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GEOLOGY

Hydrothermal Alterations of Modern Organic Sediments at the Ashadze-1 Hydrothermal Field, Mid-Atlantic Ridge, 13° N

I. F. Gablina[a], E. A. Popova[b], T. A. Sadchikova[a], T. A. Khusid[c], N. S. Os'kina[c], V. E. Bel'tenev[d], and V. V. Shilov[d]

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Abstract—For the first time detailed investigations of hydrothermal alterations on microbiota of ore-bearing sediments of the Ashadze-1 field (13° N, Mid-Atlantic Ridge) were carried out and local mineral–geochemical zoning was established. For the first time for the region, enriching of Mg sediments related with hydrothermal activity was revealed. It was concluded that hydrotherms affecting sediments are characterized with a high Mg content.

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Ore-bearing sediments widespread in the regions of high hydrothermal activity on the ocean bottom were studied for a long time. Definitive data about ore-bearing ocean sediments are presented in the basic works [1–3]. Study of alterations of sediments in relation to modern hydrothermal activity is important both as a search attribute and for understanding the deep processes inaccessible for direct observations.

New mineral formations within the bottom sediments of the modern hydrothermal Ashadze-1 field of the Mid-Atlantic Ridge (13° N) directly in the outlet of hydrotherms and at various distances from it are the subjects of the present study. Determination of the nature of mineral components is difficult in investigation of ore- and metal-bearing sediments. These components can be of an autigenous, terrigenous, and edaphogenous nature. To facilitate solving the problem, organic matter of sediments which is uniform by composition on the sedimentogenesis stage along the whole ocean was selected as the main subject for the research. The organic matter of sediments is presented with calcite shells of dead plankton and benthos. The difference of their transformation can be related with different diagenesis conditions only. Based on this difference, mineral–geochemical zoning of the Ashadze field sediments related with hydrothermal alterations was determined. It was concluded that hydrotherms affecting sediments are characterized by high Mg content.

We studied samples of sediments taken by scientists of the All-Russia Scientific Research Institute Oceanology during the 26th voyage of R/V *Professor Logachev* realized by the Federal State Unitary Enterprise *Polyarnaya ekspeditsiya* in 2005. Sediments were taken with a tele-clamshell by a sublatitudinal profile crossing the ore field from the east to the west (Fig. 1).

Ashadze 1 field with an area of 450 × 350 m is at a depth 4100–4200 m and prolonged sublatitudinaly. It is situated near the foot of the western slope of the rift valley in the high-active field of crossing of the edge deep break with the zone of sublatitudinal tectonic deformations. The geological structure of the field is presented by gabbroids and serpentinized peridotites. Ultrabasites are covered with modern biogenic carbonic and clay-carbonic foraminifera-coccolith sediments with fragments of modified rocks in the lower layers.

According to early investigations, the thickness of sediments is more than 3 m, but near the hydrothermal buildings, it is reduced to 0.5 m and less. The ore field is presented by two ore bodies with relic and active hydrothermal buildings and ore-bearing sediments (Fig. 1). Anomalous values of the turbidity and temperature and the content of soluted Fe and Mn are recorded in the bottom layers of water. Bottom waters have low density related with the presence of gases in significant quantities, especially hydrogen and methane [4, 5]. The temperature of solutions within the

[a]Geological Institute, Russian Academy of Sciences, Moscow, Russia
[b] Gramberg All-Russia Research Institute for Geology and Mineral Resources of the World Ocean, St. Petersburg, Russia
[c] Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia
[d]Polar Marine Geosurvey Expedition (PMGE), St. Petersburg–Lomonosov, Russia
e-mail: gablina@ilran.ru, popova@vniio.ru, tkhusid@mail.ru, nsoskina@mail.ru, ocean-party@peterlink.ru

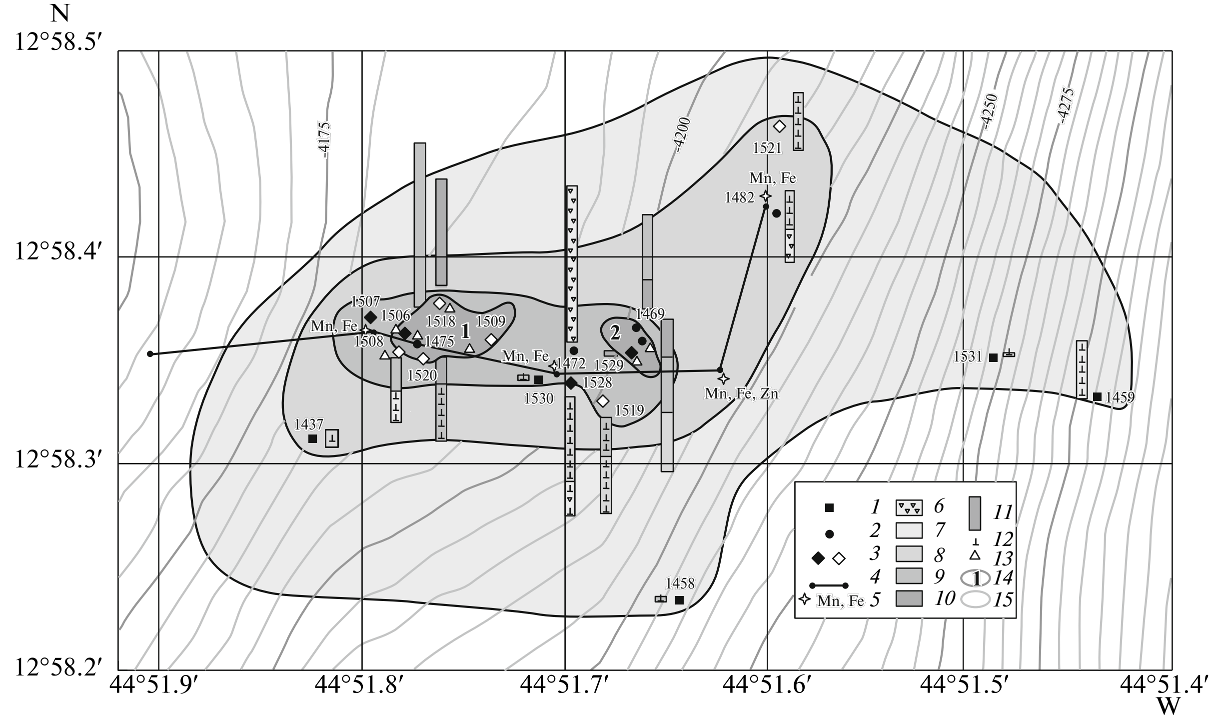

Fig. 1. Distribution scheme of ore-bearing sediments of the hydrothermal field Ashadze-1. (1–4) Testing stations and their numbers (white icons are the samples studied in this work, black icons show the data on chemical composition were used): (*1*) box-shaped sampler; (*2*) vibrate-percussive arrangement; (*3*) tele greifer; (*4*) hydrophysical bore; (*5*) geochemical anomalies of near-bottom waters; (*6–10*) types of sediments: (*6*) nonmetal-bearing with modified peridotites (Fe < 10%, Cu+Zn < 0.25%); (*7*) metal-bearing (Fe > 10%, Cu+Zn < 0.25%); (*8*) metal-containing (Fe 7–10%, Cu+Zn > 0,25%); (*9*) ore-containing (Fe 10–30%, Cu+Zn > 0.25%); (*10*) ore (Fe > 30%, Cu+Zn > 0.25%); (*11*) columns of sediments (vertical scale 1 : 20); (*12*) carbonate; (*13*) sulfides; (*14*) contours of ore bodies and their numbers; (*15*) contours of distribution of sediments.

field comes to 353°C; the pH is no less than 3.5, and mineralization is 0.8–1.3 from the seawater salinity [6]. The absolute age of sulfide ores from hydrothermal buildings, according to the thorium–uranium technique, varies from 2100 ± 300 to 7200 ± 1800 years [7].

The samples from columns of stations 1508, 1509, 1518, 1520, 1519, and 1521 were investigated. Sediments are broached at the depth 5–60 cm. To compare with ore-bearing and metal-bearing sediments, we studied samples of background sediments broached 1 km northward (station 1515) and 1–2 km southward (station 1430, 1525) from the ore field center. During investigations, the next types of analysis were used: biostratigraphic, granulometric, chemical, optical, radiographic, and electron-microscopic analyses.

Chemical analysis of sediments revealed zonal distribution of rock-forming and ore elements. From the northeast to the southwest (towards ore body 1), the carbonate content of sediments is reduced in order of magnitude. On the contrary, the content of Fe, Mn, Mg, Si, and Cu increases. Ore body 1 is characterized by a high Fe content in the sediments (10–30% and higher). Along the distance from ore body 1 to the southwest field side (1437 station, Fig. 1), the carbonate content increases and the magnesium content and the content of ore components decrease (Table 1).

The *rentgenodiphractometric* technique was used for investigation of clay fractions (≤0.001 mm) by the columns of the stations 1430, 1508, 1515, 1519, 1520, 1521, and 1525. Clay fractions were not found in the samples of ore-bearing sediments (stations 1509, 1518). In almost all columns, except station 1508 on the southwest periphery of ore body 1, the dominant clay mineral is kaolin. At station 1508 the most widespread is Fe-smectite with Ca and Mg in interlayers. The same cation composition of smectite dominates in the samples where it is an impurity mineral, except for station 1521 situated on the northeast periphery of the ore field. This station is the most distant from the ore deposits and stations 1430, 1515, and 1525 situated out of the ore field. The most widespread mineral is kaolin, and smectite is presented with the form of K and Na in interlayers.

Biostratigraphic investigations were carried out at stations 1519, 1520, and 1521. In samples 1508 and 1518, organic sediments are almost completely mineralized and irreducible for determination. In the studied samples, the microbiota comes up to 80–90% of the sand and aleurite fractions of sediments. It is presented with plankton and benthos foraminifera, coccoliths, shells of ostracods, spicules of sponges, and rare specimens of silica radiolarians. Plankton fora-

Content of basic rock-forming and ore components in sediments of the Ashadze-1 field (Mid-Atlantic Ridge) by the section of columns from northeast to southwest (wet chemistry, chemical laboratory of the All-Russia Research Institute Oceanology; C_{org} is wet chemistry, chemical laboratory of the Geological Institute, Russian Academy of Sciences)

No of station	No of sample (interval, cm)	SiO_2	Fe_2O_3 (total)	MgO	MnO	CaO	Cu	CO_2	S (total)	C_{org}
1521	1521-1 (0–1)	14.40	4.94	3.45	0.045	**33.00**	0.14	**28.20**	0.08	**0.69**
	1521-2 (1–10)	13.30	4.76	2.90	0.10	**36.00**	0.15	**28.60**	0.16	**3.62**
	1521-2 (10–20)	13.35	4.53	2.30	0.10	**39.50**	0.13	**31.66**	0.16	**1.09**
	1521-2 (20–30)	12.60	4.29	2.10	0.098	**38.00**	0.089	**30.66**	0.19	**2.44**
1519	1519-2 (2–10)	15.40	9.52	2.10	0.11	**26.75**	**1.25**	**23.45**	0.45	**0.33**
	1519-3 (10–20)	11.20	5.80	1.95	0.11	**36.30**	**0.29**	**29.25**	0.23	0.22
	1519-4 (20–30)	11.20	4.23	1.55	0.12	**36.70**	0.13	**30.32**	0.34	**1.15**
	1519-5 (30–40)	14.20	4.16	1.80	0.11	**35.00**	0.1	**28.66**	0.19	**0.32**
1528	1528-1 (0–5)	16.30	5.08	3.20	0.14	**33.50**	0.14	**26.66**	0.01	**0.35**
	1528-2 (5–10)	11.30	4.27	1.40	0.10	**38.50**	0.16	**30.80**	0.32	**0.26**
	1528-4 (20–30)	**19.95**	5.62	2.50	0.13	**31.00**	0.097	**24.06**	0.03	0.22
	1528-6 (40–55)	**26.50**	6.54	**11.70**	0.18	**20.70**	0.045	**16.68**	0.10	≤0.1
1520	1520-1 (0–4)	15.80	**38.12**	3.60	**0.48**	5.00	**4.5**	5.45	**4.00**	**0.77**
	1520-2 (4–15)	14.60	**44.23**	3.60	**0.70**	2.12	**5.63**	1.56	**4.50**	**1.31**
	1520-4 (25–35)	13.40	6.15	2.20	0.079	**33.00**	0.17	**27.10**	**0.20**	**0.84**
1518	1518-2 (2–15)	12.20	**51.48**	**7.62**	0.009	0.49	**5.55**	2.18	**20.27**	0.12
	1518-4 (25–35)	17.40	**47.86**	**10.44**	0.007	0.25	**3.89**	3.02	**21.61**	≤0.1
	1518-6 (45–55)	7.40	**58.14**	4.64	0.019	0.29	**6.54**	6.50	**26.75**	≤0.1
1475	1475-1 (0–20)	**29.60**	**14.88**	**18.00**	**0.55**	4.20	**1.88**	6.07	**2.67**	0.15
	1475-2 (20–30)	**30.00**	**14.55**	**18.75**	**0.52**	4.18	**1.84**	6.00	**2.84**	≤0.1
	1475-4 (40–50)	**29.80**	**15.60**	**18.15**	**0.55**	3.88	**1.89**	5.44	**3.37**	≤0.1
	1475-6 (60–70)	10.80	**36.46**	**6.04**	0.11	0.95	**16.30**	1.15	**19.23**	≤0.1
	1475-8 (80–90)	**22.20**	**25.83**	**14.00**	**0.30**	1.67	**9.32**	2.06	**11.00**	≤0.1
1508	1508-2 (2–12)	**37.10**	**18.27**	**21.80**	0.14	1.17	**0.28**	0.45	0.36	0.20
	1508-3 (12–22)	**25.46**	**32.00**	**9.00**	**0.75**	0.87	**0.26**	0.52	**2.11**	≤0.1
	1508-4 (22–32)	**23.64**	**32.60**	**8.88**	**1.42**	1.22	0.097	0.62	**2.16**	0.26
	1508-5 (32–45)	12.82	**38.00**	**9.80**	**1.51**	1.38	0.041	12.38	**20.35**	≤0.1
1437	1437-1	11.60	4.70	2.28	0.11	**35.80**	0.11	**28.80**	0.06	0.12
	1437-2	12.80	4.77	5.10	0.11	**35.50**	0.11	**29.70**	0.10	0.22

Note: Extra bold is the increased contents of basic oxides and ore-forming elements.

miniferas and coccoliths are dominants. Based on the complex of factors, the age of sediments is Holocene–Late Pleistocene (0–30000 years) [8]. The investigated complexes of plankton and benthos foraminiferas are characteristic for the tropical zone of the Atlantic Ocean. From the Holocene to the Late Pleistocene, the number of species and the total amount of benthos foraminiferas, coccoliths, and ostracods are increased [9].

Mineralogical investigation of sediments of ore-bearing (enriched of Fe, Cu, Zn) horizons of stations 1519 and 1520 and ore columns of stations 1508 and 1518 by means of electron microscopy showed that the degree and nature of shell mineralization strongly modify from east to west. The shells from station 1519 are less changed and of calcite. The surfaces of some shells have Fe hydroxides and Fe–Mn crusts. In the column of station 1520 from the periphery of ore body 1, calcite of shells sometimes contains impurities of Mg, Cu, and Si. Fe–Mn crusts sometimes with impurities of Cu, Si, Ni, crystals of anhydrite, hematite (?), and barite are often presented on surfaces of the shells. Within ore body 1 (station 1518) and to the west of it, in the zone of increased magnesium content (station 1508), intensive hydrothermal transformations of sediments occurred. They appeared in the substitution of calcite shells with second minerals and cement formation. Second minerals are presented with silicates: tremolite-actinolite, serpentine, Fe–Mg smectites, saponite (?), possibly, palygorskite (sepiolite); carbonates Mg–Mn-containing siderite; sulfides pyrite, and sulfides of Fe and Cu (Fig. 2). Analogous new mineral formations as well as a little barite, anhydrite, and quartz overgrow the shells forming a crust and pore cement of sediments. Newly formed silicates and carbonates are characterized with a high content of Fe and Mg. During the substitution of foraminiferas with pyrite and its following recrystallization and oxidation, shells fully lost their habits. Only the same sizes and sphere-shaped form of pyrite aggregates and sometimes relics of primary shell structures enable us to guess about the primary biogenic nature of the sand fraction of the sediments (Fig. 2c). Pyrite to a variable degree is oxidized and contains inclusions of Cu sulfides. By the whole section of columns, traces of carbonaceous matter are found on the shells.

The most widespread new formations are pyrite and siderite. Mg and Mn combine into siderite in abundance. Apparently, they isomorphously replace Fe. Hence, thin-crystallized siderite replacing calcite shells are characterized by a higher content of Mg (9.55–11.36%, on average by 6 measurements 10.9%) and Mn (6.07–7.21%, on average 6.19%) in comparison to the later siderite of cement. The Mn content in siderite varies from 0.84 to 10.9%, of the average by 6 measurements 7.42%, and Mn from 3.25 to 6.78, on average 4.96%. The crystal structure of mineral conforms to siderite (the strongest lines 3.590, 2.78, 2.127, 1.726).

By the composition of dominant second minerals, the next zones are distinguished: (1) the sulfide zone, agreeing with ore body 1; (2) zone of minerals of increased magnesium content, partly agreeing with ore body 1, exceeding its limits on the west and south-west; (3) development zone of Fe–Mn crusts on the south periphery of ore bodies 1 and 2. The processes of solution and substitution of carbonate shells by secondary minerals decay toward the edges of the hydrothermal field.

Educed mineral–geochemical zoning in sediments of the Ashadze-1field is related with superposed

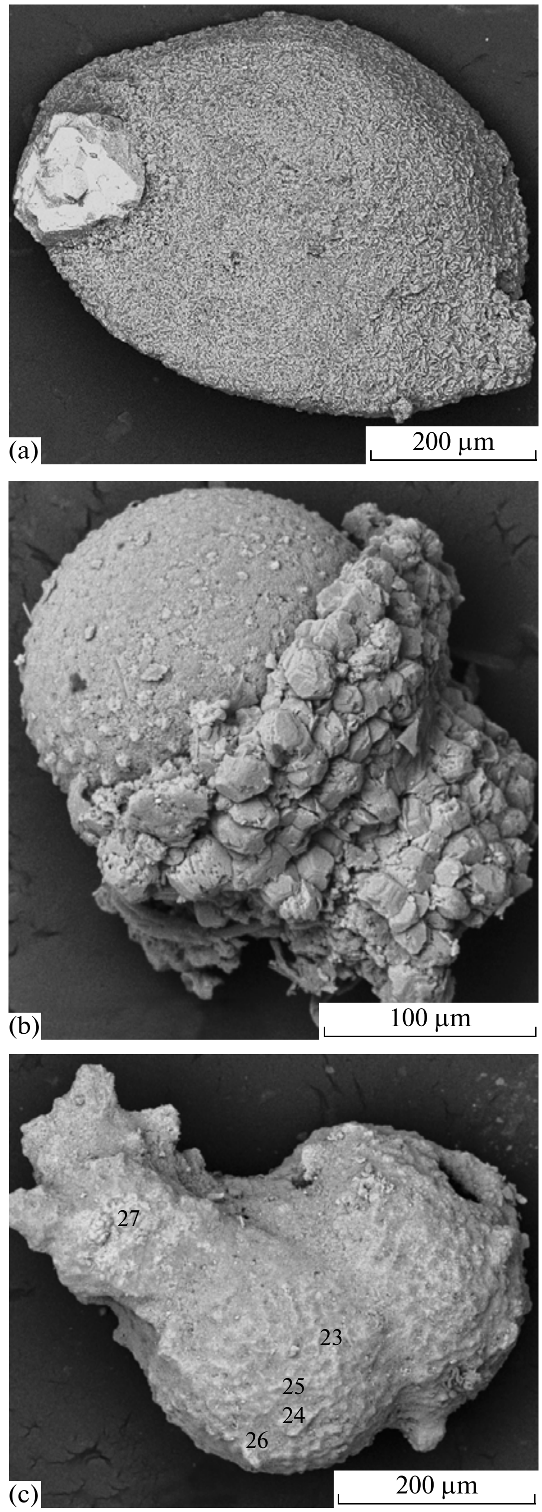

Fig. 2. Behavior of foraminifera shells of organogenic sediments of the Ashadze-1 field. Chemical composition by the data of PCMA (CamScan MV2300 with built-in energo-dispersive analytic system INCA Energy 200, Geological Institute, Russian Academy of Sciences); (a, b) station 1508, interval 32–45 cm. (a) Shell of the benthic foraminifera *Quinqueloculina seminula* (Linne) replaced with thin-crystal Mg–Mn-containing siderite in total, in the mouth is pyrite crystal; (b) shell of the plankton foraminifera *Orbulina universa* Orbigny fully replaced with Fe–Mg–smektite (composition, mass concentration, %: Mg 9.46, Al 5.04, Si 26.29, Ca 2.29, Fe 11.93, O 44.99) and submerged in crystal-granular Mg–Mn-containing siderite. The relic of thorns of the same compositions like the majority of pseudomorphoses on shells; (c) station 1518, interval 25–35. Figure on images is the numbers of measurements. Pseudomorphos of the different oxidized pyrite (measurements 23–26) with inclusions of Cu sulfides (measurement 27) on the two-dimensional shell of the *Globigerinoides* sp. with relic of weak structure and mouth.

hydrothermal processes. It is known that Mg-containing silicates in association with sulfides, silica, and anhydrite mark the plots of hydrothermal discharge in the Red Sea [1]. It is important that Mg is contained in hydrotherms of the Red Sea, which is uncharacteristic for an ocean hydrothermal source. Usually they have no Mg at all [10]. The peculiarity of the hydrothermal Ashadze-1 field is the presence of siderite in the zone of increased magnesium content of siderite. Siderite is enriched with Mg and Mn in association with Fe–Mg-containing silicates including Fe–Mg clay minerals. A wide distribution of minerals enriched with Mg in the hydrothermal-transformed ore-bearing ocean sediments testifies to the high content of this element in fluids acting on the sediments. The presence of Mn in composition of siderite conforms to the data of its increased content in the plume above the hydrothermal Ashadze-1 field [4, 11]. Quantitative ratios of Fe, Mg, and Mn consisting of siderite of different generations testify to the gradual decrease in the Mg and Mn content in the mineral-forming solutions.

Thus, for the first time, detailed investigations of hydrothermal transformations of ore-bearing sediments of the Ashadze-1 field on the microbiota were carried out; substitution of foraminifera shells with pyrite and sulfides of copper (within ore body 1) and with high magnesian accompanying minerals was discovered.

The educed zone of increased magnesium content apparently testifies to a high rate and short way of transport of hydrothermal solutions. It can be related with the proximity of the magmatic chamber and the tectonic location of the ore field, in the high active near-break area.

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