Origin and distribution of Fe-montmorillonite in the metalliferous sediments from the axial zone of the East Pacific Rise (20°30' — 22°00' S)

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Abstract. High dispersive minerals of the metalliferous sediments from the axial zone of ultra-fast spreading center in the South part of the East Pacific Rise (20°30' — 22°00' S) were studied by XRD methods. It is established that the high dispersive part of the studied sediments is almost totally composed of X-ray amorphous Fe and Mn oxihydroxides. Among the crystalline phases of greater importance is the Fe-montmorillonite with different degree of crystallinity. Goins away from the rise axis illite of terrigenous origin appears. It is established that during the pulsed hydrothermal processes the degree of Fe-montmorillonite crystallinity changes. The Fe-montmorillonite formed during the low temperature phases of the hydrothermal stages is better crystallized than that one formed during the high temperature phases. The processes of crystallization are most probably controlled by the physico-chemical parameters of the venting from the oceanic crust hydrothermal fluids.

Introduction

The study of some clay and other high dispersive minerals is of great importance for the origin and the distribution of the metalliferous sediments in the World Ocean. The overall amount of the clay minerals, their degree of crystallinity and the content of X-ray amorphous materials depend on the source of their input. Biscaye (1965) and Hayes (1973) established that clay minerals are stable enough in time and can be transported to long distances without changing their crystallographic peculiarities. Well crystallized dioctahedral illites and chlorites are very often of terrigenous origin and are transported by wind and water. The smectite minerals are the main part of the high dispersive deposits, formed on volcanic materials as a result of halmirolysis.
The peculiarities of the formation of the high dispersive minerals from the metalliferous sediments of the East Pacific Rise (EPR) were pointed out by several authors (Горбунова, 1976, 1981, 1982; Горбунова, Лисицын, 1980, 1981; Hein et al., 1979; M c M u r t y , Y e h , 1981 etc.). They established, that the high dispersive part from the surface sediment layer was composed mainly of X-ray amorphous material. The clay minerals are normally in the early stage of crystallinity in the form of Fe-montmorillonite. Going away from the rise axis in the zone with metalliferous sediments, situated along the EPR to the West and to the East, the degree of the Fe-montmorillonite crystallinity increases and that is also true of the amount of the clay minerals. The red abyssal clays normally contain a high amount of clay minerals and at the same time they have better crystallinity than the ones in the metalliferous sediments.

The detailed studies of Gorbunova and Lissitzin (Горбунова, Лисицын, 1981) based on data from several cruises in the South-East parts of the Pacific Ocean allowed them to create for the first time distribution maps of the main groups of clay minerals in that region. A map of the main clay mineral provinces was designed.

The study of the degree of crystallinity of the Fe-montmorillonite in the metalliferous sediments, as well as the relation clay minerals — X-ray amorphous material showed fluctuations in time (Горбунова, 1981, 1982, 1987, 1990; Горбунова, Лисицын, 1981). The above cited authors pointed out that these changes coincided with the cyclic input of material from the sources with endogenous origin.

Geological setting

The large territory of metalliferous sediments situated along the EPR axis to the South-East of the Pacific Ocean which excludes 10 billion km² is the object of study of many authors (Лисицын, 1976, 1979; Скорнякова, 1964; Востром, 1966 etc.). In order to study the submarine hydrothermal activity and the related massive sulfides and metalliferous sediments the 4th cruise of R/V “Geolog Fersman” took place in 1987-1988. The area of investigations was situated at the western flank of the ultra-fast (from 16 to 20 cm. year⁻¹) (H e r r o n , 1972; R e a , 1978; R e a , L e i n e n , 1986) spreading segment of EPR (20°30'-22°00' S) between two zones of overlapping (П о р о ш и н а et al., 1992) (Fig. 1). In the rift zone of the rise, fields of massive sulfides and high temperature hydrothermal activity were established (Краснов et al., 1988; М а р ч и г et al., 1986, 1988, 1989). The cores with metalliferous sediments were taken along three profiles situated at 10, 20 and 40 km from the spreading axis (Fig. 1). The situation of the profiles to the West of the EPR was predetermined mainly by the

Fig. 1. Scheme of the studied region and the core locations: 1 — fields of massive sulfides in the rift zone of the East-Pacific rise (according to L i s i t z i n et al., 1900); 2 — spreading center axis
fact that the hydrothermal material was transported there mainly to the West (Лисицын, 1976; Марчиг et al., 1986).

Sedimentological and biostratigraphic studies of the samples (Левитан et al., 1990) as well as age dating giving the rates of deposition (Деков, Купцов, 1990, 1992) were carried out. The carbonate varieties predominate among the metalliferous sediments. The CaCO₃ contents there normally are about 50-70%. The carbonate material is composed of coccoliths, foraminiferas and their fragments. In the ore part of the sediments iron and manganese oxihydroxides are established. In the lythogenetic part of the deposits small quantities of predominantly edaphogenic components, as well as terrigenous ones (mainly of eolic origin) are found out.

Methods of investigations

The X-ray diffractometry analyses is the main method applied in the present study. It was been carried out in the Institute of Oceanology of the Russian Academy of Sciences by diffractometers DRON-2 and DRON-4, in the Geological Institute of the Russian Academy of Sciences — diffractometer DRON-2 and in the Geological Institute of the Bulgarian Academy of Sciences by diffractometer D-500 SIEMENS. CuKα and FeKα tubes and graphite monochromators were used. The results were processed by IBM PC/AT standard packets of programs. The standard method of specimen preparation was used — washing by ionized water and separation of the fraction under 1 μm. Parallel to this bulk samples were studied too. Oriented specimens (sedimented on glass) and tablets were used untreated and after treatment by Na-acetate-acetic acid buffered to pH 5.0. The specimens were analyzed: 1) untreated; 2) glycerine treated; 3) after heating at 550°C. The different samples were studied after heating in 1 N HCl for one hour in order to differentiate the iron varieties of the clay minerals. Many specimens were analyzed by SEM (JEM 7a) in order to study the morphology of the authigenous minerals.

The quantitative estimation of the clay minerals is a very difficult problem. A number of authors estimated the relations between the different groups of minerals (Бискаев, 1965; Скафе, Кунце, 1971) without taking into consideration the amount of the amorphous material. In the present paper we decided that it was not possible to apply these methods because the amorphous material predominated in the greater part of the studied samples while the clay minerals due to their small amounts were difficult to evaluate.

Results and discussion

The high dispersive part of the studied sediments after their decarbonatization is almost totally composed of X-ray amorphous material such as iron oxihydroxides and opal. Among the crystalline phases the montmorillonite with different degree of crystallization is of great importance. This mineral is characterised with basal spacing of d=14.7 Å in Mg-saturated state, with glycerine — d₀₀₁=18 Å, d₀₀₂=9.3 Å spacing is not well expressed. After heating at 550°C a wide diffuse peak with d=10 Å and weak peaks with 3.30 and 3.18 Å appear; d₀₀₂ are absent. These data show a higher iron content in the montmorillonite mineral. After treatment with 1 N hot (80°C) HCl the montmorillonite peaks disappear or become obviously smaller the peak at d₀₀₀=1.501 Å shows that the mineral is dioctahedral (Fig. 2). The electron microscope pictures demonstrate clearly the authigenous-diagenetic crystals of the Fe-montmorillonite with specific worm-like or highly segmented forms (Pl. I, figs 1, 2, 3, 4). Fe-oxihydroxides, terrigenous clay minerals and zeolites can also be very well seen on the pictures.

Different ideas were put forward to explain the origin of Fe-montmorillonite. The most widely spread model was presented in the paper of Hein et al. (1979). McMurtry and Yeh (1981) made their contribution to that model using the results about the formation temperature of the Fe-montmorillonite on the basis of ¹⁸O/¹⁶O data. According to that model the Fe-montmorillonite is probably formed under lower temperature hydro-
hermal processes (30-50°C) as a result of the oxidation and cooling of the unstable, high temperature, sulfides (380°C ± 30°C) and the interaction of the formed Fe-oxihydroxides with silica (hydrothermal or biogenic) or as a result of the penetration of the hydrothermal fluids through the basalts and the sediments. The distribution of this mineral takes place as colloid phases probably as a result of the erosion of the hydrothermal mounds by the bottom currents.

However the diageneric origin of the Fe-montmorillonite formed onto terrigenous material and hialoclasts is also possible. As it has already been demonstrated by A. G. Kossovskaya (Kossovskaya et al., 1975) the basalt hialoclasts undergo an interaction with ocean water under the conditions of high porosity and segmented relief giving birth to authigenous clay minerals. The degree of crystallinity of the formed minerals probably depends on the deposition rate which partially controls the duration of the basalt contact with the ocean water. The presence of Al-montmorillonite in some samples (a clear 002 peak (Konyama, 1970)) allowed the Japanese scientists to suggest (Aoki et al., 1979) that this mineral was formed on ash material differing from its iron varieties.

We can conclude that the high dispersive minerals in the metalliferous sediments come from three sources: 1) endogenous — as colloids from the vent fields at spreading center (such as X-ray amorphous Fe-oxihydroxides and Fe-montmorillonite); 2) authigenous — Al-montmorillonite and mixed-layered illite-montmorillonite, formed on products of halmirolisis of the volcanic material; 3) terrigenous — illite, chlorite, kaolinite.

According to the main clay mineral provinces map (Горбунова, Лисицын, 1981) the studied region is situated in the montmorillonite province with the predomi-
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PLATE I

SEM pictures of metalliferous sediments:
1 — core 85, 142-145 cm, $\times$ 10 000 — Fe-montmorillonite;
2 — core 85, 108-109 cm, $\times$ 3000 — philipsite, Fe-montmorillonite;
3 — core 85, 153-158 cm, $\times$ 2000 — Fe montmorillonite and accumulations of iron oxihydroxides;
4 — core 87, 20-22 cm, $\times$ 3000 — Fe-montmorillonite, terrigeneous clay minerals slightly diagenetically altered;
5 — core 87, 15-16 cm, $\times$ 1000 — philipsite, terrigeneous clay minerals;
6 — core 93, 0-1 cm, $\times$ 2000 — zeolites
rance of amorphous material. Its comparatively small area and locality situated along the rise axis prevent the demonstration of the main regularities of the Fe-montmorillonite spatial distribution. It can be suggested that Al-montmorillonite is present in the sediments on the ten kilometer profile and close to the spreading axis together with the increased content of hialoclasts. Approaching the flanks the degree of crystallinity of the Fe-montmorillonite increases and illite appears (core 87). The illite is characterised with series of peaks at 10.5 and 3.3 Å, which do not change after glycerine treatment and after heating. After heating in 1 N HCl these peaks do not disappear which shows their terrigenous origin. Clay-sized quartz and feldspars are present in small amounts in almost all samples. In some of the samples of the 40 km profile (core 87, 15-16 cm; core 93,0-1 cm) authigenous phillipsite is found (Pl. I, figs 4, 5, 6).

The problem about the alteration of the authigenous Fe-montmorillonite in time, as it was mentioned above, was discussed in the literature. Irregular changes in the degree of its crystallinity has been established.

In the present paper we tried to establish the behavior peculiarities of the Fe-montmorillonite at the time of the assumed pulsed hydrothermal process. To come to the solution of this problem 6 samples from the lower part of core 85 were studied by XRD. Using the contents of Fe (calculated on carbonate free basis (GFB)) as hydrothermal indicator we had a clear picture of the stages of hydrothermal impulses and calm periods (Fig. 3a). The samples were taken from the maximum and minimum of the vertical distribution of the iron content. On Figure 3b the curve of the vertical distribution of the amorphous silica (GFB) and the details from the low angles diffractograms (Fig. 3c) of the studied samples are given. Considering the present state of knowledge of the hydrothermal processes in the ocean (Лицицын et al., 1990) it can be assumed that the maximums Fe content register the high temperature phase of the hydrothermal stages. And the maximums of the amorphous silica content appearing with a half phase before the "iron" maximums (Fig. 3), most probably reflect the low temperature phase of these stages which logically precede the high temperature ones. The Fe-montmorillonite crystallinity was studied using its peaks at d_{001}=14.7 Å in Mg-saturated stage (Fig. 3c). Clear narrow peaks at 14.7 Å show a high while the broad diffuse ones — low degree of crystallinity of this mineral. Analyzing the diffractograms it can be concluded that at the time of the low temperature phase of the hydrothermal stage well crystallized Fe-montmorillonite is formed (T_{formation}=27-39°C), while during the high temperature phase — a poor crystallized one. The control of this process is probably carried out by a change in the amorphous silica concentrations in the hydrothermal fluids (maximum for the low temperature phases) in connection with the temperature change of the latter. It can be suggested that the formation of poor crystallized Fe-montmorillonite in the high temperature phases of the hydrothermal process is related to the physicochemical features of the environment and the possible activity of the peripheral low temperature vents.

Conclusions

a). The high dispersive part of the studied metalliferous sediments is almost totally composed of X-ray amorphous oxihydroxides of iron and manganese. The Fe-montmorillonite with different degree of crystallinity is of highest importance among the crystalline phases. Illite of terrigenous origin appears in the sediments away from the ridge axis.

b). During the pulsed hydrothermal process the degree of crystallinity of the Fe-montmorillonite changes regularly. The Fe-montmorillonite formed at the time of the low temperature phases of the hydrothermal stages is better crystallized than the one formed during the high temperature phases. The crystallization processes are most probably controlled by the physicochemical parameters of the venting in the ocean floor hydrothermal fluids.

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