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GEOCHEMISTRY

Native Metals in Kimberlite Pipe Aureoles of the Arkhangelsk Diamondiferous Province

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It is generally considered that the impact of kimberlite pipes upon host rocks is insignificant and that the alteration zone does not exceed 10–15 m. In 1991, Kisel established that the above concept is invalid for the Arkhangelsk diamondiferous province. Kimberlite pipes of this province are accompanied by hidden (primarily micropetrographic) fracture zones. Epigenetic hydrothermal mineralization can also be developed in such zones. Rock alteration in the contact zone commonly attenuates with increasing distance from the kimberlite body.

It was subsequently established that these structural-textural and mineralogical anomaly (hereafter, SMA) zones are almost comparable or slightly greater than primary geochemical aureoles in terms of linear parameters. In 1995, Kisel proposed criteria for the subdivision of host rocks into normal and anomalous types. He also found a technical resolution for the implication of these rocks as a source of information that can be used in prospecting for hidden kimberlite bodies with a low content of indicator-minerals. This communication presents the first results of the instrumental investigation of intricate mineralogical features of host rocks from SMA zones.

We studied more than 50 samples on a JSM-6400 scanning electron microscope equipped with a Link ISIS-300 energy-dispersive spectrometer. The samples were taken from the core collection of ZAO Terra representing the entire Vendian–Carboniferous terrigenous sequence penetrated by boreholes. The kimberlite-hosting sequence primarily consists of fine-grained sandstones and mudstones with a clayey admixture.

We examined structural–textural patterns of rocks and minerals in approximately 300 SEM images. We also scrutinized more than 500 quantitative analyses of minerals. This made it possible to reveal typical morphological–chemical features of accessory minerals and their exotic paragenetic assemblages in terrigenous rocks. We deciphered more than ten mineralogical features that can be used in prospecting for kimberlite bodies.

The comprehensive study of terrigenous rocks from the alteration zone of kimberlite pipes resulted in the discovery of numerous segregations of native metals with diverse forms and dimensions (Fig. 1). Native copper, zinc, and ferrochrome (Fe_7Cr) commonly make up chains, while other metals are observed as rare grains and flakes. Native metal concentration in some samples is very high (up to 100*n* grains/cm^2). The size of individual segregations is generally not more than a few micrometers (average 4–8 μm, maximum 100 μm). They are often arranged as straticulate clusters.

Findings of native metals and intermetallic compounds in kimberlite pipe aureoles are particularly interesting in connection with the discovery of metallic films on diamond crystals [4, 7, 11]. The list of 24 species (9 metals plus 15 alloys and intermetallic compounds) found in altered rocks includes the following phases: Au, Ag(S), Fe, Ni, W, Fe–Cr, Fe–Ni, Fe–Ni–Cu, Fe–Ni–Cr, Ni–Cr–Fe–W–Mo, Fe–Mn–Si, Cu–Ni, Cu–Ni–Sn(Fe), Cu–Sn, Cu–Zn, Cu–Zn–Sn, Cu–Zn–Ni, Cu–Al, Cu, Sn, Zn, Pb, Pb–Sb, and Pb–Cu–Zn. In [6], we published a list of more than 40 species of metallic films on diamond crystals and described their morphological and chemical features. The metallic films on diamond crystals, including those from the Lomonosov Pipe, are compositionally very similar to native metals in host rocks. The contamination of natural samples with technical metals is ruled out, because the samples were carefully prepared from fresh rock chips. The composition and metal ratios in natural alloys differ from those in technical alloys.

Electron-microscopic images of native metals indicate that they are confined to carbonate matrix in pores and overlain by other minerals. Their composition is irregular even within a single grain, suggesting that they are natural formations. We detected typical accordion-shaped crystals that are also known as "crystal-booklets" (Figs. 1b, 1d, 1f). Such native metal crystals are already known in many geological settings. They were probably generated from metalliferous fluids in a

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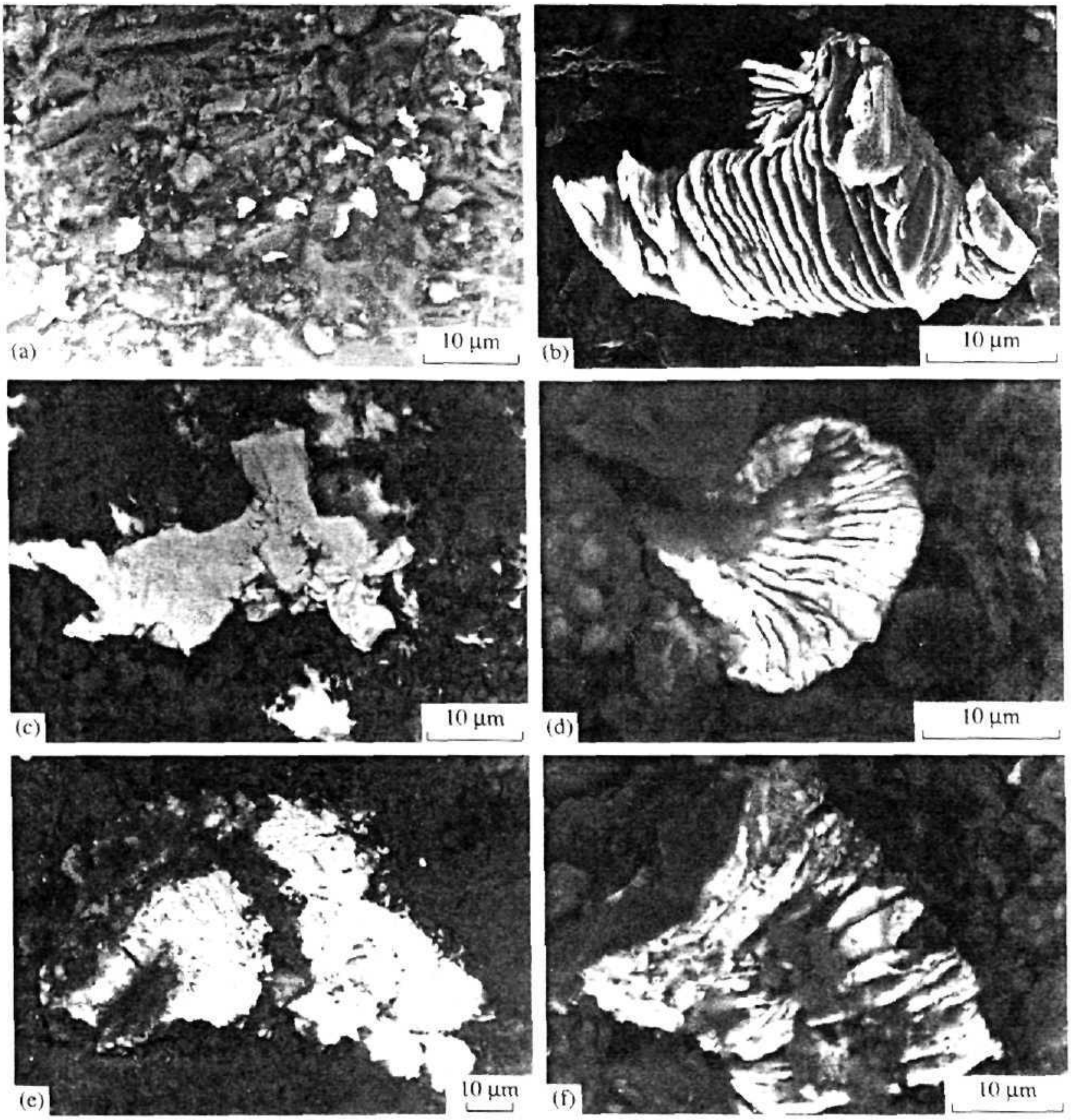

Fig. 1. SEM images of native metal segregations in carbonatized sandstones. (a) Chain of ferrochrome (Fe_7Cr) segregations; (b) crystal-booklet of natural brass (Cu_2Zn); (c) native copper; (d) crystal-booklet of natural Fe–Ni–Cu alloy; (e) large native zinc; (f) crystal-booklet of natural Fe–Ni alloy.

reductive environment. Mantle gases with hydrogen and methane could serve as the reducers. Gaseous inclusions in rock-forming minerals from ultramafic rocks [2, 5] and diamond crystals [1] show that the concentration of reductive gases in the mantle-hosted mineral-forming medium was sufficient for the existence of native metals in the mantle, kimberlites, and ultramafic rocks [3, 9]. For example, large segregations of native copper and aluminum, several millimeters in size, are known in kimberlite pipes of the Arkhangelsk diamondiferous province.

A part of 140 quantitative analyses of native phases is presented in the table. We also carried out a few hundred qualitative analyses of native metals based on energy-dispersive spectra. Metals and alloys of iron-group elements are the most widespread phases. Alloys of the Fe–Ni–Cu system account for more than 50%. Their data points are plotted on the Fe–Ni–Cu ternary

Normalized chemical compositions of native phases (wt %) and their dimensions (μm)

Fe	Ni	Cr	Cu	Sn	Zn	W	Au	Pb	Sb	S	Total	Dimension
87.62	0.29	12.09	–	–	–	–	–	–	–	–	100.0	10 × 24
1.54	–	–	78.31	20.15	–	–	–	–	–	–	100.0	6 × 10
0.26	0.03	–	–	–	–	–	99.70	–	–	–	100.0	2 × 2
0.37	–	–	65.85	33.78	–	–	–	–	–	–	100.0	4 × 6
46.92	37.38	–	15.45	–	–	–	–	–	–	0.24	100.0	6 × 8
51.19	48.63	–	0.17	–	–	–	–	–	–	–	100.0	3 × 4
95.46	4.54	–	–	–	–	–	–	–	–	–	100.0	5 × 7
0.49	–	0.27	44.92	–	54.32	–	–	–	–	–	100.0	8 × 12
1.43	0.10	–	86.03	12.38	–	–	–	–	–	0.06	100.0	5 × 7
77.39	8.86	13.76	–	–	–	–	–	–	–	–	100.0	2 × 3
0.38	0.04	–	–	0.71	–	–	98.53	–	–	0.33	100.0	2 × 3
0.37	0.30	–	6.67	–	–	–	91.80	–	–	0.87	100.0	2 × 3
73.22	0.91	24.20	1.17	–	0.45	–	–	–	–	0.05	100.0	4 × 5
1.33	98.48	0.19	–	–	–	–	–	–	–	–	100.0	2 × 4
0.76	0.46	–	60.58	–	38.18	–	–	–	–	0.02	100.0	2 × 3
0.32	0.33	–	95.39	–	3.97	–	–	–	–	–	100.0	5 × 8
1.03	0.00	–	–	98.97	–	–	–	–	–	–	100.0	4 × 6
0.88	0.17	–	75.31	18.87	–	–	–	–	–	4.77	100.0	3 × 8
39.83	14.82	–	45.00	–	–	–	–	–	–	0.35	100.0	6 × 8
21.43	5.37	–	57.78	–	–	–	–	–	–	15.42	100.0	2 × 3
0.76	0.20	0.03	–	–	–	99.00	–	–	–	–	100.0	0.5 × 1
0.55	0.00	0.01	–	–	–	99.44	–	–	–	–	100.0	1 × 1
11.85	25.95	–	44.93	17.18	–	–	–	–	–	0.10	100.0	3 × 4
25.47	3.64	–	65.25	5.54	–	–	–	–	–	0.10	100.0	2 × 3
1.67	–	–	0.29	–	97.70	–	–	–	–	0.33	100.0	1 × 2
0.12	–	–	0.08	–	99.79	–	–	–	–	–	100.0	100 × 70
0.84	–	–	93.09	–	0.03	–	–	–	–	6.04	100.0	5 × 6
11.29	9.63	–	77.95	0.90	0.22	–	–	–	–	–	100.0	12 × 12
39.61	30.84	0.09	24.52	4.95	–	–	–	–	–	–	100.0	40 × 10
99.38	0.02	0.09	0.17	0.04	0.29	–	–	–	–	–	100.0	4 × 5
63.22	29.13	0.10	6.71	0.17	0.20	–	–	–	–	0.47	100.0	35 × 18
0.21	0.23	0.07	99.49	–	–	–	–	–	–	–	100.0	5 × 7
0.97	0.18	0.05	58.54	–	38.80	–	–	–	–	1.46	100.0	2 × 2
71.97	24.46	0.09	3.47	–	–	–	–	–	–	–	100.0	100 × 30
–	–	–	–	0.24	–	–	–	97.50	1.63	0.63	100.0	10 × 20
0.46	–	–	22.30	–	15.27	–	–	62.56	–	0.09	99.97	4 × 5
15.02	84.20	–	0.46	–	0.32	–	–	–	–	–	100.0	10 × 10
0.71	0.21	–	0.72	0.24	0.08	–	–	87.93	4.17	5.88	99.94	3 × 4
56.11	38.01	–	5.78	–	–	–	–	–	–	0.10	100.0	10 × 8
74.96	20.90	–	4.07	–	–	–	–	–	–	0.07	100.0	5 × 5
–	–	–	0.04	–	–	–	–	91.20	8.53	0.23	100.0	10 × 10
43.39	34.98	–	16.71	–	0.30	–	–	–	–	0.03	95.41	200 × 35
30.26	58.09	–	6.90	0.50	0.23	–	–	–	–	0.10	96.08	10 × 6
3.08	25.28	–	26.30	–	42.54	–	–	–	–	2.80	100.0	5 × 6
1.92	97.30	–	0.58	–	–	–	–	–	–	0.19	99.99	1.5 × 1
1.66	–	–	0.50	–	0.50	–	–	85.56	11.03	0.93	99.98	1 × 1
4.54	64.25	31.21	–	–	–	–	–	–	–	–	100.0	3 × 4
2.77	0.19	–	53.01	–	37.33	–	–	6.70	–	–	100.0	25 × 15
5.62	0.68	–	59.93	–	26.09	–	–	7.42	–	0.26	100.0	5 × 6
1.29	–	–	–	–	–	–	–	91.02	6.68	1.01	100.0	2.5 × 3

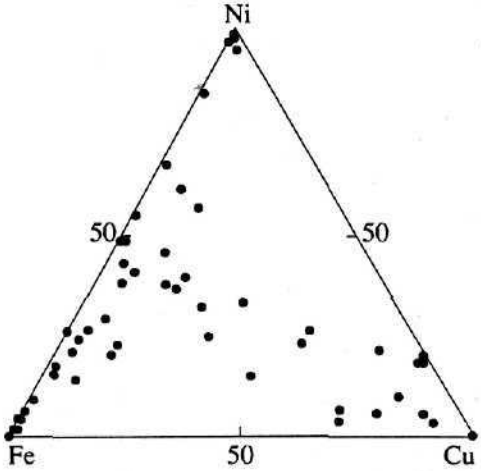

Fig. 2. Data points of natural alloys of the Fe–Ni–Cu system.

diagram (Fig. 2). Alloys of the Fe–Cr–Ni system contain an admixture of W and Mo. The detected natural alloys are compositionally similar to those used as various (stainless and armor) steels in technology. Ferrochrome with the stable chemical formula Fe_7Cr is known as a natural intermetallic compound [8]. Native alloys of the Fe–Cr–Ni system were detected in only three boreholes near an anomaly zone.

Native alloys of copper and zinc make up the second group (Fig. 1c). The intermetallic compound Cu_2Zn, the most stable phase in this system, is widespread in the studied rocks and similar to brass with a stoichiometric composition. It is also known in Alpine-type ultramafic rocks [3] and kimberlites [9].

Rare grains of natural alloys of the Cu–Sn(Ni,Fe) system with the composition of technical brass were encountered in all of the studied samples.

Findings of intermetallic compounds of lead and antimony in tuffisites are very interesting (Fig. 1e). They are observed in both kimberlitic and problematic tuffisites. Native alloys of the Pb–Sb system are known in conglobreccias from the Sidorov sector of the Ichet"yu deposit (Middle Timan) and diamondiferous rocks in the Visher area (Polyudov Ridge) [10]. These alloys may serve are indicators of tuffisites.

Two samples contained small grains of native gold. Native tungsten was detected in the other two samples.

Some native alloys turned out to be unstable in natural conditions. They are gradually transformed into oxides, sulfides (e.g., Ag_2S), sulfates, and others. For example, the surface of Cu–Sn alloys is covered with fine sulfate crystals, while native metals are contaminated with some sulfur.

The abundance of fine-dispersed metallic phases of different compositions in kimberlitic aureoles and the development of metallic films on diamond crystals suggest that native metals are genetically associated with diamond. At the same time, they are also observed as accessory members of kimberlite pipes at the contact with host rocks.

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