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GEOCHEMISTRY

Silver Spheroids in Graphite-Bearing Rocks of the Maksyutov Complex, Southern Urals

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Findings of graphite pseudomorphs after diamond and metamorphic nanodiamonds have been reported in the recent literature [1, 2]. Therefore, we attempted to extract and scrutinize graphite pseudomorphs and diamond particles from graphite-bearing rocks of the Maksyutov Complex. We used the thermochemical dissolution method applied for the extraction of microdiamonds. The byproduct of the insoluble residue in the experiments contained unusual spherical particles mainly represented by very interesting spheroids of native silver (Fig. 1).

We investigated the graphite-bearing interbed in quartzites of the Yumaguza Formation in the upper part of the Maksyutov Complex. The sampling site is located approximately 2 km east of the settlement of Ivanovka on the left bank of the Tirgamysh River. The quartzites are intensely dislocated and transformed into stressed (often isoclinal) folds. The rocks contain a significant amount of graphite, but graphite-rich interbeds are scanty. The sampled graphite-bearing interbed is traced by debris of large blocks.

The crushed and powdered fraction of graphite schists was fused with NaOH at 500°C. Subsequently, the fraction was leached and treated with HCl. The insoluble residue left after decomposition was separated in bromoform. The heavy fraction obtained from 15 g of the initial sample of graphite-bearing quartzite yielded 132 spheroids approximately 20–50 μm in size.

In general, the spheroids show a silvery luster and positive chemical reaction with nitric acid for Ag. The reaction yields a very thin transparent film on the surface of the initial spheroids. Their identification with the Debye–Scherrer (Table 1) and microprobe (Table 2) methods confirmed reliably the affiliation of spheroids to native silver. Some particles contain Cu (<1%). The surface of spheroid silver particles is commonly coated with a friable nanogranular film (thickness ~300 nm, size ~100 nm or less). The grains are characterized by a lack of crystallographic form and the presence of quite equant outlines (Fig. 2). Such a film is developed either as a uniform coating on silver particles or can be presented by segments. The consequent "football" pattern of spheroids is observed distinctly in reflected electron images (Fig. 3). At the same time, granular particles similar to grains of a consolidated film can make up relatively rare sinuous chains on the surface of spheroids.

Study of the elemental composition of granular films revealed that they contain not only Ag, but also as much as >10% Br (Table 2). The presence of Br is likely related to its absorption by the loose surface of film on the native silver during the extraction of the heavy fraction with bromoform. However, we cannot rule out the natural origin of Br in the film.

We also considered the technological influence during the thermochemical processing of the sample. It is worth noting that the thermochemical processing was aimed mainly to remove the silicate rock-forming component. Therefore, its influence on the remaining min-

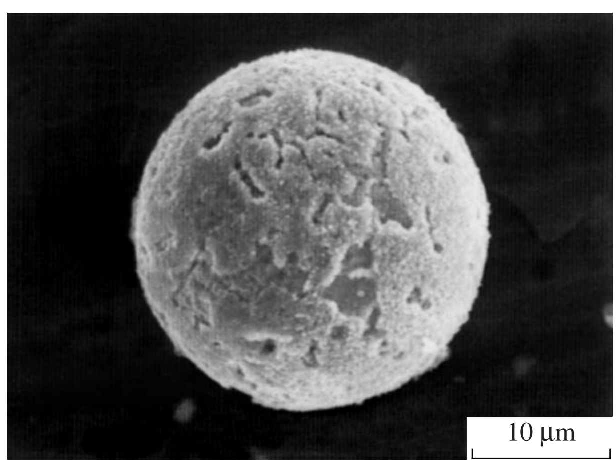

Fig. 1. Native silver spheroid. Maksyutov Complex, southern Urals. Secondary electron image.

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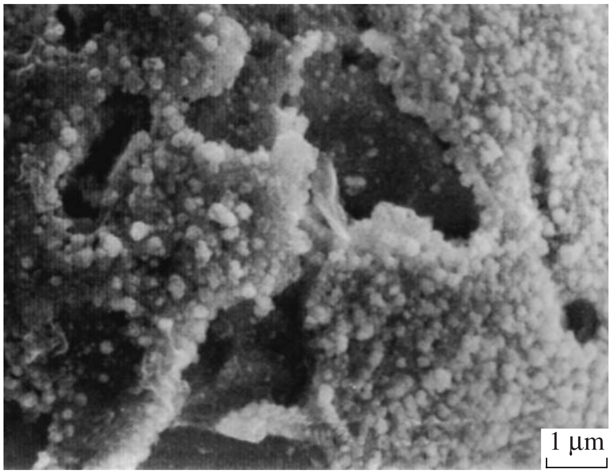

Fig. 2. Silver bromide film on the silver spheroid surface. Secondary electron image.

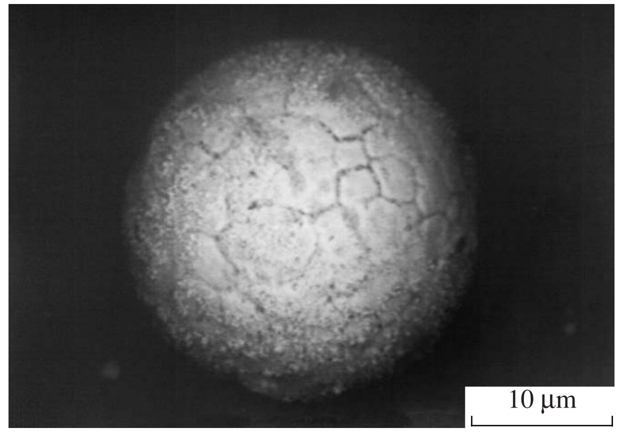

Fig. 3. Silver spheroid with a Br-bearing coating presented by angular segments. Back-scattered electron image.

eral components was insignificant. Native components and intermetallides are retained during the processing. A check analysis of the sample yielded other unique spheroid particles, including Ce–La–Fe particles with an iron hydroxide coating, a hematite spheroid, and an ovoid hydrocarbon (?) particle. We also detected Pb–Sn–Br intermetallides marked by a highly variable composition (with or without a Cu admixture) and several cuprite crystals.

The results of atomic absorption analysis showed that the Ag content in the graphite-bearing quartzites is at the detection limit. Based on the semiquantitative spectral analysis, they are slightly enriched in Pb, but depleted in Mn, V, Cu, Ti, Co, Ni, Zr, Y, and Yb, relative to similar carbonaceous rocks in the Near-Polar Urals.

Findings of unusual (spheroid) mineral particles and the presence of intermetallides indicate a natural origin of the native silver. Study of the Maksyutov Complex revealed unique mineral microparticles that should be scrutinized in further investigations.

It has long been known that native noble mineralization can be developed in carbonaceous rocks and this type of mineralization can produce large deposits. However, their formation mechanism and mineral

Table 1. Debye–Scherrer data on spheroid silver particles

Interplanar distance, nm	Intensity, scale	Plane lattice index, *hkl*	Interplanar distance, nm	Intensity, scale	Plane lattice index, *hkl*
0.235	5	111	0.0935	2	331
0.203	2	200	0.0912	1	420
0.1438	1	220	0.0833	1	422
0.1227	2	311	0.0786	2	
0.1175	1	222			

Table 2. Microprobe data on spheroids of the native silver

Element	Sample, wt %					
	MK-187/2-1	MK-187/1	MK-187-C1	MK-187-C1-1	MK-187-C2	MK-187-C2-1
Ag	98.07	94.93	98.27	99.41	91.69	87.73
Cu	–	–	–	0.60	0.91	–
Br	2.35	2.21	–	–	5.67	10.64
Total	100.25	97.14	98.27	100.01	98.27	98.67

forms were insufficiently studied. Our investigations have demonstrated that the native silver can occur as perfect spheroid particles. The spheroid morphological variety of the native silver has been detected for the first time.

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