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# Silica-Metal Spherules in Ignimbrites of Southern Primorye, Russia

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**ABSTRACT: A comprehensive mineralogical-geochemical and petrological study of ignimbrites from the Yakut-Gora volcanic depression (Primorye, Far Eastern Russia) revealed a wide distribution of silica-metal spherules ("globules") that are typical liquid immiscibility resultant. The metallic portion of a spherule (composition varies from low-carbon iron to cohenite) borders gas pores and is rimmed by symplectite that consists of quartz, magnetite, and silica-potassic glass. This allows us to consider that the whole formation formed through reduction of the enclosing silicate melt. Abundant evidence of high reduction states of ignimbrite melts and the presence of iron carbides suggest an $H_2$-$CH_4$ composition of the fluidal phase in ignimbrite magmas.**
**KEY WORDS: spherule, native iron, ignimbrite, tektite, Primorye, Russia.**

## INTRODUCTION

Spherules, chondrules, globules, pellets, fly ash—this is a short enumeration of rounded formations found sporadically in very different rock types all over the globe (Gieré et. al., 2003; McCall, 2001; Detre, 2000; Sokol et al., 2000; Lefevre et al., 1986; Fredriksson and Martin, 1963 et alias). However, not counting the uncertainty of their genesis—extraterrestrial, anthropogenic, or terrestrial—in all cases the physicochemical conditions of their development are beyond question. Their shape, morphological features, mineral and chemical compositions, and the presence of gas inclusions in glasses testify to their formation under conditions of very low oxygen fugacity and rapid crystallization. In this connection, the identification of these features in ignimbritic rocks in Primorye (Far Eastern Russia) described below shed an interesting new perspective.

It is likely that there are few so well-known and yet puzzling phenomena of nature as ignimbrite eruptions. The attention paid to ignimbrites since the beginning of the past century is due not only to their widespread distribution in different regions of the world, but because of the unique nature of their development within the process of catastrophic eruptions. However, to date, there is no unified opinion about the problems regarding their origin and the proper mode of ignimbrite magma eruptions.

As delineated below, these silica-metal spherules resulting from ignimbrite melt crystallization in the Yakut-Gora volcanic depression (VD), are the morphological analogs of meteoritic chondrules, and will be shown to be the missing link in solving the problem of fluid behavior of ignimbrite volcanism.

## GEOLOGICAL DESCRIPTION OF THE YAKUT-GORA VD AND SAMPLING

In previous works (Grebennikov and Maksimov, 2006; Grebennikov, 1998), the authors described in

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detail the geology, petrology, and geochemistry of the Yakut-Gora VD, so here I offer only a brief description. The depression, like others similar to it, is situated towards the continental side of the East Sikhote-Alin volcano-plutonic belt (Shcheglov, 1984) and terminates its development (Fig. 1). In morphology, the VD is a subsidence caldera elongated northwest for 40 km and ranging up to 20 km across. At the modern level of the section it is restricted by rectilinear and arcuate faults, often filled with rhyolite and granite-porphyry bodies. The history of the volcanic structure includes two stages. During the first (Maastrichtian) stage, pyroclastic deposits of moderately felsic composition accumulated, forming the basement distinguished as the Siyanovsky volcanic complex. During the second (Paleocene–Early Eocene) stage, the ignimbrite units of rhyolites of the Bogopolsky complex were formed.

In the Yakut-Gora VD, five stratified units (Ignimbrites 1–5) are distinguished (upwards), and each of them shows a zoned structure (Fig. 2). In the lower part of the composite geological section, the rocks are represented by poorly sintered lithoclastic rhyolitic tuffs grading into a more compact zone of the sintered and welded tuffs and then into the ignimbrites. Among the ignimbrites, a zone of massive black obsidian is sometimes (Ignimbrites 2 and 4) observed. The uppermost part of the flows is composed again of the poorly sintered pyroclastic deposits. The units exhibit a total thickness of 600 to 650 m. The Rb-Sr isochronous age is 59.7–54.8 Ma (Grebennikov, 1998).

Intrusive facies in the complex consist of porphyritic rhyolite dikes and granite stocks. The intrusions break the ignimbrites and some extrusive bodies of the Bogopolsky complex. According to Rb-Sr dating, the age of the intrusive formations is 55.3 Ma.

The extrusive-vent facies composing the domes can be divided into two types. The first type includes elongated, platy, or isometric pyroclastic extrusives of rhyolites that at the lower hypsometric level grade into the rhyolite-porphyries of subvolcanic appearance. The second type is represented by a set of extrusive domes (Nezhdanka Mount, Berezovyi Spring) composed of spherululoidal rhyolites and volcanic glasses grading sometimes into short and thick lava flows. Their intrusions (52.9 Ma) culminate in the Yakut-Gora VD formation.

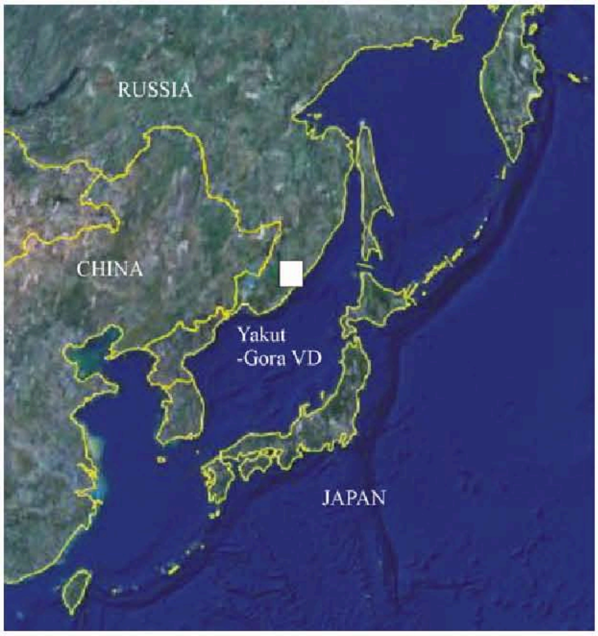


**Figure 1. Location of Yakut-Gora VD.**

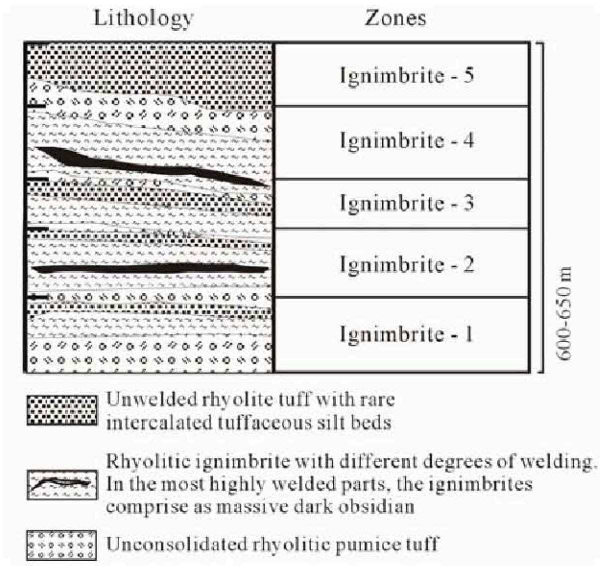


**Figure 2. A schematic cross-section of typical ignimbrite sequences of the effusive rocks in the Yakut-Gora VD.**

The ignimbrite rocks contain phenocrysts of quartz, sanidine ($Or_{70}$), oligoclase ($An_{29}$), ferrohypersthene ($Ca_3Mg_{27}Fe_{70}$), and ferrohedenbergite ($Ca_{44}Mg_2Fe_{54}$) or Fe-rich augite ($Ca_{41}Mg_{21}Fe_{38}$), biotite ($Annite_{70-77}$), ferro-hornblende, olivine ($Fa_{89}$–$Fa_{99}$), ilmenite, and traces of zircon, apatite, and allanite. Not all of these occur in every unit.

The spherules are sporadically found in thin sections and magnetic concentrates of all types of the rocks but they are prevalent in rhyolitic obsidian and spheruloidal rhyolites of lava-filled extrusives.

## ANALYTICAL METHODS

Minerals and glass were analyzed using the electron probe JXA 8100 (Japan) with three wave spectrometers and energy-dispersion spectrometer INCA (Oxford, England), which make possible the analyzing of element varieties from B to U at the Far East Geological Institute (Russia) and at the Shimane University (Japan). Accelerating voltage and current on the samples were 15–20 kV and $2\times10^{-8}$ A, respectively. Resolution of EDS was 137 eV. Natural and synthesized minerals, repeatedly proven as such in many laboratories, were used as standards. For the quantitative analysis of carbon, samples and standards were coated with gold. Analysis of the metallic portion of a spherule showed that when the samples were coated with graphite, carbon concentration increases by 5 wt.%–6 wt.%. X-ray-diffraction studies were carried out using an ARS-2 apparatus (Russia) with monochromatic FeKα radiation, with an X-ray emitter and Debye camera (*d*–57.3 mm).

In view of the low content, the silicate-metallic spherules were either separated by washing out the heavy fraction of rock eluvium on a wooden tray in field conditions, or by magnetic separation from crushed rock. The roll and jaw crushers were eliminated from the separating process and the hand crushing in Fe-free agate mortars completely excluded the possibility of material contamination with alien impurities, especially with Fe compounds. The sampling was made in a remote uninhabited area among the single-type volcanic rocks, excluding both the possibility of anthropogenic pollution and contamination by the minerals of other complexes. That the spherules belong to a primary material was confirmed by the fact that they were found directly in thin sections and in growths with volcanic glass.

## RESULTS

The spherules have a spherical form and glossy surface (Fig. 3 to Fig. 8) that, at high magnification (up to 8 000×), displays an irregular, “corroded” relief probably resulting from the symplectite aggregate structure (Fig. 3). The spherule sizes range from 0.1 to

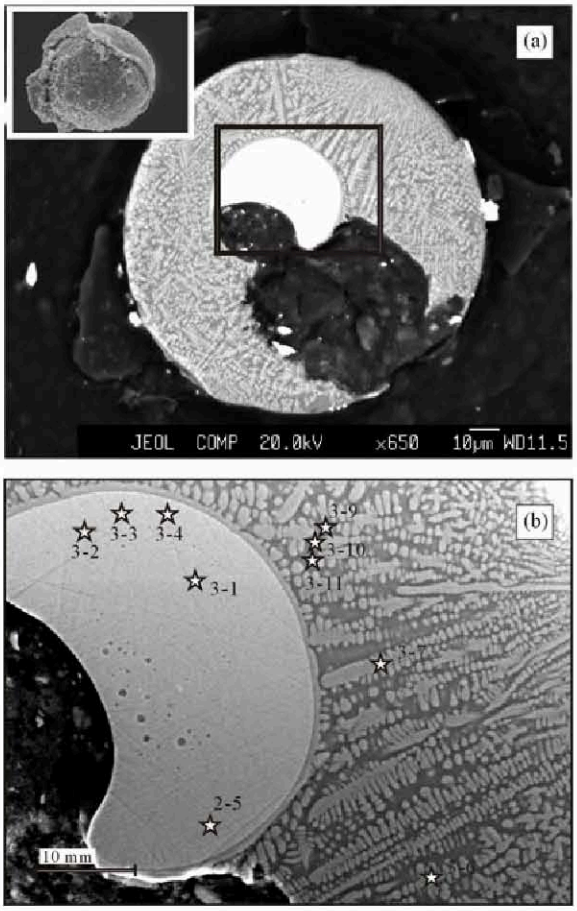


**Figure 3. Spherule coated by enclosing glass from ignimbrite of Mt. Yakut-Gora. Secondary electrons (hereinafter). (a) General view and morphology (inset); (b) magnified fragment with points of analyses.**

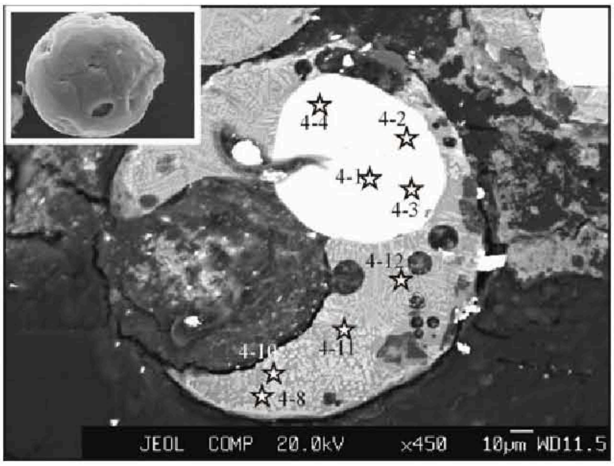


**Figure 4. Spherule from fluidal lavas of the Mt. Nezhdanka extrusive. General view with points of analyses and morphology (inset).**

**Table 1 XRD analysis of the spherule**

| No. | d/n | I | Phase |
|---|---|---|---|
| 1 | 3.300 | 10 | Q |
| 2 | 2.920 | 3 | Sp |
| 3 | 2.500 | 9 | Sp, Q |
| 4 | 2.224 | 1 | Q |
| 5 | 2.090 | 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 | 1.045 | 2 | Sp, Q |
| 20 | 1.012 | 3 | Q |
| 21 | 0.986 | 1 | Sp, Q |

Note: $a_o$cp – 8.36 Å. $a_o$: Sp. magnetite, Q. quartz.

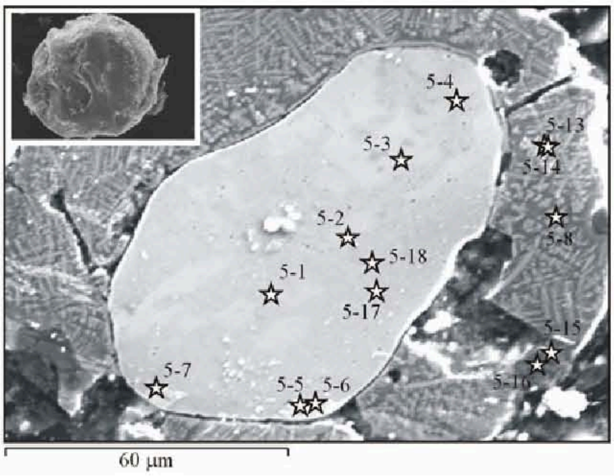


**Figure 5. Spherules with non-uniform core (light) and inclusions of glass in symplectite from fluidal lavas of the Mt. Nezhdanka extrusive. General view with points of analyses and morphology (inset).**

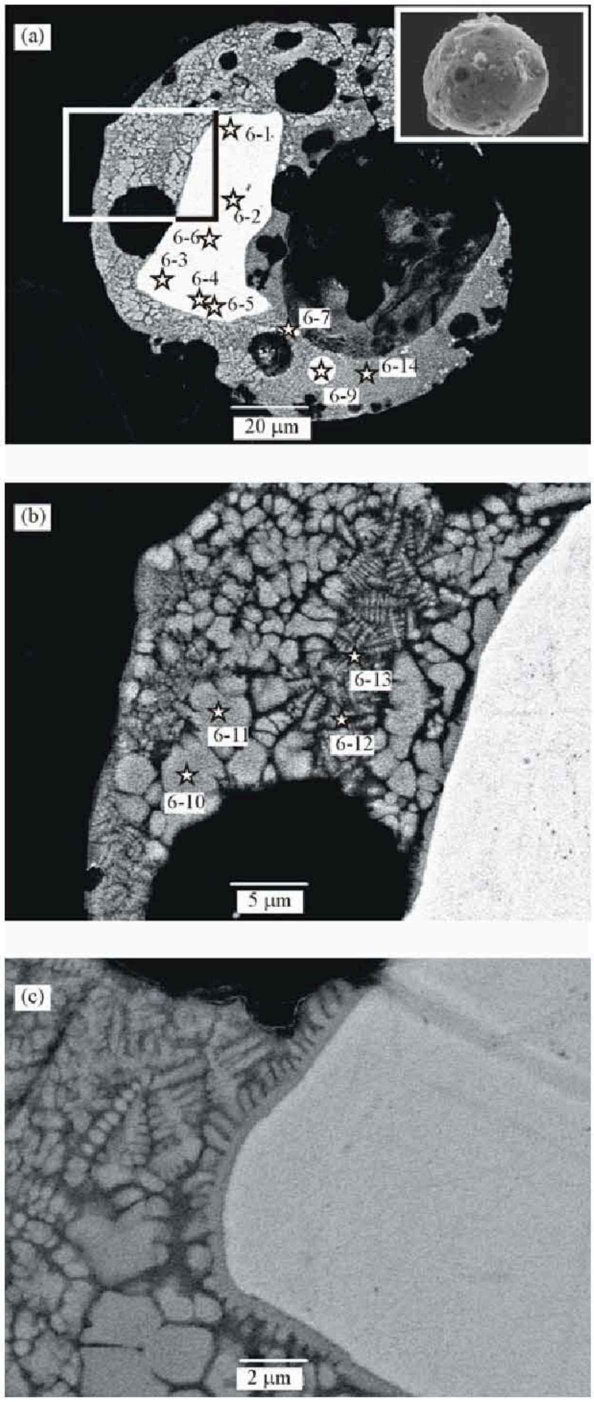


**Figure 6. Coarse-pored spherule with a core of irregular form from the Sedaya Mt. dacite dike. (a) General view and morphology (inset); (b) magnified fragment of interporous space with non-uniform structure of symplectite. Spotted and platy separations of carbon are seen in the core; (c) magnified fragment of the core with magnetite rim and glass fringe.**

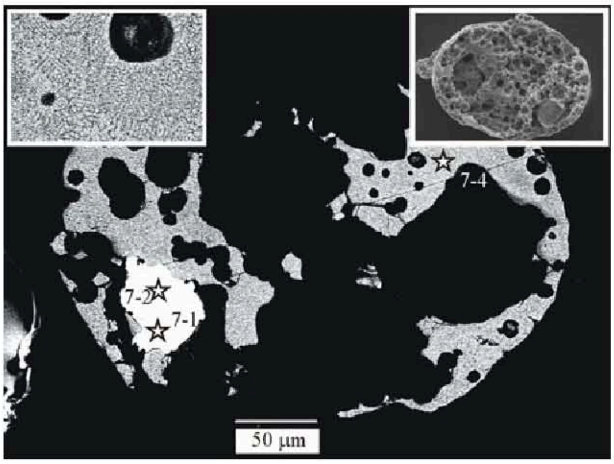


Figure 7. Coarse-pored spherules from fluidal lavas of the Mt. Nezhdanka extrusive. General view with points of analyses. Insets: in the right upper corner—morphology of spalling; in the left upper corner—magnified fragment of fine-grained symplectite.

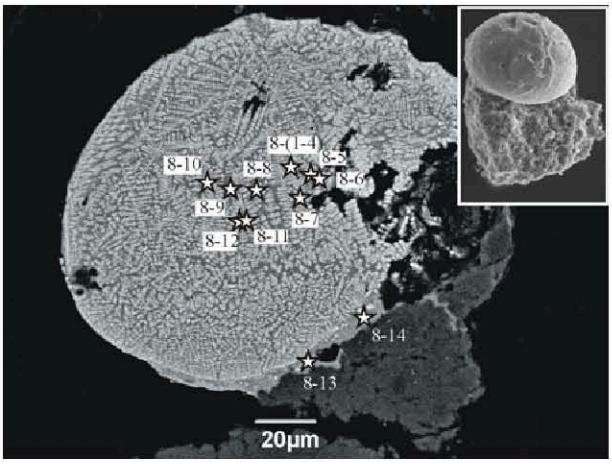


Figure 8. Free of metallic core spherule with a fragment of enclosing glass from spheruloidal rhyolitic lava of the Mt. Nezhdanka extrusive. General view with points of analyses and morphology (inset).

**Table 2 Chemical compositions of the spherule metallic part**

| No. | C | Si | Mn | Fe | Ni | Σ | Me/C atom % |
|---|---|---|---|---|---|---|---|
| 3-1 | 7.47±0.82 | - | - | 92.16 | 1.34 | 100.97 | 2.69 |
| | 27.10 | | | 71.91 | 0.99 | 100.00 | |
| 3-2 | 6.87±0.76 | - | - | 91.79 | 1.21 | 99.87 | 2.91 |
| | 25.58 | | | 73.50 | 0.92 | 100.00 | |
| 3-3 | 6.46±0.72 | - | - | 91.52 | 1.27 | 99.25 | 3.09 |
| | 24.46 | | | 74.56 | 0.98 | 100.00 | |
| 3-4 | 7.31±0.81 | - | - | 90.02 | 1.35 | 98.68 | 2.69 |
| | 27.13 | | | 71.85 | 1.02 | 100.00 | |
| 3-5 | 6.69±0.77 | - | - | 90.88 | 1.40 | 98.96 | 2.97 |
| | 25.21 | | | 73.71 | 1.08 | 100.00 | |
| 4-1 | 4.58±0.51 | - | - | 95.37 | 0.57 | 100.52 | 4.51 |
| | 18.16 | | | 81.37 | 0.47 | 100.00 | |
| 4-2 | 4.12±0.46 | - | 0.55 | 95.75 | - | 100.42 | 5.03 |
| | 16.58 | | 0.49 | 82.93 | | 100.00 | |
| 4-3 | 4.10±0.45 | - | - | 94.62 | 0.59 | 99.31 | 4.99 |
| | 16.69 | | | 82.82 | 0.49 | 100.00 | |
| 4-4 | 4.15±0.46 | - | 0.48 | 95.13 | - | 99.76 | 4.96 |
| | 16.78 | | 0.43 | 82.79 | | 100.00 | |
| 5-1 | 3.17±0.35 | 0.33 | 0.83 | 97.94 | - | 101.93 | 6.71 |
| | 12.90 | 0.57 | 0.74 | 85.79 | | 100.00 | |
| 5-2 | 2.38±0.26 | 0.30 | 0.91 | 96.47 | - | 99.77 | 8.78 |
| | 10.17 | 0.55 | 0.85 | 88.43 | | 100.00 | |
| 5-3 | 3.84±0.43 | 0.30 | 0.87 | 96.57 | - | 101.28 | 5.46 |
| | 15.41 | 0.51 | 0.76 | 83.32 | | 100.00 | |

**Continued**

| No. | C | Si | Mn | Fe | Ni | Σ | Me/C atom % |
|---|---|---|---|---|---|---|---|
| 5-4 | 3.57±0.39 | 0.24 | 0.59 | 96.76 | - | 100.93 | 5.86 |
| | 14.52 | 0.42 | 0.52 | 84.54 | | 100.00 | |
| 5-5 | 5.80±0.64 | 0.11 | 0.05 | 92.23 | - | 98.08 | 3.42 |
| | 22.51 | 0.18 | 0.04 | 76.99 | | 100.00 | |
| 5-6 | 6.92±0.77 | 0.11 | 0.07 | 92.35 | - | 99.34 | 2.87 |
| | 25.65 | 0.18 | 0.06 | 73.65 | | 100.00 | |
| 5-7 | 6.64±0.74 | 0.31 | 0.83 | 90.51 | - | 97.98 | 2.96 |
| | 25.00 | 0.49 | 0.68 | 73.26 | | 100.00 | |
| 5-17 | 4.56±0.51 | 2.18 | 4.12 | 85.74 | - | 94.78* | 4.25 |
| | 18.48 | 3.05 | 3.65 | 74.82 | | 100.00 | |
| 5-18 | 5.00±0.56 | 2.92 | 5.93 | 80.31 | - | 91.90** | 3.71 |
| | 20.42 | 3.88 | 5.29 | 70.41 | | 100.00 | |
| 6-1 | 5.90±0.65 | - | 0.58 | 93.61 | - | 100.08 | 3.43 |
| | 22.56 | | 0.48 | 76.96 | | 100.00 | |
| 6-2 | 6.64±0.74 | - | 0.13 | 93.58 | - | 100.35 | 3.04 |
| | 24.78 | | 0.11 | 75.11 | | 100.00 | |
| 6-3 | 6.69±0.74 | - | 0.97 | 92.49 | - | 100.15 | 3.00 |
| | 24.97 | | 0.79 | 74.24 | | 100.00 | |
| 6-4 | 4.77±0.53 | - | 0.22 | 93.49 | - | 98.47 | 4.23 |
| | 19.14 | | 0.19 | 80.67 | | 100.00 | |
| 6-5 | 4.91±0.55 | - | 0.35 | 92.73 | - | 97.99 | 4.08 |
| | 19.70 | | 0.31 | 80.00 | | 100.00 | |
| 6-6 | 6.00±0.67 | - | 0.43 | 92.45 | - | 98.88 | 3.33 |
| | 23.10 | | 0.36 | 76.54 | | 100.00 | |
| 6-7 | 7.93±0.88 | 0.48 | 1.01 | 91.49 | - | 100.92 | 2.45 |
| | 28.29 | 0.73 | 0.79 | 70.19 | | 100.00 | |
| 6-9 | 9.38±1.04 | - | - | 90.66 | - | 100.04 | 2.08 |
| | 32.48 | | | 67.52 | | 100.00 | |
| 7-1 | 11.25±1.25 | - | - | 86.87 | 0.61 | 98.73 | 1.67 |
| | 37.43 | | | 62.16 | 0.42 | 100.00 | |
| 7-2 | 10.67±1.18 | - | - | 87.70 | 0.24 | 98.60 | 1.77 |
| | 36.07 | | | 63.76 | 0.17 | 100.00 | |

In numerator, wt.%; in denominator, atom %. *. +P (0.36%); **. +P (0.40%)+S (0.25%).

0.2 mm. Sometimes fragments of minerals (sanidine) or enclosing glass are welded to them, but more often a "leg", which links them with the enclosing melt, branches off from the surface. In the spallings, a coarse porosity is observed. The spherule inner struture is shown in Figs. 3–8. In all cases, in their core, one large pore or several small rounded ones occur, and a metallic "drop" joins to them. The "drop", in turn, is surrounded by aggregates of quartz, glass, and magnetite in the symplectite intergrowth. The presence of magnetite was supported by XRD analysis (Table 1). In rare cases a spherule is entirely composed of a symplectite aggregate (Fig. 8). The metallic "drop" has a rounded, rarely angular form (Fig. 6). At the contact with symplectite, they are rimmed by magnetite "fringe" (Fig. 6c). Etching with HCl and X-ray microanalysis reveals an inhomogeneity in carbon distribution in the metallic portion of a spherule

(Figs. 5 and 6) with Fe/C ranging from 2 to 9 (Table 2). Some "drops" are homogeneous in composition, and in this case Ni admixtures appear in them. In non-homogenous "drops", the Mn admixture is considerable, and its content reaches 6 wt.% in the rounded hollows within the iron matrix (Table 2, Nos. 5-17 and 5-18). In this case, P and S admixtures appear in their compositions, being, probably, the constituents of mineral aggregates sublimated on the walls of the gas pores. It should also be noted that in the low-carbon varieties, a stable admixture of silicon in the absence of Al, Na, and K is established that testifies to the contribution of an iron-silicide component.

At high magnification (Figs. 6 and 7), heterogeneity of the symplectite structure is revealed—in the medium-grained matrix the fine-grained filamentary separations originate and connect pores as channels. This is probably caused by rapid loss of the gas phase and quenching of the melt. The rims around symplectite (Table 3, Nos. 8-13 and 8-14) are composed of potassic glass that predominates in the symplectite of, a spherule without an iron core. We succeeded in

**Table 3 Chemical compositions of the spherule silicate part with magnetite admixture (wt.%)**

| No. | | $SiO_2$ | $Al_2O_3$ | FeO | MnO | $Na_2O$ | $K_2O$ | Σ |
|---|---|---|---|---|---|---|---|---|
| I | 3-7 | 2.18 | - | 88.68 | 1.80 | - | - | 92.64 |
| | 4-8 | 2.63 | 0.79 | 87.82 | 0.37 | - | - | 92.05 |
| | 6-10 | 0.25 | 0.20 | 88.16 | 0.66 | - | - | 89.27 |
| | 6-11 | 0.18 | 0.30 | 87.89 | 0.56 | 0.07 | 0.08 | 89.08 |
| | 7-4 | 3.95 | 0.93 | 85.06 | 0.69 | - | 0.21 | 90.85 |
| | 8-1 | 1.89 | 0.61 | 88.75 | 0.22 | - | - | 91.46 |
| | 8-2 | 2.96 | 0.75 | 88.83 | - | - | - | 92.54 |
| | 8-3 | 3.67 | 0.81 | 88.03 | 0.60 | - | 0.33 | 92.85 |
| | 8-4 | 2.04 | 0.81 | 88.82 | 0.33 | - | - | 91.83 |
| | 8-5 | 1.42 | - | 90.57 | - | - | - | 92.32 |
| | 8-6 | 1.51 | - | 89.68 | - | - | - | 91.18 |
| | 8-7 | 2.16 | 0.67 | 90.12 | - | - | - | 92.94 |
| II | 6-12 | 15.74 | 2.26 | 71.42 | 0.87 | 0.09 | 1.10 | 91.48 |
| | 6-13 | 12.46 | 2.00 | 76.29 | 0.87 | 0.39 | 0.96 | 92.98 |
| | 6-14 | 12.96 | 2.11 | 73.81 | 0.71 | 0.13 | 1.22 | 90.95 |
| | 8-11 | 11.00 | 1.21 | 79.43 | 0.98 | - | 0.78 | 93.40 |
| | 8-12 | 10.99 | 1.19 | 79.76 | 0.95 | - | 0.85 | 93.74 |
| III | 3-9 | 27.79 | 2.55 | 64.83 | 1.46 | 1.05 | 1.01 | 98.69 |
| | 3-10 | 27.62 | 2.27 | 66.45 | 1.33 | 0.85 | 1.16 | 99.67 |
| | 3-11 | 28.05 | 2.49 | 65.55 | 1.41 | 1.01 | 1.01 | 99.52 |
| | 4-11 | 26.83 | 2.95 | 66.73 | 1.38 | 1.01 | 1.17 | 100.07 |
| | 4-12 | 27.58 | 2.97 | 63.71 | 1.28 | 0.77 | 1.19 | 97.49 |
| | 5-13 | 26.06 | 3.21 | 65.44 | 1.20 | 0.89 | 1.42 | 98.23 |
| | 5-14 | 28.71 | 3.36 | 62.45 | 1.02 | 1.05 | 1.21 | 97.80 |
| | 8-8 | 25.52 | 2.40 | 69.37 | 0.98 | 0.32 | 1.57 | 100.15 |
| | 8-9 | 23.32 | 2.02 | 68.20 | 1.32 | 0.38 | 1.56 | 96.81 |
| | 8-10 | 24.46 | 2.55 | 64.32 | 1.36 | - | 2.05 | 94.74 |
| | 8-13 | 26.47 | 4.66 | 58.09 | 1.06 | - | 3.33 | 93.61 |
| | 8-14 | 28.27 | 4.68 | 56.59 | 1.42 | - | 2.25 | 93.21 |

I. Magnetite+quartz; II. symplectite (square scanning); III. glass+magnetite+quartz (pointed analyses).
Total iron as FeO.

**Table 4 Calculated chemical compositions of silica portion from spherules without magnetite (wt.%)**

| | No. | $SiO_2$ | $Al_2O_3$ | FeO | $Na_2O$ | $K_2O$ | Σ | Mt/(Gl+Q) |
|---|---|---|---|---|---|---|---|---|
| II | 6-12 | 81.20 | 11.66 | 1.00 | 0.46 | 5.68 | 100.00 | 79 |
| | 6-13 | 78.02 | 12.52 | 1.00 | 2.45 | 6.01 | 100.00 | 83 |
| | 6-14 | 78.14 | 12.72 | 1.00 | 0.78 | 7.36 | 100.00 | 81 |
| | 8-11 | 83.84 | 9.22 | 1.00 | 0.00 | 5.94 | 100.00 | 86 |
| | 8-12 | 83.50 | 9.04 | 1.00 | 0.00 | 6.46 | 100.00 | 86 |
| III | 3-9 | 84.91 | 7.79 | 1.00 | 3.21 | 3.09 | 100.00 | 67 |
| | 3-10 | 85.71 | 7.05 | 1.00 | 2.64 | 3.60 | 100.00 | 68 |
| | 3-11 | 85.29 | 7.57 | 1.00 | 3.07 | 3.07 | 100.00 | 67 |
| | 4-11 | 83.12 | 9.14 | 1.00 | 3.12 | 3.62 | 100.00 | 68 |
| | 4-12 | 83.98 | 9.05 | 1.00 | 2.34 | 3.63 | 100.00 | 67 |
| | 5-13 | 81.69 | 10.06 | 1.00 | 2.79 | 4.45 | 100.00 | 68 |
| | 5-14 | 82.79 | 9.69 | 1.00 | 3.03 | 3.48 | 100.00 | 65 |
| | 8-8 | 84.99 | 7.99 | 1.00 | 1.07 | 5.22 | 100.00 | 70 |
| | 8-9 | 84.63 | 7.33 | 1.00 | 1.38 | 5.66 | 100.00 | 72 |
| | 8-10 | 83.33 | 8.69 | 1.00 | 0.00 | 6.99 | 100.00 | 69 |
| | 8-13 | 76.05 | 13.38 | 1.00 | 0.00 | 9.57 | 100.00 | 63 |
| | 8-14 | 79.50 | 13.17 | 1.00 | 0.00 | 6.33 | 100.00 | 62 |
| * | 5-15 | 80.53 | 10.77 | 0.91 | 2.69 | 5.73 | 100.64 | |
| | 5-16 | 81.96 | 10.28 | 0.94 | 2.39 | 5.57 | 101.13 | |
| ** | AV-24/5 | 77.68 | 12.60 | 0.45 | 2.97 | 4.85 | 99.67 | |
| | AV-24/6 | 77.40 | 12.82 | 0.31 | 1.38 | 6.54 | 99.62 | |

Calculation of magnetite portion has been carried out via elimination of 1 wt.% FeO (average value in ignimbrites) and combination of FeO residue with MnO with subsequent calculation of the sum for magnetite stoichiometry: $Mt/(Gl+Q)=(FeO+MnO-1)*100/(\Sigma-MnO)$, wt.%. *. Glass from symplectite (EPMA); **. spheruloidal rhyolite lava-filled extrusives (bulk).

analyzing magnetite and glass in the symplectite (Table 3). Magnetite turned out to be highly manganese and free of admixtures of other elements (Ti, Cr, V, Al, Mg) that are not characteristic of the high-temperature magmatic magnetites from felsic rocks (Shcheka et al., 1980) and allows us to connect its appearance with the crystallization of the immiscible high iron and silica melts. Larger (3–5 μm) separations of glass in the symplectite aggregate and fringes around it are represented by a potassic (without $Na_2O$) variety close in composition to the bulk composition of spheruloidal rhyolite lava (Table 4, AV-24/5 and AV-24/6) for which the liquid immiscibility nature is assumed. The bulk composition of the symplectite was obtained by square scanning of its areas with the beam (Table 3, II). The ratios of the magnetite and silicate portion are within 79 wt.%–86 wt.%. It is interesting that in the point analyses (Table 3, III) Mt/(Gl+Q) ratios in all areas are lower—about 62 wt.%–72 wt.%. After the magnetite admixture was excluded by calculation (Table 4), the glass composition in a spherule turned out to be close to the composition of residual glass from ignimbrites with somewhat increased potassium content, i.e. this is likely to be the melt enclosing spherules that were partially transformed in the process of its reduction.

## DISCUSSION

Recent publications strongly suggest that spherules are rather widespread, found in different geological settings, and have a terrestrial origin.

Magnetic spherules were found in the Senomanian–Eocene rhyolites and andesites of the south Sikhote-Alin, Primorye (Filimonova et al., 1989). They show similar outer habits with a smooth or rough dull surface of grey color. Particles are very brittle and porous. A complicated inner structure is conditioned by the content of iron oxidized to various degrees. The chemical compositions of spherules are close to that of the phases of ferrispinel composition. Taking into account the restriction of spherules to volcanite cavities, their porous texture, drop-like form, and specific composition, Filimonova et al. (1989) concluded that they could be crystallized under reducing conditions created by compounds of hydrogen and carbon through their quenching.

In the crushed samples of different rocks of ultrabasic massifs of the Koryak plateau (Kamchatka), native iron, copper, chrome, aluminium, tin, and lead and solid solutions of copper and zinc (analogs of α-ß-brass) as well as carbides of tungsten and titanium have been identified. Spherical forms of metallic and accompanying silicate-oxide separations, the presence of glass in the latter and dendritic textures of their aggregates, and the presence of gas bubbles in the metallic and silicate-oxide microspherules indicate active participation of high-temperature gas-reductants in the processes of crystallization of these minerals (Rudashevsky et al., 1987).

In the Middle Devonian eruptive breccias of the Priazovsky massif—Donets basin junction zone, some peculiar particles were found: (a) magnetic plates and spherules, (b) weakly magnetic black opaque glassy spherules and slag-like particles, and (c) non-magnetic transparent glassy spherules. The spherules were composed of native iron and the products of its high-temperature oxidation. The oxidation degree makes it possible to trace a regular series from pure iron with initial evidence of oxidation in the liquid state to martitized magnetite. The spherules were often hollow inside. In some metallic spherules, cohenite was found. The features of morphology, inner structure, and mineral and chemical compositions and presence of gas inclusions, pseudobrookite, wustite, ulvospinel, and native iron in glasses testify that they were developed from a gas-saturated high-temperature melt in a greatly reducing medium at rapid drops of temperature and pressure (Tsimbal et al., 1985).

Spherical titanomagnetite formations are widespread in the Elekmonarsky granite pluton of the North Altai (Bazhenov et al., 1991). Liquid immiscible separation of ore matter from the original basic magma occurred as a high-titanium and manganous monocrystalline ore drop of ferrite containing 96.40% Fe; 2.30% Si; 0.40% Mn; 0.07% Cr; 0.03% Ni. Appearance in the titanomagnetite decay structure of ulvospinel, associated persistently with graphite, clearly points to the reducing conditions of the ore matter separation.

Numerous spherical formations were found in the volcanic rocks from an area about 600 km$^2$ and about 700 km deep (according to bore hole data) of the Kuril-Kamchatka Island arc (Sandimirova et al., 2003; Rychagov et al., 2002). In the samples, fragments of volcanic glass with spherical native iron impregnation were found together with the spherules. The considerable amount of graphite flakes and carbonaceous particles of irregular shape as well as isolated grains of moissanite and iron carbide found together with the spherules suggest that the matter was deposited at high reducing fluid.

Isometric, rounded grains 0.05–0.5 mm in size and grey-yellow in color with a dull metallic luster were found within the mineralization of the “Trubka” fumarole located on the Second Cone of the north break of the Large Tolbachinsky eruption (Kamchatka). These grains were composed of iron-cohenite aggregates that had various myrmekite-like eutectoid structures. Gas flows participating in the formation of native metal-bearing associations were characterized by a high reduction degree and were enriched in carbon compounds (Glavatskikh and Generalov, 1996).

Magnetic spherules have been described in several environments, usually characterized by their reducing conditions and often by their high iron and carbon contents in deep sea sediments (Freeman, 1986) and limestone or biodegraded oil (McWhinnie et al., 1990; McCabe et al., 1987).

Describing such spherule formations, one cannot help but note the large quantity found in meteoritic matter. Most meteorites that fall on earth (chondrites) are characterized by the presence of round grains called chondrules.

So what are chondrules? Chondrules (after the ancient Greek word “chondros” or grain) are spherical or elliptical formations representing rapidly quenched drops of the molten silicate matter of meteorites. Chondrules can range in diameter from just a few micrometers to over 1 cm.

Unity of supercooling conditions of the chondrule melts its fragments, and the matrix cementing them testifies that they were formed through catastrophic explosions in accordance with the model of two-stage development of the chondritic planets that initially possessed hydrogen mantles like the planets of the Jupiter group (Marakushev et al., 2003, 1995).

Finally, we will note the findings of spherules of metallic iron in tektites—glass-like rocks displaying peculiar and composite shapes and sculptures. The metallic spherules, from less than 0.1 to as much as 5 mm in diameter, are completely embedded in tektites, perfectly spherical, shiny, and fresh—without the slightest trace of oxidation or alteration. The major mineral phase is α-iron or kamacite. The spherules contain more than 95% Fe and 1.2% to 3.2% Ni (Chao et al., 1962). Most tektites are rather close to obsidians (O'Keefe, 1963) and, in particular, to low-water volcanic glasses of ignimbrites. They represent quite amorphous natural glass free of microlites. All tektites show fluidal texture, and almost all of them contain lechatelierite and other glass-like inclusions. With high silica content (68%–82% $SiO_2$) they, like ignimbrites, are undersaturated with alkalis but saturated with siderophiles (Fe, Ni, Cr, Ti, Co, V) by 1 to 2 orders of magnitude, so their extraterrestrial nature is beyond question (Table 5). Their water content is lower than 0.02 vol.%, and hydrogen content in the gas phase is 35 vol.%–41 vol.% with the absence of ferric iron. Glasses display a high thin (≤1 μm) porosity, and pressures in the pores were determined instrumentally to be lower than $10^{-3}$ atom (Suess, 1951). The last fact, along with the presence of kamacite and a more mafic composition, allowed Izokh and Le (1983) to suggest that these tektites are delivered to the cosmic vacuum by volcanic explosions of one of the giant planets of our solar system (for example, Jupiter's satellite). Now it is known that such volcanoes actually exist. With this example the author

**Table 5 Average chemical compositions of volcanics of the Yakut-Gora VD and tektites**

| | Ignimbrite | Extrusive volcanic glass | Extrusive spherulitic rhyolite | Bediasite | Moldavite | Indochinite | Philippinite | Javanite | Australite |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 72.49 | 74.15 | 77.68 | 76.37 | 80.07 | 73.00 | 70.80 | 72.32 | 73.45 |
| $TiO_2$ | 0.14 | 0.11 | 0.09 | 0.76 | 0.80 | 0.73 | 0.79 | 0.75 | 0.69 |
| $Al_2O_3$ | 13.22 | 12.05 | 12.60 | 13.78 | 10.56 | 12.83 | 13.85 | 11.68 | 11.53 |
| $Fe_2O_3$ | 0.52 | 0.14 | 0.17 | 0.19 | 0.15 | 0.64 | 0.70 | 0.85 | 0.58 |
| FeO | 1.03 | 0.70 | 0.44 | 3.81 | 2.29 | 4.37 | 4.30 | 4.81 | 4.05 |
| MnO | 0.05 | 0.01 | 0.00 | 0.04 | 0.11 | 0.09 | 0.09 | 0.16 | 0.00 |
| MgO | 0.16 | 0.02 | 0.05 | 0.63 | 1.46 | 2.48 | 2.60 | 2.75 | 2.05 |
| CaO | 0.88 | 1.97 | 0.16 | 0.65 | 1.87 | 1.91 | 3.09 | 2.89 | 3.50 |
| $Na_2O$ | 3.65 | 3.73 | 2.97 | 1.54 | 0.51 | 1.45 | 1.38 | 1.78 | 1.28 |
| $K_2O$ | 4.21 | 1.93 | 4.85 | 2.08 | 2.95 | 2.40 | 2.40 | 2.35 | 2.28 |
| $P_2O_5$ | 0.02 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.09 | 0.03 |
| Cr | | *0–5* | | | | *20–425* | | | |
| Ni | | *1–4* | | | | *8–220* | | | |
| Co | | *0–3* | | | | *4–20* | | | |
| V | | *0–24* | | | | *18–100* | | | |
| Mf | 0.20 | 0.29 | 0.06 | 0.88 | 1.31 | 1.68 | 1.97 | 1.84 | 1.97 |
| K' | 0.43 | 0.25 | 0.52 | 0.47 | 0.79 | 0.52 | 0.53 | 0.46 | 0.54 |

Note: mf=$(Fe_{tot}$+Mg+Ca)/(Na+K), atom; K'=K/(K+Na), atom. Major elements are given in wt.%, trace element, in ppm. Tektite data are from O'Keefe (1963).

wishes to emphasize that the formation conditions of the terrestrial ignimbrites and cosmic tektites are similar in many respects.

The study of the ignimbrites of the Yakut-Gora VD that did not experience any secondary alteration (rather rare cases) shows their high degree of reduction to be striking. Analyses of glasses revealed that the iron oxidation degree ($Fe^{+3}/\Sigma Fe$) is extremely low (15 at.%–30 at.%), though it can still be lower because the rocks cooled down when they came in contact with the oxygen of the atmosphere. This quantity is comparable with those in the tholeiitic basalts where the main gas components are $H_2$ and $CH_4$, and much lower in the "oxidized" alkaline basaltoids with a carbon-dioxide-haloid composition of volatiles (Shcheka, 2004). This is supported by anomalous iron content of the Fe-Mg silicates, predominance of ilmenite and rare magnetite, and finally, the ubiquitous appearance of the described "globules" of native iron.

The metallic part of the studied spherules, surrounding a gas pore, has a composition of low-carbon iron ($Fe_9C$–$Fe_5C$) to cohenite ($Fe_3C$). This suggests that the reducer fluid of the silicate melt is the $H_2$-$CH_4$ admixture (CO and $CO_2$ portion is infinitesimally low at this oxygen fugacity). As noted above, the magnetite-glass-quartz symplectite surrounding the metallic phase is probably an intermediate product of reduction (according to the reaction $FeO+H_2\rightarrow Fe+H_2O$; $Fe_2O_3+3H_2\rightarrow 2Fe+3H_2O$; $2FeO+CH_4\rightarrow 2Fe+H_2+CO+H_2O$) of the enclosing silicate melt in its contact with a "gas bubble". It should be noted that the glass composition in symplectite strongly differs from that of the host ignimbrite glass (Tables 3, 4), which may be explained by the liquid immiscibility mechanism of formation whose real existence in the system $K_2O$-$FeO$-$Al_2O_3$-$SiO_2$ has been proven experimentally (Roedder, 1951), where a high potassium-silica melt was formed around the iron particles. Additionally, it is supported by the data of Naumov et al. (1993), who observed two immiscible melts (high silica and high iron ones) in the quartz phenocrysts from ignimbrite. Thus, in their mineralogy, morphology, and composition the studied silicate-metallic spherules are related to the process of the silicate melt immiscibility under the effect of the reduced gases (Oleinikov et al., 1985; Marakushev, 1979).

## CONCLUSIONS

(1) The pursued investigations of the silica-metal spherules found in the ignimbrites of the Yakut-Gora VD together with analysis of the scientific literature reporting such spherules in diversified geodynamic settings allowed the conclusion regarding their volcanic origin.

(2) The availability of the spherules and other evidence of the reduction degree of magmatic melts and their iron-carbon composition (low-carbon iron—cohenite) testify to the $H_2$-$CH_4$ composition of fluids of ignimbrite magmas that initiated the processes of reduction of the silica melt.

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