Silicate—Metallic Spherules and the Problem of the Ignimbrite Eruption Mechanism: The Yakutinskaya Volcanic Depression

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Abstract—In the course of detailed mineralogical, geochemical, and petrological studies of volcanic rocks in the Yakutinskaya volcanic depression of the Eastern Sikhote—Alin volcanic belt (Primorye) silicate—metallic formations (small balls) were found to occur widely. This suggests a new approach to the evaluation of the mechanism that is responsible for the formation of specific large-volume "hot" explosions. The metallic nuclei (whose compositions vary from low-carbon cast iron to cohenite) are surrounded by symplectite, which consists of quartz, magnetite, and siliceous—potassic glass (without Na); thus, the entire formation can be considered as a siliceous—metallic spherule. Based on analyses of the gas phase, the spherules consist of hydrogen and methane. The calculation of oxidation reactions that involve these gases shows that the process entails a significant decrease of volume and heat release. This suggests that the mechanism of "hot" ignimbrite explosions consists of the collapse of the roof of the magma chamber into the explosion zone and the formation of a collapse caldera with the ejection of the melt and its subsequent dispersion on the surface. This is facilitated by significant overheating of magma and its saturation with hydrogen, which is accompanied by a sharp decrease in viscosity by several orders of magnitude, even for such highly siliceous melts.

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INTRODUCTION

Ignimbrite eruptions are among the grandiose and at the same time ominous natural phenomena that are no less dangerous to humanity than the collision of the Earth with space objects. The enormous masses (thousands of cubic kilometers) of ejected materials, high temperatures of both lavas and ashes, and their welding to the earth surface, all indicate the specific character of the ignimbrite eruption mechanism. The problem of these eruptions has been noted since the early 20th century, both because their products occupy huge areas in Italy, Japan, California, New Zealand, Kamchatka, Primorye and other regions and because the eruptions are highly destructive and have repeatedly resulted in environmental disasters. The term ignimbrite 'fiery rock dust cloud' from the Latin igni-(fire) and imbri- (rain) was introduced in the 1930s by P. Marshall [1935], whose classical work on New Zealand ignimbrites is still of importance, especially as regards the observation part of this work. Marshall defined the basic geological and petrologic features of ignimbrites: (1) highly uniform rock textures with signs of fluidity; (2) volcanic material are welded so intensively that even forms interbeds of volcanic glass; (3) the absence of visible volcanic edifices (cones), which attests to the fissure character of explosions. This author, while allowing the ejection of dispensed

We also believe that ignimbrites were formed from pyroclastic flows of the hot-sand avalanche type that were ejected as a very mobile gas—liquid emulsion that consists of fragments and drops of melt, incandescent ash particles, and other pyroclastic material. Expanding gases provide the high mobility of the flow. A gas liquid (molten) magmatic emulsion saturated with crystals of minerals, ash, and rare fragments of rocks flies like a burning avalanche with tremendous speed over tens and hundreds of kilometers without a break

hot material, hypothesized its lithification due, not to ordinary welding with the formation of secondary melt (fiamme), but through the adhesion of hot particles. Papers that consider the problems of ignimbrite generation present a wide range of rather controversial views, not only on their origin, but also on the mechanism of ignimbrite magma eruption. All the known opinions on this matter may be classified into three major hypothesis: the usual tuff hypothesis [Zavaritskii, 1947; Marshall, 1935, and others], the hypothesis of lava flow [Vlodavets, 1961; Levinson-Lessing, 1928; Beck and Robertson, 1955; Kennedy, 1955; Lacroix, 1930 and others] with the related theory of liquation splitting of melts [Marakushev, 1979; Steiner, 1960], and the hypothesis of an incandescent pyroclastic "downpour" [Rittmann, 1960].

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in the continuity of the ejected material and, having cooled, preserves a specific lava-like appearance.

Summing this up, we may conclude that the solution of the problem of ignimbrite generation is closely related to understanding the role and character of the fluid regime, as well as the specific features of eruption products, which is the goal of this paper.

Studies of magmatic rocks of the Bogopolsky complex (Early Paleogene) in the Yakutinskaya volcanic depression (VD) that were carried out using modern analytical techniques yielded original mineralogical and isotope-geochemical data on their composition and revealed a clear vertical zonation in the ignimbrite distribution and cyclicity of volcanic eruptions [Grebennikov, 2003; Grebennikov and Maksimov, 2006]. These studies showed that ignimbrite-generating melts are highly reduced. In addition to the domination of ferrous over ferric iron in ignimbrite minerals (the exclusively ilmenite composition of Fe–Ti oxides, low oxidation of volcanic glasses, and the extremely ferruginous composition of pyroxenes and olivines), this conclusion is also supported by silicate-metallic globules that contain native iron and cohenite, which were discovered by the authors of the works referred to above.

MATERIALS AND METHODS

Microanalysis of minerals and glasses was carried out using a JXA 8100 electron microprobe (Japan) with three wave spectrometers and an INCA energydispersive spectrometer (Oxford, England) in the Far East Geological Institute and at the University of Shimane, Japan. The accelerating voltage and electric current were 15-20 kV and $2 \cdot 10^{-8}$ A, respectively. The semiconductor detector resolution was 137 eV. Natural and synthesized materials that have been repeatedly approved in many laboratories were used as standards. Gold-sprayed coating of samples was used for quantitative analyses of carbon. In the analysis of the metallic part of the spherule it was found that under graphite coating the content of carbon increased by 5-6 wt %. The determination of the micro- and macroelements in the rocks was performed largely by the X-ray fluorescence method using a Rigaku RIX 2000 spectrometer (University of Shimane, Japan). Some of the silicate analyses were carried out at the Far East Geological Institute using the standard "wet" chemistry technique.

X-ray structural studies were carried out using an ARS-2 instrument with monochromatic FeK α radiation with an IRIS source and an RKD camera (d = 57.3) using photography.

Experimental charges of $100-200 \ \mu g$ of monomineral fractions and glass were taken for analyses of gas phases in the minerals. The charges were found using the thermal method ($800-1000^{\circ}C$) in a pure helium atmosphere with subsequent determination of H₂, N₂, CO, CH_4 , CO_2 , and H_2O using an LXM-8MD chromatograph.

Spherules were separated either by electromagnetic separation out of crushed rocks or by washing the heavy fraction from eluvium. The relationship of the spherules with the primary material is supported by their presence in thin sections and "intergrowths" with host ignimbrite glass.

BASIC DATA

A Brief Geological Description of the Yakutinskaya VD

Detailed geological, petrologic, and geochemical characteristics of the Yakutinskaya VD have been given previously in many papers [Grebennikov, 2003; Popov and Grebennikov, 2000, 2001; Grebennikov, Maksimov, 2006]; thus, our explanation here is short. The structure under discussion is located in the back part of the Eastern Sikhote Alin volcanic belt [Vulkanicheskie ..., 1984]. It extends in the northwestern direction for 40 km and is up to 20 km in width (see Fig. 1). At the present-day surface it is limited by linear and arcuate faults that steeply dip to its inner part. The faults are filled with rhyolite porphyry dykes and subvolcanic granite bodies. Morphologically, the structure is a depression with a basement at a depth of 2.5 km and granite bodies underneath. It is expressed as an intense minimum in the gravity field [Mikhailov, 1989]. The western and northwestern parts of the structure are considerably eroded to the level of the subsurficial magma chambers, which are composed of hypabissal granites. Stratified rocks are consequently known only in the southern part of the Yakutinskaya VD.

Two phases are recognized in the history of this volcanic structure. During the first (Maastrichtian) phase the moderately acidic pyroclastic deposits of the Siyanovsky Complex that compose its base were accumulated. These rocks are found in outcrops in the walls of the caldera and in erosion windows among strata of ignimbrites and rhyolite tuffs of the Bogopolsky complex, which formed in the second phase (Danian– Eocene).

The Bogopolsky Complex involves effusive (flows, sheets, and units), extrusive–vent (necks, volcanic vents, and extrusive domes), and hypabissal facies (the roots of volcanoes, which consist of dykes, stocks, and laccolites). As a whole, the complex has a high silicic composition of its igneous rocks, wide occurrence of volcanic glasses, and the domination of ignimbrites and tuffs, which are welded to various extents. We emphasize that the rocks of the Bogopolsky Complex are found only within this VTS and are unknown in the nearest vicinity.

The section of the Yakutinskaya VD consists of five members (counting downward, below in the text they are denoted as ign. 1-5). The total thickness of the deposits is 600-650 m (see Fig. 2). The lower part of each member contains lithic rhyolite tuffs that are



Fig. 1. Geological sketch-map of the Yakutinskaya VD (1) Terrigenous rocks of the basement; (2) Siyanovsky volcanic complex; (3–6) Bogopolsky volcanic complex: tuffs of various degrees of welding and ignimbrites with horizons of volcanic glasses (sheets) (3), granites and rhyolite-porphyries (hypabissal bodies) (4) granites and rhyolite porphyries (subvolcanic bodies); (5) rhyolites (brecciated extrusions) (6), spherulitic glasses (extrusions); (7) major faults. Insert shows the geographical location of the structure. Cross section A-B see in Fig. 7.

gradually replaced by rocks in a more compact welding zone and then in ignimbrites proper. The uppermost part of a member is again formed by crystal—lithic and lithoclastic units. According to Rb—Sr isochrone measurements, the age is 59.7–54.8 Ma [Grebennikov, 1998].

The hypabissal facies of the complex consist of fissure intrusives, dykes, and stocks that consist of rhyodacite-porphyries and hypabissal granites. The intrusions cut across rhyolite tuffs and some extrusive bodies. The Rb–Sr age of these rocks is 55.3 Ma. Two types of extrusive-vent domes are recognized. The first type is found in the form of elongated, plateshaped, or isometric rhyolite extrusions whose margins are of effusive appearance and on the lower hypsometric levels become hypabissal granite-porphyries. The second type includes some zoned extrusive domes (Nezhdanka and Berezovyi Klyuch Mts) that are composed of spherulitic rhyolites and perlites in the center; in the periphery they sometimes turn into short and thick lava flows. Their age is 52.9 Ma [Grebennikov, 1998].

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Fig. 2. A schematic crosssection of typical ignimbrite sequences of the effusive rocks in the Bogopolskaya suite. (1) Poorly welded rhyolite tuffs with occasional interlayers of tufogenic silt material; (2) ignimbrites with different degrees of welding and zones of massive black glass; (3) unconsolidated rhyolite tuffs.

The Petrography and Mineralogy of Rocks

Field studies have shown that the facies diversity of stratified fragmental volcanogenic rocks of the Yakutinskaya VD is due to different phases of explosive ignimbrite generation. The composite geological section involves five members of ignimbrites (ignimbrite 1-5 from bottom to top) of complex structure. Poorly sorted and relatively unconsolidated lithic and crystalloclastic tuffs (which are referred to as tuffs proper below) compose the top parts of the ignimbrite sheet. In lower parts they are found in a more compact zone of rocks of varying degrees of welding and then in ignimbrites proper. The lowest parts of the flow are composed of litho- and crysalloclastic tuffs. Pheno- and xenocrysts, as well as xenoliths, are irregularly distributed in the matrix. This distribution of facies varieties is typical of each of the five cycles, with the exception of the second and fourth ones (ign. 2 and 4), where ignimbrites proper involve interlayers and lenses of massive black perlites.

Welded tuffs have a massive structure and are composed of uniform clasts (about 0.5 mm) that consist of angular quartz grains (15–20 vol %), hypidiomorphic crystals of potassic feldspar (15 vol %), oligoclase (5 vol %), altered mafic minerals (0.5–1 vol %), and fragments of fine crystal tuffs. It is worth noting that as the rocks become more like typical ignimbrites they are found to be more monolithic. The welding of rocks is only observed under a microscope and is expressed in the appearance at the boundaries of contacting fragments of a welding strip and by the presence of hyaline, axiolite, and eutaxitic textures in the bonding mass. The basic difference of tuffs from ignimbrites proper is the absence of fiamme and the solid-phase deformations of glass fragments. Sometimes thin interlayers of unconsolidated ash tuffs are observed among ignimbrite sheets. These tuffs have a vitroclastic texture with rounded and fork-shaped clasts of volcanic glass (7–10 vol %, 0.5 mm) and quartz grains (5–7 vol %), as well as grains of sanidine (5 vol %) and oligoclase (2–3 vol %). The accessory minerals are allanite (0.6 mm), ilmenite (0.3 mm), and very rare balls of native iron (0.1 mm). The mafic minerals (0.5–1 vol %) are usually completely chloritized and evenly distributed among the ash matrix.

The ignimbrites consist of a compact matrix of strongly extended and intricately deformed ash particles of fluid texture. The matrix (originally an ash mass) contains phenocrysts of minerals and fiamme. The last are arranged conformably to the fluidity. The ignimbrites contain quartz, sanidine, plagioclase, ferrohypersthene (Ca₃Mg₂₇Fe₇₀), and ferrohedenbergite $(Ca_{44}Mg_{2}Fe_{38})$ in ign. 2 and 4 or ferroaugite $(Ca_{41}Mg_{21}Fe_{38})$ in ign. 1, 3, and 5, along with biotite, ferruginous hornblende, and favalite. The accessory minerals are dominated by allanite, ilmenite, zircon, and apatite. Magnetite is extremely rare. In each of the members the mineral composition varies to some extent. The fluid structure is emphasized by wavy bent strips in which fragments of volcanic glass are arranged parallel to these lines in the matrix. The characteristic feature of ign. 1 and 3 are numerous fragments of underlying sedimentary and volcanic rocks, which are rare in ign. 2 and 4; this is related to the domination of loose explosive products in the former (see Fig. 2). Finally, we emphasize one common feature of all ignimbrites, viz., cataclasis of impregnations and embayment contours of grains.

The fiamme are elongated flattened, stretched formations, lens-shaped with flame-like ends (split or lens-like wedging-out in shape), with a long axis of 0.5-6 cm and a short axis of 1-2 mm, rarely 3-9 mm. The fiamme are not normally crystallized and consist of volcanic glass of darker color compared to the glass in the matrix. Sometimes they are slightly devitrificated, so that when viewed at a high magnification their fluidity is highly emphasized; this is expressed in the alternation of absolutely black and slightly devitrificated glasses of a lighter color. The contents of crystal clasts in fiamme are somewhat lower than in the matrix. They consist of broken-down feldspars, quartz, and biotite, with the fiamme being selectively enriched in the latter. It is of interest that both the fragments of feldspars and biotite flakes are arranged conformably with the fiamme.

The granites and rhyodacite-porphyries compose hypabissal bodies and are leucocratic coarse porphyry rocks that consist largely of quartz, potassic feldspar ($Or_{57-58}An_{0.6-0.8}$), oligoclase ($An_{14-18}Or_{9-11}$), and biotite (fe* = 73–79). Orthopyroxene, zircon, allanite, and ilmenite occur in accessory amounts. Granite porphyries are of a typical hypidiomorphic granular texture. Gradual transitions from mega porphyry to micro por-

Compo- nent	ign. 1, rhyodacite	ign. 2, rhyodacite	ign. 3, rhyodacite	ign. 4, rhyodacite	ign. 5, rhyodacite	Extrus. (margin), perlite	Extrus. (center), spherulitic rhyolite	Dyke, porphyritic rhyodacite	Stock, granite
	AV-15/2	AV-23/1	AV-23/3	AV-23/7	AV-23/10	AV-24/1	AV-24/5	AV-25	AV-28/6
SiO ₂	69.64	72.49	72.47	71.56	72.55	72.55	77.68	70.24	78.08
TiO ₂	0.22	0.14	0.28	0.18	0.19	0.10	0.09	0.00	0.08
Al_2O_3	12.74	13.22	13.87	13.64	14.13	12.24	12.60	14.78	12.53
Fe ₂ O ₃	1.23	0.52	0.29	0.10	1.31	1.01	0.00	2.82	0.18
FeO	1.22	1.03	1.91	1.42	0.64	0.15	0.45	0.45	0.91
MnO	0.03	0.05	0.05	0.04	0.02	0.01	0.00	0.09	0.02
MgO	0.23	0.16	0.23	0.18	0.21	0.04	0.05	0.71	0.04
CaO	2.20	0.88	1.21	0.97	0.84	0.74	0.16	1.49	0.42
Na ₂ O	3.38	3.65	3.47	3.82	3.34	4.05	2.97	4.52	3.51
K ₂ O	3.40	4.21	4.37	3.97	4.53	2.18	4.85	3.96	4.93
P_2O_5	0.10	0.02	0.07	0.03	0.02	0.00	0.00	0.15	0.04
H_2O^-	1.09	0.28	0.30	0.40	0.30	1.83	0.10	0.24	0.00
L. O. I.	4.32	2.98	2.21	3.29	1.64	4.89	0.72	0.70	0.00
Total	99.80	99.63	100.73	99.60	99.72	99.79	99.67	100.15	100.74
Q	39.60	36.80	36.34	35.60	38.00	45.27	43.37	28.82	38.80
Or	24.93	28.20	29.80	27.09	30.16	14.95	30.18	27.03	30.31
Ab	35.47	35.00	33.87	37.32	31.84	39.78	26.45	44.15	30.89
K/(K+Na) at %	39.83	43.15	45.31	40.61	47.16	26.15	51.80	36.57	48.03

Table 1. The representative compositions of the volcanic rocks of the Yakutinskaya VD

phyry varieties are characteristic of rhyodacites. The former typically have porphyry texture with potassic feldspar ($Or_{65}An_{1.2}$), albitized plagioclase ($Or_{0-8}An_{0.1-26}$), quartz, biotite (fe* = 66–70), and completely chloritized pyroxene. The accessory minerals are amphibole, ilmenite, allanite, and zircon. As the rocks become aphyric rhyodacites, the concentration of biotite decreases until it vanishes altogether. Gradual transitions from porphyritic to aphyric textures are observed.

Extrusive facies (Nezhdanka mount) consist of three major rock types: perlitic volcanic glasses and rhyolite clastolavas at the periphery and spherulitic rhyolites in the center. The phenocrysts are composed of quartz, plagioclase ($An_{18-24}Or_{9-4}$), and sanidine ($Or_{63-68}An_{1.2}$). Allanite, ilmenite, and balls of native iron occur in accessory amounts.

The composition of the rocks of the Yakutinskaya VD (see Table 1) is close to the average rhyolite after Daly. The volcanic glasses (fiamme and matrix) are overall more siliceous than the bulk composition of the same rocks and are characterized by the ubiquitous domination of sodium over potassium (see Table 2). A deficit of the total in EPMA (2–4 wt %) reflects the perlitic composition of the glasses. The chief peculiar-

ity of all the rocks is their highly siliceous and highly aluminous corundum-normative composition, which is due to a relative deficit of strong cations (Ca, Na, and K), which form the normative feldspar molecule.

A comparative geochemical analysis of the effusive and intrusive rocks of the Yakutinskaya VD [Grebennikov and Maksimov, 2006] suggests the preliminary separation of these rocks into two groups. The first group includes hypabissal granites and "highly" siliceous ign. 2 and 4, the second contains dykes of porphyritic rhyodacites and "poorly" siliceous ign. 1, 3, and 5. The former have more sodium (Na/K) and are more ferruginous (Fe/Mg). The concentrations of Ti, Ca, and Mg are somewhat lower. Rocks of this group are enriched in Sc, Rb, Y, Nb, Sn, Cs, heavy REE, Ta, Pb, and U. They are characterized by low contents of Sr, Ba, and Eu and, accordingly, are somewhat enriched in radiogenic strontium (87Sr/86Sr is 0.7074– 0.7081) compared with ign. 1, 3, and 5 (87 Sr/ 86 Sr is 0.7066-0.7072). Paired ratios of indicative rare elements (K/Rb (116-197) and Ti/Zr (1.6-5.4)) are lower, but Rb/Sr (2.1-239) are higher than in the group of "low" siliceous rocks.

The chemistry of the rocks in the Nezhdanka zonal extrusion is peculiar (see Table 1). The spherulitic rhy-

Table 2. R	epresentati	ve composi	itions of vo	lcanic glass	of the Yakı	utinskaya V	D							
Compo-		Ignim	brite 1			Ignimb	orite 4		Nezhdan	ıka Mount	extrusion	Nezhdar	nka Mount	extrusion
nent	fiamme	fiamme	matrix	matrix	fiamme	fiamme	matrix	matrix	(marg	in) Perlite ((glass)	(center)	Spherulitic	: rhyolite
SiO_2	77.70	77.35	77.59	77.68	76.57	76.17	76.74	77.49	75.67	74.57	73.30	77.53	77.83	77.84
TiO_2	0.06	0.04	0.04	0.05	0.06	0.03	0.07	0.03	0.00	0.04	0.04	0.02	0.07	0.06
Al_2O_3	12.17	12.46	12.19	12.32	12.38	12.36	12.18	12.41	12.32	12.01	12.13	12.44	12.22	12.58
FeO^*	1.06	0.87	0.88	1.00	1.07	1.03	0.99	1.15	0.69	0.33	0.40	0.96	1.00	1.00
MnO	0.00	0.00	0.02	0.03	0.04	0.02	0.06	0.04	0.01	0.00	0.00	0.05	0.12	0.04
MgO	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.01	0.00	0.04	0.02	0.02
CaO	0.54	0.35	0.44	0.44	0.39	0.81	0.46	0.47	0.86	0.91	0.89	0.25	0.23	0.21
Na_2O	4.01	4.29	3.68	3.53	3.84	3.70	3.63	3.72	2.82	3.00	3.21	3.31	3.28	3.38
K_2O	2.98	3.12	2.84	2.89	2.20	2.31	2.38	2.26	1.08	1.09	1.12	2.34	2.44	2.47
P_2O_5	0.01	0.00	0.02	0.02	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.04
Total	98.54	98.47	97.69	97.95	96.61	96.46	96.52	97.57	93.44	91.96	91.10	96.95	97.22	97.63
SiO_2	78.85	78.55	79.42	79.31	79.25	78.97	79.51	79.42	80.97	81.09	80.46	79.96	80.06	79.72
TiO_2	0.06	0.04	0.04	0.05	0.06	0.03	0.07	0.03	0.00	0.04	0.04	0.02	0.07	0.06
Al_2O_3	12.35	12.65	12.48	12.58	12.81	12.82	12.62	12.72	13.19	13.06	13.32	12.84	12.57	12.89
FeO^*	1.07	0.89	0.90	1.02	1.11	1.06	1.03	1.18	0.74	0.36	0.44	0.99	1.02	1.02
MnO	0.00	0.00	0.02	0.03	0.04	0.02	0.06	0.04	0.01	0.00	0.00	0.05	0.12	0.04
MgO	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.01	0.00	0.04	0.02	0.02
CaO	0.55	0.36	0.45	0.44	0.41	0.84	0.48	0.48	0.92	0.99	0.98	0.25	0.23	0.22
Na_2O	4.07	4.36	3.77	3.61	3.98	3.84	3.76	3.82	3.02	3.26	3.53	3.41	3.37	3.46
K_2O	3.03	3.16	2.91	2.95	2.28	2.39	2.47	2.32	1.16	1.19	1.23	2.41	2.51	2.53
P_2O_5	0.01	0.00	0.02	0.02	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.04
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
δ	44.39	41.70	47.77	48.67	49.29	49.18	49.98	50.21	63.51	61.46	58.72	53.50	53.32	52.46
Or	19.02	19.62	18.28	18.64	14.52	15.41	15.69	14.86	7.72	7.83	8.08	15.37	15.97	16.10
Ab	36.59	38.68	33.95	32.69	36.20	35.41	34.33	34.93	28.77	30.71	33.20	31.14	30.71	31.44
Note: Elect	ron probe n	nicroanalyzeı	r (EPMA). <i>i</i>	Analysts A.A	. Kabanov ar	nd N.I. Ekim	iova (FEGI)). FeO* den	otes total irc	u				

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olites in the central part with supposed liquating formation have a higher potassic content, K/(K + Na) of 51.8 at %. The volcanic glasses in the marginal part contain more sodium, K/(K + Na), viz., 26.2 at %, and are less siliceous. The concentrations of calcium and iron are somewhat higher [Grebennikov, 2003].

The presence of spherical objects with metallic iron in the glasses is a characteristic feature of the volcanic rocks discussed here. An analysis of the literature convincingly shows that such globules are of terrestrial origin and occur widely. They are known in the eruptive breccias of the Priazov massif [Tsymbal et al., 1985], in Altai granitoids [Bazhenov et al., 1991], in the Alpine-type ultramafic rocks of the Koryak Upland [Rudashevskii et al., 1987], in the volcanic rocks of Southern Sikhote-Alin [Filimonova et al., 1989], in the exhalation products of the Tolbachik Volcano [Glavatskikh and Generalov, 1996], in the pyroclastic sediments of the Barombi Mbo caldera lake (Western Cameroon) [Cornen et al., 1992], and in the volcanic rocks of the Kuril-Kamchatka island arc [Sandimirova et al., 2003]. Finally, similar globules are known in such problematic formations as tektites [Tektites, 1963]. V.M. Khosseini and V.L. Rusinov [1999] demonstrated that spherical segregations are confined to cylinder-shaped channels that are vertically oriented in vents of acidic intrusions.

Similar objects were found by the authors in eluvium and crushed samples of all the rock varieties of the Yakutinskaya VD. They are the most abundant in extrusive spherulitic rhyolites on Nezhdanka Mount.

RESULTS

The Mineralogy of Silicate–Metallic Spherules

The micro objects under consideration have spherical shapes with glossy surfaces (see Fig. 3). Their size varies within 0.1-0.2 mm. Sometimes fragments of host glass are welded onto them, but more often a spherule is provided with a "leg" that connects it with the host melt. Coarse porosity is observed in chips. Their internal structure is shown in Figs. 4a–4d. In all cases the nucleus of a spherule contains one or several small rounded pores with an adjacent metallic "drop." The drop in turn is surrounded by a symplectite of quartz, glass, and magnetite. The last fact is proven by X-ray structural analysis (see Table 3). Around the pores and at the edges of spherules the symplectite texture becomes fine-grained, possibly due to degassing and cooling of the melt. At the contact with the symplectite the "drops" are surrounded with a glass fringe of constant thickness (Figs. 4a, 4c).

HCl etching and X-ray microanalysis revealed inhomogeneity in the carbon distribution in the metallic parts of spherules, with the Fe/C ratio varying from 3 to 9 at % (see Table 4). Some "drops" are homogeneous in composition (nos. 4a1–4; 4b1–4) and contain admixtures of Ni. The inhomogeneous Note: a_0 average is 8.36 Å. The lines of the calculation for a_0 are underlined: S_p denotes magnetite and Q, quartz.

ones involve a considerable admixture of Mn (nos. 4c17-18) with concentrations reaching 6 wt % in rounded holes in the ferruginous matrix (no. 4a). When this is the case, admixtures of P and S occur in them, which is probably related to the salt films of gas pores. We also note that low-carbon varieties were found to contain a persistent presence of silicon, while Al, Na, and K are absent, which attests to the presence of iron silicide. Only a qualitative evaluation of the composition of the fringe that is in contact with the symplectite (nos. 4c10–11) is possible because of its thinness, viz., in addition to Fe and C (from the "drop"), K, Al, and Si are present, which may indicate potassic glass. In the symplectite we analyzed the magnetite (see Table 5, no. 4a7) and silicate components. The magnetite turned out to be highly manganous and free of other elements (Ti, Cr, V, Al, and Mg), which is not typical of high-temperature magmatic magnetites [Shcheka et al., 1980] and suggests its origin by the disintegration of a liquation silicon-iron melt. The composition of the silicate part was determined by areal

Table 3.	An X-ray powder photograph of spherule compo-
sition	

No.	d/n	Ι	Phase
1	3.300	10	Q
2	2.920	3	Sp
3	2.500	9	Sp, Q
4	2.224	1	Q
5	<u>2.090</u>	7	Sp
6	1.811	4	Q
7	1.705	1	Sp
8	1.664	1	Q
9	1.595	5	Q
10	1.468	7	Sp, Q
11	1.368	6	Q
12	1.314	1	Sp
13	1.269	1	Sp, Q
14	1.224	1	Q
15	1.193	1	Q
16	1.177	1	Q
17	1.150	1	Q
18	1.091	1	Sp, Q
19	<u>1.045</u>	2	Sp, Q
20	1.012	3	Q
21	<u>0.986</u>	1	Sp, Q



Fig. 3. Morphology and internal structure of magnetic spherules. EVO 50-XVP (Germany). Secondary electrons.

 $(5 \times 6 \,\mu\text{m})$ scanning and point-by-point analyses (see Tables 4 and 5). According to the first method, the silicate part of the symplectite consists of quartz and feldspar. After recalculation with the exclusion of magnetite (according to its composition in no. 4a7, and on the assumption of 1% FeO and 0.06% MnO in the silicate part) it was found (see Table 6) that the bulk composition of the symplectite includes about 80% magnetite, while the silicate part consists of quartz (60%) and potassic feldspar (40%) with no albite at all. The edge around the spherule is of the same composition (nos. 4c10, 4c11). Spot analyses of the silicate part revealed the presence of Na up to compositions of glasses close to ignimbrites (see Table 4, no. 4c15-16). These localities are confined to the symplectite edges or to breaks in its continuity and possibly reflect the metallization of the ignimbrite melt around gas pores. The magnetite content is lower here, as low as 66-67%.

Therefore, the studied "balls" in terms of mineralogy, morphology, and composition are typical double silicate—metallic spherules whose generation is related to metallization of the silicate melt affected by reduced gases [Marakushev, 1979; Oleinikov et al., 1985].

DISCUSSION

The above materials demonstrate that the problem of ignimbrite volcanism has two important aspects: (1) what are the variations of ignimbrite melt compositions and what are their causes? and (2) what are the peculiarities of ignimbrite eruptions?

Numerous points of view exist on the first problem [Vlodavets, 1961; Zavaritskii, 1947; Levinson-Lessing, 1928: Marakushev, 1979: Beck and Robertson, 1955; Kennedy, 1955; Lacroix, 1930; Marshall, 1935; Tektites, 1963; Rittmann, 1960; Steiner, 1960, and others]. They appeal, e.g., to the phenomenon of the splitting (liquation) of a primary melt into two (or more) immiscible liquids under the influence of different fluids and fluid-gravitation segregation of melts. Finally, there are numerous ideas on the significant role of assimilation of host rocks and welding (up to melting) of hot-ash material. The actual existence of liquation processes during petrogenesis has been reliably proven not only by observations but also in many experiments [Marakushev et al., 2003; Shcheka et al., 1999; Roedder, 1951, and others]. However, while the appearance of immiscible liquids in such systems as silicate-sulphide, silicate-carbonate, silicate-metal is beyond question, in natural silicate melts the explanation of so-called globular rocks based on this mechanism involves difficulties in many cases. None the less, we show below in this paper that ignimbrite volcanism does involve liquation, although its role is limited.

Processes of differentiation (thermogravitational diffusion or emanation crystallization) leave their mark on the formation of the material inhomogeneity of the melt, not only in zones of its generation in abyssal conditions but also in intermediate chambers. We show this using the example of the Yakutinskaya volcanic depression, but by no means pretend that this option is universally applicable.

In terms of chemistry we classified the magmatic formations of the Yakutinskaya structure into two groups, "high" and "low" silicic. This is clearly demonstrated in Fig. 5, where the first group includes the compositions of ign. 2 and 4, granites, and zonal extrusions. We note that spherulitic rhyolites of the central parts of extrusions are lumped together with granites, but the marginal glassy parts are similar in composition to ignimbrites (2 and 4). At the top of the diagram with the sum (FeO, CaO, MgO, and TiO₂) of more than 3 wt %, the data points of ign. 1, 3, and 5 and dykes of rhyodacite-porphyries occur. The latter, being "glassy" analogs of granites, have a trend common with these, thus indicating melt differentiation during crystallization in intrusive conditions.

As a whole, the major characteristics of chemistry of the structure's rocks are reduced to variations of three main oxides: SiO₂, K₂O, and Na₂O. The diagram (Fig. 6) shows the concentrations of these oxides as normative molecules of quartz (Q), albite (Ab), and potassic feldspar (Or). The data of experimental studies for H₂O-saturated granite system at P = 0.3-4 kbars are also shown. It follows from this diagram that the bulk compositions (phenocrysts, xenocrysts + glass) of rocks that are generated during all the cycles of ignimbrite eruptions, as well as granites, are located along a strip that is somewhat stretched out along the Ab–Or axis, i.e., they characterize K–Na differentiation with enrichment of residual liquid by the Ab component. It is of interest that on the experimental curve of a water-saturated granite melt this area occupies the interval of 1-2 kbars, which probably indicates certain baric conditions of magmas. A similar distribution of silicic acid and alkalis (based on probe analyses) is observed for glasses that are found in the matrix and fiamme (see Table 2). Fiamme (independently of ignimbrite type) have more sodium contents (see Fig. 6). At the same time, compared with the bulk compositions, fiamme are enriched in the Ab and Q components, thus indicating the general $Or \rightarrow Ab \rightarrow Q$ evolution of the primary melt. At the same time, glasses from "high" siliceous ignimbrites are more sodic and silicic, while from "low" siliceous they are more potassic. This in turn attests to the fact that the fiamme are not fusions or liquates but represent a residual melt that has differentiated along the $Or \rightarrow Ab \rightarrow Q$ direction. The same pattern is characteristic for the periphery of the Nezhdanka Mount extrusion. These zones of glass compositions are extended along the Ab–Q axis, reflecting an extreme saturation in SiO_2 .

Within the spherules two areas of the silicate part (of the melt), viz., Q–Or and Q–Or–Ab, are recognized. According to some experimental results [Roedder, 1951], they probably characterize two immiscible liquids, viz., ferruginous potassic and siliceous sodic– potassic.

All this demonstrates that the magma composition of the Yakutinskava VD generally evolved in the direction $Or \rightarrow Ab \rightarrow O$, i.e., with the accumulation of silica and sodium and decreasing potassium. The data presented here attest to the fact that cyclic changes in the compositions of ignimbrite melts depended to a larger extent on the processes of the fluidal-silicate cluster differentiation of the primary homogeneous melt. Its partial crystallization in the upper parts of a chamber in the direction $Or \rightarrow Ab \rightarrow Q$ results in the appearance of a residual melt that evolves in the $Ab \rightarrow O$ direction, which is reflected in the matrix glass. This process was repeated many times in cycles under the conditions of the Yakutinskaya structure during 6 million years [Grebennikov and Maksimov, 2006] from the first cycle to final extrusions with successive progressive accumulation of silica (see Fig. 6). Alternation of cycles, as will be shown below, might be caused by the replacement of a water regime by a methane-hydrogen regime.

The dimensions (for the Yakutinskaya VD, about 300 km³) and high temperature of ash material (890°C as estimated by P. Marshall) are characteristic features of ignimbrite volcanism, which attests to the unusual mechanism of such eruptions. The first feature to be noted in unweathered ignimbrites is their highly reduced state. Thus, precision analysis of glasses shows that the degree of oxidation of iron (Fe⁺³ Σ Fe) is rather low (15-30 at %) although it was possibly even lower because the cooling of rocks took place in surface conditions in contact with the atmosphere. This value is comparable with values in tholeiitic basalts, whose major fluid components are H_2 and CH_4 , and much lower than in "oxidized" fluid systems of alkaline basaltoids with their carbonic acid-haloid composition of volatiles [Shcheka, 2004]. This is supported by the anomalous ferruginous content of Fe-Mg silicates, domination of ilmenite and rare presence of magnetite, and, finally, the ubiquitous occurrence of silicate-metallic spherules that contain native iron (cohenite) in nuclei.

The metallic parts of spherules that surround gas pores have compositions that vary from low-carbon iron cast (Fe₉C-Fe₅C) to cohenite (Fe₃C). This suggests the hypothesis that the reducer ("metallizer") of the silicate melt was an H₂-CH₄ mixture (the percentage of CO₂ at oxygen fugacity of Fe–FeO is negligible). As mentioned above, the magnetite–glass– quartz symplectite around the metallic phase is possi-



Fig. 4. Silicate metallic spherules with points for analysis. JXA-8100 (Japan). Secondary electrons.







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No. of point of analysis	С	Si	Mn	Fe	Ni	Total	Me: C at.
4b1	$\frac{7.47}{27.10}$			<u>92.16</u> 71.91	$\frac{1.34}{0.99}$	$\frac{100.97}{100.00}$	2.69
4b2	$\frac{6.87}{25.58}$			$\frac{91.79}{73.50}$	$\frac{1.21}{0.92}$	$\frac{99.87}{100.00}$	2.91
4b3	$\frac{6.46}{24.46}$			$\frac{91.52}{74.56}$	$\frac{1.27}{0.98}$	$\frac{99.25}{100.00}$	3.09
4b4	$\frac{7.31}{27.13}$			$\frac{90.02}{71.85}$	$\frac{1.35}{1.02}$	$\frac{98.68}{100.00}$	2.69
4c1	$\frac{4.58}{18.16}$			$\frac{95.37}{81.37}$	$\frac{0.57}{0.47}$	$\frac{100.52}{100.00}$	4.51
4c2	$\frac{4.12}{16.58}$		$\frac{0.55}{0.49}$	$\frac{95.75}{82.93}$		$\frac{100.42}{100.00}$	5.03
4c3	$\frac{4.10}{16.69}$			$\frac{94.62}{82.82}$	$\frac{0.59}{0.49}$	$\frac{99.31}{100.00}$	4.99
4c4	$\frac{4.15}{16.78}$		$\frac{0.48}{0.43}$	$\frac{95.13}{82.79}$		$\frac{99.76}{100.00}$	4.96
4c5	$\frac{3.17}{12.90}$	$\frac{0.33}{0.57}$	$\frac{0.83}{0.74}$	$\frac{97.94}{85.79}$		$\frac{101.93}{100.00}$	6.71
4c6	$\frac{2.38}{10.17}$	$\frac{0.30}{0.55}$	$\frac{0.91}{0.85}$	$\frac{96.47}{88.43}$		$\frac{99.77}{100.00}$	8.78
4c7	$\frac{3.84}{15.41}$	$\frac{0.30}{0.51}$	$\frac{0.87}{0.76}$	$\frac{96.57}{83.32}$		$\frac{101.28}{100.00}$	5.46
4c4	$\frac{3.57}{14.52}$	$\frac{0.24}{0.42}$	$\frac{0.59}{0.52}$	$\frac{96.76}{84.54}$		$\frac{100.93}{100.00}$	5.86
4c5	$\frac{5.80}{22.51}$	$\frac{0.11}{0.18}$	$\frac{0.05}{0.04}$	$\frac{92.23}{76.99}$		$\frac{98.08}{100.00}$	3.42
4c6	$\frac{6.92}{25.65}$	$\frac{0.11}{0.18}$	$\frac{0.07}{0.06}$	$\frac{92.35}{73.65}$		$\frac{99.34}{100.00}$	2.87
4c7	$\frac{6.64}{25.00}$	$\frac{0.31}{0.49}$	$\frac{0.83}{0.68}$	$\frac{90.51}{73.26}$		$\frac{97.98}{100.00}$	2.96
4c17	$\frac{4.56}{18.48}$	$\frac{2.18}{3.05}$	$\frac{4.12}{3.65}$	$\frac{85.74}{74.82}$		$\frac{94.78*}{100.00}$	4.25
4c18	$\frac{5.00}{20.42}$	$\frac{2.92}{3.88}$	$\frac{5.93}{5.29}$	$\frac{80.21}{70.41}$		$\frac{91.90*}{100.00}$	3.71

Table 4. The chemical composition of the metallic part of the spherules

Note: Numerator is in wt % and the denominator is in at %. * - +P(0.36%); ** -+P(0.40%) + S(0.25%).

bly an intermediate product of "metallization" (by the reaction $MeO + H_2 = Me + H_2O$) of the host silicate melt in contact with a gas 'bubble." It should be noted that the melt composition in symplectite radically differs from the composition of the host melt (see Fig. 6),

which is a peculiar feature of spherulites in extrusions with the supposed liquation mechanism of formation.

Based on the major parameters of their composition and fluid component regimes, all silicate melts are subdivided into two essentially different types: the

No. of analysis point	SiO ₂	Al ₂ O ₃	FeO	MnO	Na ₂ O	K ₂ O	Total	K/(K+Na) at.
4a7	2.18		88.66	1.80			92.64	
4a8*	15.00	1.42	77.40	0.83		0.53	95.17	1.00
4b7*	16.62	1.93	75.78	1.01		0.78	96.12	1.00
4c12*	16.75	2.36	77.52	0.85		0.93	98.42	1.00
4c10	24.46	2.55	64.32	1.36		2.05	94.74	1.00
4c11	11.00	1.21	79.43	0.98		0.78	93.40	1.00
4a10	27.62	2.27	66.45	1.33	0.85	1.16	99.67	0.47
4b14	26.83	2.95	66.73	1.38	1.01	1.17	100.07	0.43
4b15	27.58	2.97	63.71	1.28	0.77	1.19	97.49	0.51
4c15	80.53	10.77	0.91		2.69	5.73	100.64	0.58
4c16	81.96	10.28	0.94		2.39	5.57	101.13	0.61
AB-24/5**	77.68	12.60	0.45		2.97	4.85	99.67	0.52
AB-24/6**	77.40	12.82	0.31		1.38	6.54	99.62	0.76

Table 5. The chemical composition of the silicate part of spherules with admixture of magnetite (wt %)

Notes: * is by scanning $(5 \times 6 \mu m)$; the others are point-by-point analyses, ** spherulitic rhyolites of the Yakutinskaya VD.

No. of analysis spot	SiO ₂	Al ₂ O ₃	FeO	MnO	Na ₂ O	K ₂ O	Total	$\frac{Mt}{(Or + Ab + Q)}$ wt %
4a8	87.55	8.29	1.00	0.06	0.00	3.10	100.00	82
4b7	85.05	9.89	1.00	0.06	0.00	4.00	100.00	80
4c12	82.69	11.66	1.00	0.06	0.00	4.59	100.00	79
4c10	83.27	8.69	1.00	0.06	0.00	6.99	100.00	69
4c11	83.78	9.22	1.00	0.06	0.00	5.94	100.00	86
4a10	85.68	7.03	1.00	0.06	2.64	3.59	100.00	67
4b14	83.08	9.12	1.00	0.06	3.12	3.62	100.00	67
4b15	83.93	9.04	1.00	0.06	2.34	3.63	100.00	66

Table 6. Calculated chemical composition of the silicate part of the spherules minus magnetite (wt %)

Note: Mt stands for magnetite, Or for orthoclase, Ab for albite, and Q for quartz.

feldspar (quartz-hypersthene-normative) type and the feldspathoid (i.e., undersaturated in SiO₂, alkaline) types. The first are characterized by "reduced" methane-hydrogen volatiles, the second type contains "oxidized" haloid-phosphorous-carbon acid volatiles [Shcheka, 2004]. The presence of low mobility CO_2 , P_2O_5 , Cl_2 , and F_2 in the melt is reliably determined by their presence in gas-liquid, saline, and melt inclusions in minerals; however, hydrogen due to its extreme mobility, escapes from melts or oxidizes to water as the thermodynamic parameters become lower [Slobodskoi, 1981]. Its presence in melts is expressed in lower oxidation of iron in minerals and glasses of feldspar rocks along with frequent occurrence of native iron in them. Instrumental studies revealed [Slobodskoi, 1981; Cruikshank et al., 1973, and others] that the gas flares that are observed during present-day eruptions often result from hydrogen burning, while the content of hydrocarbon is low. On the basis of studies of gases that were sampled directly from magmatic melts of Ploskii Tolbachik Volcano (Kamchatka) I.A. Menyailov et al. [1980] showed that their composition is dominated by hydrogen (63–93 vol %). When the temperature decreases and the hydrogen comes in contact with air, it oxidizes to water, which forms fumaroles. The concentrations of other gases are insignificant: CO₂, 2–10%; O₂, 0.36–5%; and CH₄ + CO < 1–2%. High H₂/H₂O ratios in near-surface conditions of some volcanic systems are also supported by the dissipation of large volumes of hydrogen from "Golubye ozera" (Blue Lakes) thermal



Fig. 5. Variation of the silicity and basicity of Yakutinskaya VD (1-5) ign. 1-5; (6-7) glassy (6) and spherulitic (7) rhyolites of Nezhdanka Mt. extrusion; (8-9) rhyoliteporphyry dykes (8) and granite stocks (9).



Fig. 6. Chemical composition of rocks of the Yakutinskaya VD with experimental data for water-saturated granite systems, from 0.3 to 4 kbars [Tuttle and Bowen, 1958]. (1) ign. 1, fiamme and matrix (EPMA); (2) ign. 4, fiamme and matrix (EPMA); (3) ign. 1 and 3 (bulk); (4) ign. 2 and 4 (bulk); (5) rhyolite porphyry, dyke (bulk); (6) granites (bulk); (7) monolithic glasses, extrusion (bulk); (8) monolithic glasses, extrusion (EPMA); (9) glass from spherule (EPMA); (10) calculated compositions of silicate part of spherule. EPMA denotes Electron probe microanalisis, bulk stands for bulk analysis.

sources within the Baranskii hydrothermal-magmatic system [Znamenskii and Nikitina, 1985].

Finally we note that, in our opinion, investigators of ignimbrite generation unjustifiably pay little attention to their comparison with tektites. None the less, in many features they are rather similar [Tektites, 1963]. While having a high content of silica (72–79% SiO₂), tektites are also undersaturated in alkalis. Water content is lower than 0.01 % and the hydrogen content in the gas phase is 35–41 vol %, with no ferric iron. As a rule, they contain micro spherules of metallic iron. The glasses typically have a fine ($\leq 1 \mu m$) porosity, with the instrumental determination of pressure in these

pores being below 10^{-3} at. The last fact, along with their more mafic composition (enrichment in Ti, Cr, Ni, Mg, Fe, and Ca) allowed E.P. Izokh [Izokh and Le Dykh An, 1983] to propose the hypothesis that tektites are supplied to the vacuum of space by volcanic explosions on one of the satellites of the giant planets in the Solar System. As is now known, such volcanoes really exist. By this we wish to emphasize the fact that the oxidation—reduction conditions for the generation of ignimbrites, which are definitely terrestrial, and space tektites are similar in many aspects.

For estimation of possible composition of volatile components in the Yakutinskaya VD melts, chromatography analysis of thermic extracts from minerals of ignimbrites of all the five eruption cycles was carried out (see Table 7). The results probably do not reflect the primary (juvenile) gas composition, but they permit making some qualitative evaluations. Thermodynamic calculations show that the obtained gas mixtures are disequilibrium for real P-T parameters. The reasons for this have been repeatedly discussed in the literature. The chief one is that a thermic extraction includes the gross composition of gases (primary, retained, admixture-mineral, secondary components). None the less, these results reveal that admixtures of the air (nitrogen) component are near zero. In spite of the hydrogen loss during degassing, the C/H ratios are extremely low, i.e., the admixture of CH_4 in the primary gas did not exceed a few percent. The results also show that in the I, II, and IV cycles the hydrogen portion is significant (see Table 7) but in III and V and in final extrusions hydrogen is oxidized to water. The explanation may be found in the structure of the Yakutinskaya VD section (Fig. 2) where the composition of "hydrogen" cycles is dominated by ignimbrites, while among "oxidized" ones unconsolidated tuffs are found in considerable amounts. This is possibly related to the oxidation of the gas component of the tuffs, both under the influence of oxygen in the air during cooling on the surface and due to the influence of the water that formed during the explosion of the detonating mixture. Therefore, the above data suggest that the basic gas component of ignimbrites is hydrogen.

Based on this, the volume effects of possible oxidation-reduction gas reactions were calculated. The preliminary step was to use the "Selector" program [Karpov, 1981] to find the molecular volumes of real gases for the conditions P = 1 kbars and $T = 700^{\circ}C$, i.e., for the conditions of the supposed intermediate chamber (see Table 8). The following reactions are possible:

> (I) $2H_2 + O_2 = 2H_2O \Delta Q + 137 \text{ kcal/mol};$ $\Delta V = 168.25 \text{ cm}^3/\text{mol} (-56.9\%)$

(II) $CH_4 + 2O_2 = CO_2 + 2H_2O \Delta Q + 192 \text{ kcal/mol};$ $\Delta V = 84.2 \text{ cm}^3/\text{mol} (-27.3\%)$

Component	Ign. 1, rhyodacite	Ign. 2, rhyolite	Ign. 3, rhyodacite	Ign. 4, rhyolite	Ign. 5, rhyodacite	Extrusion, perlite	Extrusion, spherulitic rhyolite	Extrusion, spherulitic rhyolite
	Kfs	Kfs	Kfs + Q	Kfs + Q	Kfs + Q	Kfs	Pl	Pl
H ₂	9.24	16.47	1.03	5.80	0.00	0.97	1.10	1.21
N ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
CO	5.55	10.34	1.08	3.05	0.36	0.47	` 0.40	0.63
CH ₄	0.31	0.47	0.03	0.12	0.29	0.42	0.63	0.23
CO ₂	2.89	4.91	0.42	1.73	0.65	1.04	0.96	0.61
H ₂ O	82.01	67.81	97.43	89.30	98.70	97.09	96.92	97.29
V, cm ³ /kg	2087.10	1011.40	7411.20	1629.80	3032.30	2612.80	3025.50	2062.60
CO ₂ /CO	0.52	0.47	0.40	0.56	11.80	2.21	2.40	0.98
H_2O/H_2	8.87	4.11	94.59	17.57	-	100.09	88.10	80.40
C/H	0.05	0.09	0.01	0.03	0.01	0.01	0.01	0.07
$log f O_2^{CO}$	-16.68	-19.08	-16.93	-18.92	-15.59	-20.55	-20.50	-21.28
$log f O_2^{HO}$	-14.45	-17.17	-12.39	-16.02	—	-16.87	-16.99	-17.06
logfO ₂	-14.87	-17.51	-13.05	-16.42	-12.71	-17.88	-18.11	-17.78
T°C	900	800	900	800	900	700	700	700

Table 7. The composition of the gas phase from minerals from the Yakutinskaya VD and some parameters of the fluid regime during their crystallization

Notes: Kfs denotes potassic feldspar; Pl, plagioclase; and Q, quartz.

As seen from the equations, the reactions involve significant loss of volume. It was shown earlier that the concentration of carbon component is insignificant and the active component of the process is actually the explosion reaction of detonating mixture (I). At low P and T it is stimulated by shock agents (sparks, flashes, pressure jumps), but at temperatures above 600°C the mixture $2H_2 + O_2$ ignites spontaneously [Nekrasov, 1962]; i.e., the reaction is real in the conditions of the intermediate chamber of the Yakutinskaya VD. Notable shrinkage in the apical part of the chamber at the instant of the explosion should result in momentary magma injection to the surface along conduits with the simultaneous formation of a subsidence caldera. The high (+ 137 kcal) exothermal effect of reaction (I) and saturation of melt with hydrogen lead to overheating up to 1300°C according to measurements at the hydrogen flare of the Ploskii Tolbachik Volcano (O.N. Volynets, personal communication), where spherules [Glavatskikh and Generalov, 1996] and dilution of several orders of magnitude [Persikov et al., 1986] were also found. This facilitates the ejection and spattering of the liquid melt. Clusters (adhesion and coalescence) of its particles form as fiamme.

A hypothetical model of ignimbrite generation in the Yakutinskaya VD may be as follows (see Fig. 7). The intrusion of deep-seated high-temperature melts into upper crust layers results in partial melting of host rocks and formation of an intermediate chamber of siliceous magma. This chamber might reach a significant size due to the constant supply of heat and fluids from the deeper chamber. A homogeneous melt (its composition may be identified with the composition of ign. 1) occurs in a closed system at the level of higher oxygen fugacity in contact with cooler rocks. Since the gradients of temperature and volatiles are the highest in the area of interaction between magma and host rocks, a zone saturated with volatile components forms exactly at the top of magmatic column. The decrease in temperature from the bottom to the top due to conductive or hydrothermal cooling convection is compensated by an increased content of hydrogen and other volatile components. The temperature of the melt's liquidus line decreases, resulting in

Table 8. Molecular volumes of gases ($T = 700^{\circ}C$, P = 1 kbars)

Gas	$V, \mathrm{cm}^3/\mathrm{mole}$
H ₂	97.70
O_2	100.45
H ₂ O	63.80
CO_2	95.77
CO	109.80
CH_4	106.70

Note: The values were calculated using the Selector software [Karpov, 1981] for real gases.



Fig. 7. Proposed dynamic model of ignimbrite volcanism of the Yakutinskaya VD. (1) Sedimentary rocks of the basement; (2) Late Cretaceous volcanogenic rocks of the Siyanovsky Complex; (3) "basic" ignimbrite-generating melts and their derivates; (4) "acidic" ignimbrite-generating melts and their derivates; (5) granites and rhyolite-porphyries (hypabissal bodies); (6) perlites and spherulitic glasses (extrusions).

a diminishing amount of phenocrysts from the bottom to the top of the magmatic column. Such a zonality in the distribution of the temperature and composition of volatile components is inseparably linked with enrichment of the melt with various components. The latter causes the direction of crystallization to be $Or \rightarrow Ab \rightarrow Q$. This is accompanied by enrichment of the residual melt, at first by Na, then by the SiO₂ com-

ponent. The slow inflow of hydrogen and methane from the deeper chamber leads to its oxidation, both by reduction of FeO and Fe₂O₃ according to the reactions: FeO + H₂ \rightarrow Fe + H₂O; Fe₂O₃ + 3H₂ \rightarrow 2Fe + $3H_2O$; and $2FeO + CH_4 \rightarrow 2Fe + CO_2 + 2H_2O$ and because of a higher general fO_2 (compared to deeper segments of the chamber on this level). In a homogeneous melt, in "hydrogen pores" iron-silicate "drops" (intermediate phases of iron reduction) segregate, which in turn disintegrate into metallic and silicate components. The modeling of such a process, which was experimentally supported by E. Roedder [Roedder, 1951], was conducted with a Fe-FeO buffer using metallic iron, around which immiscible potassic, siliceous, and high-ferrous melts formed. In the latter, iron crystallized as an "oxidized" phase (magnetite) which in our case was probably caused by interaction of spherules with the more oxidized host melt. The liquation character of the silicate part of micro objects is supported by the constantly contrasting highly potassic composition in all the studied samples. This also agrees with the data of V.B. Naumov et al. [1993] who studied melt inclusions in quartz phenocrysts of ignimbrites in the Kurama mountains (Tien Shan). In these, liquation segregation into a highly siliceous potassic melt and iron (similar to those described in this paper) globules was clearly observed.

The highly reduced character of the fluids probably favored the appearance of such a specific extremely ferruginous parageneses of minerals and native iron. Alternation of, so to speak, "low" siliceous and "high" siliceous rhyolites, with specific petrochemical and mineralogical characteristics, serves as a complement to the zonality of the magma chamber, which periodically arises at the top of the column. The concentration in the fluidized melt of alkalis and coherent components with large ion radii and the depletion of bivalent alkaline-earth cations (Ca, Ba, Sr, and Mg) also explains the appearance of overcooled silicate fluids (volcanic glasses and hyaloignimbrites).

In our opinion, the possible mechanism of the formation of the Yakutinskaya VD may be presented as follows. The strike-slip regime within Eastern Sikhote Alin in the Paleogene [Geodinamika ..., 2006] brought about the ascent of deeper gas flows of a highly reduced (hydrogen) composition, decompression melting of crust material, and the initiation of a chamber with a highly fluidized siliceous composition. At the initial stages of caldera development the volcanic activity only involved some insignificant eruptions of "loose" pyroclastics (Plinian type of eruptions after R. Smith [1979]). The growth of the intermediate magma chamber in the near-surface conditions resulted in the formation of open detachment fractures in host rocks in a considerable area. Asymmetric subsidence of rock blocks took place along these fractures (the most voluminous was in the southwestern part of the structure) and air penetrated into the top of

the intermediate chamber, where the pressure was several orders lower than in the atmosphere. When there is a constant supply of hydrogen from a deeper chamber into an intermediate one, the silicate melt must be diluted (a decrease in viscosity by several orders of magnitude occurred) and saturated with hydrogen. After a certain pressure is reached and the temperature rises above 700°C, the volume ratio between hydrogen and oxygen might reach 2: 1, i.e., acquire the composition of a "detonating gas"; this resulted in the explosion of this mixture in the entire volume of the intermediate chamber. This process occurs as a chain reaction and is exothermal, being accompanied by an enormous decrease of the gas mixture volume. This resulted in further subsidence of the roof of the magma chamber (in the southwestern direction) with the formation of a collapse caldera. Due to the practical incompressibility of liquids, the overheated liquid melt was ejected upward along weakened zones, in accordance with hydrodynamic principles. For narrow magma conduits the speed of melt movement might be rather great. Heat release and the generation of enormous volumes of water fluid, with accompanying oxidation of hydrogen, increased the wettability of particles and fragments, resulting in subsequent welding to produce monolith masses. Since water is a product of the reaction described above, water will dominate the composition of the gases under analysis, which is supported by studies of the gas phase in ignimbrites [Grebennikov, 2003].

The cyclicity of ignimbrite eruptions in the Yakutinskaya VD (ign. 1–ign. 5) reflects the change of volume and duration of each cycle with the appearance, depending on the phase that was in progress, of "high" or "low" siliceous portions of ignimbrite-generating melts in the zonal magma chamber. We wish to note that all ejected products occur exclusively within the depression.

These characteristics prove the reality of the suggested mechanism of ignimbrite eruptions of the Yakutinskaya VD. We note that although this mechanism does not embrace all of the diversity of the phenomena of ignimbrite formation, the principal difference between vacuum "hot" ignimbrite explosions from the ejection of "cold" material from the chamber roof due to the growth of volatile phase pressure is indisputable. Finally, the basic aspects of the suggested model are completely supported by experimental data [Yamamoto et al., 2008], which indicates the intense fragmentation and ejection of melt that is saturated with gas and compressed up to 2.6 MPa when decompressed.

CONCLUSIONS

(1) Detailed studies of silicate—metallic spherules from ignimbrites of Primorye, along with other factors, demonstrate the probability of the participation of hydrogen and methane in fluid component of ignimbrite melts. The periodicity of the oxidation– reduction reactions controls the cyclicity of ignimbrite explosions.

(2) The cyclic changes of the mineral-chemical composition of ignimbrite magma in the course of volcanism are quite satisfactorily explained by fluid-silicate segregation of an acidic melt in the intermediate chamber with the participation of reduced fluids. The distribution of SiO₂, K₂O, and Na₂O in glasses of fiamme and the host matrix similar to those for "high" siliceous ignimbrites in the apical and "low" siliceous ones in the deeper parts of the magma chamber attest to the fact that fiamme could not be a product of melt liquation or welding of ash material, but are derivatives of the residual melt after differentiation of the primary melt in the direction Or \rightarrow Ab \rightarrow Q.

3. It is supposed that the fundamental difference between ignimbrite eruptions and other volcanic explosions is the significant shrinkage of the space above the chamber at the moment of the explosion of corresponding gas mixtures and the collapse of the chamber roof. This should be accompanied by the formation of numerous magma conduits and the ejection of the melt from the chamber along narrow channels with the simultaneous formation of a collapse caldera.

4. The substantial exothermal effects of oxidation reduction reactions and saturation with hydrogen lead to the overheating and dilution of highly siliceous magma, thus facilitating its ejection to the surface and pulverization in the form of an emulsion.

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