.15	0.21	0.03	0.03	3.648	3.130
10	8		B3. Manganoan	2	5.98	3.97	5.69	1.01	0.49	0.48	0.23	0.24	0.864	0.544
11	5			1	0.11	0.07	0.14	0.11	0.27	0.18	—	—	1.542	0.678
12	8			3	12.11	4.02	0.65	0.25	0.09	0.12	0.01	0.02	0.010	0.025
13	10	D. Metallic spherules		3	0.27	0.35	2.53	3.23	0.38	0.38	0.02	0.03	3.914	3.701
14	3		C1. In Fe-and Ti-spherules	1	6.77	7.71	2.85	4.00	0.20	0.21	2.43	3.01	0.152	0.178
15	1		C2. In Fe-tektite	1	2.88		16.07		0.11		0.14		0.142	
16	2		C3. In glassy carbon	1	4.10	0.14	21.55	0.50	0.06	0.09	0.10	0.01	0.140	0.062
17	13	E. Silicate-ferrous glasses and cinders	D1. Ferrous	1	0.17	0.14	0.03	0.04	0.48	0.35	0.02	0.02	—	—
18	2			2	0.35	0.06	0.40	0.15	2.05	1.66	0.02	0.02	0.105	0.147
19	8		D2. Ti-Fe	1	0.89	0.38	0.59	0.47	0.45	0.17	0.07	0.07	—	—
20	2			2	7.36	0.13	0.65	0.12	0.81	0.08	0.99	0.08	—	—
21	9	E. Silicate-ferrous glasses and cinders	E1. Vesicular silicate glasses	1	2.37	1.35	4.66	3.34	1.20	0.40	2.04	0.69	0.373	0.561
22	2			3	1.73	0.37	1.62	0.15	0.51	0.71	3.04	0.97	—	—
23	2			3	3.36	0.29	25.20	11.36	0.46	0.12	1.58	1.95	0.038	0.052
24	5		E2. Ferrous-silicate cinders	1	3.18	3.24	1.37	0.94	0.53	0.39	4.12	1.07	—	—
25	1	F. Silicate-ferrous cinders		2	3.69		2.75		0.91		2.32		1.783	
26	8		E3. Silicate-ferrous cinders	1	0.95	0.90	2.16	1.88	0.82	0.30	0.42	0.81	—	—
27	1			2	1.09		0.52		—		—		0.228	
28	28		E4. Ferrous cinders	1	0.23	0.43	0.24	0.31	0.18	0.20	0.02	0.03	—	—
29	2			2	—	—	—	—	—	—	—	—	—	—

Table 2. (Contd.)

No.	Numbers of samples	Group	Type	Sub-type	SO ₃		Cr ₂ O ₃		NiO		CoO		Cl ₂ O	
					x	s	x	s	x	s	x	s	x	s
1	12	A. Silicate glasse—volkhovites	A1. Magnesian volkhovites	1	0.998	0.474	0.054	0.052	—	—	—	—	—	—
2	13			2	1.148	0.093	0.029	0.035	0.046	0.047	0.041	0.031	0.007	0.013
3	26		A2. Calcic volkhovites	1	2.449	0.569	0.027	0.041	—	—	0.008	0.023	0.008	0.027
4	5			2	0.563	0.413	0.075	0.134	—	—	—	—	—	—
5	69		A3. Manganian volkhovites	1	0.198	0.175	1.024	0.127	—	—	—	—	0.007	0.016
6	13	B. Inclusions in volkhovites		2	0.222	0.139	0.991	0.104	0.044	0.035	0.073	0.065	0.005	0.008
7	1			3	0.497	—	1.134	—	—	—	—	—	—	—
8	2		B1. Magnesian	1	1.166	0.038	0.020	0.026	0.060	0.037	0.052	0.014	0.013	0.017
9	2		B2. Calcic	1	0.657	0.141	0.052	0.014	0.505	0.712	0.184	0.258	0.010	0.011
10	8		B3. Manganian	2	0.128	0.116	4.035	6.106	0.047	0.068	0.058	0.069	0.114	0.138
11	5	C. Inclusions in other newly formed grains		1	1.489	1.031	1.181	0.571	0.102	0.117	0.140	0.270	0.007	0.012
12	8			3	0.018	0.016	54.900	13.674	0.058	0.138	0.032	0.065	0.016	0.019
13	10			3	9.529	15.118	5.765	4.506	0.164	0.243	0.113	0.183	0.013	0.019
14	3		C1. In Fe-and Ti-spherules	1	0.390	0.645	0.034	0.039	—	—	0.045	0.074	0.164	0.165
15	1		C2. In Fe-tektite	1	0.277	—	0.769	—	—	—	0.128	—	0.058	—
16	2	D. Metallic spherules	C3. In glassy carbon	1	0.105	0.147	0.035	0.048	—	—	—	—	0.062	0.009
17	13		D1. Ferrous	1	—	—	0.069	0.054	—	—	—	—	—	—
18	2			2	1.299	0.284	0.117	0.070	—	—	0.085	0.067	0.179	0.083
19	8			1	—	—	0.225	0.186	0.017	0.046	0.030	0.074	0.018	0.032
20	2		D2. Ti-Fe	2	0.017	0.023	0.137	0.023	—	—	—	—	—	—
21	9	E. Silicate-ferrous glasses and cinders	E1. Vesicular silicate glasses	1	0.020	0.032	0.043	0.047	0.012	0.033	0.007	0.019	—	—
22	2			3	0.095	0.059	—	—	—	—	—	—	—	—
23	2			3	0.725	1.023	0.437	0.617	—	—	—	—	—	—
24	5		E2. Ferrous-silicate cinders	1	0.118	0.107	0.023	0.030	—	—	—	—	—	—
25	1			2	0.778	—	—	—	0.158	—	0.075	—	0.280	—
26	8		E3. Silicate-ferrous cinders	1	0.216	0.407	0.028	0.033	—	—	—	—	—	—
27	1			2	0.009	—	0.033	—	—	—	—	—	0.018	—
28	28		E4. Ferrous cinders	1	0.065	0.172	0.064	0.069	—	—	0.005	0.018	—	—
29	2			2	—	—	0.914	0.019	0.256	0.158	—	—	—	—

Note: The subtypes correspond to (1) normal, (2) abnormal, and (3) anomalous varieties of the selections. The oxide concentrations are given in wt %; x is the mean concentration; s is the standard deviation; and the minus sign indicates concentrations below the microprobe detection limit.

binocular magnifier and often translucent in polished thin sections. The manganian volkhovites are commonly dark green to black, occasionally green to pale green (the latter are occasionally transparent), and very rarely greenish brown. In thin sections, black manganian volkhovites are translucent and show clearly visible greenish color shades.

When the average concentrations of major oxides are compared in the three groups of volkhovites, differences can be identified at the 0.01–1% significance level of the Student criterion, and the absolute values of the latter may reach 30–100. These contrasting differences are caused by very low dispersions of the major oxides. For example, the standard deviations of Al_2O_3 are 0.27% for magnesian and 0.21% for manganian glasses (the mean concentrations are 11.7 and 4.9%, respectively). This means that the coefficient of variation for Al_2O_3 in these glasses is as low as 2–4%. However, if all volkhovite types are included in the sampling, the statistics principally changes (mean = 7.4%, standard deviation = 3.1%), and the coefficient of variation increases to 42%.

In order to study the compositional variability of volkhovites within individual grains, we analyzed the cores and peripheral portions of 20 grains. No statistically significant differences were detected, and only one grain (sample 516) displayed an increase in Si and Al concentrations in the protruding “tail” of a droplet-shaped grain. Thus, volkhovites show significant differences between the three glass groups, only weak differences within each of these groups, and no compositional variability within individual grains. Note that the three glass groups show no statistically significant differences in P, Ni, Co, and Cl, but when the method of main components is applied to these groups, they are subdivided into two subtypes according to the second factor. These subtypes can be conventionally referred to as normal and abnormal. The list of elements identified according to the Student criterion is somewhat different for the three groups: magnesian volkhovites (+Co, Ni, Al, Ti, and P; –Ca and K), calcic volkhovites (+Si, K, Fe, and P; –Ca, Mn, S, and Na) and manganian volkhovites (+Ni, Co, and P), where the plus sign denotes enrichment in an element in the abnormal volkhovite. Hence, the most important indicative elements of the abnormal glasses are (+P, Ni, and Co; –Ca). The results of the correlation and factor analyses of the compositions of the glasses corroborate the conclusions stated above. If the statistical sampling includes the glasses of all types, then the factor diagram shows two clearly separated volkhovite types. When each of them is considered separately, normal and abnormal glasses can be distinguished. The separate processing of statistical data for each subtype yields an isotropic diagram of factor values.

Inclusions in volkhovites. As follows from microprobe examination, many volkhovites contain inclusions. The size of the inclusions increases from the

magnesian glasses (0.006 mm) to calcic (0.01 mm) and manganian (0.14 mm). The number of grains increases from 3 to 5 and 30% in the same direction. While magnesian and calcic volkhovites contain similar inclusions, manganian volkhovites are distinguished by calcite amygdules surrounded by silicate rims, chains of coalescent grains with a retained silicate rim between, and high-Cr inclusions, along with undecrepitated and decrepitated spherules.

Differences between the inclusions are most clearly seen in a diagram for the factor values of a random selection (Fig. 3). Inclusions in magnesian volkhovites are spherical (grains 243 and 315), small (5–8 μm) equant grains of a silicate–ferrous composition, with the predominance of FeO, SiO_2 , CaO, and MgO (Table 2). These inclusions are enriched in P_2O_5 (1.17%) and SO_3 (1.17%). The maximum enrichment was detected in two spherules (samples 519 and 554) found in calcic volkhovites that contain 3.65% P_2O_5 , 0.66% SO_3 , 0.50% NiO, 0.18% CoO, and 91.9% FeO.

The inclusions in manganian volkhovites are common undecrepitated spherules (samples 303, 513, and 517). They are characterized by the highest concentrations of Fe, most likely, in the metallic form and relatively low contents of P, S, Cr, Ni, and Co, perhaps, in the form of oxides. The decrepitated spherules (samples 238 and 514), which are characteristic only of magnesian volkhovites, are characterized by anomalously high concentrations of P, S, Cr, Ni, and Co. The redistribution of material was noted only in the decrepitated spherules: from the bottom portions of the microspherules to their necks, the element concentrations gradually (sample 238) or abruptly (sample 514) change. In sample 238, the concentrations systematically increase (Fe $\rightarrow$ Mn $\rightarrow$ Cr, S $\rightarrow$ P $\rightarrow$ Ca, Ni, Co); in sample 514, its bottom portion is notably enriched in Fe, whereas the neck, in Mg, Co, Cr, P, S, and Ni. The spot analysis 514.15 yields (wt %) 13.1 Cr_2O_3 , 10.6 P_2O_5 , 3.2 SO_3 , 0.65 NiO, and 0.41 CoO.

Five volkhovite grains (samples 214, 250, 410, 533, and 535) contain inclusions with anomalously high Cr_2O_3 concentrations (25.1–66.5%). In the case of the highest Cr_2O_3 concentrations, Cr-spinel is readily identified by its crystal habit. At lower Cr_2O_3 concentrations, a noncrystalline Cr–Fe phase appears. All transitions between these end members of the chromian inclusions can be observed within a single grain, which is composed of four coalescent spherules (sample 410). The silicate–ferrous rims retained between the spherules are also enriched in Cr, P, and S and are depleted in silica and enriched in Al, Mn, Mg, and Ca. A calcite amygdule in manganian volkhovite (sample 113) is characterized by a variable composition (from calcite to mangancalcite) and contains relics of a concentrically zoned silicate rim 5–10 μm wide, which is similar to the rim in sample 410.

Metallic spherules. We distinguished three types of the spherules: (1) Fe, (2) Ti–Fe, and (3) Cu–Au, which

can be readily identified. The ferrous spherules are characterized by a steel-gray color, an ideal spherical shape, a small size (~100 μm , on average), the occurrence of spherical cavities, and a uniform composition. These glasses are depleted in most major oxides (~2%). These spherules basically differ from the Cr-Fe inclusions in volkhovites in having low concentrations of Cr_2O_3 (<0.2%). Two of these spherules were determined to contain Na_2O (2.1%), SO_3 (1.3%), and Cl_2O (0.18%).

The Ti-Fe spherules differ from the above type in having lower concentrations of FeO (41.5–81.9%), anomalously high concentrations of TiO_2 (7.3–52.1%), and notably elevated SiO_2 (11.3) and MnO (6.4%). As mentioned above, practically all of these spherules are decrepitated with the release of the silicate phase. The Ti-rich undecreepitated spherules (sample 417) were recognized as an individual subtype. They are enriched in SiO_2 (16.7%), Al_2O_3 (7.7%), MnO (12.1%), and MgO (7.4%), which makes them compositionally similar to manganian volkhovites.

The Cu-Au spherules and grains were found by V.M. Semikolennykh in loam samples with low volkhovite contents (20–100 grains per kg of rock). The gold specks are dominated by irregularly shaped grains up to 0.1-mm across. The grains occasionally reach 0.3 mm in size with small offsets (sample 701), corroded hemispheres are less abundant (sample 702), and sporadic grains are ideal spheres up to 0.06 mm in diameter (sample 705). The results of microprobe analyses of five grains indicate that Au concentrations vary from 49 to 76%, while the copper concentration increases from 19 to 43%. The grains always contain 4–13% silver, and one spot analysis indicated palladium (0.08%). The Au concentration systematically decreases from spherical grains (sample 705) to corroded semispheres (samples 702 and 703) and irregularly shaped grains (sample 704) (76, 66, and 58% Au, respectively), while the Cu concentration increases (19, 23, and 35%, respectively). Au is uniformly distributed within individual grains, and only one large gold grain (sample 701) has an offset with a much higher Cu concentration (up to 43.6%).

Glasses and cinders. This group (Fig. 2) includes all glasses markedly differing from volkhovites in the occurrence of a clastic structure, the absence of aerodynamic morphologies, in having a typical black color, and bearing numerous cavities up to 0.1 mm across, which makes their texture similar to those of pumice-cinder and allows us to refer to them as Vesicular glasses. Similarly to the glasses, the cinders have clastic structures, a black or occasionally brown color, extremely heterogeneous inner structures, and a very diverse morphology: platelets, irregularly shaped fragments, and strongly elongated grains. According to their chemical composition, the glasses and cinders are classified into four types with a systematically decreasing concentration of Si (55, 39, 16, and 2%) and an increasing Fe concentration (7, 31, 69, and 97%). These

types were termed vesicular glasses and ferrous-silicate, silicate-ferrous, and ferrous cinders.

The vesicular silicate glasses are close to basic and intermediate igneous rocks (45–68% SiO_2) in composition and noted by elevated FeO and Al_2O_3 . One of the grains abounded in cavities (sample 428) contains up to 1.3% P_2O_5 , 0.08% Cr_2O_3 , and 0.1% NiO. A grain with the highest Al_2O_3 (sample 412) does not contain P_2O_5 , but is enriched in SO_3 (0.09%) and Cr_2O_3 (0.12%). The subtype of high-Mn Vesicular glasses (sample 416) is characterized by very high MnO concentrations (15–17%) and strongly differs from Mn-volkhovites in having high SiO_2 and Al_2O_3 concentrations. The subtype of high-Ca glasses (17–33% CaO) is distinguished by high concentrations of SO_3 (up to 1.5%) and Cr_2O_3 (0.87%).

The **ferrous-silicate cinders** are close to basic and ultrabasic rocks (35–48% SiO_2). These cinders are very heterogeneous, even within individual grains (sample 424), but have persistently high concentrations of Al_2O_3 , Fe_2O_3 , and K_2O (3.4–5.4%). The maximum Ca concentrations in cinders are characteristic only of this subtype. Sample 209 principally differs from all other samples of this group. In this sample, cinder that contacts a large black shungite-like grain contains (wt %) 1.8 P_2O_5 , 0.78 SO_3 , 0.16 NiO, 0.07 CoO, and 0.28 Cl_2O , so that this sample was recognized as an individual subtype. It should be emphasized that individual grains often reveal gradual transitions from ferrous-silicate to silicate-ferrous cinders (sample 424) and even to ferrous cinders (sample 405). The *silicate-ferrous cinders* were recognized as an individual type by FeO prevalence over SiO_2 . The SiO_2 concentrations in these cinders show a bimodal distribution (with modes at 35 and 4–11%), which is compensated by unsystematic variations in TiO_2 (up to 2%), Al_2O_3 (up to 8%), MnO (up to 3%), CaO (up to 6%), Na_2O (up to 1%), and K_2O (up to 2%). The cinders do not show elevated concentrations of P, S, Cr, Ni, and Co. The distinguished subtype of abnormal cinders (sample 203.1) is characterized by very high concentrations of TiO_2 (7.3%) and MnO (15%). It is noteworthy that this cinder was found within a Ti-Fe spherule and largely inherited its composition. The **ferrous** cinders are composed of native iron (97% Fe) with a minor admixture of silicate material. One grain (sample 610), which was recognized as an individual subtype, had high concentrations of Cr_2O_3 (0.9%) and NiO (up to 0.37%). During the course of further research, the cinders probably will be reclassified into two types: (1) ferrous (up to 20% SiO_2) and (2) ferrous-silicate (>30% SiO_2).

Inclusions in other newly formed grains. These inclusions are innumerable and were found occasionally in unusual aggregates: Fe-Ti spherules, Fe-tektite, and glassy carbon (?). The Fe-Ti spherules (samples 203 and 504), which are no larger than 0.5 mm, show clearly discernible indications of an explosion. Their central parts are often hollow and contain cinder frag-

ments and microlites of quartz, potassic feldspar, calcite, and chlorite. The peripheral zone of the Fe-Ti spherules contain numerous microspherules (Fig. 2, sample 504), which often contains microlites of the aforementioned minerals or, more rarely, consist of glassy masses (samples 203.2, 203.6, and 504.5) of a composition approaching that of the high-Si aluminous Vesicular glasses (group 21) with the maximum concentrations of SiO_2 (72.4%), Al_2O_3 (26.1%), and K_2O (5.9%).

Ferrous tektite-like aggregates were found only in one grain, in which filamentous and irregularly shaped tektite is interlaced with irregularly shaped Mn-volkhovite (Fig. 2, sample 615). This sample provides evidence that the volkhovite and Fe-tektite were formed simultaneously. The glass included in the Fe-tektite (sample 615-6) is compositionally identical with Mn-volkhovite.

Interesting glass inclusions (sample 124) were detected in a fragment of blue glassy carbon (?), whose peripheral part contained minute (1–10 μm) agglomerated fragments of various glasses and minerals that were welded with filaments of silicate glass. The filaments were 5–10- μm thick and up to 300- μm long and had a composition intermediate between those of Mg- and Ca-volkhovites, most closely approximating their varieties rich in volatile components. The main difference between the filamentous glasses and volkhovites is the high concentrations of SiO_2 (57.5%) and Al_2O_3 (16.1%) at relatively low CaO (21.5%). Some fragments of ferrous cinders are overgrown by felty fuzzy aggregates of glasses of a similar composition.

Minerals. In selecting samples of volkhovites and related spherules, glasses, and cinders for microprobe analysis, much attention was paid to minerals able to characterize some unusual conditions. Sample 2012 was determined to contain apatite, barite, biotite, glauconite, garnet, diopside, dolomite, ilmenite, calcite, quartz, magnetite, millerite, monazite, feldspar, hornblende, serpentine, thorite, chlorite, spinel, and zircon. Their tentative examination revealed the presence of varieties notably enriched in Mg, K, P, S, Cr, Ni, Co, Cl, Ba, Ce, La, and Th. Some of these mineral grains were possibly genetically related to volkhovites and associated glasses, cinders, and spherules.

DISCUSSION

Model justification. The statistical processing of a selected sampling from the combined database for samples 2012 and 2035 by the principal-component method of factor analysis (Fig. 3) allowed us to establish that major elements can be classified into the following three clearly individualized groups: (1) P, Ni, Co, Fe, and S; (2) Cr, Ti, Mn, Mg, and Ca; and (3) K, Si, Na, and Al. The first group of elements is characteristic of inclusions in volkhovites, ferrous cinders, and spherules; the second one is typical of volkhovites, sil-

icate-ferrous cinders, and spherules; and the third group is preferably contained in aluminosilicate minerals and, more rarely, silicic cinders and glasses. In the diagram for the factor values, these three groups of elements are plotted as three fields: *a*, *b*, and *c*. We believe that the boundaries between fields *K1* and *K2* have genetic implications. Indeed, all of the examined aluminosilicate minerals plot to the right of line *K2*, with mafic minerals plotting near *K2* and felsic minerals clustering away from this line. From its upper part downward, pyroxenes systematically give way first to amphiboles and then to garnet and biotite. Because of this, line 2 can be provisionally regarded as the boundary between the lithosphere and asthenosphere. Note that the data points of Mn-volkhovites lie below *K2*, the point of Ca-volkhovite (point 3) is situated exactly on line *K2*, and Mg-volkhovites (points 1 and 2) plot to the left of the line. It is, thus, reasonable to suggest that the magmatic chambers of Mn-volkhovites were hosted in the upper lithosphere, and those of Ca- and Mg-volkhovites were located at the lithosphere-asthenosphere boundary. The boundary between fields *a* and *b*, which was drawn along line *K2*, is less clearly defined, but it is also recorded in petrochemical data and marked by a significant change in the concentrations of ore elements: *a*—Co, Ni, and Fe; *b*—Cr, Ti, and Mn. In the terminology proposed by Larin (2005), line *K2* separates the lower part of the metallosphere and it has the asthenosphere as its upper part. According to these data, the following two petrogenetic sequences of elements can be proposed for the rocks in question: (1) metallospheric—P, Ni, Co, Fe, S, Cr, Ti, and Mn; and (2) lithospheric—Mg, Ca, K, Si, Na, and Al.

The available data allowed us to attach a genetic interpretation to our statistical model and, thus, consider once again the principal characteristics of volkhovites and related metallic spherules, glasses, and cinders.

Volkhovites. Although tektite-like glasses of a composition approaching those of mafic rocks have been described in the geological literature (Schulte et al., 2003; Glass et al., 2004), they were found very rarely. We are not aware of any finds of microtektites of an ultramafic composition, particularly in association with mafic microtektites (Mn-volkhovites), diverse metallic spherules, glasses, cinders, etc. Rare glasses of an ultramafic composition similar to that of volkhovite were found in three territories in Russia (Zharkov and Mal'kov, 2000). "Volcanic" glasses whose composition corresponded to low-Fe varieties of Ca-volkhovites were found at deep levels of the Aikhal, Mir, and Udachnaya diamond-bearing pipes in Yakutia and in Pliocene deposits in the Nem Highland of the Timan Range, and a glass bead of the Late Permian age and a composition close to volkhovite was found at the Severnaya Dvina River. No glasses closely resembling volkhovites have ever been found in areas of active volcanism.

Volkhovites display unique petrochemical features, which differ between their three distinguished types. Mg-volkhovites consist only of four major oxides: SiO_2 , CaO , MgO , and Al_2O_3 . Note that high concentrations of the latter two oxides are prohibited for igneous rocks. Conspicuous “carbonatite” features are shown by Ca-volkhovites, which contain about 35% CaO . Mn-volkhovites are no less individualized and are noted for anomalous MnO concentrations (approximately 12%) and the persistent presence of Cr_2O_3 (about 1%). These features of volkhovites led us to suggest that magmatic reservoirs of a corresponding composition could occur in the upper part of the lithosphere when volkhovites were produced (or are present there even now). Another noteworthy feature of volkhovites is the absence of differences between the P, Ni, and Co concentrations in the three types of glasses. This can most realistically be explained only by the supply of these elements of the metallospheric series into the magmatic reservoirs with vigorous gas flows, which is, in turn, possible if the concept of an originally hydride Earth (Larin, 2005) is considered plausible.

It should be stressed that volkhovites exhibit indications of such processes as liquid immiscibility (the occurrence of the outer silicate parts of the spherules and their segregated metallic phases) and the active release of gaseous components from the decrepitated spherules. The explosive processes resulted in the ejection of sprays of minute silicate melt droplets at the surface, with these droplets immediately solidifying when falling down. This is evident from the abundance of aerodynamic shapes, the typical “knead” and dumbbell-shaped morphologies of volkhovite grains and the interlacing of filamentous volkhovite glasses with metallic tektite-like aggregates.

Metallic spherules. Other very unusual aggregates are ferrous spherules, whose composition is completely identical to that of the ferrous cinders. P, Ni, or Co were not detected in these spherules, but the abnormal spherules are characterized by high concentrations of S and Cl and elevated concentrations of Cr and Co. The number of analyses of the ferrous spherules is still insufficient for settling this problem. Equally mysterious problems are the presence of abundant silicate phases in the Ti–Fe spherules and the mechanisms producing the spherules of cuprian gold.

Glasses and cinders. The clastic nature of the glasses, their Vesicular structures, and their saturation with gases testify that these glasses were produced earlier than volkhovites as products of differentiation in the asthenosphere. The already solid glasses and cinders were blasted by powerful gas flows and ejected at the surface. During their active movements, they often became saturated with all elements of the metallosphere series. A principally important feature of volkhovites and the cinders is their association with shungite-like aggregates. Having no information about the conditions under which these rocks were formed,

we can only hypothesize that they were brought to the surface from the deepest zones.

Minerals. Most of the examined minerals were formed in the lithosphere. However, when volkhovites were generated, Th phosphates could be produced, the geochemistry of the earlier minerals could be modified, and these minerals could be redeposited. All of these issues call for further investigation.

Genetic model. We proposed a cryptomagmatic model for the genesis of volkhovites as a new type of endogenic tektite-like glass. It is suggested that volkhovites were formed during three evolutionary stages of geological processes: (1) pre-Holocene, (2) cryptomagmatic, and (3) final.

Pre-Holocene stage. The Archean–Middle Proterozoic folding episode, the Late Proterozoic–Neogene platform stage, and the Quaternary glaciation, which ended 10000 years ago with the deposition of loams of the Valdaian glaciation, are recognized in the geological history of the local lithosphere. Loam blankets cover concealed deep faults, whose intersections could be favorable for the development of younger cryptomagmatic activity. During the pre-Holocene stage, the metallosphere (Larin, 2005) underwent strong differentiation, a process that resulted in the enrichment of the lower levels of the metallosphere in P, Ni, Co, Fe, and S, whereas its upper levels are enriched in Fe, S, Cr, Ti, and Mn in compliance with the aforementioned metallospheric succession of elements. The asthenosphere became enriched in various glasses and cinders, with their Fe-rich varieties localized at the deep levels of the asthenosphere and silicate constituents at its upper levels. The magmatic reservoirs hosted in the upper asthenosphere in the Quaternary likely contained melts of quite a different composition: (a) Fe-rich, with Au and Cu derivatives at the lower levels and Cr, Ti, and Mn melts at the higher levels; (b) basic Ca-rich; and (c) ultramafic K-rich (lamproitic ?).

Cryptomagmatic stage. The greatest catastrophe in the Earth’s evolutionary history (Izokh, 1997) at about 10000 years ago was followed by extensive cryptomagmatic activity. It is thought that a planetary zone of the generation of hydrogen flows responsible for the formation the Australo-Scandinavian tektite belt was localized in the upper part of the core. A few of the most powerful gas jets, which reached the surface later, entrained fragments of shungite-like aggregates and silicate–ferrous cinders and intruded the asthenosphere as cinder–stone–gas mixtures. These ascending plumes penetrated through asthenospheric magmatic reservoirs and captured melt droplets, fragments of silicate glasses and cinders, and intruded the lithosphere in the form of cinder–melt–gas “cryptomagmatic” mixtures. In the lithosphere, the plumes became additionally enriched in rock and mineral fragments from the Precambrian basement, as well as in swelled Cambrian clay and Ordovician limestone, and were ejected under high pressure within local zones in the form of cinder–

melt–mud–gas mixtures. Melt droplets practically instantaneously solidified in midair as tektite-like glasses, and the erupted tuffisite-like mixture was mixed with the fluvioglacial loams.

Final stage. The cryptomagmatic stage in the genetic history of volkhovites is believed to have been followed by a rapid temperature decrease and the transformation from strongly reducing to oxidizing conditions. This was associated with metasomatic activity and the emplacement of additional portions of clay material. The latter conclusion is confirmed by numerous finds of blue endogenic (?) clay among the dark brown and variegated loams. The subsequent erosion largely obliterated the results of the cryptomagmatic activity, and anthropogenic processes further complicated the identification of the natural glasses.

Some implementations and consequences. Below, we formulate some problems to be further explored in light of our results.

An issue of primary importance is the development of our concept of magmatic differentiation, the role of volatiles in deep geological processes, the genesis of hydrocarbons, etc. (Marakushev, 1999). Our data may lead to a principal revision of the tuffisite model for the genesis of the Krasnovishersk diamond deposits (Chaikovsky, 2001) and the concept concerning magmatic tuffisites (Petrovsky et al., 2004; Makhlaev and Golubeva, 2006). An important applied aspect of our research is the highlighted necessity of the geological surveying of the Kirishi structure as a target for the exploration of the Quaternary endogenic ore mineralization. In this context, it seems to be particularly important that visible gold particles were found there together with volkhovites. Attention should be focused on P, Cr, Ni, and Co ore occurrences, which might be found at a relatively shallow depth. Also, we cannot rule out that the volkhovite-bearing loams are prospecting guides for hidden diamond-bearing Paleozoic tuffisite types and that diamond mineralization of the Holocene age could be discovered in the area.

CONCLUSIONS

The principal results of our research can be summarized as follows.

(1) Volkhovites are a new type of tektite-like endogenic glasses of a basic and ultrabasic composition that occur as relatively small (1–3 mm) grains of a specific aerodynamic morphology and are well preserved. The volkhovites were provisionally dated at 10000 years, i.e., younger than the Valdai glaciation. They are classified into three types: magnesian, calcic, and manganoan with no transitional varieties in between. Petrochemical data accentuate the principal compositional differences between the discrete glass types, weak differences within the types, and practically unvarying compositions within individual grains. Inclusions in volkhovites are Fe-rich metallic phases, which occur as

spherules and rare mineral segregations enriched in P, Ni, Co, S, and Cr.

(2) The metallic spherules comprise Fe-rich, Fe- and Ti-rich, and Cu- and Au-rich varieties; the latter contain 49–76% Au, much Cu, and 4–13% Ag. The glasses and cinders accompanying volkhovites were classified into ferrous, silicate–ferrous, and ferrous–silicate cinders and Vesicular silicate glasses of an intermediate–basic composition.

(3) Statistical analysis of the petrochemical data allowed us to recognize two genetic series of elements in volkhovites, glasses, and cinders: a deep-seated series of P, Ni, Co, Fe, S, Cr, Ti, and Mn and a lithospheric series of Mg, Ca, K, Si, Na, and Al. Based on these data, we propose a cryptomagmatic model, which suggests that the Vesicular glasses and cinders were formed during the pre-Holocene stage in the asthenosphere, and volkhovites were generated at the asthenosphere–lithosphere boundary and then broke through to the surface in the form of a cinder–stone–melt–mud–gas mixture. Upon their ejection, the melt droplets practically instantaneously solidified in the form of tektite-like glasses when in midair, and then the erupted tuffisite-like mixture mingled with the fluvioglacial loams.

ACKNOWLEDGMENTS

We thank M.N. Tolkachev for conducting most of the analytical work; D.G. Skublov for his invaluable help in the computer processing of the data; and geologists M.N. Afanasov, A.P. Kazak, and M.S. Leikum for solving some of the problems encountered during the course of this research.

REFERENCES

1. I. I. Chaikovsky, *Petrology and Mineralogy of the Diamond-Bearing Intrusive Pyroclastites from the Vishera Urals* (Perm State Univ., Perm, 2001) [in Russian].
2. V. E. Barnes, "Tektite Research 1936–1990," *Meteoritics* **25**, 149–159 (1990).
3. J. A. Barral, B. M. Jahn, and J. Amosse, et al., "Geochemistry and Origin of Libyan Desert Glass," *Geochim. Cosmochim. Acta* **61**, 1953–1959 (1997).
4. M. D. Belonin, V. A. Golubeva, and G. T. Skublov, *Factor Analysis in Geology* (Nedra, Moscow, 1982) [in Russian].
5. V. I. Bouska, et al., *Natural Glasses* (Acad., Praha, 1993).
6. J. C. Davis, *Statistics and Data Analysis in Geology* (Wiley, New York, 1973; Nedra, Moscow, 1990).
7. A. Deutsch, M. Ostermann, and V. L. Masaitis, "Geochemistry and Neodymium–Strontium Isotope of Tektite-Like Objects from Siberia (Urengoites, South Ural Glass)," *Meteor. Planet. Sci.* **32**, 679–686 (1997).
8. V. I. Feldman, *Petrology of Impactites* (Moscow State Univ., Moscow, 1990).

9. P. V. Florensky and A. I. Dabizha, *The Zhamanshin Meteoritic Crater* (Nauka, Moscow, 1980) [in Russian].
10. B. P. Glass, H. Huber, and C. Koeberl, "Geochemistry of Cenozoic Microtektites and Clinopyroxene-Bearing Spherules," *Geochim. Cosmochim. Acta* **68**, 3971–4006 (2004).
11. K. Heide, G. Heide, and G. Kloess, "Glass Chemistry of Tektites," *Planet. Space Sci.* **49**, 839–844 (2001).
12. G. Heide, B. Müller, and G. Kloess, et al., "Structural Classification of Natural Non-Crystalline Silicates," *J. Non-Crystal. Solids* **323**, 68–71 (2003).
13. G. Heinen, *Tektites: Witnesses of Cosmic Catastrophes* (Luxembourg, 1998).
14. E. P. Izokh, "Australian-Asian Tektites and Global Catastrophe about 10 000 Years Ago Caused by Collision of the Earth with a Comet," *Geol. Geofiz.* **38** (3), 638–660 (1997).
15. *Impaktites* (Moscow State Univ., Moscow, 1981) [in Russian].
16. J. A. O'Keefe, *Tektites and Their Origin* (Elsevier, Amsterdam, 1976).
17. J. A. O'Keefe, "Reply to Taylor and Koeberl," *Meteoritics*, No. 29, 743–744 (1994).
18. C. Koeberl, "Geochemistry of Tektites and Impact Glasses," *Ann. Rev. Earth Planet. Sci.* **14**, 323–350 (1986).
19. C. Koeberl, "Tektite Origin by Hypervelocity Asteroidal or Cometary Impact: Target Rocks, Source Craters, and Mechanisms," in *Large Meteorite Impacts and Planetary Evolution*, Ed. by B. O. Dressler, R. A. F. Grieve, and V. L. Sharpton, (Geol. Soc. Am. Spec. Paper **293**, 1994), pp. 133–151.
20. A. A. Marakushev, *Origin of the Earth and the Nature of Its Endogenic Activity* (Nauka, Moscow, 1999) [in Russian].
21. A. A. Marakushev, O. S. Bogatyrev, A. D. Fenogenov, et al., "Impactogenesis and Volcanism," *Petrologiya* **1** (6), 571–595 (1993).
22. F. Marini, "Natural Microtektites Versus Industrial Glass Beads: An Appraisal of Contamination Problems," *J. Non-Crystal. Solids* **323**, 104–110 (2003).
23. Yu. B. Marin, G. T. Skublov, and B. G. Vanshtein, *Petrochemical Evolution of Phanerozoic Granitoids* (Nedra, Leningrad, 1983) [in Russian].
24. L. V. Makhlaev and I. I. Golubeva, "Magmatogenic Fluidized (Pseudoliquefied) Systems and Their Role in Rock Formation and Associated Minerageny," in *Problems of Geology and Mineralogy* (Geoprint, Syktyvkar, 2006), pp. 143–159 [in Russian].
25. A. Montanari and C. Koeberl, *Impact Stratigraphy: The Italian Record* (Springer, Berlin, 2000).
26. V. N. Larin, *Our Earth: Origin, Composition, Structure, and Evolution of the Initially Hydride Earth* (Agar, Moscow, 2005) [in Russian].
27. I. A. Nechaeva, *Multiple Meteorite Explosions as Geological Factors* (Nedra, Moscow, 1982) [in Russian].
28. E. G. Panova, A. P. Kazak, and K. E. Yakobson, "Mineralogy of Devonian Terrigenous Rocks of the Northwestern Russian Platform in Connection with Their Diamond Potential," *Zap. Vseross. Mineral. O-va* **133** (3), 12–24 (2004).
29. V. Petrovsky, L. Makhlaev, A. Pystin, et al., "Diamond-Bearing Visherites as a Possible Key to Solution of the Secret of the Nature of Brazilian Phyllites, Australian Lamproites, and Arkhangelsk Kimberlites," *Vest. Inst. Geol. Komi Nauchn. Tsentra*, No. 12, 15–30 (2004).
30. H. Povenmire, *Tektites. A Cosmic Paradox* (1997).
31. H. Scholze, *Glass* (Springer, Berlin, 1990).
32. P. Schulte, W. Stinnesbeck, D. Stüben, et al., "Fe-Rich and K-Rich Mafic Spherules from Slumped and Channelized Chicxulub Ejecta Deposits in the Northern La Sierrita Area, NE Mexico," *Int. J. Earth Sci.* **92**, 114–142 (2003).
33. G. T. Skublov and O. M. Tyugai, "Petrochemical Model of Formation of Tektite-Like Glasses in the Zhamanshin Crater and Association with the Moon Impactogenesis," *Zap. Vseross. Mineral. O-va* **133** (6), 95–117 (2004).
34. S. G. Skublov and O. M. Tyugai, "Geochemistry of Impact Glasses from the Zhamanshin Crater: Ion Microprobe Data," *Geokhimiya* **43** (7), 779–785 (2005₁) [*Geochem. Intern.* **43** (7), 708–714 (2005a)].
35. S. G. Skublov and O. M. Tyugai, "Distribution of Trace Elements in Impact Glasses from the Zhamanshin Crater: Comparison with Tektites," *Geokhimiya* **43** (11), 1228–1234 (2005b) [*Geochem. Intern.* **43** (11), 1128–1134 (2005b)].
36. S. G. Skublov, V. A. Lovyagin, G. T. Skublov, and O. M. Tyugai, "Geochemistry of Microtektites of the Zhamanshin Crater," *Vest. St. Petersburg Gos. Univ., Ser. 7.*, No. 4, 17–25 (2005).
37. W. Vogel, *Glaschemie* (Springer, Berlin, 1992).
38. V. A. Zharkov and B. A. Mal'kov, "Kimberlite Glass, Problems of Kimberlite Volcanism, and Diamond Potential of the Southern Regions of Komi Republic" *Vest. Inst. Geol. Komi Nauchn. Tsentra*, No. 8, 4–5 (2000).