Cu-Ag-Au Microspherules in Igneous Rocks: Morphology, Composition, Diagnostic Criteria and Possible Origin

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Abstract: Igneous rocks from the Russian Far East contain Cu-Ag-Au microspherules with distinct exterior and interior structures, compositions and assemblages of Cu-rich micro-inclusions. Natural microspherules are compared in this study with technogenic Cu-Ag-Au microspherules, which are experimentally produced and extracted from gold scrap jewelry. The following set of diagnostic criteria are considered to distinguish natural from technogenic microspherules on a genetic basis as follows: (1) compacted-related features versus cellular appearance of the exterior; (2) lack of exsolution- or crystallization-related features in natural and domain-type internal structure in technogenic microspherules; (3) absence of spherical copper-oxide inclusions along with meniscus-type textural boundaries in technogenic microspherules; (4) pure copper-oxide composition of inclusions versus the common presence of Fe, Ni, Zn, Cu and Na in natural microspherules. The diagnostic characteristics of natural Cu-Ag-Au microspherules suggest extremely fast cooling rates during their formation, which is possible during violent explosive volcanic eruptions or injection of partially molten, pulverized metal alloys into shallow intra-crustal cavities and fault-related tectonic gashes.

Keywords: Cu-Ag-Au microspherules; natural versus technogenic origins; microspherule genesis; diagnostic criteria; liquid immiscibility; explosive volcanic eruptions

1. Introduction

Recent studies of magmatic rocks in the Russia Far East using such methods as scanning electron microscopy (micro-metallogeny) revealed presence of substantial quantities of microspherules composed of Cu-Ag-Au alloys [1,2]. Compositionally similar, but texturally non-spherical Cu-Ag-Au alloys were also reported from subduction-related plutonic complexes and adakite lavas in the Mesozoic Stanovoy suture zone [3–5], Cr-Ni ores in orogenic peridotites and pyroxenites of the Beni Bousera massif in the Atlas Mountains of Morocco [6], ophiolitic chromitites and peridotites [7–9], layered mafic-ultramafic intrusions such as Skaergaard [10] and Norilsk [11], Miocene-Pliocene adakites from northern Kamchatka [5], Quaternary high-K dacites from the Bolivian Andes [12], Eocene trachytes from the Virginian Appalachians [12], basaltic lavas from Kilauea and Mauna Loa volcanoes in Hawaii [13] and glassy MORB-type submarine lavas from the Chile Ridge (southeastern Pacific Ocean) [13]. The occurrence of Cu-Ag-Au alloys in intrusive rocks is interpreted as result of transport of ore elements in mafic plutonic systems under fluid-saturated, relatively reduced conditions [3,4,10], while the formation of Cu-Ag-Au alloys in volcanic environments implies either fast cooling of metal droplets in the course of violent explosive eruptions [1,2] or pre-concentration of precious (Au, Ag) and base (Cu) metals during lava solidification before later-stage hydrothermal remobilization of the host lava flow or igneous dike [12–14]. Presence of Cu-Ag-Au alloys in mantle wedge xenoliths and host primitive ankaramite lava at the Avachinsky volcano in Kamchatka suggests that refertilized sub-arc lithospheric or asthenospheric mantle was the ultimate source of these
alloys in the wide range of subduction-related (arc, collisional, post-collisional, etc.) tectonic environments [14–19].

Compounds with different Cu:Ag:Au ratios and tendency towards pure Cu-Au and Ag-Au compositional end-members were also described in various hydrothermal and contact metamorphic rocks [20,21], where their origins have been attributed to fluid–rock metasomatic interactions under relatively low-temperature (<400 °C) and variably oxidized conditions [22,23]. Primarily due to the general rarity of well-documented magmatic occurrences, precise conditions of formation of Cu-Ag-Au alloys in igneous environment are still rather poorly constrained by the data available from natural systems, thermodynamic calculations or experimental studies [1–5,14,24–31].

Discovery of precious and base metal microspherules in volcanic rocks opens up new avenues for better understanding of emergence of metal-rich alloys and mineral phases in silicate and sulfide melts, as well as processes leading to the formation of precious metal mineralization in high-temperature magmatic settings. The Cu-Ag-Au microspherules are viewed as bona fide evidence for high-temperature transport of primary magmatic gold by melts originating from metal-rich, deep-seated sources in the mantle [1,2,13,14,27,31]. This primary magmatic gold can contribute to a range of economic metal deposits [32] and, upon chemical and morphological transformations under oxidized upper crustal conditions, form classic epithermal Au-Ag mineralization in subvolcanic ore-forming environments [1,2,4,12,33–36]. Determination of compositional and textural features of microspherules and establishment of clear diagnostic criteria for their primary igneous origins in the context of the development and evolution of mineralized gold-bearing magmatic-hydrothermal systems are especially important in the light of their apparent potential applications as a powerful exploration tool in cratonic and accreted terranes, Andean-type continental margins and orogenic belts.

Our paper presents textural and compositional data on Cu-Ag-Au microspherules in magmatic rocks from the Lesser Khingan Range in Russian Far East combined with some experiments on the formation of these alloys at atmospheric pressure and different cooling regimes. In this respect, we aim to determine specific diagnostic criteria of natural versus technogenic origins for this potentially very important metal association in igneous rocks, either intrusive (plutonic) or extrusive (volcanic).

2. Materials and Methods

2.1. Geologic Background and Samples

The Cu-Ag-Au microspherules were detected in ores, mafic to felsic explosive breccias and tuffs, as well as associated basaltic and carbonatite-like rocks from the Poperechny, Kostenga and Kaylan iron-manganese deposits in the Jewish Autonomous Region of the Russian Far East (Figure 1). Formation of these deposits is linked to Mesozoic explosive volcanism within the Bureya Terrane of the Central Asian Orogenic Belt (CAOB) [1,2]. Mesozoic felsic magmatism within the Bureya Terrane appears to be related to the amalgamation of various crystal blocks in the eastern CAOB into a single Amur superterrane and its collision with the North Asian Craton [37,38]. Mesozoic magmatism, terrane accretion and intraplate tectonism within the southeastern part of the Russian Far East and bordering region of NE China records general westward flat subduction of the Izanagi lithospheric plate in Middle Jurassic to Early Cretaceous time [39–41].

Samples used in this study represent several prominent and typical rock types that occur within the three iron-manganese deposits studied in detail in the Bureya Terrane of the Russian Far East (Figure 1). The sampled rock types include magnetite-rich lava from the Kostenga deposit, mineralized tuff from the Kaylan deposit and carbonatite-like rock from the Poperechny deposit. Details of textural relationships, mineralogy and major and trace element geochemistry of these rock formations can be found in [1,2,42].
In order to study the internal structure of individual microspherules, the Scotch tape with attached microspherules was coated with epoxy resin and disconnected from the sample holder. The remainder of the Scotch tape was washed away (cleaned up) with ethanol and the epoxy with microspherules was ground down until the exposure of representative internal structures. After that, microspherules were studied using a scanning electron microscope with the energy dispersive spectrometer (SEM-EDX) system VEGA 3 LMH (TESCAN, Brno, Czech Republic) fitted with the X-Max 80 energy dispersive spectrometer (Oxford, UK). The following analytical conditions were used during microspherule studies: accelerating voltage of 20 kV, beam current of 530 pA, beam diameter of 0.2 µm, maximum counting time of 20 s. A set of reference materials including 37 natural and synthetic oxides, minerals and native metals (Oxford/108699 # 6067) was used as reference standards. Co-standard Oxford Instruments/143100 # 9864-15 was used for routine daily instrument calibration. The EDS compositions are considered to be precise within approximately ±0.1 mas.%, which is deemed satisfactory for the purposes of the current study.

X-ray diffraction (XRD) analysis of gold-bearing particles was conducted using the Miniflex II diffractometer (Rigaku, Tokyo, Japan) under the following set of conditions: CuKα-radiation, accelerating voltage of 30 kV and beam current of 15 mA.

For the studies of the exterior morphological features of microspherules, the latter were mounted onto the conductive Scotch tape of the scanning microscope sample holder. In order to study the internal structure of individual microspherules, the Scotch tape with attached microspherules was coated with epoxy resin and disconnected from the sample holder. The remainder of the Scotch tape was washed away (cleaned up) with ethanol and the epoxy with microspherules was ground down until the exposure of representative in-
ternal cross-sections and subsequently polished. Ultimate care was paid in order to prevent over-polishing to avoid the appearance of an internal relief due to heterogeneous internal structure of individual microspherules and possible display of the effect of stretching of the softer material over the surface of the harder mineral phase.

3. Results

3.1. Exterior Features of Cu-Ag-Au Microspherules

Microspherules containing Cu, Ag and Au predominantly display spherical shapes combined with sizes ranging from first microns to first tens of microns. The surface of individual Cu-Ag-Au microspherules is very rarely smooth and typically is sculptured and covered with compaction-related deformations, reflecting fast cooling in the absence of crystallization (Figure 2A,B). Exterior features of all studied microspherules lack any evidence for penetration by internal crystals or sub-crystalline phases. We have, however, frequently observed external crusts and fragments of copper-rich phases immiscible with the Cu-Ag-Au alloy on the surface of the individual Cu-Ag-Au microspherules (Figure 2C).

Figure 2. Back-scattered electron (BSE) images of the exterior features of typical Cu-Ag-Au microspherules. (A) Linear compaction-related deformations on microsphere in the magnetite lava from the Kostenga deposit. (B) Compaction-related depressions and “shagreen”-type exterior of microsphere in mineralized felsic tuff from the Kaylan deposit. (C) Partially preserved Cu-rich immiscible phase crust on microsphere in carbonatite-like magmatic rock from the Poperechny deposit. Locations of microspherule sites are shown in Figure 1.

3.2. Internal Structure and Composition of Cu-Ag-Au Microspherules

Internal structure and composition of Cu-Ag-Au microspherules were determined with SEM-EDS on polished cross-sections. Out of 74 studied microspherules, only 8 individual spherules displayed texturally and compositionally homogeneous internal structure (Figure 3A). Additional detailed X-ray diffraction studies confirmed the absence of crystalline phases within these microspherules and the internal homogeneity of their chemical composition [1].

Most of the studied spherules contain very small inclusions of predominantly copper-oxide composition with minor admixtures of Ni, Zn, Cr and Fe (Figure 3B–F). It is important to emphasize that presence of Ag, Au and, partially, Cu in SEM-EDX analyses of copper-oxide micro-inclusions is due to the compositional influence of the surrounding Cu-Ag-Au matrix [1]. The concentration of copper in micro-inclusions consequently leads to its relative depletion in the matrix, although general copper content in the bulk microsphere (determined using areal SEM-EDX scanning of the entire interior cross-section of an individual microsphere) remains approximately constant. Copper-oxide inclusions typically display circular (Figure 3B), dendritic (Figure 3C) or polygonal (in most cases, hexagonal; Figure 3D) shapes. In rare cases, inclusions with different shapes occur within the individual Cu-Ag-Au microsphere (Figure 3E). Some larger copper-oxide inclusions exhibit clear textural evidence for liquid immiscibility represented by internal meniscus-type boundary (Figure 3F) typically interpreted as co-existence of two compositionally different liquids [43,44].
Figure 3. Internal structure and composition of Cu-Ag-Au microspherules (BSE images). (A) Internally homogeneous microspherule in compositionally evolved tuff from the Kaylan deposit. (B) Microspherule with rounded Cu-O inclusions in the carbonatite-like rocks from the Poperechny deposit. (C) Microspherule with dendritic Cu-O inclusions in evolved tuff from the Kaylan deposit. (D) Microspherule with faceted Cu-O inclusions in magnetite lava from the Kostenga deposit. (E) Microspherule with combined rounded, dendritic and faceted inclusions in magnetite lava from the Kostenga deposit. (F) Rounded Cu-O inclusion with meniscus-type textural boundary indicative of liquid immiscibility in magnetite lava from the Kostenga deposit. Arrows indicate precise locations of tabulated SEM-EDA analyses. Insets reveal the general internal structure of individual microspherules. Images (B,F) are modified after [1]. Locations of the microspherule sites are shown in Figure 1.

3.3. Diagnostic Criteria for Cu-Ag-Au Microsphere Identification

Figure 4 summarizes compositional variations of principal components (copper, gold and silver) in the Cu-Ag-Au microspherules from the Lesser Khingan deposits we investigate here.

Figure 4. Compositional variations in natural Cu-Ag-Au microspherules compared with the 14 karat (14K) gold alloy composition used in our investigation [45].
Data in Figure 4 suggest that compositional variations in natural Cu-Ag-Au are broadly similar to the 14K “red” gold alloy, which is typically used in gold jewelry manufacturing [46,47]. This startling coincidence led us to an investigation specifically designed to eliminate any possibility of contamination of our samples with natural microspherules from human-worn pieces of standard gold jewelry. Under this special investigation, we are also seeking to develop some reliable morphological and compositional and textural criteria to distinguish between microspherules of possible natural and technogenic origins. In order to achieve these goals, we supplemented our data on natural microspherules from the Lesser Khingan iron-manganese deposits with SEM studies of experimentally produced Cu-Ag-Au microspherules and scrap jewelry products.

We used pure copper, silver and gold metals to synthesize technogenic Cu-Ag-Au microspherules. Smelting of pure metals was performed in crucibles with borax flux heated by the standard gas torch flame gun. Spherical micro-portions of Cu-Ag-Au alloy were then liberated from the easily solvable flux matrix and investigated with the same methods that were previously applied to natural microspherules. The same sampling methods were applied to broken crucibles previously used in the manufacturing of the 14K gold jewelry. Results of the SEM-EDX studies of technogenic microspherules are presented in Figure 5.

![Figure 5. BSE images of microspherules with 14K gold alloy external relief and composition experimentally produced from scrap jewelry materials. (A) Exterior features of experimental microspherules. (B) Internal structure of experimental microspherules. (C) Internal structure of experimental microspherules emphasized under enhanced contrast conditions of the SEM instrument. (D–F) Results of scanning of cross-section (B) in characteristic emission rays Cu Kα1 (D), Ag Lα1 (E) and Au Mα1 (F).](image)

In comparison with the natural samples, technogenic Cu-Ag-Au microspherules completely lack any compaction-related deformational features along their surfaces. Typical technogenic spherule surface display a very characteristic cellular (“mesh”-or “honeycomb”-like) appearance, most probably due to crystallization processes involved in their formation (Figure 5). This suggestion is further supported by the high contrast regime scanning of internal cross-sections of technogenic microspherules along with clear difference in separate spot analyses (chemical compositions) of dark and light zones that occur inside the technogenic spherules (Figure 5C). It is important to emphasize here that the SEM-EDX area scanning of the entire internal section of an individual microspherule will result in...
the average “bulk” composition of this particular spherule (Figure 5B). Distribution of individual chemical elements between sub-crystalline zones within the individual microspherule is best demonstrated with SEM-EDX scanning of its internal cross-sections using characteristic radiation Au M\(_\alpha\)1 (Figure 5D), Cu K\(\alpha\)1 (Figure 5E) and Ag L\(\alpha\)1 (Figure 5F).

Oxygen intake, achieved during our experiments either through smelting in the air (room atmospheric conditions) or limiting the amount of borax flux in the crucible, results in the formation of Cu-Ag-Au microspherules almost completely covered with a copper-oxide crust (Figure 6A). Removal of the Cu-oxide crust exposes a surface relief texturally similar to the spherules generated in fully fluxed smelting experiments (Figure 6B).

Cu-Ag-Au microspherules exposed to oxygen-rich conditions during their formation typically contain dendritic copper oxide inclusions and are depleted in copper with specific reference to their gold contents (Figure 6C).

**4. Discussion and Genesis of the Cu-Ag-Au Microspherules**

Results of our SEM-EDX studies of natural and technogenic microspherules can possibly lead to some important practical and fundamental implications. Data presented in this paper provide some additional firm criteria to identify natural versus technogenic origins of microspherules, which, we believe, can and should be used in future studies of similar spherical objects [48–50]. Fundamental aspects of this study can be potentially linked to our better understanding of gold, silver and copper partitioning in the mantle–crust system and transport and evolution of precious and chalcophile metals in the upper crustal hydrothermal environments [4,12,14,51–59].

Our data highlight four principal diagnostic criteria to distinguish between natural and technogenic microspherules. It is important to emphasize here that our comparisons are drawn on the basis of 14K gold alloy composition, which occurs naturally [1–9] and is also typically used in jewelry manufacturing [45–47]. It is possible that for Cu-Ag-Au alloys of different composition (e.g., different proportions of Au, Ag and Cu), these diagnostic criteria would be different. The first diagnostic criterion involves details of surface relief of the spherules, which is characterized by compaction-related textural features (Figure 2A, B) in natural samples and displays a cellular (“mesh”- or “honeycomb”-like) appearance in microspherules of technogenic and anthropogenic origin (Figure 6B). The second criterion is closely tied in with the first, in that natural spherules do not exhibit any evidence for exsolution (e.g., lamellae, etc.) or crystallization, while technogenic spherules possess internal domain structures due to the initial decomposition of the homogeneous primary alloy into various sub-crystalline phases. The third distinction involves the character and appearance of copper oxide inclusions. Technogenic spherules do not carry spherical copper oxide micro-inclusions or micro-inclusions with immiscibility-related, meniscus-type textural boundaries such as those shown in Figure 3F. Finally, copper oxide micro-inclusions...
in natural versus technogenic microspherules display subtle, but distinct compositional
differences. Besides the presence of some Ag and Au due to some matrix contributions
from sample areas affected by instrumental X-ray excitation from the SEM source [1],
inclusions in technogenic microspherules are composed exclusively of copper and oxygen,
while spherical inclusions in natural microspherules almost always contain Fe, Ni, Zn,
Cr and some occasional Na. Apparently, the natural environment of formation for the
Cu-Ag-Au microspherules was saturated in respect to these chemical elements, while the
manufactured 14K gold alloys are depleted in them totally.

Textural and compositional comparisons between natural and technogenic Cu-Ag-Au
microspherules presented in this study shed light on their origins under natural conditions.
It became abundantly clear that these unique mineralogical objects can only form in nature
under strongly reducing conditions (logP(O₂) under ~3) [1,60] typical of deep horizons of
the terrestrial lithosphere. Any oxygen intake during formation of natural Cu-Ag-Au alloys
at temperatures in excess of 260 °C immediately triggers oxidation of the copper component,
resulting in the formation of a copper-oxide crust on the surface and copper-oxide inclusions
in the interior of microspherules. This oxidation process is most probably the primary
reason for the rarity of these microspherules in the upper crust, as most of the Cu-Ag-Au
spherules will be completely oxidized in shallow epithermal environments associated with
magmatic-hydrothermal plumbing systems and terrestrial volcanoes. Consequently, the
studied natural Cu-Ag-Au microspherules may represent the “primary magmatic gold”
sourced in the deep-seated lithosphere, which, upon oxidation and preferential copper loss,
leads to the formation of precious metal deposits with the typical Au-Ag composition of
hydrothermal ores [61–65].

Studies of natural Cu-Ag-Au microspherules and their experimentally produced
compositional analogues suggest that their formation in nature is facilitated by high to
extremely high cooling rates, resulting in the absence of high-temperature exsolution
features (lamellae) and preservation of spherical shapes of internal copper-oxide (cuprite)
micro-inclusions. Moreover, some copper-oxide inclusions display clear textural evidence
(Figure 3F) for oxidation and liquid immiscibility, most probably triggered by contact of
microspherules with either strongly oxidized fluids (epithermal environments in the upper
crust) or with atmospheric oxygen (violent explosive eruptions). Extremely fast cooling
rates resulted in the preservation of Cu-Ag-Au alloys and their oxidized micro-inclusions in
the metastable state. These cooling rates were not achieved, even in experiments involving
the dropping of a molten Cu-Ag-Au droplet into cold water. However, similar extremely
high cooling rates in nature can be achieved during high-energy volcanic explosions (e.g.,
the “Minoan” Plinian eruption of Santorini volcano in Greece, the 1974 sub-Plinian eruption
of Fuego volcano in Guatemala, the 1977 fire-fountain eruption of Seguam volcano in the
Aleutians [66,67]) or injection of partially molten, pulverized metal alloys into shallow
intra-crustal cavities and fault-related tectonic gashes.

5. Conclusions

We can formulate the following diagnostic criteria for natural Cu-Ag-Au microspherules on the basis of data presented in the current study.

1. Surface relief and appearance. Natural microspherules are characterized by compaction-related surficial deformations, while technogenic products display cellular surfaces indicative of proto-crystallization processes.
2. Natural microspherules do not show any solid solution evidence for exsolution or post-formation crystallization, while technogenic spherules display a well-defined internal domain microstructure due to decomposition of the initial homogenous alloy into several sub-crystalline phases.
3. Technogenic spherules totally lack spherical copper-oxide micro-inclusions and micro-inclusions with meniscus-type textural boundaries, indicative of liquid immiscibility at the early stages of their formation and compaction.
4. Copper-oxide micro-inclusions in natural Cu-Ag-Au spherules always contain some Fe, Ni, Zn, Cr and, to a lesser extent, Na, while inclusions in technogenic microspherules are composed exclusively of copper and oxygen, as suggested by SEM-EDX microanalysis.

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