

Native aluminium in metalliferous sediments from the East Pacific Rise axial zone (21°S)

Vesselin M. Dekov ^a, Elena D. Mandova ^b, Kalin B. Dimitrov ^c,
Krassimir N. Rekkalov ^c

^a Department of Geology and Paleontology, Sofia University, 15, Tzar Osvoboditel Boulevard, 1000 Sofia, Bulgaria

^b Laboratory of Marine Geology, Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str, bl. 24, 1113 Sofia, Bulgaria

^c Section of Mineralogy, Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str, bl. 24, 1113 Sofia, Bulgaria

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Abstract

An endogenous model of the formation of small amounts of >100 µm metallic aluminium particles from the metalliferous sediments of the East Pacific Rise (21°S) is proposed on the basis of a detailed study of their morphology, chemical composition, X-ray data, spatial and temporal distribution. According to this model native aluminium is formed as an accessory mineral during the process of the pre-chamber evolution of basic and ultrabasic systems in the spreading zones, under high *P-T* and low *fO₂* conditions, as well as during the later serpentinization of basites and ultrabasites from the second and third oceanic layer. As a result of the active tectono-magmatic processes in the rift zones the native aluminium particles are carried upwards into the seafloor water layer by the upwelling vent fluids of the hydrothermal circulation cells. During periods of high hydrothermal activity, the number of Al⁰ particles carried upwards increases. The spatial distribution of the particles depends on the energy of the hydrothermal system and the direction and energy of the seafloor currents. The thin oxyhydroxide, silicate and chloride crusts formed on the surface of the Al⁰ particles, as well as a monoatomic oxide film, prevent further alteration of the particles.

1. Introduction

In the geological environment native metals are usually found only in ancient volcanic rocks and hydrothermal ores (Ramdohr, 1975; Smirnov, 1976; Guilbert and Park, 1986; Pirajno, 1992). Their distribution and origin have been described elsewhere (Ramdohr, 1975; Novgorodova, 1983). The presence of native metals in pelagic sediments is thus a little strange as it is well known that such sediments are usually formed under strongly oxidizing conditions. However, native metals and alloys have been found, although rarely, in Recent and Meso-Cenozoic oceanic sediments (Hollister

et al., 1972; Schlanger et al., 1976; Shterenberg and Vassileva, 1979; Lazur et al., 1984). A wide spectrum of these minerals has been identified in recent years (Arsamakov et al., 1988; Shterenberg, 1993). A peculiarity of their distribution is that they only occur in the active tectonic regions of the ocean floor, including zones of transform faults, mid-ocean ridges and back-arc spreading centres.

Native metals in sediments have been found in the vicinity of the sulphide-rich hydrothermal mounds at 21°N East Pacific Rise (EPR) (Cronan, 1979), in the Clarion fault zone (Shterenberg and Vassileva, 1979; Shterenberg et al., 1980; 1986;

Arsamakov et al., 1988), in the metalliferous sediments of the EPR axial zone (Shterenberg et al., 1981; Marchig et al., 1986), in the vicinity of Marcus–Nekker seamounts and the Hess rise (Shnjukov et al., 1981) and in the J₃–K₁ limestones and volcanic siltstones and sandstones immediately overlying basalt basement at several DSDP sites (Hollister et al., 1972; Jenkyns, 1976; Schlanger et al., 1976). Noble metals in the form of discrete minerals have been identified in polymetallic sulphide deposits from the EPR near 21°N (Hekinian et al., 1980), the TAG field, Mid-Atlantic Ridge (Hannington and Scott, 1989; Hannington et al., 1986, 1988, 1992; Rona et al., 1993) and from the Lau back-arc spreading centre (Herzig et al., 1990). Native metals are also present in pelagic Fe–Mn nodules (Baturin and Dubinchuk, 1984; Yushko-Zakharova et al., 1984).

The limited abundance of the native metals in oceanic sediments limits studies of their genesis. The published data is fragmentary and suggest that the largest abundances of native metals are in the metalliferous sediments that occur in the axial zone of the spreading centres and whose formation is related to hydrothermal activity in the rift.

This paper presents the results of a detailed investigation of metallic aluminium in metalliferous sediments, with the emphasis on its spatial and temporal distribution and aimed at gaining an insight into its origin.

2. Geological setting

In the present study samples of sedimentary material from the EPR axial zone (20°30′–22°00′S) (Fig. 1A and B) collected during the fourth cruise of R/V *Geolog Fersman* (in late 1987 and early 1988) is used to investigate the origin and fate of Al³⁺.

In the southeastern Pacific Ocean along the flanks of the EPR and the adjacent parts of the deeps is located the largest known compact field of metalliferous sediments; this region is the classic area for studies of hydrothermal sediments (Boström and Peterson, 1969; Boström, 1973; Dymond et al., 1973; Heath and Dymond, 1977).

Research was carried out on samples from five geological sites (Fig. 1B; Table 1) within the axial

zone and the upper part of the western EPR flank, between the two zones of overlapping (20°30′ and 22°00′S). Four of the sites are located opposite fixed active hydrothermal fields in the southern part of the area (Backer et al., 1985; Renard et al., 1985; Krasnov et al., 1988; Marchig et al., 1988). The fifth site is located opposite another hydrothermal field in the northern part of the area (Macdonald et al., 1986).

The selection of the studied area is favoured by several factors:

(1) The studied ridge sector is isolated from the continental masses and is influenced by fluvial inflow.

(2) In the seafloor water layer, high concentrations of Fe, Mn and ³He (elements indicative of recent active hydrothermal processes) have been detected (Hudson et al., 1986; Krasnov et al., 1988).

(3) The spreading centre is characterized by a high spreading rate: 16.2 cm/yr (Rea, 1978).

(4) Investigations of the sediments from the axial zones of the EPR and the Galapagos Rift show that the maximum concentrations of hydrothermal material [70–80% on a carbonate free basis (CFB)] are found in the section between 14° and 42°S (Walter and Stoffers, 1985).

(5) A large number of massive sulphide chimneys have been identified in the rift zone between 18° and 23°S (Francheteau and Ballard, 1983; Hekinian and Bideau, 1985; Backer et al., 1985; Renard et al., 1985; Macdonald et al., 1986; Krasnov et al., 1988; Marchig et al., 1988).

(6) The seafloor currents carry most of the hydrothermal precipitates westwards from the ridge crest (Lupton and Craig, 1981; Edmond et al., 1982; Marchig and Gundlach, 1982; Marchig et al., 1984).

The sedimentary cover of the studied area consists of a large variety of metalliferous sediments (Levitan et al., 1990). The sediments are strongly oxidized, horizontally bedded oozes of a variety of brown colours. They consist of: biogenic calcium carbonate, hydrothermal Fe and Mn oxyhydroxides, basalt clasts, authigenic clay minerals and very small amounts of allochthonous aeolian material. The first two components together make up 75–95% of the bulk sediment.

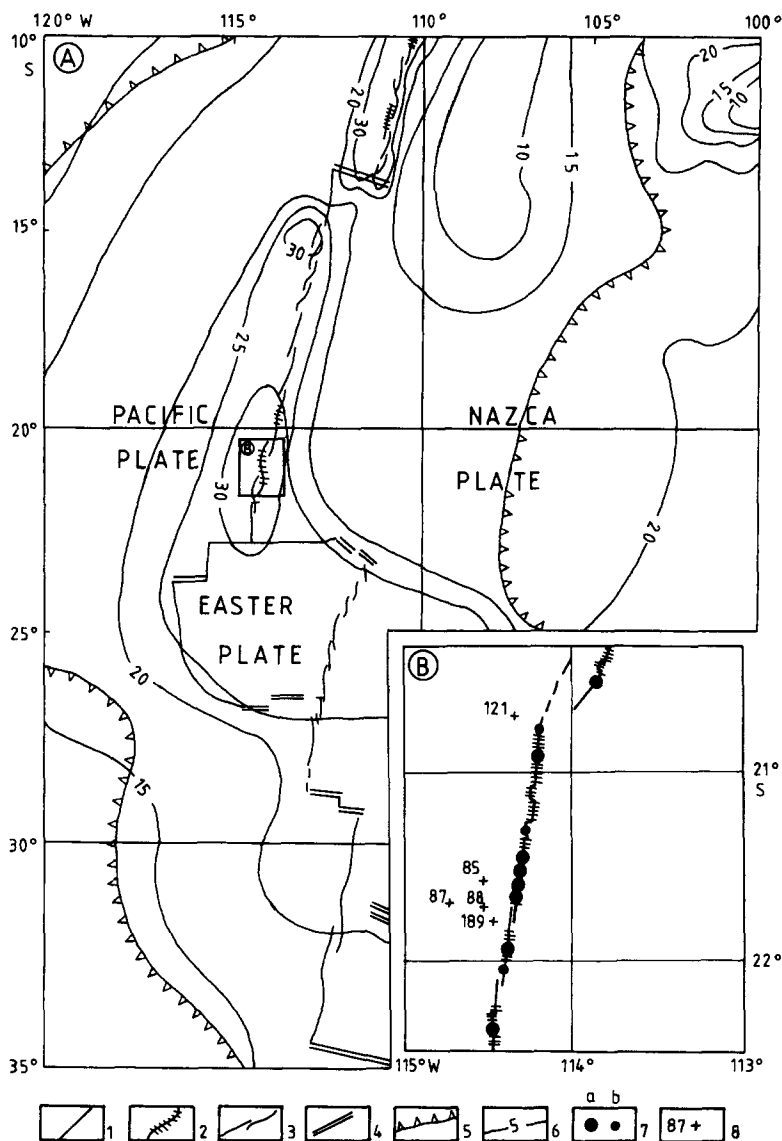


Fig. 1. (A) Sketch map of hydrothermal ore-bearing sediments of the southern part of the EPR (after Krasnov et al., 1992). (B) Diagram showing the location of the sampling stations. Legend: 1 = EPR axial zone without graben or with poorly developed graben; 2 = the same with well developed graben; 3 = zone of overlapping; 4 = transform fault; 5 = outer EPR boundary; 6 = contours of Fe + Mn (in %, on a CFB); 7 = location of the fields of massive sulphides in the EPR rift zone (after Backer et al., 1985; Renard et al., 1985; Macdonald et al., 1986; Krasnov et al., 1988; Marchig et al., 1988): a = large fields, b = smaller fields; 8 = location of sampling stations.

3. Sample material and analytical techniques

For the purpose of clarifying the spatial distribution of Al^{IV} , the surficial horizons of all cores were investigated (Table 1). To establish objective

trends of Al^{IV} distribution through time and its possible genetic link with the evolution of the hydrothermal process the cores 4F-121 and 4F-189 were studied in more detail (Table 1).

Equal amounts of 100 ml of natural wet samples

Table 1
Studied cores, intervals and fractions

Core identification	Latitude (°S)	Longitude (°W)	Water depth (m)	Distance from ridge axis (km)	Collection device*	Core intervals (cm)	Studied fractions (mm)	Number of Al ³⁺ particles
4F-85	21°33.7'	114°30.6'	3140	20	T	0–2	0.10–0.25	2
							0.25–0.50	1
4F-87	21°41.9'	114°43.4'	3220	40	S	0–2	0.10–0.25	2
							0.25–0.50	–
4F-88	21°43.3'	114°31.0'	3010	20	S	0–2	0.10–0.25	3
							0.25–0.50	2
4F-121	20°42.8'	114°15.9'	3225	20	T	0–1	0.10–0.25	3
							0.25–0.50	–
						7–8	0.10–0.25	2
							0.25–0.50	–
							0.10–0.25	4
						15–16	0.25–0.50	6
							0.10–0.25	–
						25–26	0.10–0.25	–
							0.25–0.50	–
						29–30	0.10–0.25	–
							0.25–0.50	–
						30–31	0.10–0.25	3
							0.25–0.50	–
						33–34	0.10–0.25	2
							0.25–0.50	1
						37–38	0.10–0.25	3
0.25–0.50	–							
50–51	0.10–0.25	2						
	0.25–0.50	1						
52–53	0.10–0.25	3						
	0.25–0.50	–						
62–63	0.10–0.25	2						
	0.25–0.50	2						
65–66	0.10–0.25	4						
	0.25–0.50	4						
78–79	0.10–0.25	2						
	0.25–0.50	–						
80–81	0.10–0.25	3						
	0.25–0.50	1						
4F-189	21°47.1'	114°26.8'	3140	10	G	0–2	0.10–0.25	3
							0.25–0.50	3
						9–11	0.50–1.00	–
							0.10–0.25	6
							0.25–0.50	4
						20–22	0.50–1.00	–
							0.10–0.25	18
							0.25–0.50	10
							0.50–1.00	3
							1.00–2.00	–
> 2.00	–							

*T = Flow-through tube; S = square sampler; and G = bottom grab.

of metalliferous sediments, hermetically sealed in polythene bags, were washed with distilled water to remove soluble salts. The grain size distribution was determined through sieve analysis and sediment fraction separation.

The extremely low contents of metallic aluminium particles prevented the use of conventional bulk mineralogical techniques (e.g. XRD) for Al⁰ diagnostics.

It is difficult to examine Al⁰ particles from the fine (<0.10 mm) sediment fractions for the following reasons. (1) Their fine size makes systematic microscopic examination and separation from the other heavy minerals (Fe and Mn oxyhydroxides, some sulphides and magnetite) with similar optical properties (lustre and colour) practically impossible. (2) The specific gravity of aluminium (2.70) is very similar to that of the light minerals—calcite (2.71), plagioclases (2.61–2.76) and quartz (2.65) (which together make up >98% of the bulk sediment), and does not allow the aluminium particles to be separated by means of heavy liquids. (3) The very small amounts and the physical properties of the Al⁰ particles also make centrifugal, magnetic and electromagnetic separation impossible.

Therefore, only the coarse fractions (0.10–0.25, 0.25–0.50, 0.50–1.00, 1.00–2.00, >2.00 mm) were examined by reflected light microscopy for metallic particles (Table 1). Particle form, colour and lustre were also determined. The morphology, size and chemical composition of the metallic aluminium particles were investigated by SEM JEOL T-300 with a Link 860-500 EDS and ZAF/PB program and by SEM JEOL Superprobe-733 with a System-5000 ORTEC EDS and SPRINT-III program. The spatial variations in the chemical composition of individual particles were examined in cross and longitudinal sections. For this purpose the Al⁰ particles were mounted in organic resin and polished sections were prepared. The following standards and X-ray lines were used: Al₂O₃ (Al K_α), FeCuS₂ (Fe K_α), diopside (Si K_α) and chlor-apatite (Cl K_α).

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

4. Results

4.1. Morphology and size of the particles

Particles of metallic aluminium were found in almost all the samples examined (Table 1). All 105 particles studied had thin, in most cases almost isometric lamellae (Fig. 2A), silver white in colour with a strongly metallic lustre. Crescent-shaped lamellae of irregular shape or elongated along one of the axes are also found. All the particles have a smooth or slightly uneven surface. Despite their high plasticity, their edges are rarely rounded and in most cases are uneven and sharp, with well shaped thin, parallel, sometimes curved, crumbled microlayers (Fig. 2B).

The size of the Al⁰ lamellae, as measured along two perpendicular axes (a and b) usually ranges from 100 to 250 μm (Table 1). Larger particles (600 × 900 μm) are also found, as well as smaller lamellae (20 × 50 μm) present in the finer sediment fractions. Of special interest are four identifications of aluminosilicate grains with sharp, rough edges. Thin lamellae of metallic aluminium can be observed to be closely attached to the grain surface (Fig. 2C). Some of the edges of the lamellae are incorporated into the main mass of the aluminosilicate grain (Fig. 2D).

4.2. Chemical composition

The examined particles represent extremely pure aluminium (98–100% Al, Fig. 3A). The amounts of Fe, Cl, Ti, Ca and Si present usually range from 0.1 to 1% (Table 2). Rarely some of these elements (Ti, Ca, Si) reach 1–5%. In these cases the content of Al decreases to 95%. For comparison, published data on the chemical composition of native aluminium particles from ocean sediments and basic and ultrabasic igneous rocks have been compiled in Table 2. These data show that in natural Al⁰ particles the trace elements Mg, Si, Fe, Ca, Ti (in descending order) occur more frequently and in higher concentrations. The amounts of Cu, Zn and Mn are lower and rare, whereas Pb, Cr, Sn and Cl are very rarely present.

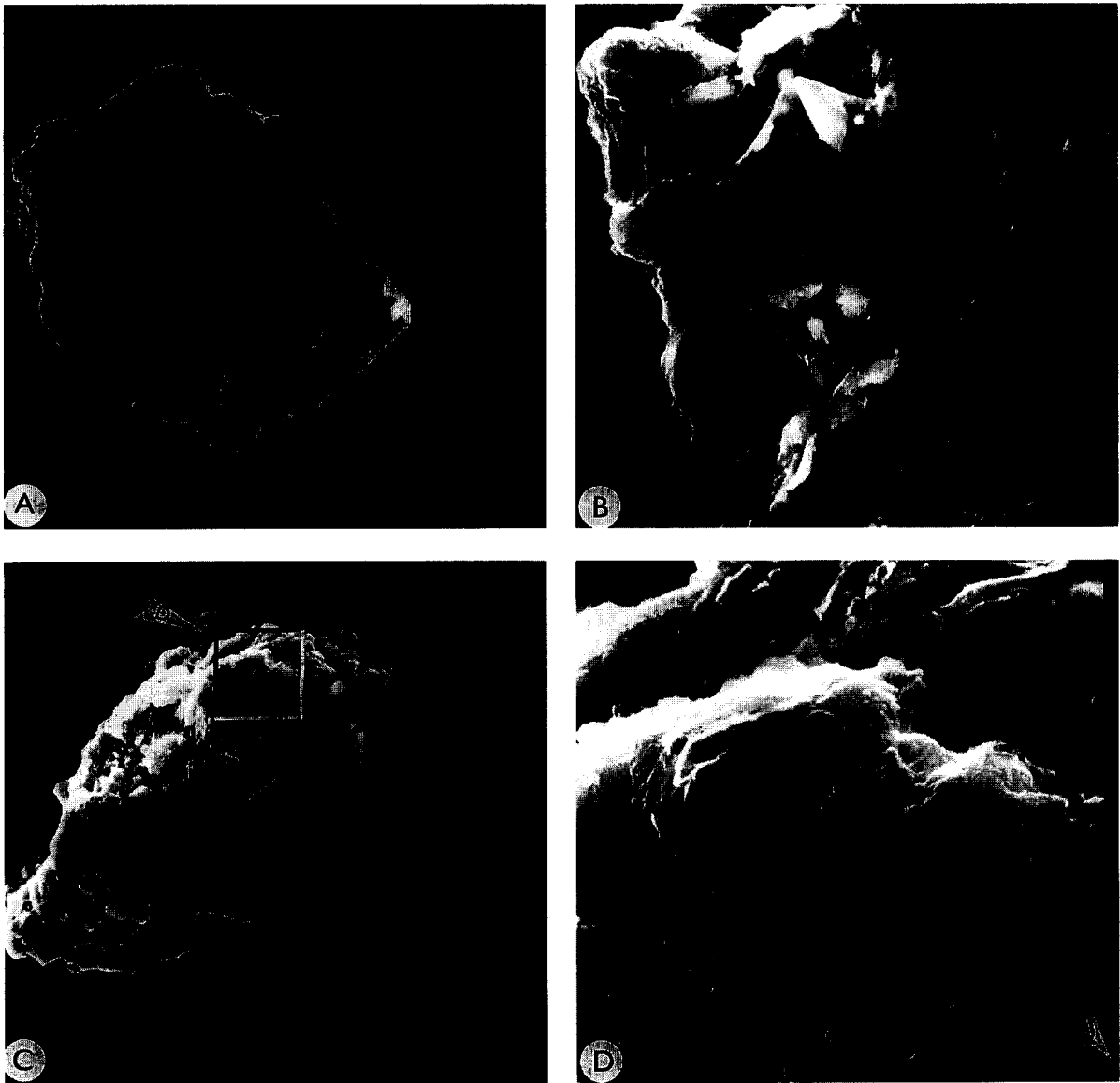


Fig. 2. Scanning electron micrographs of native aluminium particles. (A) General view of a native aluminium particle (H20.S6); (B) uneven, curved, parallel microlayers on the periphery of an Al⁰ particle (H13.S3); (C) aluminosilicate grain with a thin Al⁰ lamella (square) closely attached to it (H16.S2); (D) enlargement of the Al⁰ lamella indicated by square in (C); a lamella edge (arrow) issuing from the aluminosilicate grain can be clearly seen. Scale bars equal 100 μm (A) and 10 μm (B–D).

Back-scattered electron images (BEI) (Fig. 4A) and X-ray mapping (Fig. 4B and C), as well as microprobe analyses of cross and parallel sections of the Al⁰ particles, indicate that other trace elements are present in insignificant amounts and have an irregular areal distribution.

4.3. X-ray diffraction studies

The X-ray diffraction data proved the examined particles to be Al⁰. The sharp and clear reflections on the X-ray diffraction patterns show that the particles are well crystallized. The split of the

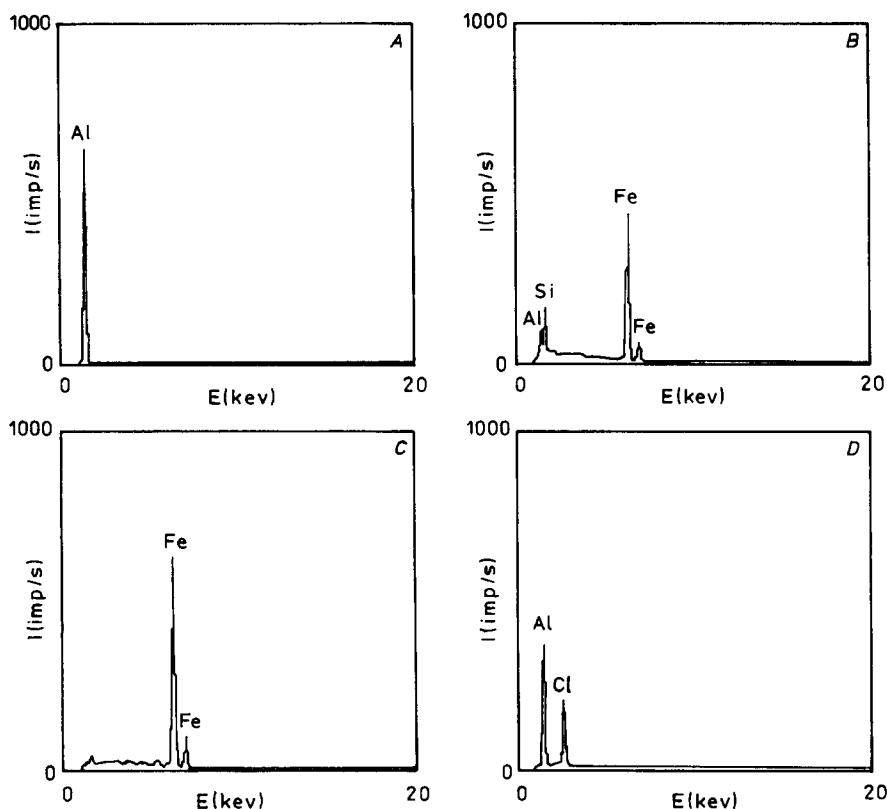


Fig. 3. X-ray spectra of: (A) native aluminium particle (H22.S5); (B) light orange, poorly transparent colloform crust on the surface of an Al° lamella (H2.S1); (C) reddish brown crust on an Al° lamella (H15.S1); (D) white semi-transparent, massive crust on the surface of an Al° lamella (H13.S1) with hydration cracks.

$K_{\alpha 1}$ – $K_{\alpha 2}$ doublet ($d=0.781$ – 0.779 Å) indicates that the blocks making up the mosaic structure are relatively large, that the particles are free from internal tensions and that they are well crystallized. The X-ray diffraction data for native aluminium from ocean sediments and for basic and ultrabasic igneous rocks are in excellent agreement (Table 3).

4.4. Spatial and temporal distribution of the metallic aluminium particles

The search for trends in the Al° distribution in space and time was suggested by antecedent studies, in which a hypothesis had been proposed of a genetic relation between native metals and the tectono-magmatic active zones.

In the present investigation of the surface sediment layer negative correlations of both the

number of Al° particles in the samples and the particle size with the distance from the spreading axis are evident (Table 1; Fig. 5A).

In the light of modern concepts of a pulsed development of the hydrothermal processes in the ocean rift zones (Lissitzin et al., 1990) and their influence on the chemical and mineral composition of the sediments being formed, it was decided to undertake a careful study of cores 4F-121 and 4F-189. Stages of high hydrothermal activity and stages of relative quiescence can be distinguished in the sediments from these cores using concentrations of the main ore-forming element [Fe (on a CFB)] as a criterion of hydrothermal activity (Fig. 6). During stages of high hydrothermal activity (i.e. maximum Fe content), the number of metallic aluminium particles in the sediments increases relative to their number during periods

Table 2
Chemical composition of native Al^o particles from different natural objects

Reference:	Present study						Arsamakov et al. (1988)						
Object and area of investigation:	Metalliferous sediments, 21°S EPR						Non-carbonate zeolitic pelagic clays, NE Deep, Pacific Ocean						
Investigated particles:	1	2	3	4	5	6	1	2	3	4	5	6	7
	>10	Al	Al	Al	Al	Al	Al	Al,Zn	Al,Mg	Al,Mg	Al,Fe	Al,Pb	Al,Cu
Wt.%	10–1	–	–	Ti,Ca	–	Si	–	–	–	Zn	–	–	–
	<1	–	Fe,Cl	Fe	Fe,Si	Fe,Ca, Ca	Ca,Mg, Cu,Ti, Fe,Si	Ca,Mg, Cu,Mn	Ca,Cu, Mn,Si	Ca	Zn,Ca, Mg,Cu, Ti,Mn, Si	Ca,Mg, Cu,Fe, Si,Cr	Ca,Mg, Ti,Fe, Mn,Cr
Reference:	Shterenberg and Vassileva (1979)				Shterenberg et al. (1986)		Oleynikov et al. (1978)			Kovalski and Oleynikov (1985)			
Object and area of investigation:	Terrigenous–pyroclastic clay sediments, Clarion FZ, Pacific Ocean				Pelagic red clay, Clarion FZ, Pacific Ocean		Anorthositic gabbro–dolerites, Ust-Hanninski intrusive, Siberian Platform			Kimberlite tube “Leningrad”			
Investigated particles:	1	2	3	4	1	1	2	3	1	2	3		
	>10	Al	Al	Al	Al,Si	Al	Al	Al,Mg, Si	Al,Cu	Al	Al	Al	
Wt. %	10–1	–	Ti	Si	Zn	–	Mg	–	Mg	–	–	Cu,Mg	
	<1	Si,Fe, Ca,Mn, Sn	Mg,Si, Fe,Ca, Mn,Cu, Zn	Mg,Fe, Ca,Cu, Mn	Mn,Mg, Fe,Ca, Cu	Zn	–	–	–	–	Fe	Mn,Si, Zn	

of low hydrothermal activity (Fig. 6). The Al^o lamellae deposited during hydrothermal activity peaks are larger than those deposited when the hydrothermal process is relatively quiescent (Fig. 5B).

4.5. Mineral phases on the surface of the metallic aluminium particles

Thin variegated crusts are often present on the surface of the Al^o particles. They either partially cover the surface of the lamellae as isolated spots or otherwise completely cover one or both sides of a particle. The crusts are of three types:

(1) Greenish yellow to reddish orange, slightly

transparent, colloform crusts (Fig. 7A), made up of varying amounts of Fe, Si and Al (Fig. 3B). X-ray studies show the predominant presence of an X-ray amorphous phase and smaller amounts of poorly crystallized Fe montmorillonite and goethite (α -FeOOH). During dispersal in the hydrothermal plume and after the deposition of the Al^o particles, a mixture of primary X-ray amorphous SiO₂ and Fe oxyhydroxides is very likely to adhere to the particles' surfaces. During maturation of this material an interaction of its components and a subsequent process of crystallization with the formation of Fe montmorillonite (McMurtry and Yeh, 1981) and goethite begins.

(2) Reddish brown to brown–black crusts, occa-

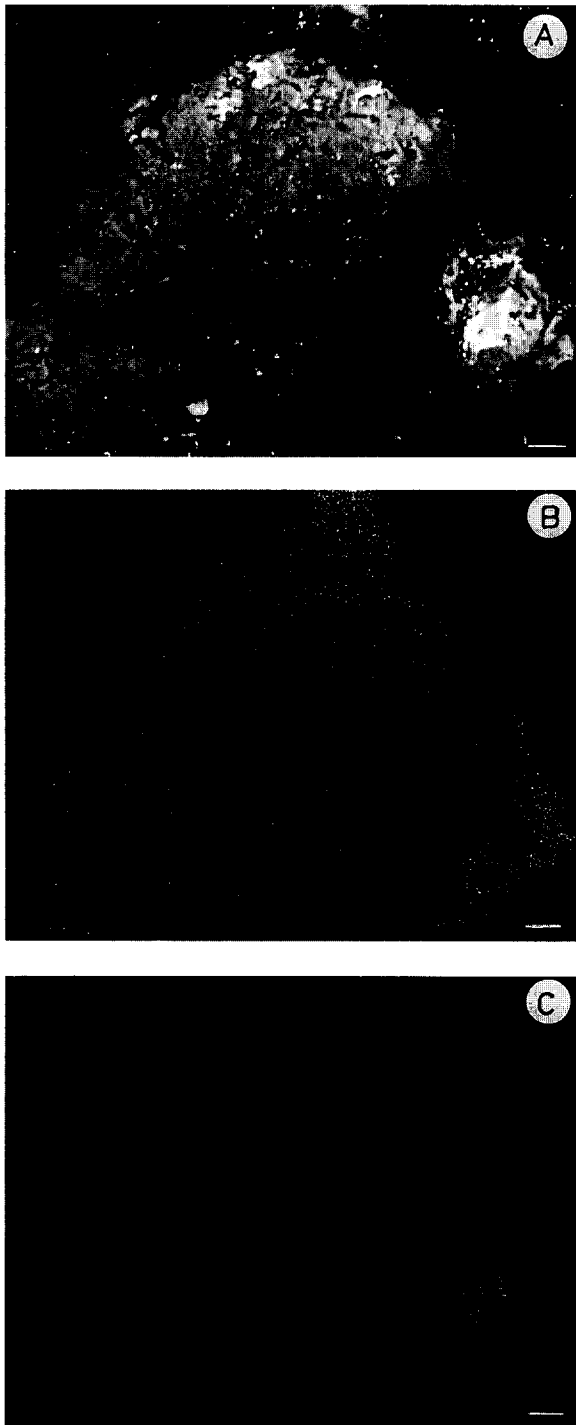


Fig. 4. (A) Back-scattered electron image of a longitudinal section of native aluminium lamella; light tones indicate decreased contents of Al; (B) electron microprobe Al K_{α}

sionally lustrous and usually colloform under the stereoscopic microscope. An initial stage of septal crystal formation is frequently observed if examined carefully. Sometimes the entire crust is made up of a mass of such well crystallized septal crystals (Fig. 7B). The results of electron microprobe analyses (Fig. 3C) and X-ray data demonstrate that the investigated material consists of X-ray amorphous Fe oxyhydroxides and goethite of varying degrees of crystallization. Ironshot bacteriomorphous structures are observed on the surface of the Fe oxyhydroxide crusts at many places (Fig. 7C). This indicates the probable participation of bacteria in the oxidation of Fe^{2+} to Fe^{3+} and the formation of Fe oxyhydroxides.

(3) Colourless to yellowish white, semi-transparent, occasionally colloform, but more often massive, crusts with hydration cracks (Fig. 7D). The data of both electron microprobe analyses (Fig. 3D) and X-ray diffraction studies indicate the presence of X-ray amorphous aluminium chlorides.

5. Discussion

It is known that native metals and alloys can form during a variety of geological processes in reducing environments. That is why the presence of metallic aluminium particles in the metalliferous sediments of the EPR, together with the highest oxidized forms of Fe and Mn is of special interest from the point of view of the genesis of the Al° .

(1) The remoteness of the studied area from the continental masses, as well as the form and the size of the studied particles suggest that a terrigenous (fluvial and/or aeolian) origin of the Al° particles is unlikely.

(2) Sampling devices (flow-through tubes, square samplers, bottom grabs, containers, chains, cables, bolts, etc., all made from stainless steel), shipboard operations, sieving (bronze sieves; wet sieving), shipboard and laboratory atmospheres

X-ray scanning micrograph of the same area as shown in (A); and (C) electron microprobe Fe K_{α} X-ray scanning micrograph of the same area shown in (A); particle H2.S5. Scale bars equal 10 μm (A–C).

Table 3
X-ray diffraction data for native Al^o particles from different natural objects

Reference	Present study	Butuzova et al. (1987)	Arsamakov et al. (1988)	Shterenberg and Vassileva (1979)	Yushko-Zakharova et al. (1984)	Oleynikov et al. (1978)	Mikheev (1957)
Object and area of investigation	Metalliferous sediments, 21°S EPR	Metalliferous sediments, Atlantis-II Deep, Red Sea	Non-carbonate zeolitic pelagic clays, NE Deep, Pacific Ocean	Terrigenous pyroclastic clay sediments, Clarion FZ, Pacific Ocean	Fe–Mn nodules, Pacific, Indian and Atlantic Oceans	Anorthositic gabro–dolerites, Ust-Hanninski intrusive, Siberian Platform	
Sample identification (20–22)	4F-189	387(50–60)	–	100	37-1a	OB-242/3	Al _{syn}
Analytical conditions							
Radiation	CuK _α	CoK _α	FeK _α	FeK _α , CoK _α	FeK _{α,β}	FeK _α	MoK _α
Filter	Ni	–	–	Fe	–	–	Zr
U (kV)	40	–	10	–	–	–	30
I (mA)	19	–	18	–	–	–	30
Exposition time (h)	34	5–6	–	–	10	5	–
Camera	57.3 mm Gandolfi	57.3 mm Debye–Sherrer	57.3 mm Debye–Sherrer	57.3 mm Debye–Sherrer	57.3 mm Debye–Sherrer	57.3 mm Debye–Sherrer	D = 40.64 cm
Results							
	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)	<i>I</i> <i>d</i> (Å)
			6 (2.57)	2 2.58 1 2.36	10 2.35		
	10 2.33	10 2.34	10 2.33 4 (2.24)	10 2.32 2 2.23		10 2.320	10 2.34
	8 2.03	9 2.03	9 2.02 2 1.574	8 2.02	9 2.03	6–7 2.010	9 2.03
	5 1.436	8 1.43	9 1.428 4 (1.344) 1 (1.285)	8 1.43 1 1.34 10 1.27	9 1.436	4–5 1.423	8 1.432
	6 1.227	10 1.22	9 1.221	9 1.225	9 1.225	6–7 1.215	10 1.221
	3 1.170	5 1.16	5 1.168	6 1.17	4 1.175	1 1.163	5 1.169
	1 1.012	4 1.01	3 1.023	3 1.02	2 1.023		
	4 0.929		3 1.011	2 1.00			4 1.013
	2 0.907				5 0.928		7 0.926
	4 0.829				5 0.904		7 0.905
	1 0.827				4 0.824		5 0.825
	4 0.781				4 0.780		
	2 0.779						6 0.778
<i>a</i> (Å)	4.048–4.060	–	–	–	–	–	4.046 ± 0.002

Intensities estimated visually.

exclude any possibility of artificial contamination of the samples by Al^o particles. The composition of the investigated particles differs from that of anthropogenic alloys. In most cases the particles

are of pure Al (>99%) (Table 2) and the admixtures characteristic of anthropogenic alloys are absent. Copper which is the main alloying metal in sheet and bar aluminium (approx. 5%) and

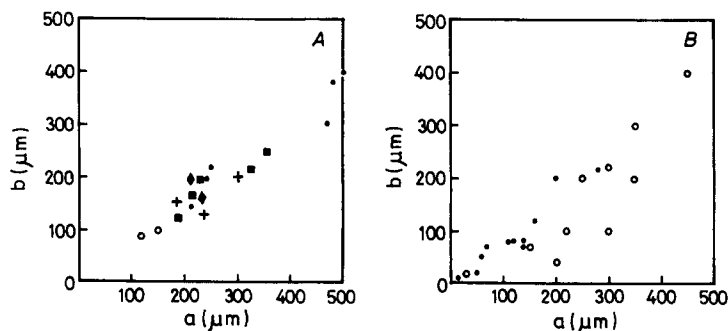


Fig. 5. Grain size distribution of the studied native aluminium particles by their normally oriented axes a and b . (A) In the surficial sediment layer. Open circles represent sample 4F-87 (0–2) (40 km from ridge axis), squares = sample 4F-88 (0–2) (20 km from ridge axis), crosses = sample 4F-85 (0–2) (20 km from ridge axis), diamonds = sample 4F-121 (0–1) (20 km from ridge axis) and dots = sample 4F-189 (0–2) (10 km from ridge axis). (B) During the pulsed hydrothermal process. Circles represent sample 4F-121 (15–16) (stage of high hydrothermal activity) and dots = samples 4F-121 (0–1), 4F-121 (7–8), 4F-121 (30–31), 4F-121 (33–34) (periods of low hydrothermal activity). See Fig. 6.

manganese, one of the most typical components of industrial aluminium alloys, are missing. The bulk of the particles are found in sediment layers formed in pre-tectonic times (older than 10 ka) (Fig. 6). These facts, in our opinion, confirm the natural origin of the metallic Al⁰ particles.

(3) A meteoritic origin of the particles also has to be rejected as the cosmogenic metalloids consist mainly of Fe, Ni and Cu compounds (Fron del, 1975; Lavrukhina and Baryshnikova, 1978) and have spherical or drop-like shapes.

(4) A biogenic origin is another alternative advanced mainly by those studying native metals in Fe–Mn nodules (Shnjukov and Orlovskii, 1980; Baturin and Dubinchuk, 1984; Yushko-Zakharova et al., 1984). According to this hypothesis native metals and alloys can be formed through the action of bacteria which settled, with microflora particles of biogenic detritus, on the Fe–Mn nodules' surface. This creates reducing microzones with sharp gradients of physico-chemical parameters. Within these zones the intensity of reducing processes can reach sufficiently high levels to reduce some elements to the metallic state. The oxidation of the native metals is hindered by their surface being covered by a protective film of Fe–Mn oxyhydroxides, condensed organic matter or clay minerals. This mechanism can also operate in the oxidizing conditions under which the metalliferous sediments form, but in our opinion it is unlikely to have been

the leading mechanism in the present case because of the following considerations. The bacterial genesis presumes the presence of cryptocrystalline minerals with poorly ordered microcrystallites, whereas the investigated Al⁰ particles are all well crystallized, with distinct parallel microlayers and relatively big blocks of mosaic structure (split of $K_{\alpha 1}$ – $K_{\alpha 2}$ doublet).

(5) The location of the native aluminium discoveries close to the recent active tectonic zones of the ocean floor points to a direct link with the endogenous processes according to most workers (Shterenberg and Vassileva, 1979; Shterenberg et al., 1980, 1986; Lazur et al., 1984; Butuzova et al., 1987; Arsamakov et al., 1988). However, the genetic conclusions reached in published work are still inadequate.

The results of this investigation also confirm the relationship between the native aluminium particles and the tectono-magmatic processes in the rift zone of the ridge: there is an increase in the number and the size of the particles, both towards the ridge axis and during stages of high hydrothermal activity.

Any analysis of the relationship between the native aluminium particles and the hydrothermal processes in the ocean rift zones should begin with the petrological significance of the native aluminium found in the basic and ultrabasic rocks from the continents. Native aluminium particles occur

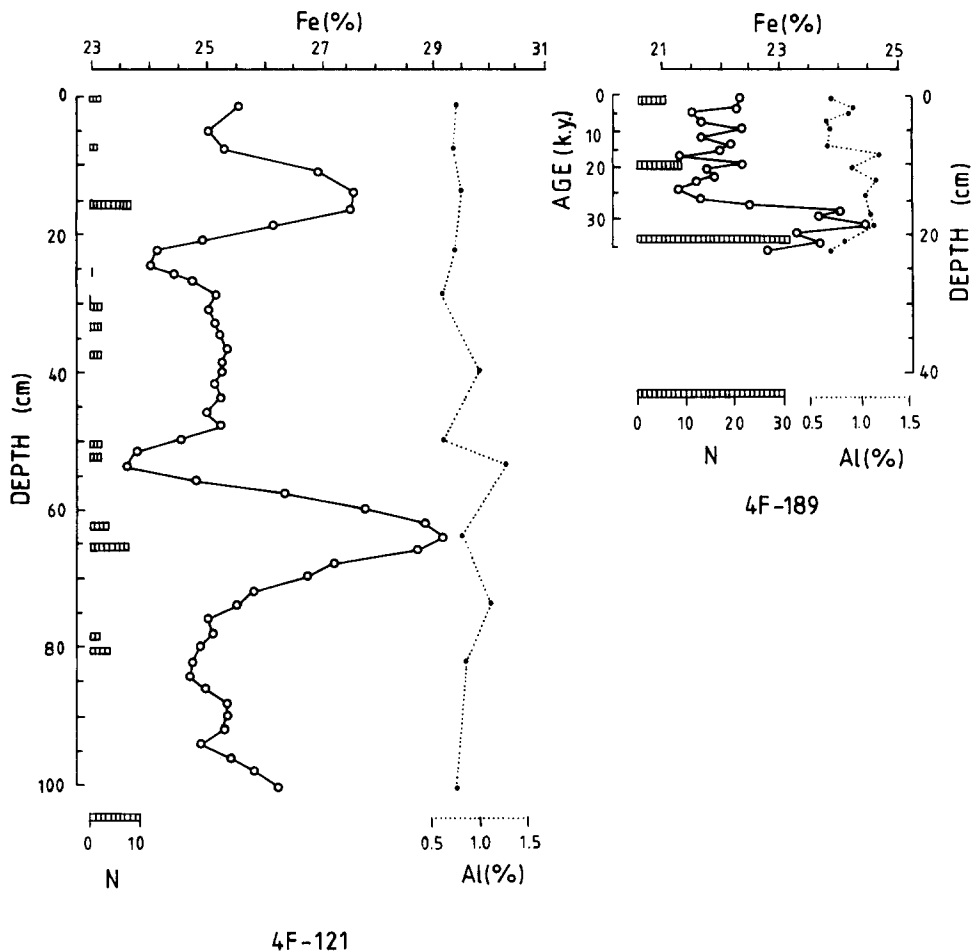


Fig. 6. Vertical distribution of Fe and Al (both on a CFB) and of the number of native aluminium particles (N) in the sediments of cores 4F-121 and 4F-189. Absolute ages determined by the radiocarbon method (Dekov and Kuptsov, 1990).

in rocks of the Siberian trap formations of the tholeiite basalt and picrite basalt series (Oleynikov et al., 1978) and in both non-altered and serpentized, basic and ultrabasic xenoliths from kimberlite pipes (Kovalskii and Oleynikov, 1983, 1985). Using thermodynamic models it can be proved that the formation of native aluminium is possible at very high temperatures in systems of extremely low oxygen fugacity (Nekrassov and Gorbachov, 1977). Oleynikov et al. (1978) proceed from the hypothesis of an initially hydride Earth (Larrin, 1975) and consider that the environment necessary for the formation of native aluminium can be realized only in the mantle under the strongly reducing conditions resulting from the input of

large amounts of intratelluric hydrogen from the deep mantle zones. The presence of native aluminium in basic and ultrabasic rocks is, according to Oleynikov et al. (1978) evidence that during the pre-chamber evolution of the magmatic systems, under high P - T and low fO_2 conditions, a stage of metallization of the silicate melt exists.

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

Osadchii and Alekhin (1984) propose a mecha-

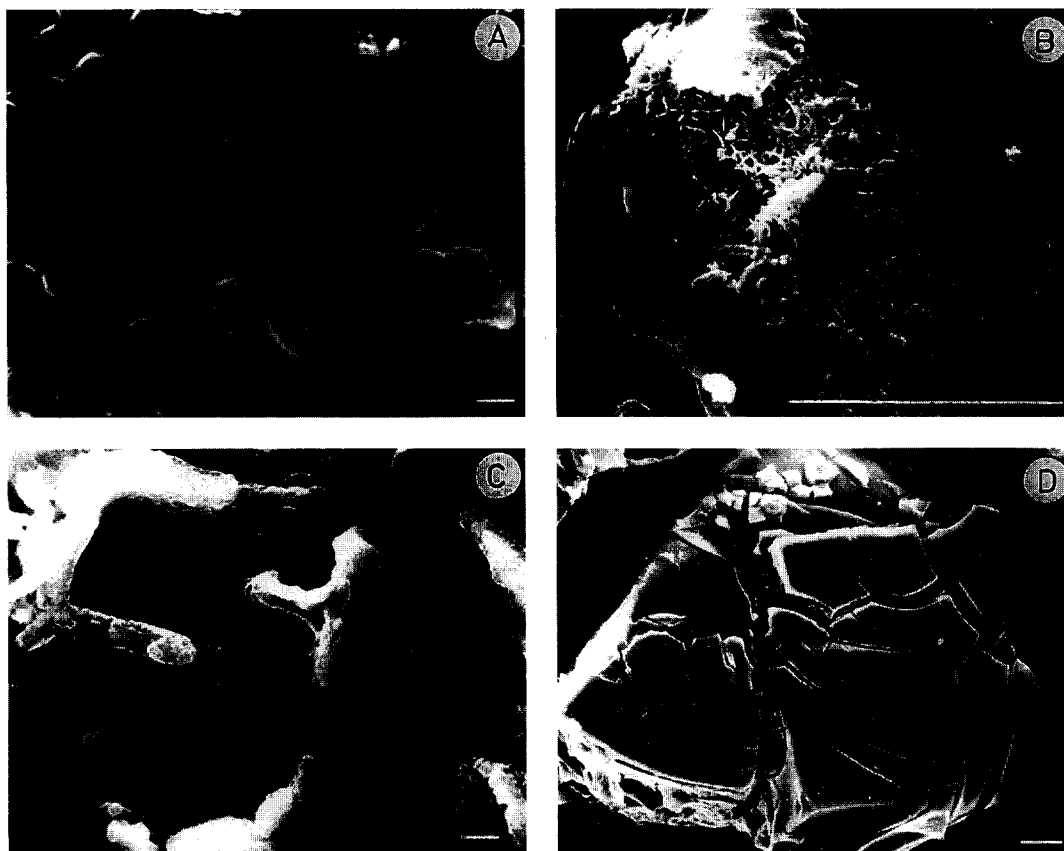


Fig. 7. Scanning electron micrographs of: (A) light orange, poorly transparent colloform crust on the surface of an Al^o lamella (H2.S1); (B) reddish brown crust on the periphery of an Al^o lamella (H2.S5) (the sharp uneven edges on the left), composed of a mass of septal crystals and colloform material (goethite of different degrees of crystallization and X-ray amorphous Fe oxyhydroxides); (C) ironshot bacteriomorphous structures on the surface of a crust of Fe oxyhydroxides (H14.S1); and (D) white, semi-transparent, massive crust on an Al^o lamella (H11.S10) with hydration cracks. Scale bars equal 10 μm (B and D) and 1 μm (A and C).

nism of native aluminium formation in response to the disproportionation of gaseous compounds of lowest valence (AlCl, AlF, Al₂O). According to these workers, AlCl is formed from the interaction of basic or ultrabasic melts that are undersaturated in SiO₂, and the host rocks or fluids containing NaCl and SiO₂. Native aluminium is formed as a result of the AlCl disproportionating on its passage through deep-seated channels, together with other fairly “dry” reducing gases.

Native metals and alloys can also be formed during the serpentinization of basic and ultrabasic rocks under conditions of oxygen deficiency (Ramdohr, 1967; Shteinberg and Chashchukhin,

1977). It is possible that the fluids from the descending branch of the deep hydrothermal cell play an important part in the serpentinization of rocks of the second and third oceanic layers in the spreading zones (Lissitzin et al., 1990).

Data on the presence of native aluminium in oceanic basic and ultrabasic rocks are not available, but in view of the above arguments, it seems possible that native aluminium may be present as an accessory mineral in these rocks.

The genetic models discussed briefly here, as well as modern concepts of the hydrothermal processes in the spreading zones (Rona, 1984; Bowers et al., 1985; Lissitzin et al., 1990) lead us

to consider that the crystallization of native aluminium is unlikely to have taken place in the submarine hydrothermal fluids.

On the other hand, the obvious relation between the native aluminium particles and the oceanic rift zones and the pulsed hydrothermal processes in them, the fresh and sharp edges of the investigated particles—evidence for a short transport distance, their chemical composition and paragenesis with aluminosilicate grains (inclusions of Al° in aluminosilicates; Fig. 2C and D), together with some of the ideas advanced by previous workers allow us to propose the following endogenous model of native aluminium formation.

6. A qualitative genetic model: summary

During the pre-chamber evolution of the basic and ultrabasic systems in the spreading zones, under high P – T and low fO_2 conditions, as well as during the later serpentinization of the basites and ultrabasites from the second and third oceanic layers, native aluminium is formed. It is possible that its formation is due not only to the input of intratelluric H_2 from the deep mantle zones but also to the disproportionation of $AlCl$ as well (witness the almost universal presence of Cl (<1%) in the native aluminium particles composition). As a result of the active tectono-magmatic processes in the rift zones, within the framework of the recycling hypothesis (Corliss, 1971), the native aluminium particles originating from the host rocks are carried upwards into the seafloor water layer by the upwelling vent fluids of the hydrothermal circulation cells. During periods of high hydrothermal activity the quantity of native aluminium particles carried upwards from depth increases. The spatial distribution of the particles depends on the energy of the hydrothermal system, as well as on the direction and strength of the seafloor currents.

Thin crusts of amorphous or poorly crystallized Fe oxyhydroxides and amorphous SiO_2 are formed on the surface of the native aluminium particles during their dispersal in the hydrothermal plume up to the time of deposition, as well as during subsequent diagenesis. The Fe montmorillonite

and goethite are most likely to have formed during the further development of these crusts.

The aluminium chloride crusts on the surface of some particles may have originated primarily during the disproportionation of $AlCl$ which resulted in the formation of Al° (Osadchii and Alekhin, 1984). A secondary genesis of these crusts is also possible in the course of transportation and sedimentation as a result of Al° interacting with chloride anions from the hydrothermal fluids or/and seawater.

The thin crusts formed this way, as well as the monoatomic oxide film present on the particles, prevent their further alteration. On the other hand, the oxyhydroxide crusts on the native aluminium particles may serve as formation nuclei for diagenetic/hydrogenetic Fe–Mn nodules. This is a possible alternative explanation for why native Al° particles are only found in the central parts of the Fe–Mn nodules (Yushko-Zakharova et al., 1984).

The interaction of seawater with ridge crest basalts at elevated temperatures in the oceanic crust considerably modifies the chemical composition of the convecting fluids. The resulting hydrothermal solutions, injected back into the seawater column, may play a significant part in determining the chemistry of the oceans.

It is evident from the chemistry of submarine hydrothermal fluids that the extreme acidity of these 350°C solutions can mobilize aluminium, a typically immobile cation, until it is enriched in vent fluids by a thousand times over normal seawater concentrations (Von Damm et al., 1985a,b; Von Damm and Bischoff, 1987; Campbell et al., 1988; Elderfield et al., 1990). The dissolved aluminium of the vent plumes is enriched over ambient seawater (Lunel et al., 1988), whereas near-vent suspended particles contain background aluminium concentrations (Trefry et al., 1985; 1986; Trocine and Trefry, 1988). The presence of a fine dusting of $AlO(OH)$ on fresh ridge crest basalt surfaces, as well as the discovery of an aluminium oxyhydroxide in the hydrothermal plumes, suggest that it may form as a hydrothermal precipitate (Howard and Fisk, 1986; 1988). This precipitate is similar to the Al–Si gels observed by Oudin (1983). The dispersal of hydrothermally produced particulate plumes is thought to be the predomi-

nant mechanism responsible for the distribution of metalliferous sediments around spreading centres. These sediments generally have very low levels of aluminium (Boström and Peterson, 1969), as observed in particles from the vent plumes. The concentrations of aluminium in the cores investigated by us (see Fig. 6 and Dekov, 1993) are approximately an order of magnitude lower than in pelagic clays (Turekian and Wedepohl, 1961). The aluminium in near-axial metalliferous sediments is considered to have been derived from both detrital and hydrothermal sources (Dymond et al., 1977) making varying contributions to the aluminium content (Leinen and Pisiyas, 1984; Barrett et al., 1987). The concentrations of Al on the EPR south of 10°S are basically controlled by hydrothermal input (Walter and Stoffers, 1985).

Thus the recently acquired data together with the endogenous model of native aluminium formation outlined above support the assumption that the hydrothermally derived aluminium material consists almost entirely of AlO(OH) and alumina-rich clays, and accessory amounts of Al^o. An evaluation of the endogenous Al^o input is a calculation fraught with difficulties. The global flux of Al^o from the world ridge crest system still cannot be quantitatively evaluated and modelled, mainly because of the lack of detailed data on other spreading centres and the extremely low Al^o contents (below the limit of detection) in the sediments investigated. Therefore, we can only state at present that native aluminium particles are not a major contributor to the oceanic aluminium balance.

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References

- Arsamakov, H.I., Kruglyakov, V.V. and Marushkin, A.I., 1988. Native metals and alloys in the pelagic sediments of the Pacific Ocean. *Lith. Ore Dep.*, 4: 122–126 (in Russian).
- Backer, H., Lange, J. and Marchig, V., 1985. Hydrothermal activity and sulfide formation in axial valleys of the East Pacific Rise crest between 18 and 22°S. *Earth Planet. Sci. Lett.*, 72: 9–22.
- Barrett, T.J., Taylor, P.N. and Lugowski, J., 1987. Metalliferous sediments from DSDP Leg 92: The East Pacific Rise transect. *Geochim. Cosmochim. Acta*, 51: 2241–2253.
- Baturin, G.N. and Dubinchuk, V.T., 1984. Sulphide mineralization in the pelagic iron–manganese nodules. *Lith. Ore Dep.*, 2: 53–61 (in Russian).
- Boström, K., 1973. The origin and fate of ferromanganese active ridge sediments. *Acta Univ. Stockholm., Stockholm Contrib. Geol.*, 27: 149–243.
- Boström, K. and Peterson, M.N.A., 1969. The origin of aluminum-poor ferromanganese sediments in areas of high heat flow on the East Pacific Rise. *Mar. Geol.*, 7: 427–447.
- Bowers, T.S., Von Damm, K.L. and Edmond, J.M., 1985. Chemical evolution of mid-ocean ridge hot springs. *Geochim. Cosmochim. Acta*, 49: 2239–2252.
- Butuzova, G. Yu., Shterenberg, L.E., Voronin, B.I. and Korina, E.A., 1987. Native metals in ore-bearing sediments in the Red Sea. *Lith. Ore Dep.*, 2: 122–125 (in Russian).
- Campbell, A.C., Palmer, M.R., Klinkhammer, G.P., Bowers, T.S., Edmond, J.M., Lawrence, J.R., Casey, J.F., Thompson, G., Humphris, S., Rona, P. and Karson, J.A., 1988. Chemistry of hot springs on the Mid-Atlantic Ridge. *Nature*, 335: 514–519.
- Cronan, D.S., 1979. Metallogenesis at oceanic spreading centers. Conference report. *J. Geol. Soc. Am.*, 136: 621–626.
- Corliss, J.B., 1971. The origin of metal-bearing submarine hydrothermal solutions. *J. Geophys. Res.*, 76: 8128–8138.
- Dekov, V.M., 1993. Distribution of chemical components in the bottom metalliferous sediments from the East Pacific Rise axial zone (20°30′–22°00′S). *Geol. Balc.*, 23: 69–84.
- Dekov, V.M. and Kuptsov, V.M., 1990. Rates of accumulation of metal-bearing sediments on the East Pacific Rise (20°S). *Oceanology*, 30: 321–324.
- Dymond, J., Corliss, J.B., Heath, G.R., Field, C.W., Dasch, E.J. and Veeh, H.H., 1973. Origin of metalliferous sediments from the Pacific Ocean. *Geol. Soc. Am. Bull.*, 84: 3355–3372.
- Dymond, J., Corliss, J.B. and Heath, G.R., 1977. History of metalliferous sedimentation at Deep Sea Drilling Site 319, in the South Eastern Pacific. *Geochim. Cosmochim. Acta*, 41: 741–753.

- Edmond, J.M., Von Damm, K.L., McDuff, R.E. and Measures, C.I., 1982. Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. *Nature*, 297: 187–191.
- Elderfield, H., Godfrey, L., Greaves, M., Mitra, A. and Rudnicki, M., 1990. Chemical dynamics of the TAG hydrothermal plume, 26°N, Mid-Atlantic Ridge. *EOS, Trans. Am. Geophys. Union*, 71: 1651.
- Francheteau, J. and Ballard, R.D., 1983. The East Pacific Rise near 21°N, 13°N and 20°S: inferences for along-strike variability of axial processes of the Mid-Ocean Ridge. *Earth Planet. Sci. Lett.*, 64: 93–116.
- Fronde, J.W., 1975. *Lunar Mineralogy*. Wiley, New York, 334 pp.
- Guilbert, J.M. and Park, C.F., 1986. *The Geology of Ore Deposits*. Freeman, San Francisco, 985 pp.
- Hannington, M.D. and Scott, S.D., 1989. Gold mineralization in volcanogenic massive sulfides: Implications of data from active hydrothermal vents on the modern seafloor. *Econ. Geol. Monogr.*, 6: 491–507.
- Hannington, M.D., Peter, J.M. and Scott, S.D., 1986. Gold in seafloor polymetallic sulfide deposits. *Econ. Geol.*, 81: 1867–1883.
- Hannington, M.D., Thompson, G., Rona, P.A. and Scott, S.D., 1988. Gold and native copper in supergene sulfides from the Mid-Atlantic Ridge. *Nature*, 333: 64–66.
- Hannington, M.D., Herzig, P.M., Tivey, M.K., Thompson, G. and Rona, P.A., 1992. Hydrothermal reworking of sulfide deposition in the TAG field, Mid-Atlantic Ridge: Evidence from the distribution of gold. *EOS, Trans. Am. Geophys. Union, Fall Meet. Suppl.*, 73: 530–531.
- Heath, G.R. and Dymond, J., 1977. Genesis and transformation of metalliferous sediments from the East Pacific Rise, Bauer Deep, and Central Basin, Northwest Nazca Plate. *Geol. Soc. Am. Bull.*, 88: 723–733.
- Hekinian, R. and Bideau, D., 1985. Volcanism and mineralization of the oceanic crust on the East Pacific Rise. In: *Metallogeny of Basic and Ultrabasic Rocks*. Inst. Min. Metall. London. Publ., pp. 1–20.
- Hekinian, R., Fevrier, M., Bischoff, J.L., Picot, P. and Shanks, W.C., 1980. Sulfide deposits from the East Pacific Rise near 21°N. *Science*, 207: 1433–1444.
- Herzig, P.M., Fouquet, Y., Hannington, M.D. and von Stackelberg, U., 1990. Visible gold in primary polymetallic sulfides from the Lau back-arc. *EOS, Trans. Am. Geophys. Union*, 71: 1680.
- Hollister, C.D., Ewing, J.I. and Shipboard Scientists, 1972. Site 105: lower continental rise hills. *Init. Rep. DSDP*, 11: 219–312.
- Howard, K.J. and Fisk, M.R., 1986. Hydrothermal vent prospecting on the Gorda Ridge and President Jackson Seamounts. *EOS, Trans. Am. Geophys. Union*, 67: 1283.
- Howard, K.J. and Fisk, M.R., 1988. Hydrothermal alumina-rich clays and boehmite on the Gorda Ridge. *Geochim. Cosmochim. Acta*, 52: 2269–2279.
- Hudson, A., Bender, M. and Graham, D., 1986. Iron enrichments in hydrothermal plumes over the East Pacific Rise. *Earth Planet. Sci. Lett.*, 79: 250–254.
- Jenkyns, H.C., 1976. Sediments and sedimentary history of the Manihiki Plateau, south Pacific Ocean. *Init. Rep. DSDP*, 33: 873–890.
- Kovalskii, V.V. and Oleynikov, O.B., 1983. Minerals of native elements in xenoliths from the kimberlite pipe “Obnajennaja”. *Dokl. Acad. Sci. USSR*, 273: 1214–1217 (in Russian).
- Kovalskii, V.V. and Oleynikov, O.B., 1985. Native metals and natural polymineral alloys of copper, zinc, lead, tin and antimony in the rocks of the kimberlite pipe “Leningrad”. *Dokl. Acad. Sci. USSR*, 285: 203–208 (in Russian).
- Krasnov, S.G., Masslov, M.N., Andreev, N.M., Konfetkin, V.M., Krejter, I.I. and Smirnov, B.N., 1988. Hydrothermal ore formation in the southern part of the East Pacific Rise. *Dokl. Acad. Sci. USSR*, 302: 161–164 (in Russian).
- Krasnov, S.G., Cherkashev, G.A. and Ajnemer, A.I., 1992. Massive sulphides and metalliferous sediments of the Ocean. *Nedra, St. Petersburg*, 326 pp. (in Russian).
- Larrin, V.N., 1975. *A Hypothesis of the Initially Hydride Earth*. Nauka, Moscow, 156 pp. (in Russian).
- Lavrukhina, A.K. and Baryshnikova, G.V., 1978. Meteorite minerals. *Zap. Vses. Mineral. Obshchest.*, 2 ser., 107: 416–430 (in Russian).
- Lazur, Yu.M., Varentsov, I.M. and Ermilov, V.V., 1984. Copper–zinc mineralization in the Mesozoic sediments of the central regions of the northwestern part of the Pacific Ocean (DSDP leg 62). *Geochemistry*, 11: 1718–1725 (in Russian).
- Leinen, M. and Pias, N., 1984. An objective technique for determining end-member compositions and for partitioning sediments according to their sources. *Geochim. Cosmochim. Acta*, 48: 47–62.
- Levitan, M.A., Dmitrenko, O.B. and Ivanova, E.V., 1990. Composition and structure of the sedimentary cover of the central part of the East Pacific Rise (19°–22°30′S). *Lith. Ore Dep.*, 5: 21–32 (in Russian).
- Lissitzin, A.P., Bogdanov, Yu.A. and Gurvich, E.G., 1990. *Hydrothermal Formations of the Rift Ocean Zones*. Nauka, Moscow, 256 pp. (in Russian).
- Lukanin, O.A. and Kadik, A.A., 1984. The possible role of the partial melting in the formation of the oxidizing and fluid conditions of the upper mantle. *Dokl. Acad. Sci. USSR*, 275: 996–998 (in Russian).
- Lunel, T., Dickie, B., Elderfield, H. and Hydes, D., 1988. Al: A tracer of deep water entrainment in hydrothermal systems. *EOS, Trans. Am. Geophys. Union*, 69: 1271.
- Lupton, J.E. and Craig, H., 1981. A major helium-3 source at 15°S on the East Pacific Rise. *Science*, 214: 13–18.
- Macdonald, K.C., Haymon, R.M. and Perram, L.J., 1986. 13 new hydrothermal vent sites found on the East Pacific Rise, 20°–21°S. *EOS, Trans. Am. Geophys. Union*, 67: 1232.
- Marchig, V. and Gundlach, H., 1982. Iron-rich metalliferous sediments on the East Pacific Rise: prototype of undifferentiated metalliferous sediments on divergent plate boundaries. *Earth Planet. Sci. Lett.*, 58: 361–382.
- Marchig, V., Gundlach, H. and Backer, H., 1984. Geochemical

- indication in deep-sea sediments for hydrothermal discharge. *Mar. Geol.*, 56: 319–323.
- Marchig, V., Erzinger, J. and Heinze, P.-M., 1986. Sediment in the black smoker area of the East Pacific Rise (18.5°S). *Earth Planet. Sci. Lett.*, 79: 93–106.
- Marchig, V., Gundlach, H., Holler, G. and Wilke, M., 1988. New discoveries of massive sulphides on the East Pacific Rise. *Mar. Geol.*, 84: 179–190.
- McMurtry, G.M. and Yeh, H.-W., 1981. Hydrothermal clay mineral formation of East Pacific Rise and Bauer basin sediments. *Chem. Geol.*, 32: 189–205.
- Mikheev, V.I., 1957. X-ray Data Catalogue for Minerals. Gostehizd, Moscow, 458 pp. (in Russian).
- Nekrassov, I. Ya. and Gorbachov, N.S., 1977. Study of the Cu–Fe–Sn–S–H₂O system at 300°–500°C and the origin of the cassiterite–sulphide ores. In: *Articles in Physico-chemical Petrology*. Nauka, Moscow, 7: 176–199 (in Russian).
- Novgorodova, M.I., 1983. Native Metals in Hydrothermal Ores. Nauka, Moscow, 288 pp. (in Russian).
- Oleynikov, B.V., Okrugin, A.V. and Leskova, N.V., 1978. Petrological significance of native aluminium finds in basites. *Dokl. Acad. Sci. USSR*, 243: 191–194 (in Russian).
- Osadchii, E.G. and Alekhin, Yu.V., 1984. On the origin of native aluminium. 27th Int. Geol. Cong., Abstr., 5: 131.
- Oudin, E., 1983. Hydrothermal sulfide deposits of the East Pacific Rise (21°N), Part I: Descriptive mineralogy. *Mar. Min.*, 4: 39–72.
- Pirajno, F., 1992. *Hydrothermal Mineral Deposits*. Springer, Berlin, 709 pp.
- Ramdohr, P., 1967. On the widespread paragenesis of the ore minerals formed during serpentinization (with some data on new and scantily described minerals). *Geol. Ore Dep.*, 2: 32–43 (in Russian).
- Ramdohr, P., 1975. *Die Erzminerale und ihre Verwachsungen*. Akad.-Verlag, Berlin, 1277 pp.
- Rea, D.K., 1978. Asymmetric sea-floor spreading and a non-transform axis offset: the East Pacific Rise, 20°S survey area. *Geol. Soc. Am. Bull.*, 89: 836–844.
- Renard, V., Hekinian, R., Francheteau, J., Ballard, R.D. and Backer, H., 1985. Submersible observations at the axis of the ultra fast spreading East Pacific Rise (17°30' to 21°30'S). *Earth Planet. Sci. Lett.*, 75: 339–353.
- Rona, P.A., 1984. Hydrothermal mineralization at sea-floor spreading centers. *Earth-Sci. Rev.*, 20: 1–104.
- Rona, P.A., Bogdanov, Y.A., Gurvich, E.G., Rimski-Korsakov, N.A., Sagalevitch, A.M., Hannington, M.D. and Thompson, G., 1993. Relict hydrothermal zones in the TAG hydrothermal field, Mid-Atlantic Ridge 26°N, 45°W. *J. Geophys. Res.*, 98: 9715–9730.
- Schlanger, S.O., Jackson, E.D. and Shipboard Scientists, 1976. Site 317. *Init. Rep. DSDP*, 33: 161–188.
- Shnjukov, E.F. and Orlovskii, G.N., 1980. Iron–manganese nodules of the Indian Ocean. *J. Geol.*, 40: 46–64 (in Russian).
- Shnjukov, E.F., Sobolevskii, Yu.V., Kozak, S.A. and Shcherbakov, I.B., 1981. Iozite and native iron from Maria Celesta fracture zone (Indian Ocean). *J. Mineral.*, 3: 48–54 (in Russian).
- Shtenberg, D.S. and Chashchukhin, I.S., 1977. Serpentinization of the Ultrabasics. Nauka, Moscow, 128 pp. (in Russian).
- Shtenberg, L.E., 1993. On native metals at the seafloor. *J. Mineral.*, 15: 79–85 (in Russian).
- Shtenberg, L.E., Alexandrova, V.A., Vassileva, G.L., Voronin, B.I., Gussareva, A.I., Dmitrik, A.L., Rychkova, V.B., Salyn, A.L., Stepanova, K.A. and Stepanov, S.S., 1980. Products of volcanic activity in the sediments of site 655 (North-Eastern Pacific Ocean). *Lith. Ore Dep.*, 2: 17–32 (in Russian).
- Shtenberg, L.E., Kuzmina, O.V., Laputina, I.P. and Tzepin, A.I., 1986. On the find of native aluminium in association with ZnO and ZnCl₂ in the sediments of site 647 (North-Eastern Pacific Ocean). *Lith. Ore Dep.*, 1: 137–140 (in Russian).
- Shtenberg, L.E. and Vassileva, G.L., 1979. Native metals and intermetals in the sediments from the North-Eastern Pacific Ocean. *Lith. Ore Dep.*, 2: 133–139 (in Russian).
- Shtenberg, L.E., Vassileva, G.L., Voronin, B.I. and Korrina, E.A., 1981. Gold and silver minerals in the metalliferous sediments of the Pacific Ocean. *Izv. Acad. Sci. USSR, Geol. Sect.*, 7: 151–154 (in Russian).
- Smirnov, I., 1976. *Geology of Mineral Deposits*. Mir, Moscow, 520 pp.
- Trefry, J.H., Trocine, R.P., Klinkhammer, G.P. and Rona, P.A., 1985. Iron and copper enrichment of suspended particles in dispersed hydrothermal plumes along the Mid-Atlantic Ridge. *Geophys. Res. Lett.*, 12: 506–509.
- Trefry, J.H., Metz, S., Trocine, R.P. and Nelsen, T.A., 1986. Geochemistry and history of hydrothermal precipitates in a Mid-Atlantic Ridge vent field. *EOS, Trans. Am. Geophys. Union*, 67: 1022.
- Trocine, R.P. and Trefry, J.H., 1988. Distribution and chemistry of suspended particles from an active hydrothermal vent site on the Mid-Atlantic Ridge at 26°N. *Earth Planet. Sci. Lett.*, 88: 1–15.
- Turekian, K.K. and Wedepohl, K.H., 1961. Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.*, 72: 175–192.
- Von Damm, K.L. and Bischoff, J.L., 1987. Chemistry of hydrothermal solutions from the Southern Juan de Fuca Ridge. *J. Geophys. Res.*, 92: 11,334–11,346.
- Von Damm, K.L., Edmond, J.M., Grant, B., Measures, C.I., Walden, B. and Weiss, R.F., 1985a. Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta*, 49: 2197–2220.
- Von Damm, K.L., Edmond, J.M., Measures, C.I. and Grant, B., 1985b. Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta*, 49: 2221–2237.
- Walter, P. and Stoffers, P., 1985. Chemical characteristics of metalliferous sediments from eight areas on the Galapagos rift and East Pacific Rise between 2°N and 42°S. *Mar. Geol.*, 65: 271–287.
- Yushko-Zakharova, O.E., Zakharov, V.E., Golovina, M.S., Dubakina, L.S. and Shcherbachev, D.K., 1984. Native metals in the iron–manganese nodules of the World Ocean. *Dokl. Acad. Sci. USSR*, 275: 465–467 (in Russian).