Native silver-copper alloy in metalliferous sediments from the East Pacific Rise axial zone (20° 30'-22° 10'S)

Vesselin M. DEKOV [a] and Zhelyazko K. DAMYANOV [b]

[a] Department of Geology and Paleontology, Sofia University, 15 Tzar Osvoboditel Boulevard, 1000 Sofia, Bulgaria.

[b] Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 92 Rakovski Str., 1000 Sofia, Bulgaria.

ABSTRACT

In the axial metalliferous oozes of the East Pacific Rise, accessory amounts of shiny metallic grains occur. Optical microscope, SEM, microprobe and XRD analytical techniques have permitted detailed mineralogical study of these grains and established a hitherto unknown (in seafloor sediments, rocks and ores) $Ag_{71.5}Cu_{28.5}$ alloy. An endogenous hypothesis of the formation of the extremely small amounts of these alloy particles dispersed in the metalliferous sediments is suggested on the basis of a precise investigation of alloy micromorphology, chemical composition, inner texture and temporal distribution. According to the proposed hypothesis, native silver-copper grains are formed as ultra-accessory micro-segregations in a silicate matrix during the mantle pre-chamber evolution of the basic and ultrabasic systems beneath the spreading zones, under high P-T and low fO_2-fS_2 conditions. The alloy formation was probably realized with falling temperature in the following sequence: crystallization of β crystals ($T \cong 785\,°C$) --> crystallization of $\alpha + \beta$ eutectic mixture ($T=779.4\,°C$) --> α and β exsolution ($T<779.4\,°C$) to an end composition $Cu + Ag$-Cu eutectic $+ \alpha_{ii}$ (Ag_{ii}). Mantle convection and plumes transport the silicate melt matrix and the silver-copper segregations contained therein to the earth's crust. The short residence time of the magma in the shallow crust chamber and its rapid crystallization in the crust and neovolcanic rift zone are responsible for the preservation of metallic grains in the silicate groundmass. During the cyclic tectono-magmatic processes in the rift zone, the host basic ridge rocks have undergone desintegration and native $Ag_{71.5}Cu_{28.5}$ alloy, together with other rock clasts, disperse into the near-axial metalliferous sediments. The maximum quantity of native silver-copper particles occurs in sediments formed during periods of intense volcanic activity.

RÉSUMÉ

Un alliage argent-cuivre natif dans les sédiments métallifères de la dorsale du Pacifique Est (20° 30'-22° 10'S).

Les sédiments calcaires métallifères de la dorsale du Pacifique Est contiennent des grains métalliques brillants. Une étude détaillée (microscope optique, MEB, microsonde, XRD) a permis de déceler dans ces grains un alliage $Ag_{71.5}Cu_{28.5}$ inconnu jusqu'à présent dans les sédiments, roches et minerais océaniques. La micromorphologie de l'alliage, sa composition chimique, sa structure interne et sa répartition temporelle, suggèrent une formation endogène : ces micro-ségrégations d'argent-cuivre natif se formeraient dans un milieu de composition silicate basique ou ultra-basique pendant une évolution mantellique

pré-chambre en dessous de la zone de diffusion, dans des conditions de hautes température et pression (T-P) et de basse fugacité fO_2-fS_2. L'alliage s'est probablement formé dans une période de refroidissement selon la séquence suivante : cristallisation de cristaux β (T $\cong$ 785 °C) --> cristallisation du mélange eutectique $\alpha + \beta$ (T = 779.4 °C) --> exsolution α et β (T < 779.4 °C), pour aboutir à la composition finale Cu + Ag-Cu eutectique + α_{ii} (Ag_{ii}). La convection et les plumes mantelliques déplacent le magma porteur des éléments argent-cuivre dans la croûte terrestre. Le bref temps de résidence du magma à faible profondeur dans la chambre magmatique crustale et sa cristallisation rapide dans la croûte terrestre dans la zone dorsale néo-volcanique sont responsables de la conservation des grains métalliques dans la matrice silicate. Pendant les cycles tectono-magmatiques de la zone du rift, les roches basiques se désintègrent et l'alliage natif $Ag_{71.5}Cu_{28.5}$ se disperse avec des particules rocheuses dans les sédiments métallifères à proximité de l'axe de la dorsale. La plus grande quantité de particules d'argent-cuivre natif se trouve dans les sédiments formés pendant les périodes d'activité volcanique intense.

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INTRODUCTION

The zero-valent state of a number of elements in some hydrothermal ores and metasomatites is well known (Ramdohr, 1975; Novgorodova, 1983, 1994). Various native metals and alloys have been discovered in the past 25 years, during intensive study of the accessory minerals in sedimentary formations and igneous complexes (from acid to ultrabasic) from the continental parts of the lithospheric plates (Kovalskii, 1981; Novgorodova, 1984, 1994). Unknown before then, native nickel (Ramdohr, 1967), cadmium (Oleynikov et al., 1979), chromium (Yusupov et al., 1982), titanium (Trunilina et al., 1988) and manganese (Kim et al., 1989) were found. Still debated are the findings of high-oxygen affinitive elements ($\Delta G_f^o < 0$) in a metallic state, such as silicon (Bird and Weathers, 1975; Novgorodova et al., 1989; Pankov and Spezius, 1989) and aluminium (Oleynikov et al., 1978; Novgorodova, 1979).

The genesis and preservation of the native metal and alloy particles presented in various seafloor formations have recently been intensively studied. It has been established that the pelagic sediments formed in a strong oxic environment (Shterenberg and Vassileva, 1979; Arsamakov et al., 1988; Shterenberg, 1993) and Fe-Mn nodules (Baturin et al., 1984; Yushko-Zakharova et al., 1984), as well as seafloor tholeiitic basalts (Shnyukov et al., 1981; Shterenberg et al., 1993), contain the same assemblage of native metals and alloys. The spatial and temporal distribution of native particles in the various seafloor formations and the occurrence of native metals in the hydrothermal plumes (Jedwab and Boulègue, 1984) are thought to result from tectono-magmatic activity at the active plate boundaries - mid-ocean ridges, back-arc spreading centres and transform fault zones (Shterenberg, 1993; Dekov et al., 1995).

Copper is one of the most widespread native minerals in the hydrothermally altered basalts of the second oceanic layer (Leinen et al., 1986), massive sulphides of the ocean rift zones (Minniti and Bonavia, 1984; Hannington et al., 1988; Rona, 1988) and metalliferous sediments

immediately overlying the basalt basement of the ocean floor (Zemmels et al., 1972; Jenkyns, 1976; Marchig et al., 1986). Findings of native silver are rather rare in the oceanic massive sulphides (Hekinian et al., 1980; Minniti and Bonavia, 1984; Rona, 1988; Halbach et al., 1993), metalliferous sediments (Shterenberg et al., 1981, 1988) and ferromanganese crusts (Bolton et al., 1986).

The present work extends the Dekov et al. (1995) study on metallic occurrences in hydrothermally influenced sediments. The first findings, to our knowledge, of a natural silver-copper alloy in the metalliferous sediments of the East Pacific Rise (EPR) axial zone (20° 30'-22° 10' S) are reported here.

GEOLOGICAL SETTING

In late 1987 and early 1988, the 4th cruise of R/V *Geolog Fersman* (VNIIOkeangeologiya, St. Petersburg) was conducted in the southeastern Pacific Ocean (Fig. 1A), the main objective being to collect novel data about the tectono-magmatic activity along the EPR crest. The largest field of metalliferous sediments in the world is located in this region, which is why it has become the classic area for studies of recent hydrothermal activity and related massive sulphides and hydrothermal sediments (Boström, 1973; Dymond et al., 1973; Marchig et al., 1986; etc.).

Research was carried out on sediment samples collected by means of flow-through tubes, square samplers and bottom grabs during the above-mentioned cruise from twenty geological sites (Fig. 1B). Detailed results were published (Krasnov et al., 1992; Dekov, 1994). The sites were situated within the EPR axial zone between the two zones of overlapping spreading centres (20° 40' and 22° 08' S after Francheteau and Ballard, 1983 and Krasnov et al., 1988, respectively).

The studied ridge sector is far from landmasses and is uninfluenced by fluvial inflow. The spreading centre is characterized by an ultra-high accretion rate - 16.2 cm/yr (Rea, 1978). A large number of massive sulphide chimneys
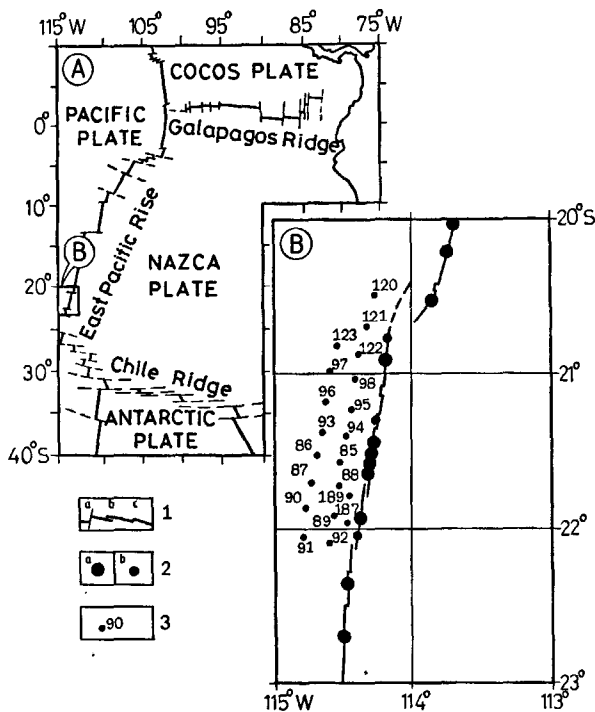
Figure 1

(A) Sketch map of the southeastern part of the Pacific Ocean. (B) Diagram of the survey area. 1 = ridge axis discontinuities: a = transform faults, b = zones of overlapping spreading centres, c = devals; 2 = location of the fields of massive sulphides in the EPR rift zone (after Bäcker et al., 1985; Renard et al., 1985; Krasnov et al., 1988; Marchig et al., 1988): a = large fields, b = smaller fields; 3 = location of sediment sample stations.

have been detected in the narrow axial rift valley during submersible dives and seafloor television survey (Bäcker et al., 1985; Renard et al., 1985; Krasnov et al., 1988; Marchig et al., 1988).

The sedimentary cover of the studied area comprises a large variety of strongly oxidized, horizontally bedded calcareous metalliferous oozes. These consist of: biogenic $CaCO_3$ (foraminiferal and coccolith tests); hydrothermal Fe- and Mn-oxyhydroxides; basaltic clasts, authigenic clay minerals; and very small amounts of allogenic aeolian material (Dekov, 1994).

MATERIALS AND METHODS

The aim was to clarify the spatial and temporal distribution of the expected metallic particles and their possible genetic link with the evolution of the tectono-magmatic events. Selected sediment core horizons (thickness, 1 cm; intervals between the horizons - 1 to 10 cm) from all twenty sites were studied.

Natural wet samples (100 ml) of metalliferous sediments, hermetically stored in polythene bags, were washed with distilled water to remove soluble salts. The grain size distribution was determined through wet sieve analysis and sediment fraction separation.

The extremely low contents of metallic particles prevent the use of conventional bulk mineralogical techniques (e.g. XRD) for particle diagnosis.

It is clearly impossible to isolate and examine metallic particles from the fine (< 0.10 mm) sediment fractions, for the following reasons:

- Their fine size renders systematic microscopic examination and separation from other heavy minerals with similar optical properties practically impossible.

- The specific gravity of the most abundant metallic aluminium is very close to that of the light minerals - calcite, plagioclases, quartz, etc. (which together make up > 98 % of the bulk sediment), and does not allow the metallic particles to be separated by means of heavy liquids.

- The very small amounts and the physical properties of the possible metallic occurrences ($Al°$, $Sn°$, $Cu°$, etc.) make centrifugal, magnetic and electromagnetic separation particularly problematic.

Therefore, only coarse fractions (0.10-0.25, 0.25-0.50, 0.50-1.00, 1.00-2.00, > 2.00 mm) were examined by a binocular stereomicroscope for metallic particles. Particle form, colour and lustre were also determined. Preliminary diagnoses of the metallic grains were performed by means of semi-quantative EDS analyses on their natural faces.

The micromorphology, size and chemical composition of six representative silver-copper alloy specimens, mounted in organic resin to prepare polished sections, were investigated by SEM JEOL T-300 with a Link 860-500 EDS and ZAF/PB program, SEM JEOL Superprobe - 733 with a System-5000 ORTEC EDS and SPRINT-III program and Philips SEM-515 with an EDAX PV 9100 EDS system (with an operating voltage of 20 kV and electron beam diameter of 1 μm). The following standards and X-ray lines were used: pure synthetic silver (Ag $L\alpha$) and pure synthetic copper (Cu $K\alpha$). The detection limits were 0.5 wt.%. Area scanning (10 × 7 μm; 100 s exposition) was applied to establish the composition of the silver-copper alloy; point analyses - for diagnoses of phase inclusions; X-ray mapping and line-scanning - to clarify the spatial phase distribution.

The trace elements (those less than 0.1 wt.%) were determined semi-quantitatively by a laser microanalyzer LMA-1 (Carl Zeiss) combined with a PGS-2 spectrograph. The detection limits (in wt.%) were: 0.001 for Mg, Si, Ca, Al, and 0.0001 for Ti, Fe. The laser beam diameter was 10 μm.

The X-ray diffraction patterns of the metallic particles were obtained with a 57.3-mm Gandolfi camera employing Ni-filtered Cu $K\alpha$ radiation without internal standard (with an operating voltage of 40 kV and a beam current of 19 mA).

RESULTS

Preliminary EDS analyses of separated metallic particles have established the presence of a silver-copper alloy hitherto unknown in seafloor rocks, sediments and ores. Also present are numerous small, irregular grains of native aluminium (Dekov et al., 1995) and tin, as well as copper-zinc, tin-lead and tin-copper alloys.

Grains of silver-copper alloy (16 grains) were found only in the 4F-121 core sediments. About 70 % of them

Table 1

Studied intervals and fractions from the sediments of core 4F-121 (20° 42.8' S, 114° 15.9' W, 3225 m – depth of ocean, 20 km – distance from ridge axis, flow-through tube)

| Core intervals (cm)	Studied fractions (mm)	Number of silver-copper particles	Specimen identification
0-1	0.10-0.25	N.D.*	–
	0.25-0.50	N.D.	–
7-8	0.10-0.25	N.D.	–
	0.25-0.50	N.D.	–
15-16	0.10-0.25	N.D.	–
	0.25-0.50	N.D.	–
25-26	0.10-0.25	3	H9.S2
			H9.S3
			H9.S4
	0.25-0.50	2	H9.S1
			H9.S5
29-30	0.10-0.25	N.D.	–
	0.25-0.50	1	H8.S1
30-31	0.10-0.25	N.D.	–
	0.25-0.50	N.D.	–
33-34	0.10-0.25	3	H15.S3
			H15.S6
			H15.S7
	0.25-0.50	N.D.	–
37-38	0.10-0.25	N.D.	–
	0.25-0.50	1	H16.S3
50-51	0.10-0.25	N.D.	–
	0.25-0.50	N.D.	–
52-53	0.10-0.25	N.D.	–
	0.25-0.50	1	H18.S2
62-63	0.10-0.25	1	H19.S2
	0.25-0.50	N.D.	–
65-66	0.10-0.25	N.D.	–
	0.25-0.50	N.D.	–
78-79	0.10-0.25	3	H21.S1
			H21.S2
			H21.S3
	0.25-0.50	N.D.	–
80-81	0.10-0.25	1	H22.S8
	0.25-0.50	N.D.	–

* Examined for but not detected.
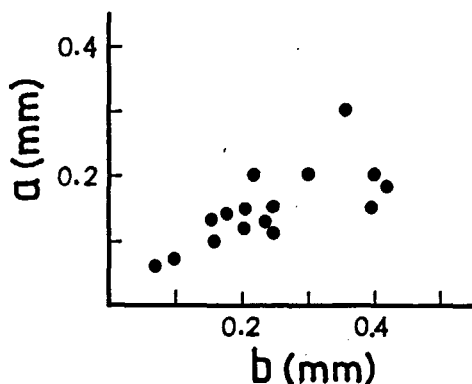
Figure 2

Grain size distribution of the studied silver-copper particles by their normally oriented axes a and b.

(11 grains) were concentrated in a fraction 0.10-0.25 mm (Table 1). The lamellar habit of the particles permitted determination of their dimensions in two perpendicular directions (minimum and maximum) (Fig. 2). The grains are length-slow in one direction reaching 420 μm and up to some tens of μm thick.

The silver-copper alloy particles consist mostly of lamella-shaped (Fig. 3A), rarely irregular-shaped isometric grains (Fig. 3B), non-magnetic, all with a metallic lustre. Specimens found in the interval from the seabottom interface to the horizon 29-30 cm are silver-white to grey-white in colour, whereas those from the rest of the core section (30-100 cm) are yellowish-white to dark yellow. On the surfaces of some specimens, parallel striations (Fig. 3A) and cracks of noncoaxial shear (Fig. 3C) are seen. They are similar to those observed on native metals and alloys from both the lunar regolith (see Fig. 1B in Ashihmina et al., 1979) and continental volcanic products (see Fig. 2 in Glavatskih, 1990). These striations and cracks might be attributable to tectonic deformation. Also clearly visible is the micro-layer inner grain texture (Fig. 3C, D) the thickness of which ranges from 2 to 5 μm. The particles are slightly soft when pressed by a steel needle.

Microprobe investigations and SEM observations in both secondary (SEI) and back-scattered (BEI) electrons revealed that the particles consist of a matrix of silver-copper eutectic mixture with scarce copper inclusions (Fig. 4A). The components of the eutectic mixture are indiscernible visually under a reflected light microscope. The matrix is optically isotropic, bright-white with a pale cream-coloured shade and without internal reflections. The fine eutectic texture (Fig. 4B) is SEI revealed after treatment by 8 g/l H_2SO_4 plus 7.6 g/l CrO_3, recommended for contrast etching of silver-copper alloys (Malishev and Roumyantsev, 1987). Native copper inclusions with a rose-yellowish shade and reflectance lower than the silver-copper eutectic mixture can be observed under higher magnifications. These are mostly elongated (isometric ones are rare), quite often oriented in one direction (Fig. 4C) up to 10 μm in length and 3-4 μm in width. The copper inclusions are not widespread and uniformly distributed in the eutectic substrate, but usually occur near the particle periphery, and "repeat" its contours (Fig. 4D).

The composition of the eutectic mixture (Table 2) was determined using area microprobe analyses because of the unusual textural features of the alloy. Fairly constant average ratios were established:

Ag/Cu (wt.%) = (71.5 ± 0.9)/(28.5 ± 0.5);

Ag/Cu (at.%) = (59.7 ± 0.7)/(40.3 ± 0.7);

Ag/Cu (at.ratio) = (2.96 ± 0.08)/2.

The small size of the copper inclusions does not permit precise quantitative analyses. Their Ag content (20 ± 3 wt.%) is much higher than the theoretical possible maximum of about 8 wt.% at 779.4 °C (Champion et al., 1981) (Fig. 5). This fact may not be due only to the inclusion of eutectic matrix volumes when analysing such fine inclusions.

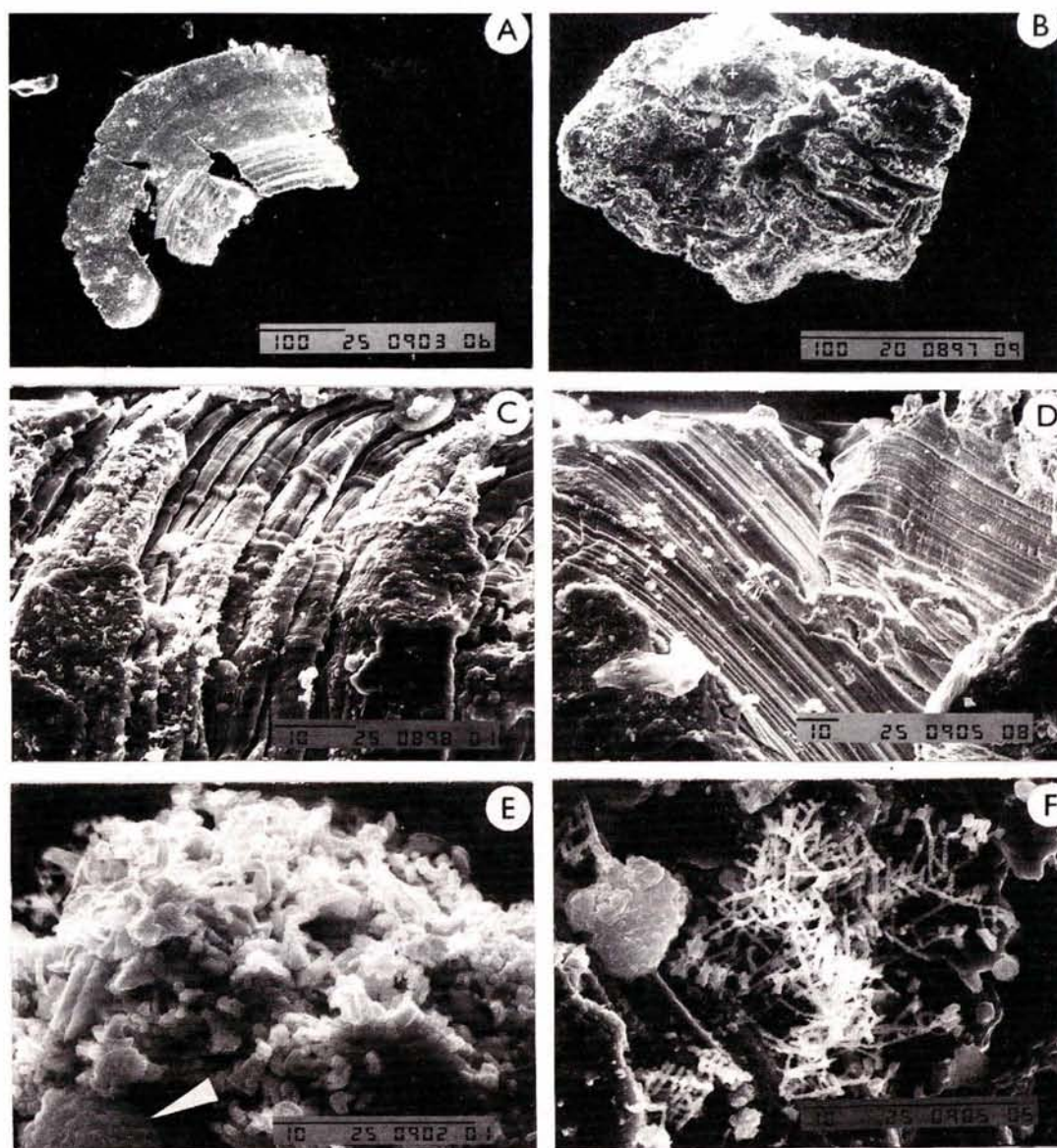Copper and silver are uniformly distributed within the eutectic mixture (of all six specimens examined) and

Figure 3

Scanning electron micrographs of native silver-copper alloy. (A) General view of a lamella-shaped silver-copper particle (H16.S3); (B) irregular-shaped isometric silver-copper particle (H9.S4) with a ferromanganese microcrust on the surface (upper part with a crest at the centre; the visible crust/particle contact is arrowed); (C) cracks of incoaxial shear on the surface of a silver-copper grain (H9.S3); (D) micro-layer texture of a silver-copper grain (H18.S2); (E) sulphur-containing isometric-grained aggregates and bacteriomorphous filaments and Fe-Mn oxyhydroxide micronodule (arrow) on the silver-copper alloy surface (H14.S3); (F) sulphur-containing bacteriomorphous filaments on the surface of a silver-copper particle (H18.S2). Scale bars equal 100 μm (A,B) and 10 μm (C-F).

the copper inclusions are notable on that background (Fig. 4G, I). Line scanning shows the narrow limits of Ag/Cu fluctuations in the eutectic mixture Fig. 4E, F.

One specimen, H8.S1, was analysed by means of a laser microspectral analyzer (four point analyses). The following trace elements (in wt.%) were detected: Ti, Mg (0.1-0.01); Si (0.01-0.001); Fe, Ca and Al (< 0.001).

All reflections of the native silver and the basic reflections of the native copper were established on the X-ray diffraction pattern of the silver-copper alloy (Table 3). The measured d_{Ag} values are slightly decreased and d_{Cu} values are increased in comparison with the standards. The same holds true in respect of the calculated cell dimensions: for silver crystal lattice $a_{(400)}$ = 4.08 Å (standard PDF # 4-783;

a = 4.0862 Å); and for copper - $a_{(311)}$ = 3.622 Å (standard PDF # 4-836; a = 3.6150 Å).

A very intriguing trend has been observed in the temporal distribution of the silver-copper particles (Fig. 6). During episodes of intense volcanic activity in the rift [fixed in the axial sediment cover by maximum contents of the geochemical and mineralogical criteria, *i.e.* Ti, olivines, basic plagioclases and glasses (Dekov, 1994)], the number of silver-copper particles in the sediments increases relative to their number in sediments formed during periods of quiescent volcanic activity synchronous with the increasing hydrothermal discharge (*i.e.* maximum Fe content) (Fig. 6).

Microscopic and electron microprobe studies identified typical hydrogenetic/hydrogenetic-diagenetic black, earthy massive to laminated Fe-Mn oxyhydroxide microcrusts and
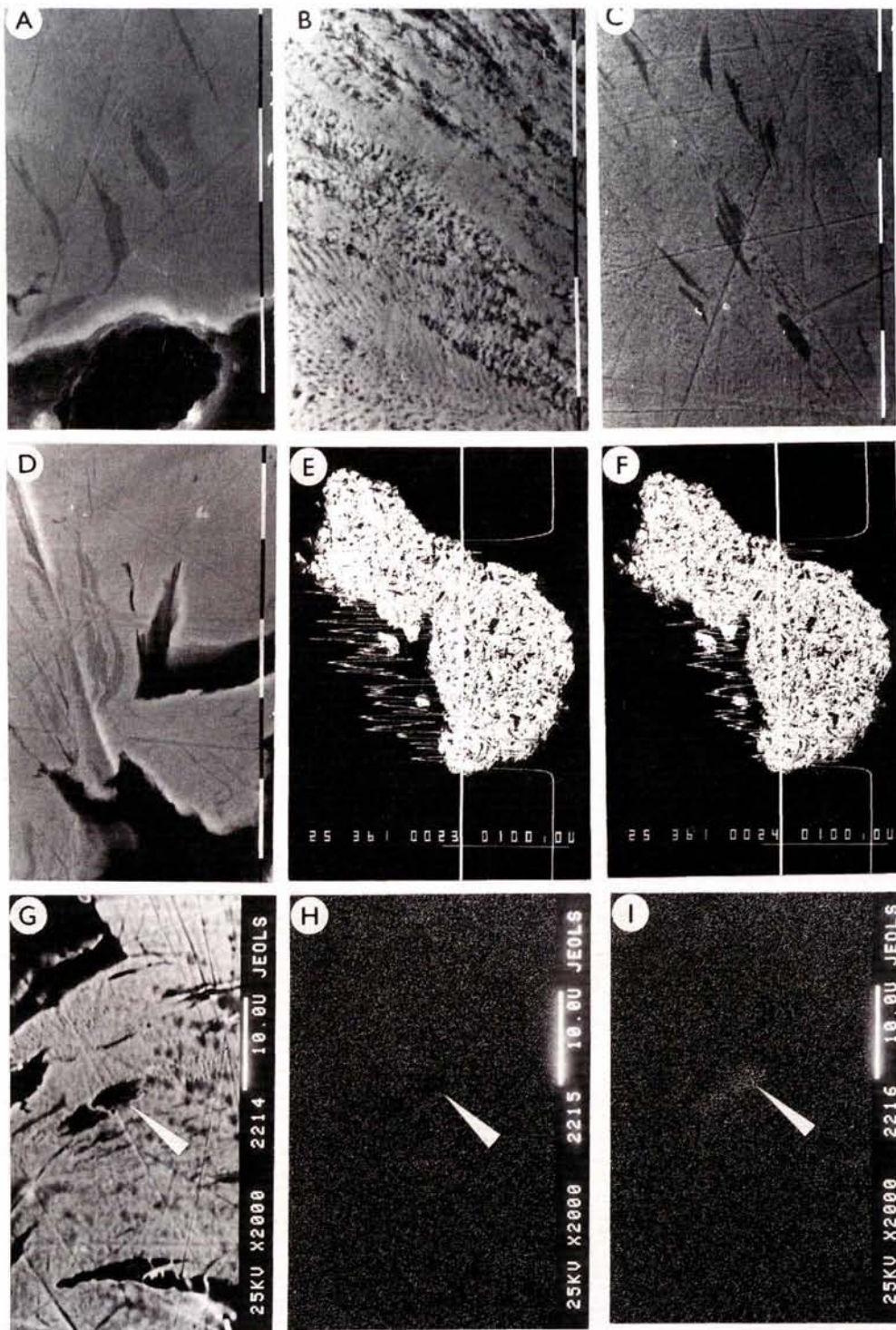
Figure 4

Internal microtextural peculiarities of silver-copper alloy. (A) Copper inclusions (dark tones) in the silver-copper eutectic matrix (SEI) (H8.S1). (B) Eutectic texture of a silver-copper matrix (after treatment by 8 g/l H_2SO_4 plus 7.6 g/l CrO_3; SEI) (H14.S3). (C) Elongated-lamellar copper inclusions (dark tones) in a silver-copper matrix (SEI) (H8.S1). (D) Copper inclusions (dark tones) subparallel to the particle periphery (SEI) (H8.S1). (E) BEI and Ag L_α X-ray line scanning of a silver-copper alloy particle (H8.S1). (F) BEI and Cu K_α X-ray line scanning of the same silver-copper particle shown in (E). (G) BEI of a copper inclusion (arrow) in a silver- copper matrix (H8.S1). (H) Electron microprobe Ag L_α X-ray mapping of the same area as shown in (G). (I) Electron microprobe Cu K_α X-ray mapping of the same area shown in (G); arrows - a copper inclusion. Scale bars equal 100 μm (E,F) and 10 μm (A-D,G-I).

micronodules on the surface of some metallic particles (Fig. 3B, E). Obviously, these ferromanganese crusts and nodules were formed on the metallic microsubstrate after the deposition of silver-copper particles. The crust thickness ranges from 100 to 150 μm. The composition (microprobe data) displayed large variations: Mn = 14.6-19.9; Fe = 16.1-13.2; Ni = 0.2-0.4; Co = 0.1-0.5 (all in wt. %).

SEM investigations have revealed accumulations of two other types of mineral microphases growing on the silver-

Table 2

Selected electron microprobe analyses (area scanning) of silver-copper eutectic mixture; specimens from the investigated sediments of core 4F-121.

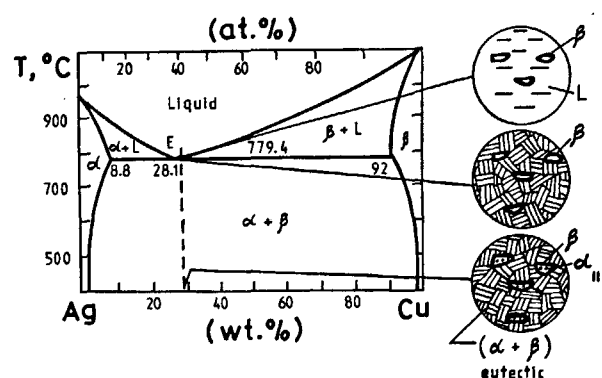| Specimen identification	Core interval (cm)	Fraction (mm)	# of analyses	Ag (wt.%)	Ag (at.%)	Cu (wt.%)	Cu (at.%)	Total (wt.%)
H8.S1	29-30	0.25-0.50	1	72.19	59.81	28.57	40.19	100.77
			2	72.55	60.44	27.97	39.56	100.52
			3	72.68	60.11	28.41	39.89	101.09
H15.S3	33-34	0.10-0.25	1	70.89	58.98	29.04	41.02	99.93
			2	71.82	59.63	28.64	40.37	100.45
			3	70.87	59.00	29.00	41.00	99.87

Figure 5

Diagram of equilibrium of silver-copper alloy (after Champion et al., 1981) and proposed microtextures at different solidification stages of native Ag$_{71.5}$Cu$_{28.5}$ alloy from the investigated sediments (see explanation in the text).

copper alloy surface. The first is represented by isometric-grained aggregates located, cluster-like or scattered, as single spherulites on the surface (Fig. 3E). Their diameter varies from 0.5 to 2.0 µm. They are spatially associated with fine bacteriomorphous filaments, 0.5-1.0 µm wide by up to 6.0 µm long (Fig. 3E, F). EDS analyses of these two mineral microphases have shown the presence of Ag, Cu and S. The fine size of the phases makes unambiguous mineral identification difficult.

DISCUSSION

Variations in the diagnostic features and physical properties of native silver and its alloys are an additive function of their composition (Atanassov, 1976). The decrease of $a_{Ag\ measured}$ compared to $a_{Ag\ standard}$ is due to the insertion of small amounts of copper (with lesser atomic radius) in the silver crystal lattice because of their low mutual solubility (Hansen and Anderko, 1958; Champion *et al.*, 1981; Malishev and Roumyantsev, 1987). Respectively, the increase of $a_{Cu\ measured}$ relative to $a_{Cu\ standard}$ is a result of the substitution of copper by silver atoms (with higher atomic radius) in the copper crystal lattice.

The theoretically unexpected high silver content revealed in the copper inclusions might be due not only to the microprobe analytical constraints ("inclusion" of matrix silver by the electron beam), but in all likehood to possible

Table 3

XRD data for silver-copper alloy from the investigated sediments of core 4F-121.

Silver-copper alloy (present study*)		Silver-3C, syn (PDF # 4-783)			Copper, syn (PDF # 4-836)		
I**	d (Å)	I/I$_1$	d (Å)	hkl	I/I$_1$	d (Å)	hkl
10	2.353	100	2.3590	111			
2	2.090				100	2.0880	111
4	2.040	40	2.0440	200			
1	1.817				46	1.8080	200
4	1.438	25	1.4450	220			
1	1.281				20	1.2780	220
5	1.224	26	1.2310	311			
3	1.170	12	1.1796	222			
1	1.092				17	1.0900	311
					5	1.0436	222
1	1.020	4	1.0215	400			
2	0.932	15	0.9375	331			
2	0.907	12	0.9137	420	3	0.9038	400
3	0.828	13	0.8341	422	9	0.8293	331
					8	0.8083	420

* Specimen H18.S2; core interval (52-53); fraction 0.25-0.50 mm; exposition time 34 h.
** Intensities estimated visually.

silver microinclusions within. This presumption is based on the fact that the copper inclusions do not contain similar high silver contents everywhere in the polished sections studied, and can be explained by analysing the silver-copper equilibrium diagram (Fig. 5).

The composition of the investigated silver-copper alloy (Table 2) is quite near to the eutectic point and localized at the hypereutectic field (Fig. 5). The formation of the hypereutectic Ag$_{71.5}$Cu$_{28.5}$ alloy was probably realized with falling temperature in the following sequence:

(i) crystallization of β crystals at T $\cong$ 785 °C -->

(ii) crystallization of α + β eutectic mixture at T = 779.4 °C -->

(iii) α and β exsolution at T < 779.4 °C to end compositions Cu + Ag-Cu eutectic + α_{ii} (Ag$_{ii}$) (Fig. 5).

The group association of the copper inclusions and their localization close to the periphery of the particles is probably an indication of density liquation resulting from the different densities of the initially formed copper crystals
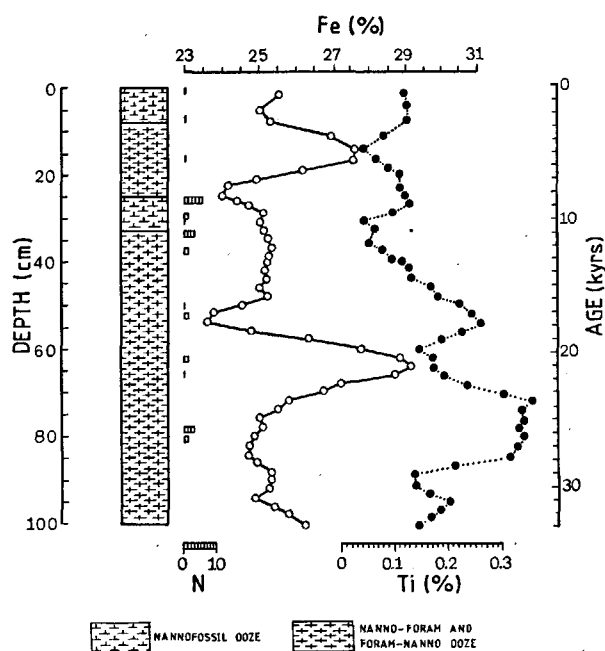
Figure 6

Lithologic section of the core 4F-121 and vertical distribution of Fe and Ti (both on a carbonate-free basis) and of the number of silver-copper particles (N) in the core sediments. Lithology described by M.A. Levitan (IO RAS). The lithologic symbols are those used in the Init. Repts. DSDP. Absolute ages determined by the radiocarbon method (Dekov and Kuptsov, unpublished data).

and the parent metallic smelt. The low-density copper crystals "float" to the upper metallic phase interface and, as a result, are situated mainly near the particle periphery (Fig. 4D), whereas in the inner grain part the eutectic predominates.

The parallel-orientated distribution of the copper inclusions (Fig. 4C) can be interpreted as a result of so called "double-cell" growth mechanism forming eutectic textures typical for native metals (Vorobev, 1990).

Native silver-copper intergrowths identified as eutectic were first described by Veen (1925) (cited in Betechtin *et al.*, 1958; Ramdohr, 1975, because of the authors' unfamiliarity with the original paper) for Lake Superiour (USA) native copper deposits. In these occurrences, the copper content is more than the silver one. The description of eutectic copper-silver mixture and copper phenocrysts in a typical "eutectophyroid" texture (Betechtin *et al.*, 1958), suggests some analogy without any commitment with regard to the genesis of those deposits. In comparison with the microscopically discernible eutectoid copper-silver intergrowths from the Lake Superiour occurrences, the eutectic mixture described here is very fine and visually inconspicuous. The latter fact is indicative of relatively rapid crystallization.

Reducing conditions are know to be required for the formation of native metals and alloys. This is why the occurrences of the unique silver-copper alloy in the oxidizing environment of the EPR metalliferous sediments are intriguing from a genetic point of view.

Some available facts lend support to the idea that the investigated – $Ag_{71.5}Cu_{28.5}$ – alloy has a natural origin.

– Sampling devices, shipboard operations, sieving, shipboard and laboratory atmospheres exclude any possibility of artificial contamination of the samples by silver-copper particles.

– The composition of the investigated particles differs from that of anthropogenic alloys. The most typical components of industrial silver-copper alloys, such as Zn, Sn and Cd (from 1.0 to 10.0 wt. %) (Precious metals, 1984; Malishev and Roumyantsev, 1987) are missing, and orthodox lithogenous admixtures (Ti, Mg, Si, Al, Ca, Fe) are present. The extremely low levels of trace-elements in the examined alloy are in agreement with the opinion that the native metals and alloys are pure and contain ultra-low trace concentrations (Zayakina, 1981).

– There is an absence of associated stainless steel flakes, which could have contaminated the samples; and an association of the silver-copper alloy with native aluminium, tin and copper-zinc, tin-lead, tin-copper alloys, which is characteristic of some oceanic sediments (Shterenberg, 1993) and continental basic and ultrabasic rocks (Kovalskii, 1981).

– All particles are found in sediment layers formed in pre-tecnogenic times (older than 9 ka) (Fig. 6). Radiocarbon, geochemical, lithologic and biostratigraphic data rule out any resedimentation (Dekov, 1994).

– There is some incrustation of silver-copper grains by Fe-Mn oxyhydroxide microcrusts and nodules. Oceanic Fe-Mn nodules and crusts are thought to have ultra-low rates of accretion - about 1 - 6 mm/Ma (Ku, 1977). Near active spreading centres these formations grow very rapidly, however (up to 100 mm/Ma (Scott *et al.*, 1974)). Assuming that the Fe-Mn crusts observed had grown at the maximum rate measured in similar conditions (~ 100 mm/Ma), about 1000 years would be necessary to form the thinnest of them (0.1 mm). In our opinion, this fact excludes the possibility of a tecnogenic origin of the substratum of these oxyhydroxide crusts.

The fresh and sharp edges and microlayers of the examined particles – evidence of a very local source (extensive alteration of shape during transport would smooth the soft grains), as well as the remoteness of the studied area from the landmasses, suggest that a fluvial and/or aeolian origin of the silver-copper particles is unlikely.

We believe that a meteoritic origin of the silver-copper particles has also to be rejected, as cosmogenic intermetals and alloys consist mainly of Fe, Ni and Cu (Ramdohr, 1973; Frondel, 1975; Lavrukhina and Baryshnikova, 1978) and have spherical or drop-like shapes.

Previous investigations of environmental influences on the distribution and enrichment of Ag in oceanic sediments have suggested that the most likely removal areas are those in which oxygen-depleted conditions are maintained (Turekian, 1968). In these environments, Ag is believed to be precipitated as silver sulphide after initial supply to the sediments with accumulating organic carbon. We have found no convincing evidence for similar environmental controls acting on the sediments studied. The near-axial sediment cover hosting the metallic particles shows no signs of significant oxygen depletion, lying much deeper

(> 2900 m) than the oxygen minimum zone. Therefore, it is supposed that a pelagic *in situ* origin of the metallic silver-copper particles under study is hardly possible.

With the foregoing considerations in mind and given the results of detailed studies on the micromorphological, structural and chemical peculiarities of the $Ag_{71.5}Cu_{28.5}$ alloy and its associations and temporal distribution, it is possible to assume a local ridge-crest source of this natural alloy, related to the tectono-magmatic processes in the rift zone.

The current understanding of hydrothermal processes in the spreading centres (Rona, 1984; Lissitzin *et al.*, 1990) leads us to believe that the crystallization and precipitation of an alloy composed of chalcophiles ($Ag_{71.5}Cu_{28.5}$) in submarine hydrothermal fluids with high sulphur activity (Von Damm *et al.*, 1985 *a*, 1985 *b*; Von Damm and Bischoff, 1987) are thermodynamically impossible.

Bacterial-like filaments on the surface of studied metallic grains (Fig. 3E, F) and the grain inner structure (Fig. 4A-C) permit speculation concerning a bacterial genesis (direct or mediated) of the silver-copper alloy. We consider our studies are not sufficient to advance a meaningful biogenic hypothesis, and the question of a bacterially mediated origin of the Ag-Cu alloy remains open to further discussion.

The lack of dendritic crystals typical for hypergenetic silver and copper (Posukhova, 1978; Novgorodova, 1989) precludes a ready explanation of a hypergenetic origin for the investigated alloy. On the other hand, the close associations of native silver and copper observed in the zones of weathering of some polymetallic deposits (Ramdohr, 1975) have different features: lamellae of native silver are covered by rims or spots of native copper as a result of secondary replacement. Hence, it is difficult to explain the formation of the examined alloy by weathering of ridge-crest massive sulphides.

Native metals and alloys can also be formed during the serpentinization of basic and ultrabasic rocks under conditions of oxygen deficiency. It has been suggested that the reducing agent is hydrogen released during serpentinization (Ramdohr, 1967). We consider that low-temperature syn-serpentinization reduction reactions could not produce the observed eutectic high-temperature silver-copper alloy. Furthermore, petrological examinations on the bedrock recovered from the rise axis in the 21° S area (Renard *et al.*, 1985; Dill *et al.*, 1992) have revealed that these rocks consist of several types of basalt. No serpentinized species have been observed.

Experiments on the interaction between basaltic glasses and model fluids (Mironov *et al.*, 1988) have corroborated the assumption that native silver could have formed during hydrothermal alteration of ridge basalts. Silver has been intensively leached from the glasses and fixed in their periphery as metallic microlamellae ($Ag°$). Whether hydrothermal ridge systems could generate $Ag_{71.5}Cu_{28.5}$ alloy in this fashion, in the ridge basic rocks is difficult to say at present. Petrological studies (Dill *et al.*, 1992) suggest that high-temperature wall rock alteration in this spreading segment began at 400-350 °C. Therefore, it

appears that hydrothermal alteration of ridge rocks could not play a significant role in the formation of $Ag_{71.5}Cu_{28.5}$ alloy with similar complex textural features.

Bolton *et al.* (1986) have described occurrences of native silver grains (as large as 50 μm) in ferromanganese crusts from a back-arc setting in the southwestern Pacific. With regard to the origin of these native particles, a local metal-enriched igneous source has been seen as responsible for their presence in the Fe-Mn crusts studied. This source, on degradation, has liberated silver particles which have been entrapped in overlying Fe-Mn crusts and associated sediments. This mode of origin, according to the authors, is supported by the presence of native silver grains embedded in slightly altered basalt.

Data on the presence of native silver-copper alloy in oceanic basic and ultrabasic rocks are not available. Until unequivocal specimens of $Ag_{71.5}Cu_{28.5}$ are found *in situ*, within bedrock, the origin of this alloy will remain a matter of debate. However, in view of the above discussions, it seems possible that native silver-copper alloy may be present as an accessory mineral in these rocks. As yet unanswered is the question whether the silver-copper alloy was primarily magmatic or born through hydrothermal ridge rock alteration.

The composition and complex inner texture of the silver-copper particles, the fine grain size characteristic of endogenous native silver and microlayers (Posukhova, 1978) similar to the native silver polysynthetic twinning (Apollonov *et al.*, 1988), together with the above review, all support the idea that a high-temperature magmatic origin is responsible for the metallic particles studied here. The observed alloy features cannot be adequately explained without introducing the concept of genesis in a reducing environment.

It is presumed that the mantle has oxidation states ranging from equilibrium with $Fe°$ at the core-mantle boundary to equilibrium with Fe^{3+}-rich silicate melts in the near-crust region. Oleynikov (1981) proposes a petrologic model of metallization of the silicate melt which exists during the pre-chamber evolution of the magmatic systems, under high P-T and low fO_2 and fS_2 conditions.

A plausible model invoked by Lukanin and Kadik (1984) suggests that in the zones of nascence of basaltic magmas, the separation of the melt during progressive melting favours a further increase of the CH_4 and H_2 levels and the decrease of fO_2. This can result in the reduction of some elements to their metallic state.

Wood *et al.* (1990) have provided convincing evidence (*see* Fig. 8 in Wood *et al.*, 1990) that at fluid saturation (in the C-O system) and equilibrium with graphite, increasing degrees of melting (due to decompression or heating) would yield decreasing fO_2. Thus, mid-ocean ridges where the peridotitic upper mantle partially melts to produce MORB appear to be zones of potential reduction. Wood *et al.* (1990) have also argued that in mantle zones in the stability field of Fe and below the IW buffer, the fluids are essentially composed of reduced phases (> 80 % CH_4).

The presence of very reduced gases (such as hydrogen, hydrocarbons, carbon monoxide) trapped in some terrestrial

native metals and alloys (Bird and Weathers, 1975; Aleshin *et al.*, 1986) can be interpreted as evidence of the significant role of reduced fluid species throughout native metal formation. Also, the hydrogen/hydrogen-methane composition of the gas phases in the upper mantle rocks (Lutz *et al.*, 1976) and the high flow of abiogenic (mantle or basaltic) hydrogen and methane above the mid-ocean ridges (Welhan and Craig, 1983; Merlivat *et al.*, 1987), together with the phenomena discussed above, permit the consideration that native metal and alloy formation might preferentially occur in the mantle beneath the constructive plate boundaries.

SUMMARY

Our studies of $Ag_{71.5}Cu_{28.5}$ alloy from the EPR axial metalliferous sediments show that this alloy, hitherto unknown in seafloor sediments, rocks and ores, has unique properties, suggesting a magmatic origin. A plausible genetic hypothesis is provided here.

During the mantle pre-chamber evolution of the basic and ultrabasic systems beneath the spreading zones, under high P-T and low fO_2 and fS_2 conditions, native $Ag_{71.5}Cu_{28.5}$ alloy is formed. The mantle convection and plumes carry the silver-copper alloy segregations and other metallic phases within the magmatic melt matrix to the earth's crust. During this transport (decompression --> partial melting --> more reducing conditions maintained), the metallic microsegregations are preserved. The rapid crystallization of basic magma in the shallow crust chamber (Cann and Strens, 1982) or its short chamber residence and, in

turn, rapid quenching in the neovolcanic rift zone are responsible for further preservation of metallic phases. Rapidly quenched pillow margins are a more reduced environment than whole rocks (Wood *et al.*, 1990) and metallic particles there have more chance to survive. The native silver-copper alloy was probably formed with the falling temperature in the following sequence: (i) crystallization of β crystals near 785 °C; (ii) crystallization of $\alpha + \beta$ eutectic mixture at 779.4 °C; (iii) α and β exsolution below 779.4 °C to end composition Cu + Ag-Cu eutectic + α_{ii} (Ag_{ii}). During cyclic tectono-magmatic processes in the rift zone, the basic ridge rocks undergo active desintegration and native silver-copper alloy liberated together with other rock clasts falls into the near-axial metalliferous sediments. Thus, the sediments formed during periods of intense volcanic activity (marked by high levels of Ti, olivines, basic plagioclases and glasses) contain a maximum quantity of native $Ag_{71.5}Cu_{28.5}$ particles.

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