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NATIVE ELEMENTS AND METALLIC ALLOYS IN THE MRIYA PIPE, AZOV BLOCK OF THE UKRAINIAN SHIELD: INSIGHTS INTO THE MINERALOGY OF THE EARTH'S MANTLE

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This study examines the occurrence, composition, and origin of native metals and some other highly reduced mineral phases in kimberlite–lamproite magmatic systems, with particular emphasis on the Mriya pipe (Azov Block, the Ukrainian Shield). Native metals are extremely rare in crustal rocks due to relatively high oxygen fugacity, but are more typical of deep mantle environments. Their presence therefore, provides important insights into reduced conditions and deep geodynamic processes. SEM/EDS investigations reveal a diverse assemblage of native metals, including Pb, Sb–Pb, Sn–Pb, Cu–Zn, Fe, and Si–Ti–Fe phases. These occur both as individual grains with spherical, fluidal, and irregular morphologies, and as inclusions within titanium–manganese–iron–silicate (TMIS) spherules and Ti^{3+}-bearing corundum.

Textural features and phase relationships indicate crystallization from melts under highly reducing conditions, most likely during rapid adiabatic cooling in gas-charged flows associated with explosive volcanic activity. Integration of new data with previously published results demonstrates that certain components of the highly reduced mantle mineral association (HRMMA), such as TMIS spherules, Pb-dominated and Cu–Zn particles, are characteristic of kimberlite-like formations. The identification of similar mineral assemblages in some sedimentary deposits on the Ukraine, lacking evidence of weathering, supports their interpretation as primary pyroclastic material capable of scattering over a considerable distance.

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Possible genetic models are considered, including deep mantle sources, plume-related transport, and formation under the influence of reduced CH_4–H_2 fluids, with some hypotheses suggesting origins in the lower mantle or near the core–mantle boundary. The results underscore the significance of HRMMA minerals as potential indicators in diamond exploration and contribute to a better understanding of the formation and preservation of highly reduced mineral systems in the Earth's interior.

Key words: native metals, metallic alloys, highly reduced phases, spherules, mantle, corundum, diamond, kimberlites, the Ukrainian Shield.

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Statement of the problem. Native metals are extremely rare in the rocks of the Earth's crust that are accessible for study. In contrast, native phases are very common in extraterrestrial material. Native phases of Fe, Ni–Fe, Co–Fe, Cu, Mo, Nb, Pt, and platinum group elements (PGE), as well as highly reduced oxygen-free minerals (phosphides, nitrides, carbides, and diamond) have been found in various types of meteorites [10]. Native metals, including Ni–Fe, Ni, Cu, Cu–Zn, Cu–Ni–Zn–Fe, FeC, $(Fe,Ni)_3P$, and $(Fe,Ni,Co)_3P$, have been identified in samples of Lunar basalts and regolith delivered by the Apollo missions [4].

The geological processes associated with the formation of the Earth's lithosphere are characterised by high oxygen activity (oxygen fugacity – fO_2), which is inconsistent with the stability of native elements. Thus, the majority of known sedimentary, metamorphic, and igneous rocks are devoid of metallic phases, with the exception of the highly stable metals Au, Ag, and PGE. In the Earth's mantle, oxygen fugacity is thought to decrease with depth down to the iron-wüstite (IW) buffer and below [7]. This change in oxygen fugacity with depth likely explains the fact that known occurrences of native metals on Earth are associated with ultramafic and mafic rocks of mantle origin, including chromites, picrites, and kimberlites [1; 5; 7; 9; 13–18], and occasionally with basalts [2; 19].

Traditionally, in kimberlite geology, the main focus has been on typical kimberlite minerals, known as kimberlite indicator minerals (KIMs). Exotic native phases from kimberlites, on the other hand, were studied only in an episodic manner. However, the discovery of inclusions of ferropericlase, native metals (Pb, Ni, Fe), carbides, and nitrides in certain varieties of diamonds has provided new data to advance kimberlite geology [7; 8; 11]. Several researchers have suggested that the presence of inclusions of highly reduced phases implies a deep origin for these diamonds (the base of the upper mantle and lower mantle), known as super-deep diamonds. A deeper origin for kimberlites has also been proposed. A model for the formation of proto-kimberlite melt at the base of the lower mantle was presented by S. E. Haggerty [6]. Thin films, including 15 native metals dominated by Fe, Ni, Pd, Au, Ag, Pb, Sn, Sb, and their intermetallic alloys, have been discovered on the surface of diamond crystals from various kimberlite provinces, which is another confirmation of the syngenetic relationship between diamonds and native metals [9]. These observations highlight the importance of studying native metals and oxygen-free minerals for a better understanding of the nature of kimberlites and the diamonds they contain.

We have previously reported on the discovery of native metals in kimberlites and lamproites of the Ukrainian Shield, and in kimberlites of the Arkhangelsk and Yakutsk provinces [15; 21; 22]. The metals occur as individual aggregates of Fe, Cu, Zn, Cu–Zn, Pb, Sb–Pb, Sn–Pb, and Au phases, and also as inclusions of Fe^0 in titanium-manganese-iron-silicate (TMIS) spherules, Mn-Fe in calcium-silicate (CS) spherules, and Si–Ti–Fe in Ti^{3+}-bearing corundum (Fig. 1). All highly reduced mineral objects, including native metals, spherules, as well as associated moissanite SiC and qusongite WC, were termed as a highly reduced mantle mineral association (HRMMA). In this article, we present new results from the study of native metals from the Mriya

pipe (Azov Block of the Ukrainian Shield), as this is the most representative occurrence with a complete suite of HRMMA [22].

Analysis of previous research. There are only a few reports of native metal discoveries in kimberlites. J. B. Dawson [3] provided information on the discovery of Ni–Fe, Fe^0 (in SiC), PGE, Ag, and Cu in kimberlites from various diamond provinces around the world.

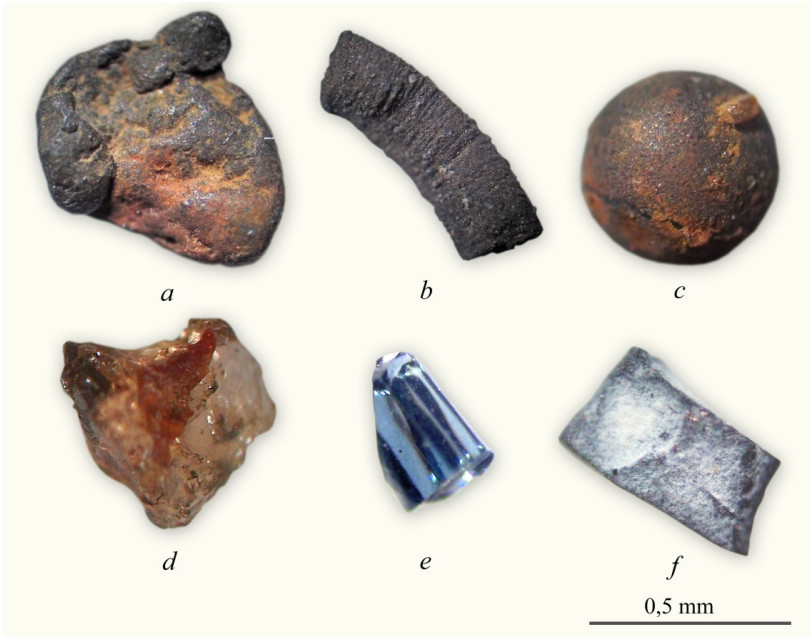

Fig. 1. Association of highly reduced mineral formations from the Mriya pipe: *a* – native lead (Pb); *b* – Zn–Cu alloy; *c* – titanium-manganese-iron-silicate (TMIS) spherule; *d* – Ti^{3+}-bearing corundum; *e* – moissanite; *f* – qusongite

V. K. Marshyntsev first described TMIS, CS, and magnetite-wustite-iron (MW-I) spherules with Fe^0 inclusions in the Mir, Udachnaya, and Aikhal pipes. The same suite of spherules, as well as Sb–Pb spherules, was discovered in the Catoca and Thiuzo pipe, Angola-Congo diamond province.

Findings of TMIS, MW-I spherules containing Fe^0, grains of native Cu, and corundum with Si–Cr–Fe inclusions from the kimberlites of the Karpinskogo-1 pipe in the Arkhangelsk Province have been reported in previous studies [22].

Spherules of pure gold have been discovered in Tertiary lamproites in Spain and in the lamproites of the Mriya pipe in the Ukrainian Shield.

Native metals, including Sb–Pb, Cu, Au, and Al, were discovered in the Ukrainian Shield by O. I. Tishchenko in the Pivdenna and Nadiya pipes, Azov Block [20]. In our previous studies, we reported on native metals discovered in another explosive volcanic structure of the Ukrainian Shield [15; 22]: TMIS spherules with Fe^0, grains of native Fe, and Cu-Zn alloy in the Zelenyi Hai pipe; TMIS spherules with Fe^0 and particles of Cu-Zn alloy in the Gruz'ka-Pivnichna pipes; TMIS lapilli with Fe^0 in the Shchors kimberlite dyke; TMIS spherules with Fe^0, CS spherules with Fe^0 or Mn-Fe inclusions, MW-I spherules, native Cu, and native Zn in the Pivdenna kimberlite pipe.

It is also worth mentioning other well-known occurrences of native metals and associated ultra-reduced phases associated with ultramafic and mafic rocks. HRMMA discovered in podiform chromitites of the Luobusa ophiolite, southern Tibet, includes PGE metal alloys (Os–Ir, Os–Ir–Ru, Pt–Fe, and Ir–Ni–Fe), base-metal alloys (Fe–Ni–Cr, and Fe–Co), native elements (Fe, Ni, Cr, Au, Cu and Si), diamond, moissanite, and iron silicide (Fe–Si) [1]. Ti^{3+}-bearing corundum with a number of highly reduced phases including native Ti, Fe–Cr, Fe–Si, Ti–Si–P, Ti–B–N–C phases, as well as zamboite $FeTiSi_2$, osbornite TiN, khamrabaevite TiC, jingsuiite TiB_2, badengzhuite TiP, zhiqinite $TiSi_2$ and qusongite WC are also present [13; 14].

W. L. Griffin and co-authors carried out detailed studies of highly reduced minerals from Cretaceous pyroclastic rocks on Mt. Carmel, Northern Israel. This mineral assemblage includes diamond, wustite FeO, MW-I spherules, native V, and Ti^{3+}-bearing corundum with entrapped ultra-reduced phases TiC, TiN, SiC, $CrSi_2$, and various Fe–Ti–Zr–(Si, P) melt derivatives [5].

Zhang Z. and co-authors reported the discovery of native gold, native copper, native zinc and moissanite grains in a picrite lava in the Lijiang area within the Emeishan large igneous province, SW China. The authors suggest that this is xenogenic material introduced into the picrite melt from the mantle with a rising plume [18].

Native metals are found in basalts from various regions. For example, Paleocene basalts from Disko Island, Greenland, contain native Fe [2]; native Fe and Cu are found in Vendian (Ediacaran) flood-basalts of Volyn, Ukraine [19].

The research purpose was to study individual particles of native metals and inclusions of native metal phases in TMIS spherules and Ti^{3+}-bearing corundum from the volcaniclastic facies of the Mriya pipe, as well as to summarise published information on native metal finds from kimberlites.

Presentation of the main material. The Mriya pipe is one of a series of lamproite volcanic bodies located in the western part of the Azov Block of the Ukrainian Shield. The Mriya pipe dates back to the Paleoproterozoic and is emplaced in the plagiogneisses and amphibolites of the Drahunsk Unit (AR_1). It is oval in plan, with dimensions of 350 × 500 m, and cup-shaped in cross-section. The main body of the pipe is filled with intrusive lamproites, with an olivine-hornblende-phlogopite composition. The upper part is made up of altered clayey-carbonate volcaniclastic rocks with xenoliths of granites, micaceous hornblendites, olivineites, and dunites with a size of 5–7 cm. The thickness of the volcaniclastic facies deposits is approximately 30 m.

A 500 kg sample of volcaniclastic rock was picked from a depth of 20 m in borehole No. 189A, which has a diameter of 1300 mm. Metal grains were hand-picked from the heavy mineral concentrates using a binocular microscope.

Microanalytical studies were undertaken to examine the compositions and textural characteristics of the metallic phases and the mineral aggregates in which they are hosted.

The inner textures of the spherules were observed using a REMMA-102-02 scanning electron microscope (SEM) at the Ivan Franko National University of Lviv. SEM equipped with a W-cathode. Images were taken using back-scattered electron (BSE) mode. Chemical compositions were obtained using an EDAR energy-dispersive spectrometer (EDS) equipped in the SEM. The optimum operating conditions were an acceleration voltage of 20 kV, a sample current of 1 nA, and a beam diameter of 0.1 μm. The instrument was calibrated in accordance with the NERMA.GEO1.25.10.74GT mineralogy standards. Additionally, at the start of the measurements, the system was fine-calibrated using Cu. Magallanes 3.2 software was used to analyse the spectra.

The HRMMA particles recovered from the Mriya pipe volcanoclastic rocks (see Fig. 1) include spherule-like metal particles, TMIS spherules, Ti^{3+}-bearing corundum aggregates, qusongite WC, and moissanite SiC.

Native metals found in the Mriya pipe can be divided into two groups. Some of them form individual grains (Pb, Pb–Sb, Cu–Zn), whereas others are incorporated into the glass matrix as inclusions in TMIS spherules (Fe^0) and Ti^{3+}-bearing corundum aggregates (Si–Ti–Fe).

Native Pb and Pb-dominated alloys occur as spherule-like particles with plastic and fluidal forms (Fig. 1, *a*; Fig. 2, *a–d*). Some particles are heterophase, with Pb and Sb–Pb phases (Fig. 3, *a*) or Sn and Pb phases (Table 1). Others consist solely of Pb (Fig. 3, *b*). The metal of some particles may contain fine angular fragments of rutile, corundum, and undetermined carbon (see Fig. 3, *b*). These angular carbon fragments exhibit positive relief on the polished surface. It is therefore more likely that this is a diamond rather than graphite or amorphous carbon.

Cu–Zn alloy particles with variable composition (Table 2) form individual grains demonstrating a variety of shapes: spherical, cylindrical, lamellar, irregular, and so on (see Fig. 1, *b* and Fig. 2, *e*, *f*).

Fe^0 inclusions in the TMIS glass spherules are spherical in shape. The size of the inclusions varies greatly, ranging from a few micrometres to hundreds of micrometres, forming the metallic core of the spherules (Fig. 3, *c*; Fig. 4; Table 3). The glass of the spherules may also contain a phase of skeletal crystals of titanium-manganese-iron oxides [3].

Si–Ti–Fe inclusions in corundum usually form a shape close to spherical. The inclusions typically consist of two–three phases with different proportions of components (see Fig. 3, *d*; Fig. 5; Table 3).

Carbides and nitrides, like native metals, carbides and nitrides can form individual grains or occur as inclusions within the corundum aggregate.

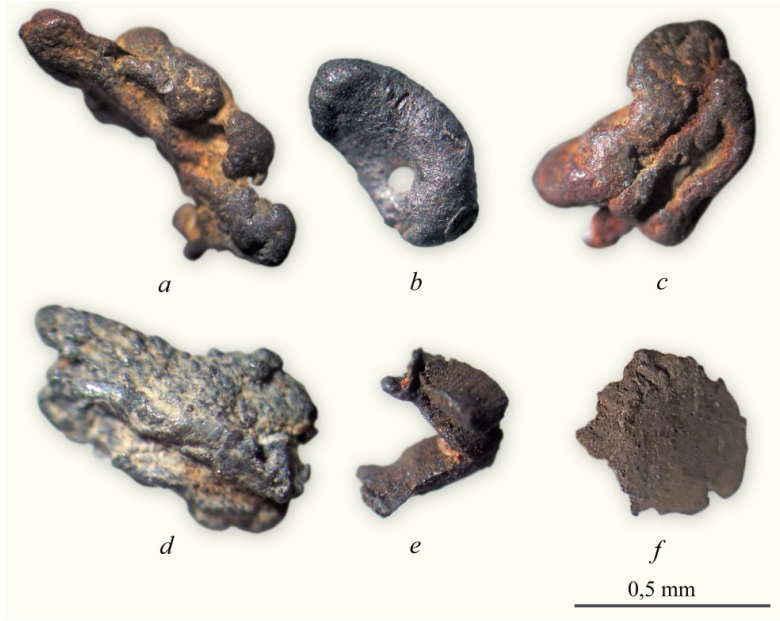

Fig. 2. Particles of native metals from the Mriya pipe: *a–d* – Sb–Pb alloy; *e*, *f* – Zn–Cu alloy

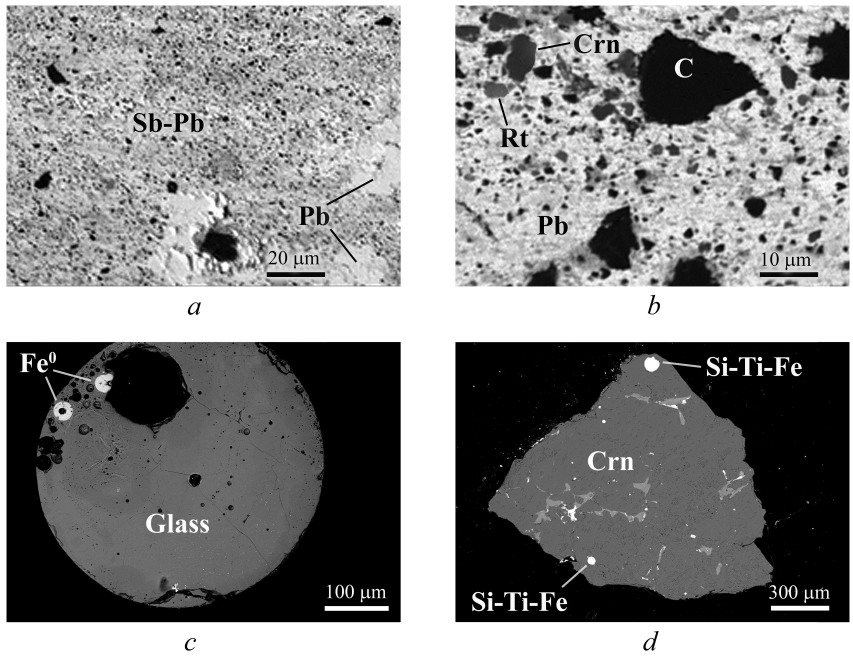

Fig. 3. Characteristic textures of individual metallic particles and inclusions of native metals, BSE-image: *a* – Sb–Pb ground mass with Pb segregations; *b* – Sb–Pb ground mass with inclusions of rutile (Rt), corundum (Crn), and unidentified carbon phase (C) – graphite (?), diamond (?); *c* – spherule composed of titanium-manganese-iron-silicate (glass with spherical aggregates of native iron (Fe^0); *d* – Ti^{3+}-bearing corundum with inclusions of the Si–Ti–Fe phases

Table 1

Composition of Pb, Sb-Pb, and Sn-Pb particles from the Mriya pipe, wt. %*

Sample Lab. No	Spot No	Ti	Fe	Cu	Ag	Sn	As	Sb	Pb	Cd	S	Total
FZ2-46	1	–	–	–	–	100.00	–	–	–	–	–	100.00
	2	–	–	–	–	–	–	–	100.00	–	–	100.00
FZ2-51	3	–	–	–	–	–	–	–	100.00	–	–	100.00
	4	–	–	–	–	–	–	82.08	17.92	–	–	100.00
FZ2-52	1	–	–	–	–	–	–	–	100.00	–	–	100.00
VG-12m	28	–	–	–	–	–	–	3.29	96.71	–	–	100.00
	31	–	–	–	–	–	–	12,67	87.33	–	–	100.00
VG-13m	33	–	–	–	–	–	–	–	100.00	–	–	100.00
	34	–	–	–	–	–	–	–	100.00	–	–	100.00
	35	–	–	–	–	–	–	–	100.00	–	–	100.00
VG-14	36	–	–	–	–	–	–	–	100.00	–	–	100.00

Continuation of table 1

K09-11	1	–	–	–	0.03	81.94	6.21	0.00	11.82	–	–	100.00
K09-14	1	–	–	–	0.81	0.17	24.28	0.00	74.74	–	–	100.00
PUT-101	1	–	–	–	–	–	–	22.01	73.42	1.25	3.32	100.00
	2	–	–	–	–	–	–	21.28	77.47	1.25	–	100.00
KR3-34	3	–	–	–	–	–	–	–	100.00	–	–	100.00
KR3-36	5	–	–	–	–	100.00	–	–	–	–	–	100.00
	6	–	–	–	–	28.56	–	–	71.44	–	–	100.00
	7	–	30.42	–	–	69.58	–	–	–	–	–	100.00
KR3-37	8	–	–	–	–	–	–	–	100.00	–	–	100.00
MR-4-5	4	2.95	3.13	3.59	–	–	–	7.25	83.08	–	–	100.00
	5	–	–	–	–	–	–	–	100.00	–	–	100.00
MR-12	1	–	–	–	–	–	–	–	100.00	–	–	100.00
MR-16	1	–	–	–	–	–	–	–	100.00	–	–	100.00
MR-17	3	–	–	–	–	–	–	7.87	92.13	–	–	100.00
MR-30	1	–	–	1.52	–	–	–	50.27	48.22	–	–	100.00

*Here and below in tables 2 and 3 – analyses by SEM/EDS; «–» (dash) – means beyond of the detection limit.

Qusongite and moissanite occur as individual angular grains. Qusongite is metallic grey in colour, transparent moissanite is coloured in shades of blue and green (see Fig. 1, *e*, *f*).

Osbornite TiN and khamrabaevite TiC are phases trapped within corundum and form near-spherical inclusions. These phases usually form individual inclusions, although khamrabaevite can also occur as a separate phase within Si–Ti–Fe inclusions.

Table 2

Composition of Cu-Zn particles from the Mriya pipe, wt. %

Sample Lab. No	Si	Ti	Fe	Cu	Zn	Sn	Total
KAR2-7	–	–	0.87	64.25	34.88	–	100.00
IYMR-19	–	–	–	87.84	7.87	4.29	100.00
IYMR-21	0.76	2.23	–	85.22	11.79	–	100.00
IYMR-23	–	–	–	65.97	34.03	–	100.00
IYMR-25	–	–	–	84.60	15.40	–	100.00
IYMR-31	–	–	–	66.33	33.67	–	100.00
IYMR-32	–	–	–	91.28	8.72	–	100.00
IYMR-33	–	–	–	56.93	43.07	–	100.00

HRMMA from kimberlite-lamproite formations exhibits distinctive features when compared to those from known non-kimberlite-type magmatic occurrences. Some highly reduced mineral formations are common to the majority of known occurrences represented by various types of igneous rocks: diamond, moissanite, Ti^{3+}-bearing corundum, MW-I spherules with Fe^0, Fe^0 grains, and wustite [1; 2; 5; 13; 14; 17].

Fig. 4. Micrographs of titanium-manganese-iron-silicate (TMIS) spherules

Table 3

Composition of Fe^0 and Si-Ti-Fe inclusions from the Mriya pipe, wt.%

Type of inclusion	Sample Lab. No	Si	Ti	Al	Cr	Fe	Mn	Mg	Ca	K	P	Total
Inclusion in TMIS spherules	FP-8	–	1.05	0.29	–	98.50	–	–	–	–	0.15	100.00
	8SH12	0.76	0.19	0.82	0.23	97.18	–	0.66	0.03	0.12	–	100.00
Inclusions in corundum	SP3-1-2	21.34	25.95	–	2.65	48.02	2.04	–	–	–	–	100.00
	SP3-1-3	15.37	4.33	–	1.75	78.50	0.05	–	–	–	–	100.00
		15.99	5.03	–	1.81	77.17	–	–	–	–	–	100.00
		20.31	29.41	–	1.87	48.02	0.39	–	–	–	–	100.00
		20.01	28.38	–	2.09	49.17	0.35	–	–	–	–	100.00
		23.02	6.90	–	2.24	67.55	0.29	–	–	–	–	100.00
		22.49	6.52	–	2.31	68.42	0.26	–	–	–	–	100.00
	SP3-1-4	16.28	4.00	–	1.53	78.19	–	–	–	–	–	100.00
		19.25	29.41	–	1.12	48.95	–	–	–	–	1.27	100.00
	KR2-16	21.39	7.22	–	1.27	69.06	1.07	–	–	–	–	100.00

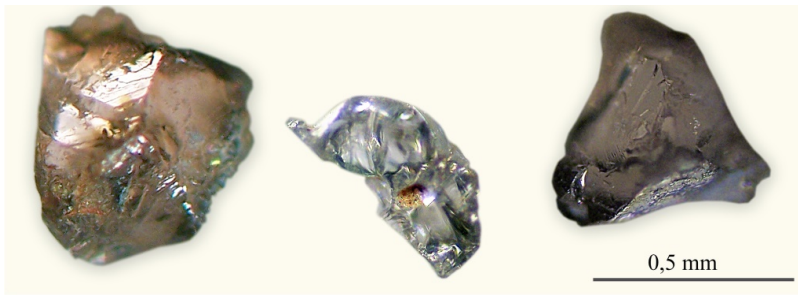

Fig. 5. Micrographs of Ti^{3+}-bearing corundum

However, others, including TMIS spherules, CS spherules, and Sb–Pb spherule-like particles, are found only in kimberlite-lampoite explosive structures [15; 20; 21]. Finds of Cu–Zn alloys and possibly native Au, Cu, and Zn also appear to be associated with kimberlite rocks in general

and with diamonds in particular. Native Pb, Sb, Cu–Zn, and Au on the surface of diamonds and as inclusions within diamonds from kimberlites are also consistent with these observations [9].

Surprisingly, kimberlite-associated varieties of HRMMA, including diamond, TMIS spherules, CS spherules, MW-I spherules, moissanite, Ti^{3+}-bearing corundum, Pb, Sb–Pb, and Au, have been found in sediments of the Vendian (Ediacaran), Cretaceous, Palaeogene, and Neogene sediments in some regions of the Ukraine [22]. It is important to note that these particles show no signs of mechanical or chemical weathering, taking into account that some of them are highly unstable to weathering (CS spherules, Pb, Sb–Pb).

These highly reduced particles may be pyroclastic rather than epiclastic. It is considered that, with rare exceptions, kimberlite pyroclastic deposits are absent beyond the crater rim [12]. It is possible that the explosive stages carrying HRMMA were relatively more energetic, which allowed them to be scattered by air over considerable distances. If this assumption is correct, then a new approach to searching for diamond deposits based on primary pyroclastic HRMMA aureoles may be viable.

The origin of native metals and other components of the HRMMA from kimberlite-lamproite rocks is an open question. Glassy TMIS spherules and spherule-like metal particles can be considered as similar objects belonging to the same class, representing droplets of solidified melt. It is likely that the fine-crystalline aggregate of Ti^{3+}-bearing corundum, which was formed not as a rock constituent but as a hardened fragment of an Al-supersaturated melt, can also be attributed to this class [5]. The shape of the mineral particles and the presence of skeletal crystalline phases imply the formation of glassy and metallic spherules, and likely corundum, from melts in gaseous flows undergoing rapid adiabatic cooling [15].

Furthermore, this flow must be sufficiently free of fragmented material. Thus, the hypothetical spherule-bearing flow and the catastrophic process of intrusion of fragmentary kimberlite material carrying ash, macro- and microcrystals, peletal lapilli, xenoliths, and other incidental material must have substantial differences. Another question is how to reconcile the differing chemistry, redox, and temperature conditions of the formation of the initial kimberlite melt and the parent melts for the glass spherules and Ti^{3+}-bearing corundum [15]. The survival of highly reduced melts within a relatively oxidised kimberlite melt seems problematic also. In essence, we must acknowledge the existence of isolated reservoirs containing metal-, TMIS-, and Al-enriched melts. The question is: where might these form, and how are they related to kimberlite-lamproite volcanism?

Previous models have proposed that native metals were formed in magmatic rocks as a result of interaction with carbonaceous deposits at shallow depths. In most recent publications, highly reduced minerals are interpreted as xenogenic mantle material introduced by rising plumes [1; 2; 11; 13–15; 17; 18]. Zhang R. Y. and co-authors suggest that some super-reducing and ultrahigh-pressure phases were transported by mantle convection from the base of the upper mantle and the mantle transition zone [17]. F. V. Kaminsky claims that super-deep diamonds containing inclusions of metals, carbides, nitrides, and ultrahigh-pressure phases were formed in the lower mantle and thus allows for the possibility of migration of highly reduced material from the mantle basement to shallow levels [7].

According to the concept developed by V. L. Griffin and his co-authors, CH_4-H_2 fluids rising into the upper mantle are responsible for the formation of ultra-reduced phases in magmas of mantle origin. This phenomenon is regarded as a fundamental process [5].

In our previous studies, we adopted a working hypothesis in which HRMMA were formed at the core-mantle boundary [22]. A theoretical model for the formation of TMIS melts (with Fe^0) in the ultra-low-velocity zone (D” layer), as a result of thermochemical interaction, was proposed [15].

Conclusions and prospects for further research. The study has shown that the volcaniclastic rocks filling the upper part of the Mriya pipe contain native metal phases, including Pb, Sb–Pb, Sn–Pb, As–Pb, Cu–Zn, Au, Fe, and Si–Ti–Fe. Pb-bearing, Cu–Zn alloys and Au occur as individual grains of spherical, plastic, and fluidal shapes. Native Fe forms spherical phases within the glass of titanium-manganese-iron-silicate (TMIS) spherules. Si–Ti–Fe phases occur as spherical aggregates trapped in Ti^{3+}-bearing corundum. An assemblage of highly reduced minerals, including diamond, qusongite, moissanite, osbornite, and khamrabaevite, has also been recognized.

A comparison of the highly reduced minerals studied from the Mriya pipe and other kimberlite-lamproitic structures with known occurrences of highly reduced minerals from various magmatic rocks around the world has shown that components such as TMIS spherules, Pb-dominated and Cu–Zn spherule-like particles are typical exclusively for kimberlite-like formations. The same assemblage of highly reduced minerals, supplemented by CS spherules, MW-I spherules, Ti^{3+}-bearing corundum, and moissanite, was also found in sedimentary deposits from various locations in the Ukraine. All these minerals can be interpreted as pyroclastic particles produced by kimberlite explosions. If this hypothesis is correct, the highly reduced minerals could be used as indicator minerals for the search for primary diamond deposits.

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САМОРОДНІ ЕЛЕМЕНТИ І МЕТАЛЕВІ СПЛАВИ ІЗ ТРУБКИ «МРІЯ», ПРИАЗОВСЬКИЙ БЛОК УКРАЇНСЬКОГО ЩИТА: ЗАГЛИБЛЕННЯ В МІНЕРАЛОГІЮ МАНТІЇ ЗЕМЛІ

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Схарактеризовано поширення, склад і походження самородних металів та високовідновлених мінеральних фаз у кімберліт-лампроїтових магматичних системах з акцентом на трубці «Мрія» (Приазовський блок Українського щита). Самородні метали надзвичайно рідкісні в земній корі через відносно високу фугітивність кисню, натомість вони більше характерні для умов глибокої мантії. Тому їхня наявність у магматичних породах є свідченням відновних умов і певних геодинамічних процесів у мантії Землі. За допомогою методів сканувальної електронної мікроскопії й енергодисперсійної рентгенівської спектроскопії (SEM/EDS) виявлено різноманітний набір природних металів, у тім числі фази Pb, Sb–Pb, Sn–Pb, Cu–Zn, Fe та Si–Ti–Fe. Вони представлені як окремими зернами зі сферичною, сферулоподібною та флюїдальною морфологією, так і у вигляді сферичних включень у титан-манган-залізо-силікатних (ТМЗС) сферулах і корунді, що містить домішку Ti^{3+} і високовідновлені мінерали.

Текстурні особливості й фазові взаємовідношення у високовідновлених частинках є доказом кристалізації з розплавів за високовідновлювальних умов, найімовірніше, під час швидкого адіабатичного охолодження в газонаповнених потоках, пов'язаних із вибуховою вулканічною активністю. Інтеграція нових даних з раніше опублікованими результатами засвідчує, що певні компоненти високовідновленої мантійної мінеральної асоціації (ВВММА) – ТМЗС сферули та Pb, Sb–Pb і Cu–Zn сферулоподібні частинки – характерні винятково для кімберлітоподібних порід. Виявлення таких мінеральних асоціацій в осадових відкладах без ознак звітрювання в деяких

регіонах України свідчить про те, що це частинки пірокластичного походження, які мають здатність розсіюватися на значній площі.

Проаналізовано вірогідні моделі походження ВВММА, які охоплюють перенесення мантійними плюмами, формування під впливом відновлювальних CH_4–H_2 мантійних флюїдів; деякі гіпотези пов'язані з можливістю формування в нижній мантії або на межі ядро–мантія.

Мінерали ВВММА, без сумніву, є потенційними індикаторами під час пошуків діамантів. Вони сприяють кращому розумінню геодинаміки формування і збереження високовідновлених мінеральних систем у надрах Землі.

Ключові слова: самородні метали, металеві сплави, високовідновлені фази, сферули, мантія, корунд, діамант, кімберліти, Український щит.

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