= GEOCHEMISTRY =

## Native Minerals and Intermetallides of Noble and Nonferrous Metals in Sediments of the Markov Deep, Mid-Atlantic Ridge

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Received December 15, 2005

**DOI:** 10.1134/S1028334X06060213

The study of modern mineralization in spreading zones of the World Ocean is mainly focused on the precipitation of minerals from hydrothermal fluids and the consequent formation of sulfide edifices [1]. However, the study of ore minerals formed in the course of the alteration of magmatic rocks is no less essential. The present paper reports the first findings of native minerals of noble metals in sediments of the Markov Deep, Mid-Atlantic Ridge.

The bottom morphology, tectonics and neotectonic movements, oceanic lithosphere composition, and bottom sediments were investigated at the Sierra Leone site in the axial Mid-Atlantic Ridge (5-7° N) in 2001-2003 [5] (cruise 10 of the R/V Akademik Ioffe [2, 3] and cruise 22 of the R/V Professor Logatchev [4]). New occurrences of massive sulfide copper mineralization were discovered among metasomatites formed in the course of hydrothermal alteration of apogabbro cataclasites on the eastern wall of the Markov rift deep [2, 4]. The panning of loose bottom sediments (total volume  $1.87 \text{ m}^3$ ) taken with the help of drag corers (15 samples) and box corers (17 samples) yielded 32 concentrates of heavy fraction minerals. The panned samples were processed under laboratory conditions and then investigated with the following standard methods: sieve analysis (fractions +1, 0.5-1, 0.25-0.5, and 0.1-0.25, and -0.1 mm); gravitational, magnetic, and electric fractionations; and complete mineralogical analysis of fractions and separation of native elements [8]. In addition, V.V. Knauf extracted native metals and intermetallides from fraction -0.25 mm of panned samples I1032 and L1147 using the gravitational separator of an original construction (AOZT NATI Patent, 1996, Russia). Table 1 shows that 13 panned samples yielded the following native minerals and intermetallides of noble and nonferrous metals that can concentrate in placers (grain size >0.1 mm): native gold (Au, Ag), isoferroplatinum (Pt<sub>3</sub>Fe), tetraferroplatinum (PtFe), native lead (Pb), native tin (Sn), native copper (Cu), and Zn-bearing copper (Cu, Zn). Samples L1093 and L1104 yielded moissanite (SiC).

Bottom sediments used for the panning are mainly composed of carbonate sediments and foraminiferal oozes with a minor admixture of the sandy fraction coupled with fragments of magmatic rocks (basalt, volcanic glass, and basic and ultrabasic rocks) and gastropods. The sandy fraction is mainly composed of foraminifers, chloritized green rock fragments, volcanic glass, quartz, calcite, and serpentine. The content of heavy fraction minerals in sediments varies from 0.n to 100*n* g. The heavy fraction is dominated by pyroxenes (primarily, clinopyroxene), magnetite, minerals of the epidote-zoisite group, and occasional chrome spinels (Table 2). The panned samples also contain indicatorminerals of hydrothermal activity, such as iron sulfides (pyrite, marcasite, pyrrhotite, and troilite); copper sulfides (chalcopyrite, chalcocite, and bornite); sphalerite, hematite, pyrolusite, atacamite, barite, aragonite, apatite, and so on; unidentified hydroxides of Fe, Mn, and subordinate Ta and Nb; and native minerals and intermetallides of noble metals. These minerals are universally found as separate grains at the Sierra Leone site. They can tentatively be united into the following mineral assemblages (Table 2): (1) pyroxene-epidote and massive sulfide assemblages (sample I1032); (2) chrome spinel-pyroxene assemblage (sample I1064); (3) magnetite-pyroxene and barite-hematite assemblages (sample I1061); and (4) magnetite-amphibole-pyroxene assemblage with a minor content of the heavy fraction (sample I1054 and others).

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	Sample											
		I1(	)32			I1(	)64		I1061			
Mineral	Grain size fraction (mm)											
	+0.5	0.5-0.25	-0.25	X	+05	0.5-0.25	-0.25	X	+0.5	0.5-0.25	-0.25	X
Magnetite	0.9	1.5	2.4	2.2	5.1	15.5	13.0	11.5	s.p.	12.7	35.1	20.0
Magnetite and rock intergrowths	n.d.	2.2	2.3	0.6	15.2	n.d.	n.d.	3.8	n.d.	0.7	0.7	0.7
Magnetite nodules	n.d.	n.d.	s.p.	s.p.	n.d.	n.d.	n.d.	n.d.	s.p.	3.3	1.5	2.8
Pyroxene group	5.0	11.8	20.0	12.3	13.5	46.5	57.4	38.9	n.d.	51.7	21.9	24.7
Epidote-zoisite group	33.1	51.1	53.2	45.9	n.d.	n.d.	n.d.	n.d.	15.0	n.d.	0.6	4.0
Olivine	n.d.	n.d.	n.d.	n.d.	s.p.	n.d.	n.d.	s.p.	n.d.	n.d.	n.d.	n.d.
Garnet	n.d.	n.d.	s.p.	s.p.	n.d.	n.d.	s.p.	s.p.	n.d.	n.d.	s.p.	s.p.
Amphibole	n.d.	1.4	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2	0.9
Chlorite group	n.d.	1.1	n.d.	0.3	6.4	n.d.	n.d.	2.3	21.0	n.d.	n.d.	5.4
Chrome spinels	0.5	1.5	s.p.	0.7	32.6	16.1	17.4	22.6	n.d.	n.d.	n.d.	n.d.
Ilmenite	n.d.	n.d.	n.d.	s.p.	n.d.	n.d.	n.d.	n.d.	n.d.	5.0	21.9	10.5
Iron sulfides	9.9	4.4	2.9	5.6	n.d.	0.8	s.p.	0.3	n.d.	n.d.	n.d.	n.d.
Copper sulfides	21.8	13.8	6.7	13.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hematite	24.8	12.3	6.2	14.3	n.d.	11.1	n.d.	3.4	20.0	20.8	6.3	14.0
Pyrolusite	n.d.	n.d.	n.d.	n.d.	n.d.	s.p.	n.d.	s.p.	n.d.	n.d.	n.d.	n.d.
Atacamite	n.d.	1.0	3.8	1.6	n.d.	n.d.	s.p.	s.p.	n.d.	s.p.	s.p.	s.p.
Rock fragments	4.0	s.p.	2.4	2.1	27.1	11.0	10.4	16.7	44.0	4.9	0.9	13.1
Zircon	n.d.	s.p.	s.p.	s.p.	n.d.	s.p.	n.d.	s.p.	n.d.	n.d.	0.7	0.2
Apatite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	0.3	n.d.	n.d.	n.d.	n.d.
Barite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	s.p.	8.1	3.3
Sphene	n.d.	n.d.	s.p.	s.p.	n.d.	n.d.	s.p.	s.p.	n.d.	n.d.	n.d.	n.d.
Aragonite	n.d.	n.d.	n.d.	n.d.	n.d.	s.p.	0.8	0.2	n.d.	0.8	n.d.	0.2
Gold	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	s.p.	n.d.	s.p.
	I	I	Magnet	ic and el	ectroma	gnetic fra	actions (	g)	I	1		I
Magnetic	0.03	0.11	0.30	0.44	0.52	1.63	0.74	2.89	< 0.01	0.02	0.06	0.08
Electromagnetic	3.09	6.21	5.83	15.13	2.04	8.91	4.60	15.55	0.06	0.10	0.08	0.24
Nonelectric	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.36	0.36	< 0.01	< 0.01	0.02	0.02
Heavy fraction in general	3.12	6.32	6.13	15.57	2.56	10.54	5.70	18.80	0.06	0.12	0.16	0.34

**Table 1.** Minerals of the heavy fraction in sediments of the Markov Deep, Mid-Atlantic Ridge (wt %)

Note: The complete mineralogical analysis was carried out by M.V. Kosolapova. (X) Mean value; (n.d.) not detected; (s.p.) single points.

Two grains of rounded equant grains of *isoferroplatinum* (size 0.1–0.15 mm) were found in sample I1032. Isoferroplatinum makes up the intergrowth with tetra-ferroplatinum (Fig. 1a) or platinum oxide. Traces of other elements of the platinum group are absent in both isoferroplatinum (Table 3, analyses 1–3) and tetraferroplatinum (analysis 4). Such isoferroplatinum and tetra-ferroplatinum are commonly found in cumulates of polyphase zonal dunite–pyroxenite–gabbro massifs (in particular, gabbro [7–9]) and placers of the platinum mineralogical–geochemical type [10].

*Native gold* was found as slightly rounded lumps in fraction 0.25–0.5 mm of sample 11061 (Fig. 1b). Intergrowths with hematite were also found. Native gold has a fineness of ~750 (Table 3, analyses 5–8). Intergrowth of the native gold with hematite and their close association with barite in panned samples (Table 2) suggest that primary ores include the gold–hematite–barite assemblage that is commonly formed at the latest stage of the deposition of massive sulfide ores [1].

*Native lead* is the most abundant mineral (Table 3). This mineral is found as lumpy, oblate, and oblong

Element	I1032 2.1.1.	I1032 2.1.2.	I1032 2.2.1.	I1032 2.2.2.	I1061 1.1.1.	I1061 1.1.2.	I1061 1.1.3.	I1061 1.1.4.
	1	2	3	4	5	6	7	8
Au	n.d.	n.d.	n.d.	n.d.	78.2	75.3	74.1	76.9
Pt	90.3	90.4	90.3	76.5	n.d.	n.d.	n.d.	n.d.
Sn	n.d.							
Ag	n.d.	n.d.	n.d.	n.d.	22.0	22.7	24.9	22.6
Cu	n.d.	n.d.	n.d.	1.5	n.d.	n.d.	n.d.	n.d.
Fe	9.2	9.3	9.6	21.7	n.d.	n.d.	n.d.	n.d.
Total	99.50	99.70	99.90	99.70	100.20	98.02	98.99	99.48
Element	I1054 1.1.1.	L1092 2.5.1.	L1116 3.3.1.	L1116 3.3.2.	L1127 3.2.1.	L1129 3.4.1.	L1130 4.1.1.	L1130 4.2.1.
	9	10	11	12	13	14	15	16
Pb	96.8	95.3	97.6	97.6	97.5	98.1	96.4	96.8
Sb	n.d.	4.38	n.d.	n.d.	n.d.	0.68	0.59	0.66
Sn	2.12	n.d.						
Ag	0.63	n.d.	n.d.	n.d.	n.d.	n.d.	0.63	0.82
Pd	0.70	n.d.	0.83	0.87	n.d.	n.d.	0.78	0.67
Total	100.26	99.69	98.46	98.43	97.46	98.81	98.40	98.91
Element	L1157 3.4.1.	I1054 1.1.2.	I1054 1.1.3.	L1147 2.6.1.	L1092 2.1.1.	L1092 2.2.1.	L1093 1.1.1.	L1105 3.1.1.
	17	18	19	20	21	22	23	24
Pb	97.0	2.73	3.38	n.d.	98.7	98.0	96.4	100.8
Sb	n.d.	3.96	3.75	n.d.	n.d.	n.d.	n.d.	n.d.
Sn	n.d.	92.7	92.0	99.7	n.d.	n.d.	n.d.	n.d.
Ag	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.	n.d.
Pd	0.76	n.d.						
S	n.d.	n.d.	n.d.	n.d.	1.41	1.48	1.38	1.40
Total	97.78	99.36	99.51	99.70	100.09	99.51	97.74	102.20
Element	L1127 3.3.1.	L1127 3.1.1.	L1130 2.2.1.	L1130 2.2.2.	L1130 2.2.5.	L1147 5.2.1.	L1147 3.2.1	L1147 7.4.1.
	25	26	27	28	29	30	31	32
Pb	98.9	n.d.						
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	35.3	36.5
Cu	n.d.	98.2	97.1	98.6	98.4	99.5	62.5	62.4
Fe	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	1.80	0.40
S	1.51	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.
Total	100.43	98.22	97.05	98.63	98.52	99.80	99.60	99.30

**Table 2.** Results of the analysis of native minerals and intermetallides (wt %) from sediments of the Markov Deep, Mid-Atlantic Ridge

Note: Analyses were carried out with a LINK-1000 energy-dispersive spectrometer at the Institute of Precambrian Geology and Geochronology, St. Petersburg (M.D. Tolkachev, analyst). Analytical conditions: accelerating voltage 25 kV, current 1–3 nA, probe diameter 2–3 μm, counting time 100 s; standards: pure metals (Pt, Os, Ir, Ru, Rh, Pd, Au, Ag, Fe, Ni, Cu, Pb, and Zn) and synthetic compounds (PbS, Cu<sub>2</sub>S, FeAsS, and PtAs<sub>3</sub>); (n.d.) not detected.



Native minerals and intermetallides of noble and nonferrous metals from sediments of the Markov Deep, Mid-Atlantic Ridge. Photomicrographs were taken by M.D. Tolkachev with an AVT-55 scanning electron microscope at the Institute of Precambrian Geology and Geochronology, St. Petersburg. (a) Aggregate of isoferroplatinum (Pt<sub>3</sub>Fe) and tetraferroplatinum (PtFe); (b) native gold (Au,Ag) and hematite intergrowth; (c) aggregation of native lead (with traces of Sn, Pd, and Ag) and native tin (with traces of Sb, Pb, and Ag) (the native lead is light-colored); (d) intergrowth of native copper with oxychlorides of Cu and Pb: (Phase 2)  $Cu_{16}Cl(OH)_{15} \cdot nH_2O$ , (phase 3)  $Pb_9Cu_5Cl_2(OH)_{26}$ , (calumetite)  $Cu(OH,Cl)_2 \cdot 2H_2O$ .

grains (0.1–2 mm) with traces of Pd, Sb, and Ag (Table 3, analyses 10–17). In one sample, we found a subgraphic aggregate of native lead and tin (Fig. 1c). The native lead contains traces of Sn, Pd, and Ag (Table 3, analysis 9), while the native tin contains traces of Sb, Pb, and Ag (analyses 18, 19). Unusual lamellar segregations (0.15–1.5 mm) with ~1.42 wt % S (analyses 21–25) can be referred to as new phase 1 (Pb<sub>11-X</sub>S). They are probably cryptocrystalline native lead–galena aggregates with an ideal constant composition (166Pb · 17PbS). One grain showed the intergrowth of phase 1 (Pb<sub>11-X</sub>S) with augite and its composition corresponds to Ca<sub>1.00</sub>(Mg<sub>0.77</sub>Fe<sub>0.28</sub>Ti<sub>0.02</sub>)<sub>1.07</sub>[(Si<sub>1.79</sub>Al<sub>0.15</sub>)<sub>1.94</sub>O<sub>6</sub>] (Table 3, analysis 21).

*Native tin* also occurs as homogeneous lumps 0.2 mm across (Table 3, analysis 9).

*Native copper* is widespread as lamellar and extended interstitial segregations (0.1–2 mm). Native copper is generally represented by the pure variety (Table 3, analyses 26–30). Analyses 31 and 32 correspond to the Fe- and Zn-bearing copper (Cu<sub>0.63</sub>Zn<sub>0.35</sub>Fe<sub>0.02</sub>). X-ray images of such Zn-bearing copper from ultramafic rocks of the Koryak Highland [11] and hydrothermal deposits of the Urals [1] indicated that this mineral is an analogue of  $\alpha$ -Cu or synthetic  $\alpha$ -brass. The rim of native copper often makes up intergrowths with oxychlorides of Cu and Pb (Fig. 1d). They include calumetite (Cu(OH,Cl)<sub>2</sub> · 2H<sub>2</sub>O), atacamite (Cu<sub>2</sub>Cl(OH)<sub>3</sub>), and

Element	I1032 2.1.1.	I1032 2.1.2.	I1032 2.2.1.	I1032 2.2.2.	I1061 1.1.1.	I1061 1.1.2.	I1061 1.1.3.	I1061 1.1.4.
	1	2	3	4	5	6	7	8
Au	n.d.	n.d.	n.d.	n.d.	78.2	75.3	74.1	76.9
Pt	90.3	90.4	90.3	76.5	n.d.	n.d.	n.d.	n.d.
Sn	n.d.							
Ag	n.d.	n.d.	n.d.	n.d.	22.0	22.7	24.9	22.6
Cu	n.d.	n.d.	n.d.	1.5	n.d.	n.d.	n.d.	n.d.
Fe	9.2	9.3	9.6	21.7	n.d.	n.d.	n.d.	n.d.
Total	99.50	99.70	99.90	99.70	100.20	98.02	98.99	99.48
Element	I1054 1.1.1.	L1092 2.5.1.	L1116 3.3.1.	L1116 3.3.2.	L1127 3.2.1.	L1129 3.4.1.	L1130 4.1.1.	L1130 4.2.1.
	9	10	11	12	13	14	15	16
Pb	96.8	95.3	97.6	97.6	97.5	98.1	96.4	96.8
Sb	n.d.	4.38	n.d.	n.d.	n.d.	0.68	0.59	0.66
Sn	2.12	n.d.						
Ag	0.63	n.d.	n.d.	n.d.	n.d.	n.d.	0.63	0.82
Pd	0.70	n.d.	0.83	0.87	n.d.	n.d.	0.78	0.67
Total	100.26	99.69	98.46	98.43	97.46	98.81	98.40	98.91
Element	L1157 3.4.1.	I1054 1.1.2.	I1054 1.1.3.	L1147 2.6.1.	L1092 2.1.1.	L1092 2.2.1.	L1093 1.1.1.	L1105 3.1.1.
	17	18	19	20	21	22	23	24
Pb	97.0	2.73	3.38	n.d.	98.7	98.0	96.4	100.8
Sb	n.d.	3.96	3.75	n.d.	n.d.	n.d.	n.d.	n.d.
Sn	n.d.	92.7	92.0	99.7	n.d.	n.d.	n.d.	n.d.
Ag	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.	n.d.
Pd	0.76	n.d.						
S	n.d.	n.d.	n.d.	n.d.	1.41	1.48	1.38	1.40
Total	97.78	99.36	99.51	99.70	100.09	99.51	97.74	102.20
Element	L1127 3.3.1.	L1127 3.1.1.	L1130 2.2.1.	L1130 2.2.2.	L1130 2.2.5.	L1147 5.2.1.	L1147 3.2.1	L1147 7.4.1.
	25	26	27	28	29	30	31	32
Pb	98.9	n.d.						
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	35.3	36.5
Cu	n.d.	98.2	97.1	98.6	98.4	99.5	62.5	62.4
Fe	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	1.80	0.40
S	1.51	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.
Total	100.43	98.22	97.05	98.63	98.52	99.80	99.60	99.30

Table 3. Compositions of minerals of native elements from sediments of the Markov Deep, Mid-Atlantic Ridge (wt %)

Note: Analyses were carried out with a LINK-1000 energy-dispersive spectrometer at the Institute of Precambrian Geology and Geochronology, St. Petersburg (M.D. Tolkachev, analyst). Analytical conditions: accelerating voltage 25 kV, current 1–3 nA, probe diameter 2–3 μm, counting time 100 s; standards: pure metals (Pt, Os, Ir, Ru, Rh, Pd, Au, Ag, Fe, Ni, Cu, Pb, and Zn) and synthetic compounds (PbS, Cu<sub>2</sub>S, FeAsS, and PtAs<sub>2</sub>); (n.d.) not detected. two new compounds that can probably be referred to as phase 2 ( $Cu_{16}Cl(OH)_{15} \cdot nH_2O$ ) and phase 3 ( $Pb_9Cu_5Cl_2(OH)_{26}$ ).

The association of native forms of lead, tin, and copper with the Zn-bearing copper is probably a middleand low-temperature product related to the metasomatism of ultrabasic and basic rocks. Intergrowths of augite with native lead, the presence of Pd in the native lead, and the admixture of Fe in the Zn-bearing copper [11] testify to the association of metasomatites with mafic rocks. This conclusion is supported by the findings of native forms of lead, tin, and copper in association with the Zn-bearing copper in massive sulfide copper deposits among metasomatites related to the hydrothermal alteration of apogabbro cataclasites on the eastern wall of the Markov Deep, Mid-Atlantic Ridge [5].

Thus, sediments of the Markov Deep contain rather large (>0.1 mm) grains of native minerals and intermetallides of noble and nonferrous metals that can be concentrated in placers. Intermetallides of Pt and Fe are likely to be derivates of the gold–hematite–barite assemblage that forms at late (low-depth) stages of the formation of hydrothermal massive sulfide ores. The association of minerals of native forms of lead, tin, and copper with the Zn-bearing copper may be related to the hydrothermal transformation of ultrabasic and basic rocks accompanied by massive sulfide copper mineralization. The association of these minerals of native elements in sediments can also serve as a prospecting guide for sulfide mineralization at both the Sierra Leone site, in particular, and the seafloor, in general.

## ACKNOWLEDGMENTS

The authors thank V.V. Knauf, M.V. Kosolapova, I.B. Markova, and E.S. Radina for assistance in the successful accomplishment of investigations, as well as all participants of cruises 10 (R/V *Akademik Ioffe*) and 22 (R/V *Professor Logatchev*).

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